CHAPTER I

INTRODUCTION

1. SOLID STATE PHYSICS AND LUMINESCENCE:

Solid State Physics is concerned with experimental investigations and theoretical interpretations of all the physical properties of solids particularly the special properties exhibited by atoms and molecules because of their association and regular periodic arrangement in crystals. In recent years it has received great attention because of the development of powerful theoretical methods and new concepts introduced and also because of its varied practical applications.

In crystalline solids, the atoms are stacked in regular manner forming a three dimensional pattern which may be obtained by a three dimensional repetition of a certain pattern unit. When the periodicity of the pattern extends throughout certain piece of material, one speaks of a single crystal while, in polycrystalline materials, the periodicity of structure is interrupted at so called grain boundaries. Further, any deviation from a perfect regular lattice is regarded as a defect or imperfection in crystal structures. In general, all crystals are in some respect imperfect. A number of important properties of solids are controlled far more by the nature of imperfections than by the nature of host crystal. The conductivity of semi-conductors may be dictated entirely by trace amounts of purposely introduced impurities. The colour of many crystals
arises from imperfections. The mechanical and plastic properties of solids are usually controlled by dislocations, a special type of imperfection. Research activity in solid state physics, therefore, is rightly concentrated on problems of "imperfections".

The phenomenon of luminescence of crystals also arises in an imperfect crystal lattice or defects. As a result, this branch has received greater experimental attention with the hope of solving the problem of the description of processes that follow absorption of energy by an insulating crystal. The position as regards the theoretical understanding is far from satisfactory mainly for two reasons: (1) in the first case, the theoretical treatment is very difficult because of complex interactions among radiation, matter and phonon. In the second case, the development of the field is largely guided by commercial considerations.

2. DEFINITIONS:

(1) Luminescence: According to Curie (2) the term luminescence includes the luminous emission which is not purely thermal in origin. However, Garlick (3) has adopted the definition of Wiedmann which states that "Luminescence is a phenomenon that involves the absorption of energy by a substance and its re-emission as visible or near visible radiation". This phenomenon has to be distinguished from thermal radiation since it does not follow Kirchoff’s law. The general term of luminescence is further sub-classified according to
the mode of excitation. Thus we have:

(a) Photoluminescence - that produced by absorption of photons.

(b) Radioluminescence - that produced by bombardment of a phosphor with high energy particles as well as radiations like X-rays or r-rays. A specific case of radioluminescence produced by cathode rays is Cathodoluminescence.

(c) Electroluminescence - that produced by the application of electric field.

(d) Chemiluminescence and Bioluminescence - as emission which accompanies a chemical reaction or biological process.

(ii) **Fluorescence and Phosphorescence** - A second basis frequently used for characterising luminescence is its persistence after the source of exciting energy is removed. Many substances continue to luminesce for extended periods after the exciting energy is cut off. The delayed light emission is generally called "Phosphorescence" while the light emitted during excitation is called "Fluorescence". The two phenomena are distinguished more precisely by Perrin (4). The phenomenon is fluorescence if the emission takes place by one or more spontaneous transitions of electrons from the excited state to the ground state. On the contrary, if the emission
occurs with the intervention of a metastable state followed by a return of the system to the excited state due to addition of energy, then, this is phosphorescence. Transition of a system from the metastable state to the ground state is assumed to be forbidden. It has first to absorb enough energy to go to the excited state from where the transition to the ground state is permitted. A study of the variation of the luminescence decay with temperature also enables a distinction to be made between the two phenomena. The decay of fluorescence is little dependent on the temperature but the duration of phosphorescence is strongly temperature dependent. Garlick (3) defines fluorescence as the luminescence with a life time of about $10^{-8}$ sec. as this is the time of relaxation of ionised gaseous ion, while, the emission which persists for longer time is phosphorescence. According to Leverenz (5) this demarcation is not very sharp and short period phosphorescence may overlap with long fluorescence.

(iii) Thermoluminescence: When a phosphorescent solid is first excited at low initial temperature, low enough to for traps not/lose their electrons, and then is warmed at uniform rate, bursts of luminescence appear at one or more limited ranges of temperature. This effect is known as "Thermoluminescence". The only difference between phosphorescence and thermoluminescence is the fixed and rising temperatures respectively of the emitter during the observation of emission. Otherwise, the two processes are the same.
(iv) Phosphors - The ability to luminesce is not confined to any particular state of matter. Luminescence is observed in gases, liquids, and solids. The passage of an electrical discharge through a gas will excite the gaseous atoms or molecules to luminesce under certain conditions. Many liquids such as oils or solutions of certain dyestuffs in various solvents luminesce strongly under ultraviolet light. Luminescence is also exhibited by many natural minerals such as scheelite, willemite, flourspar etc. A large number of solids produced artificially in the form of synthetic products luminesce under various types of excitation. The materials exhibiting the property of long after glow were originally termed Phosphor (6) - a Greek word for light carrier. Other terms commonly used by many authors are luminophor, flour or flourspor.

