CHAPTER II

LUMINESCENCE

2.1 ELEMENTARY CONCEPTS :

The key to luminescence is the propensity of electrons in atoms to jump from one energy state to another. Upon absorbing a quantum of energy from some outside source, an electron jumps to a higher, or "excited" state. It may then jump back to its original state, re-emitting the absorbed energy. In a luminescent system, part of this energy is emitted as light. The process is however, complex and certain conditions must be met to make the electron jumps produce light (luminescent radiation) rather than merely heat or other radiations. In contrast to equilibrium thermal radiation, luminescent radiation is not of an equilibrium nature. It is initiated by a comparatively small number of atoms. The quality and quantity of luminescent radiation are strongly dependent on the nature of the emitting material, whereas, in the case of thermal radiation, these depend chiefly on the temperature rather than on the nature of the emitting solid material. Thus 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 luminescent emission is greater than 10^{-9} sec.. while the Raman and Compton effects are completed in a time of about 10^{-14} sec. or less..

a) TYPES OF LUMINESCENCE :

Since the energy radiated by a system must be provided in some way, excitation of the lumenescent substance is prerequisite to luminescent emission. The various types of luminescence can be classified according to the means by which energy is supplied to excite the luminescent molecule.. When molecules are excited by interaction with photons of electromagnetic radiation, the form of luminescence is called "photoluminescence". If the excitation energy is obtained from the chemical energy of reaction, the process is "chemiluminescence". In "bioluminescence" the electromagnetic energy is released by organisms.. "Triboluminescence" is produced as a release of energy, when certain crystals are broken. The energy stored on crystal formation is released in the breaking of the crystal.. Luminescence due to bombardment of electrons is called "cathodoluminescence" ; that caused by the application of an electric field to matter is called "electroluminescence" ; that caused by the excitation with α - particles or ions is "ionoluminescence" ; "sonoluminescence" depends on the ultrasonic radiation in liquids ; and so on.

However, there is a considerable confusion in the nomenclature of luminescence. For instance, in the case of "thermoluminescence", the prefix "thermo" confusingly implies luminescence excited by heat ! Actually it has been used to denote phosphorescence obtained at various temperatures. Similarly the word "radiophotoluminescence" does not describe a mode of excitations but a sequence of processes which includes the creation of luminescence response in a non-luminescent material. That is, if stable colour centres are created by high energy radiation or fast particles, they may also act as luminescence centres when they are subsequently excited by appropriate optical frequency radiation. This is the situation described by the term "radiophotoluminescence", the radiation induced creation of new centres that are photoluminescent. Thus although they are part of the vocabulary, excessive significance should therefore be not attached to terms like the foregoing . The features common to all forms of luminescence are ; (a) excitation of the electronic system of an atom, molecule or "centre" to a higher energy state ; and