Phosphors are generally crystalline inorganic insulating materials that are very sensitive to structural changes and impurities. They may be divided into those which show luminescence in pure state and those in which luminescence is due to the addition of an activator in the form of a trace impurity. Luminescence in pure state means that the emission is not diminished by repeated purification (3). Some examples of pure state phosphors are manganous halides, salts of rare earths, platinocyanides, tungstates, molybdates and uranyl salts. Randall (7) has suggested that such materials contain groups which function like foreign molecules in the matrix
crystal from which they are separated by screening.

Phosphors can be classified into two main groups.

(a) **Photoconducting Phosphors** - In this class of phosphorescence excitation raises electrons from the valence band or from the luminescence centre to the conduction band leaving a hole behind and hence there is a strong correlation between luminescence and photoconductivity. The typical examples of such phosphors are ZnS:Ag, ZnS:Cu, CdS:Ag, etc.

(b) **Non-photoconducting Phosphors** - With this class of phosphors photoconductivity that may be present is incidental and is negligible under usual conditions of excitation, where the electron is not raised to the conduction band and hence the emitting system is quasistatic. The typical example of this class of phosphor is KCl:Tl.

This classification is suggested by Mott and Gurney (8). Leverenz (9) prefers to classify phosphors on the basis of sites occupied by the activator atom. According to him the two major groups are:

(a) Phosphors in which activator atoms occupy substitutional sites and exhibit predominantly exponential decay characteristics; for example Zn(SiSe):Mn, ZnF₂:Mn, etc.
(b) Phosphors in which activators occupy interstitial sites and exhibit predominantly power law decay, for example Zn: Cd (Si:Se): Cu ZnF₂: Cu, etc.

(v) Luminescence Centres and Transitions— To understand the mechanism of luminescence, the process has to be divided in three main stages: initial act of absorption, transport and storage of absorbed energy and the release of the stored energy in the form of emission of luminescent radiation (3). The main condition for the occurrence of luminescence emission is that the absorbed energy should be protected from any loss through radiationless transitions and should be re-emitted at the same place in the material (10). If the re-emission occurs at a different place there should be some efficient mechanism for the transfer of energy without any serious loss. In view of these considerations, the localities in a phosphor where energy is re-emitted after absorption are called luminescence centres. Luminescence centres represent those energy levels which are responsible for the spectrum of the emitted luminescence. In such centres the electron transitions responsible for luminescence emission take place with a minimum of disturbance from the surroundings. If there be any such disturbance, the probability of non-radiative transition is increased. Such centres are known as killer centres and the substances responsible for these centres are called poisons.

The nature of luminescence centres differs widely from
phosphor to phosphor (11,12). However, it is now a well established fact that these centres are created in a phosphor as a result of inclusion of some foreign constituent known as activator. The activators are supposed to provide necessary shielding for the absorbed energy which would otherwise be dissipated in the form of thermal vibrations (8). Traps provide the mechanism for storage of energy. They represent the metastable states or levels in which electrons or holes can be captured and where they remain for significant times between excitation and emission of luminescence (13). A trapped electron or hole is prohibited from moving freely through the crystal unless supplied with thermal or optical energy. When the trapped electron or hole is released, it can either recombine with luminescence centre or may be trapped again. In the latter case the ultimate phosphorescence will be delayed further.

(vi) **Luminescent Yield:** Vavilov (14) defines fluorescent yield as the part of the total absorbed radiation which is transformed into the energy of secondary fluorescent radiation. In this quantum version of definition the energy is replaced by the corresponding number of quanta. Levshin (15) however feels it necessary to couple the definition of yield with the precise definition of the state of excitation of the material. According to him, the yield of luminescence in a stationary state of excitation and luminescence is the ratio of luminescent energy liberated by the material for a definite interval of time to the energy of the exciting light absorbed by the material in the same time maintaining the given state.
of excitation.

3. (1) ENERGY TRANSFER AND SENSITIZATION:

The phenomenon in which the centre responsible for emission is not the one in which absorption has taken place is known as sensitisation. Transfer of energy in these phosphors does not involve the movement of charge. This phenomenon was discovered by Tomaschek (16) in SrS:Gd, Sm and by Rothschild (17) in CaS:Sm, Bi. Numerous studies of the effect have been made since then (18,19,20). Three different mechanisms of energy transfer are proposed:

(a) Cascade mechanism - According to this mechanism, one centre after absorbing excitation energy emits radiation which on being absorbed excites a second centre.

(b) Resonance mechanism - According to this mechanism, a resonance transfer takes place between sensitizer and activator by dipole-dipole or dipole-quadrupole or exchange interaction (21,22). On the assumption of random distribution of the sensitizer and activator ions, the distance over which such transfer can take place has been evaluated (23,24).

(c) Excitation migration - According to this mechanism, the energy transfer takes place by metastable excitons of the base lattice (25,26). Broser (27) and Balkanski (28) have shown experimentally the
possibility of the action of exciton at large distances from their point of creation.

(11) CONCENTRATION QUENCHING:

The increase in concentration of the activator in a singly activated phosphor beyond a certain value often leads to a decrease in the luminescence efficiency. Ewles and Lee (29) and Johnson and Williams (30) explain this phenomenon of concentration quenching on the assumption that quenching occurs at the centre which absorbs the exciting energy initially. It is assumed that proximity of a given activator to another activator or to a certain type of lattice defects increases the probability of a radiation-less transition in the activator. Dexter and Schulman (31) on the other hand assumed that degradation of the 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.

4. THEORIES OF LUMINESCENCE:

The interpretation of luminescence phenomenon is important for two reasons. In the first case it is possible to design and improve phosphors from fundamental considerations in view of their uses in commercial applications like fluorescent lamps, cathode ray tubes, etc. and in the second case the detailed understanding of luminescence provides insight into electronic processes in solids. The study of decay and its dependence on temperature provides information regarding
the distribution of traps and trap depths. But this study does not reveal any information regarding the actual nature of luminescence centres and the mechanism of transfer of energy. Luminescence in atomic gases is adequately explained by the concept of atomic spectroscopy but in the case of molecular gases, liquids and solids two major effects viz. shift of emission band and its breadth need special explanation. These effects are explained with the help of "Configuration Co-ordinate Model" and "Energy Band Model". Practically all interpretations of luminescence phenomenon are based implicitly or explicitly on some modifications of configuration coordinate model.

(a) **Configuration Coordinate Model:**

This model was first proposed by van Hippel (32) and was modified by Seitz (33). This is based on the consideration of interaction between the emission centre and the crystal lattice. Diagrams of total energy of the system versus position coordinates which are precisely specified as nearest neighbour distances are used to describe the transitions and re-arrangements occurring in luminescence phenomenon. In this model the ground and excited states represent different electronic states of luminescence centre. On these curves the energy of the ground and excited states are shown to vary approximately parabolically with some coordinate, usually the distance from the luminescent centre to its nearest neighbours. Fig. 1.1. There is a value of coordinates for which the energy is minimum but this value is different for the ground and
Schematic Configuration Coordinate Curves.

FIG. 1.1.
excited states because of the different interactions of luminescent centre with its neighbours. The equilibrium position of the ground state occurs at A (Fig. 1.1). If the centre absorbs light it is raised to the excited state B. The transition is a vertical one according to the Frank-Condon principle. After the centre has reached the excited state the ions of the system adjust until a new equilibrium position is reached at C, the energy difference between B and C is given off to lattice. Having reached its new equilibrium position at C, the centre may return to the ground state at D by the emission of a quantum of light. The centre relaxes from D to A, giving up energy in the form of lattice vibrations.

(i) **Stoke's Shift:**

The energy emitted is smaller than that absorbed because part of the energy is transferred to lattice. This explains the Stoke's Shift which depends on the interaction of the centre with its neighbouring ions (34).

(ii) **Band Width:**

When the system is at an equilibrium position such as at C of the excited state curve, it is not at rest but migrates over a small region around C because of the thermal energy of the system. At higher temperatures these fluctuations cover a wide range of configuration coordinates. As a result, the emission transitions are not just to a point D on the ground state curve but cover a region around D. In the vicinity of D, the ground state curve shows a rapid change of energy so that even a small range of values for the configuration
coordinate leads to a large range of energies in the optical transition. This explains the broad emission and absorption bands that are observed. An analysis of this sort predicts that the widths of the bands—usually measured in energy units between the points at which the emission or the absorption is half its maximum value—should vary as the square root of the temperature. For many systems this relationship is valid for temperatures near and above room temperature.

(iii) **Temperature Quenching**

Two other phenomena which can be explained on the basis of configuration coordinate model are temperature quenching of luminescence and the variation of decay time of luminescence with temperature. In the case of potassium chloride activated with thallium (35), it is found that at low temperatures there is very little change in brightness with temperature but at elevated temperatures the luminescence decays very rapidly. On the scheme of fig. 1.1, this is interpreted as meaning that the thermal vibrations become sufficiently intense to raise the system to the point $E$. From the point $E$, the system can fall to the ground state by radiationless transition and emitting a small amount of heat. This temperature quenching occurs more strongly for centres that would have stayed in the excited state for a relatively long period of time. As a result the decay time of emission that occurs in this temperature region is largely characteristic of centres in which transitions to the ground state have been rapid. Therefore the decay time of the luminescence is observed
to decrease. Dexter, Klick, and Russel (36) had proposed a slightly different mechanism. They had suggested that the relaxation of the system when radiationless transition occurs is much smaller than in the case of Seitz's mechanism.

(iv) **Limitations of the Model:**

Although the configuration coordinate model is successful in describing many aspects like Stoke's shift, high temperature phenomenon of thermal quenching, variation of decay time of luminescence with temperature but it also predicts that emission and absorption bands should become narrow as temperature is reduced (7). This is not the case as shown by the results of Russel and Klick (37). They have drawn a curve through the experimental points of width of the absorption band for the F-centre in potassium chloride as a function of the square root of the temperature and showed that the results are valid at high temperatures. At low temperatures the width of the band is constant. Also the applications of configuration coordinate model are limited because it does not reveal any information about the mechanism of transport of charge through the lattice. As a result of this inadequacy the phenomenon of photoconductivity could not be explained. However, in the last few years, with the realisation of the importance of zero point vibration interactions, the configuration coordinate curves have been used in a more quantitative way (38). The curves have the energy versus displacement characteristics of the simple harmonic oscillator. Its importance is that even at absolute zero the system is not at rest
but varies over a range of configuration coordinate characteristics. Further, this model is applied where photoconductivity is not associated with phosphorescence. Williams (39, 40) and others (41, 42) have successfully attempted to compute the curves in a systematic way for the thallium ion in potassium chloride lattice. They have calculated the energy levels of thallium ion as a function of configuration coordinate representing the displacement of the six chlorine ions around a thallium ion from perfect potassium chloride lattice positions. They have used approximate wave functions and treated in detail the interactions between thallium ion and the lattice. Thus, considering only fluorescence of single thallium ions substituted for alkali metal ions in the lattice, three absorption bands were found and interpreted. The absorption and emission bands as calculated by them were found to be in good accord with experiment. The chief limitation of this model is that the curves are usually constructed from experimental results. It is difficult to have configuration coordinate diagram on theoretical considerations because of the computational difficulties.

(b) Band Model:

The next phase in the interpretation of luminescence is the precise physical identity of the electron traps responsible for individual peaks and the analysis of the transfer of energy from the lattice to the activator. In luminescent systems involving transfer of charge, the luminescence is more determined by the host lattice than by the activator. A
model for this type of luminescent system was first proposed by Bloch (43) for solids which was known as the "Collective Electron Model". This model was extended further by Mott and Gurney (8) and by Seitz (44). The ideas of luminescence processes, generally accepted, are based on this model. When atoms and ions are arranged in an orderly way to form a crystal, the discrete levels of isolated atoms are broadened into bands (45). These bands of allowed energy are separated by bands of forbidden energy. In an insulator the allowed bands are either completely occupied by electrons or completely empty. The lowest empty band is usually several electron volts above the highest occupied band. As a result of absorption of radiation of suitable frequency by the crystal lattice, the electrons may be raised into the unoccupied band. This unoccupied band is generally known as the conduction band. Additional but usually discrete levels are further formed in the forbidden region between the highest filled band and the next unoccupied band as a result of traces of impurities or the presence of lattice defects which disturb the periodicity of the crystal lattice. These levels represent the normal and excited states of the impurity ions and are known as luminescent centres. Based on this band theory of solids three different types of models for a luminescence centre have been proposed by different workers.

(1) Schön and Klassens' Model: Klassens, (46) individually and also in collaboration with his associates (47), has summarised much of the current theory of luminescence for sulphides. They proposed a hole migration theory of lumines-
SCHON AND KLASENS MODEL.

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

FIG. 1.2.
cence of sulphides activated with monovalent impurities. This model is illustrated in fig. 1.2, for the case where excitation of luminescence is associated with the raising of an electron from the valence band to the conduction band. The sequence of events proposed is as follows:

1. Light is absorbed in the valence band producing a free electron and a hole leading to photoconductivity.

2. The hole may migrate towards the impurity centre. For example, if the centre is due to Ag⁺ substituted for Cd⁺⁺ in CdS, then the centre has a negative charge and attracts the hole with a coulomb-like attraction.

3. The hole is captured by impurity centre giving off a small amount of energy as infra-red radiation or a vibrational quanta.

4. The electron moves through the lattice until it finally comes near the centre.

5. The electron is captured by the centre.

The luminescence emission is given off as a result of the recombination of the hole with the electron. The electron transition may be directly from the conduction band to the ground state of the centre or may be by way of an intermediate excited state of the centre. After luminescence, the cycle is complete and the process may again be repeated. This model has been extended to include two impurity atoms, effect of
poisons, variation of luminescence colour with temperature of some phosphors, the non-linear relationship between luminescence output and the exciting intensity and similar phenomena in sulphide phosphors. But according to this model the decay characteristics and photoconductivity should be similar. This is against the actual experimental observations. The decay of luminescence is found to be more rapid than the decay of photoconductivity.

Several attempts were made to explain this feature. Bube (43) has suggested that in ZnS, the luminescence might be typical of the crystal and that the conductivity is characteristic of a small surface layer. Kallman and Kramer (49) postulate that electron transfer occurs in the crystal in some cases without electrons entering the conduction band. McKay (50) has investigated the conductivity of n-p-n junctions and inferred that the slow current decay may be characteristic of such junctions. Each of these suggestions involves the assumption that the crystal has regions in which the properties are different from those of the bulk of the crystal. A more logical solution was proposed by Lambe and Klick (51).

(ii) Lambe and Klick's Model:— This model is illustrated in fig. 1.3. The main feature of this model is that the trapping of the hole by the centre is considered to be a large energy transition and is assumed to give rise to luminescence. The sequence of events in this case is proposed as follows:
LAMBE AND KLICK'S MODEL.

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

FIG. 1.3.
(1) Light is absorbed producing a free hole and electron leading to conductivity.

(2) The hole and electron move in their respective bands and eventually the hole migrates near the impurities centre.

(3) The hole is captured by the impurity centre and luminescent emission occurs leaving the centre now neutral in charge.

(4) The electron wanders through the lattice until it finally comes near the centre.

(5) The electron is finally captured by the centre and in this capture only a small amount of energy is given off as infra-red radiation or as vibrational quanta.

The centre now returns to its original condition and the cycle can be repeated.

The essential difference between the two models is that the former assumes that luminescence results from the capture and subsequent recombination of a conduction electron whereas the latter assumes that luminescence results from the capture and subsequent recombination of a free hole. It is assumed in both the models that levels arise from sulphur ions adjacent to the monovalent activator. However, in the Lambe and Klicks' model the energy required to free an electron from one of these sulphur ions is small.
(iii) **William and Prener's Model**: Based on experiments with ZnS:Cu phosphors in which halide flux was used, William and Prener (52, 53, 54) have suggested a similar type of model which is also known as "Associated donor-acceptor model". This model is particularly applied to ZnS:Cu in which chlorine is used as flux. According to this model, centres having a ground state I (fig.1) near the valence band have a high hole capture probability while the excited state II near the conduction band has a high electron capture probability. After capture has taken place in each type of levels, emission can take place by a transition of the electron from level II to I. The only condition is that the temperature is not too high so that the electrons are not freed by activation from the type II levels before transition can take place. If such centres exist, the probability of radiative capture will be higher than for the other types of centres considered in the other two models. The transition probability will be very sensitive to the amount of overlap between the levels I and II and is essentially determined by the covalent character of the binding. This model has also been used to explain the temperature dependence of fluorescence and photoconductivity by Klassens (55) and steady state luminescence of ZnS phosphors by Ranbade (56).

(iv) **Limitations of Band Model**: If the absorption and emission processes involve transitions between states peculiar to the activator ions and the energy bands of the lattice are not involved directly, the band theory model is not
WILLIAMS AND PRENER'S MODEL.

A- Hole Capture.
B- Electron capture.
C- Transition of Electron from level II to level I giving emission.

FIG. 1.4.
particularly applicable. In other words the band model is
specially suitable for interpreting luminescence phenomenon
involving transport of electrons through the lattice. Thus
the principal limitation of the model is that the energy bands
and levels are characteristic of a particular atomic configu-
ration. The atomic rearrangement that might occur during
luminescence is ignored. Therefore, the model does not indi-
cate the origin of large quantum energy difference for absor-
ption and emission and does not suggest pronounced tempe-
ture broadening of excitation and emission energies. It is clear,
therefore, that the band model and configuration coordinate
model are complementary to each other. For some luminescence
processes one model is more suitable for other processes the
other model is better suited.

5. PROPERTIES OF PHOSPHORS:

(1) Decay Characteristics:

Becquerel (57) began the study of phosphorescence
by measuring how the intensity of phosphorescence glow decreased
with time after excitation had ceased. According to the decay
characteristics, the phosphors are divided into two categories.
With the first type, the decay rate is exponential and is indepen-
dent of temperature, while with the second type of phosphors
the decay is characterised by an initial abrupt drop in bright-
ness, probably exponential followed by a slow power-law decay.

The delay in emission of absorbed energy led the
early workers in developing a physical interpretation of glow
(45,58,59). They attributed this delay to the life time of the
excited state of the luminescence centre. It is generally agreed that the excitation of a crystal phosphor causes electrons or luminescence centre to be excited. Luminescence is then observed when an excited electron recombines with an empty centre. A delay in recombination results in a phosphor having appreciable glow. This is usually so because the electron is trapped somewhere in the crystal and is released only by receiving thermal energy from the lattice. The decay process of the first type of phosphors referred to above could be explained according to these ideas taking into consideration the transition probability for a centre in the excited state and the number of centres excited.

Suppose 'n' is the total number of excited electrons and 'p' is the transition probability for their return to the ground state then the number 'dn' that will return to the ground state in time 'dt' will be:

$$dn = -pndt$$

or

$$\frac{dn}{n} = -pdt$$

or

$$n = n_0 e^{-pt}$$

and since the luminescent intensity is given by -

$$I = \frac{dn}{dt}$$

we have

$$I = I_0 e^{-pt}$$

where

$$I_0 = p n_0$$ (initial intensity)

and

$$n_0$$ denotes the initial number of electrons excited.

This simple kinetics of first order cannot be adopted to explain the decay process of the second type of phosphors.
In this case the delay in emission of the absorbed energy is supposed to be due to the time an electron spends in a trap. Accordingly, the phosphorescence intensity will depend upon the rate of recombination of the freed electrons with the centre.

Suppose 'n' electrons are excited leaving 'n' vacant emission centres. Now, as each electron is free to recombine with 'n' emission centres and there are 'n' free electrons the probability of recombination will be proportional to \( n^2 \) and the intensity of luminescence is then given by -

\[
\frac{dn}{dt} = pn^2
\]

i.e. \( I = \frac{I_o}{(1+at)^2} \)

where \( a = (I_0p)^{1/2} \) and \( I_o \) is the initial intensity.

It is evident from the above equation that the phosphorescence intensity decreases hyperbolically with time and the form of decay depends on the initial value \( I_o \) (60, 61).

Many research workers in this field believe that in a phosphor only one process takes place but with more than a single value of one of the physical constants. The observed phosphorescence is then due to a super-position of intensities. Romanovsky et al. (62) and Urbach et al. (63) have considered the effect of superpositions of bimolecular decays due to continuous distribution of trap depths. Some investigators, however, prefer some kind of monomolecular theory in which the superposition corresponds to traps of different depths (64, 65, 66, 67). To sum up, it is rather difficult to infer specific mechanisms
or processes involved from phosphorescence decay studies. Interpretations in terms of mono or bi-molecular mechanism need only suitable assumptions about the distribution and filling of traps (68).

(2) **Thermoluminescence:**

This process provides an experimental method for determining the distribution in depths of the trapping states. In this method phosphor is first excited at low temperature which is low enough for the traps not to lose their electrons. It is then warmed in dark at uniform rate. However, it has been recently proposed that uniform rate of heating is not necessary (69, 70). The traps empty as the temperature of the phosphor rises. The intensity can then be recorded as a function of temperature of maximum thermoluminescence, the corresponding trap depth can be evaluated as each group of a trap depth gives rise to a separate maximum. The method was first proposed by Urbach (71) but its extensive use is mainly due to the researches of Randall and Wilkins (45, 59), Booth (72), Bohun (73), and Parfianovich (74) have shown independently that by using different warming rates trap depth can be evaluated from the shift of glow peaks. Halperin and Braner (75) have suggested a new method for the evaluation of thermal activation energy by using symmetry of the glow peak. Thermoluminescence equations based on a bimolecular mechanism have been obtained by a number of workers (76, 77).

**Retrapping:** Garlick and Wilkins (78) have found that even under most favourable conditions retrapping is a negligible
process in case of thermal activation. This result has been confirmed by more extensive measurements of Garlick and Gibson (79). However, some interesting evidence for re trapping comes from the experiments of Walter and Curie (80). In any case, it is generally believed that re trapping, thus, takes place on ejection of trapped electrons by long wavelength light (83).

(3) Absorption and Excitation Spectra:

The absorption spectrum of a phosphor shows the absorptions of photons by the host lattice. A set of absorption bands also arises due to transitions of electrons from luminescence centres to the conduction band or from the trap levels to the conduction band. Thus, the absorption limit is set by the width of the forbidden zone. Absorption bands may also occur due to transitions of trapped electrons to higher states. That part of the absorption spectrum which is efficient in exciting luminescence is called excitation spectrum. Usually it is shown in the form of graph of luminescent yield against wavelength of exciting radiation. Willemite and alkali halides activated with thallium possess excitation bands in the vicinity of 2500 Å. Similarly, zinc sulphide phosphors activated with copper and silver possess broad excitation bands in the vicinity of 3600 Å (84). In general, the position of optical excitation bands of luminescent materials show that excitation process has to do with the stimulation of electrons in the active centres. Further, Riehl (85) has postulated that the excited atoms of the material transmit
this excitation energy to one another in a chain like manner which terminates at the activator atom. A mathematical discussion for such excitation process is given by Frenkel (36) and others (37) which supports Riehl's theory.

(4) **Emission Spectra:**

The emission spectra of luminescent materials usually consist of one or more broad bands (39). Examples are known in which these bands are peaked at all parts of the optical spectrum from ultraviolet to infra-red (90,91). The luminescence spectra differ from atomic spectra in two basic aspects as mentioned above. In the first case, band widths of the order of hundreds of angstroms are generally observed and, in the second case, the emitted radiation is displaced to longer wavelengths compared to the absorbed radiation (2). However, it is possible to have an overlap of the long wavelength side of the absorption band and the short wavelength side of the emission band. The width of emission bands depends on the temperature of the specimen becoming narrow at low temperature (92).

The band nature of these materials is explained as due to the interaction between the emission centre and the crystal lattice (93,94). Thus, the emission characteristics are usually related to the structure and composition, valence state and the sites occupied by the activator (95,96).

(5) **Photoconductivity:**

Many luminescent materials become photoconducting
when irradiated with light which stimulates luminescence. It is suggested that, in these cases, certain of the active centres becomes ionised during the excitation process and that the conductivity is related to the presence of the freed electrons, which wander about the lattice until they are trapped by ionised centres (7). As a result of optical excitation, the centre is ionised and the electron is carried to an excited discrete level. Further, the thermal excitation supplies the remaining energy needed to carry the electron into the conduction level. According to this mechanism which is proposed by Mott (98), the photocurrent should disappear at low temperatures when the thermal energy needed to free the electrons ceases to be available. This type of vanishing photoconductivity has actually been observed in the alkali halides containing F-centres.

Since the phenomenon of luminescence is generally accompanied by photoconductivity, it appears that there exists a possible correlation between the two processes. Bube (99) has carried out extensive studies for ZnS crystals with this in view. He found that the decay of luminescence is faster than that of the photocurrent under same conditions of excitation. Further, the variation of photocurrent during excitation is found to exhibit a definite maximum whereas the emission intensity decreases continuously. In the investigations of Haering (100), wherein the applied electric field was increased linearly with time, the conductivity and luminescence displayed a sharp maximum at the same field strength. He showed that this maximum
may be used to obtain trap energy. According to Cook (101), photoconductivity can be explained in calcium tungstate by assuming exponential trap distribution if a variation of capture cross section with temperature is postulated.

6. **ALKALINE EARTH SULPHIDE PHOSPHORS:**

   (1) **Previous Work:**

   These phosphors were first studied by Lenard (102). He used Bi, Cu, Pb, Mn, and rare earths as activators. Randall and Wilkins (45,58) studied these phosphors and interpreted their results in terms of electron traps and trap depths. The studies of A.F.Wells (103) were concerned with the condition and preparation in relation to luminescence characteristics and the role of flux.

   These phosphors show phosphorescence of very long duration. In the case of CaS:Bi phosphors the emission is in the blue-violet region. Rothschild (104) had used two activators. He showed that phosphorescence efficiency could be improved by the addition of a second activator in small concentrations. The study of thermoluminescence curves reveals that each activator gives rise to its own electron trap distribution. However, it is noteworthy that composition of these phosphors is not yet well defined. They usually contain some oxide and sulphate.

   (2) **Present Work:**

   Work is going on in this laboratory on alkaline earth sulphide phosphors. Investigations have been carried out to
determine the optimum conditions for the preparation of efficient phosphors (105,106). Correct firing temperature and firing time for various systems of phosphors have been obtained. Various fluxes have been tried in different combinations and varying concentration (107). The activators chosen so far for this purpose are Bi, Cu, Gd, Sm, Mn, &c. ... Double activator system of CaS : Bi, Mn has also been studied (108). The major properties of these phosphors which are studied here are thermoluminescence and decay characteristics, crystal structure by X-ray analysis, phosphorescence and fluorescence spectra.

Zirconium, which is a transitional element and in this respect resembles other activating elements used so far, appeared to present interesting results. Moreover, very few references of Zirconium as activator are available. So it was decided to investigate calcium sulphide phosphors activated with Zirconium. In this work the following characteristics of these phosphors are being presented.

1. A number of samples with varying concentration of activator were prepared.

2. Photographs of fluorescence and phosphorescence spectra for all the samples were taken.

3. Intensities of the emission bands were measured by photographic-photometric method.

4. Peak intensity and peak wavelength of each band was evaluated.

5. Decay characteristics of the composite emission were studied on an apparatus designed and fabricated in
this laboratory.

6. Decay characteristics of the individual bands were studied on the spectrograph.

These studies reveal only a few aspects of this phosphors system. Work is in progress as regards the other aspects, namely thermoluminescence and crystal structure by X-ray analysis.
REFERENCES

1. D.L. Dexter,
   J. Chem. Phys. 21, 336, (1953)

2. D. Curie,
   "Luminescence in Crystals", Translated by

3. G.F.J. Garlick,

4. F. Perrin,
   Ann de Phys. 12, 169, (1929)

5. H.W. Leverenz,
   Science, 109, 133, (1949).

6. P. Pringsheim,
   "Fluorescence and Phosphorescence",

7. J.T. Randall,

8. N.F. Mott, and R.W. Gurney,
   "Electronic Processes in Ionic Crystals",
   Clarenden Press (1948).

9. H.W. Leverenz,
   Cornell Symposium 146, (1943).

10. R. Peierls,

11. W.A. Ruciman,

12. C.C. Klick,
13. G. J. Garlick,
14. S. J. Vavilov,
    T. Physik, 22, 266, (1924).
15. Y. L. Levshin,
16. R. Tomasechek,
    Reichsber d. Phys. 1, 139, (1944).
17. S. Rothschild,
    Naturwiss 20, 850, (1932).
18. K. H. Butler,
19. G. R. Fonda,
20. R. Leach,
21. D. L. Dexter,
22. D. L. Dexter and J. H. Schulman,
23. J. H. Schulman, J. Gunther, and C. C. Alick,
24. T. F. J. Botden,
25. H. Haken,
26. Yu. V. Konobeev,
27. I. Broser, and R. Broser-Warminsky, 
28. M. Balkanski, 
29. J. Ewles, and N. Lee, 
30. P.D. Johnson and F.E. Williams, 
31. D.L. Dexter and J.H. Schulman, 
32. A. von Hippel, 
33. F. Seitz, 
34. C.C. Klick, and J.H. Schulman, 
35. P.D. Johnson and F.E. Williams, 
36. D.L. Dexter, C.C. Klick and G.A. Russel, 
37. G.A. Russel and C.C. Klick, 
38. H. Schon, 
39. F.E. Williams, 
41. P.D. Johnson and F.E. Williams,
42. D.A. Patterson, and C.C. Klick,
43. F. Bloch,
    Z. Physik, 52, 555, (1923).
44. F. Seitz,
45. J.T. Randall and M.H.F. Wilkins,
46. H.A. Klasens,
47. H.A. Klasens, W. Ramsden, and C. Quantie,
48. R.H. Bube,
49. H. Kalman and B. Kramer,
50. K.O. Mckay,
51. J. Lambe and C.C. Klick,
52. J.S. Prener and F.E. Williams,
53. E. F. Apple and F.E. Williams,
54. F.E. Williams,
55. H.A. Klasens,

56. K.S.K. Ramnani,

57. E. Becquerel,

58. J.T. Randall and M.H.F. Wilkins,

59. G.F.J. Garlick and M.H.F. Wilkins,

60. V.V. Antonov-Romanovsky,

61. W. De Groot,

62. V.V. Antonov-Romanovsky,

63. F. Urbach, N.R. Nail and D. Pearlman,

64. F.E. Williams and H. Eyring,

65. R.H. Bube,

66. D. Curie,

67. J. Soddy,

68. M. Curie and D. Curie,
69. Tech. Louchtchik and F.H. Zaitor,

70. M. Schon,
       Techn. Wiss. Abhandl. der. Osramstudiengesellsch
       aft. 7, 175, (1953).

71. F. Urbach,
       Wien Ber II A. 135, 149 (1926)
       139, 363 (1930).

72. A. H. Booth,

73. A. Bohun,

74. I. A. Parfianovitch,

75. Halperin and A. A. Brauer,

76. A. A. Wrzesinska,

77. I. Broser and R. Broser-Warminsky,

78. G. F. J. Garlick and A. H. F. Wilkins,

79. G. F. J. Garlick and A. F. Gibson,

80. J. Malter and H. Curie,

81. B. Goldstein and J. J. Dropkin,
82. Yu. L. Lukantsever and F.N.Zat'tov,
83. G.F.J. Garlick and D.Z. Manson,
84. F.Seitz,
85. N.Riehl,
86. I.Frenkel,
87. G.Wannier,
88. F.Urbach, H.Hammendinger, and D.Pearlman,
89. J.T.Randall,
90. G.R.Fonda and H.C.Frolich,
91. H.Stanley and F.E.Williams,
92. D.A.Patterson and C.C. Klick,
93. C.C.Valm,
94. G.F.J.Garlick,
95. F.J.Studer and G.R.Fonda,
96. F.E. Williams,

97. F. Seitz,

98. N.F. Mott and R.W. Gurney,
    Electronic Processes in Ionic Crystals (1948).

99. R.H. Bube,

100. R.R. Haering,

101. J.R. Cook,

102. P. Lenard, F. Schmidt and R. Tomaschek,
    Handbuch der Experimental Physik, 23, (1928).

103. A.F. Wells,
    "Luminescent Materials" by G.F.J. Garlik,

104. S. Rothschild,

105. K.C. Chandy,
    Thesis accepted for Ph. D. degree, University of
    Saugar (India), 1956.

106. V.R. Rao,
    Thesis accepted for Ph.D. degree, University of
    Saugar (India), 1960.

107. Y.N. Khare,
    Thesis accepted for Ph.D. degree, University of
    Saugar (India), 1963.

108. N.H. Joshi,
    Thesis accepted for Ph.D. degree, University of
    Saugar (India), 1963.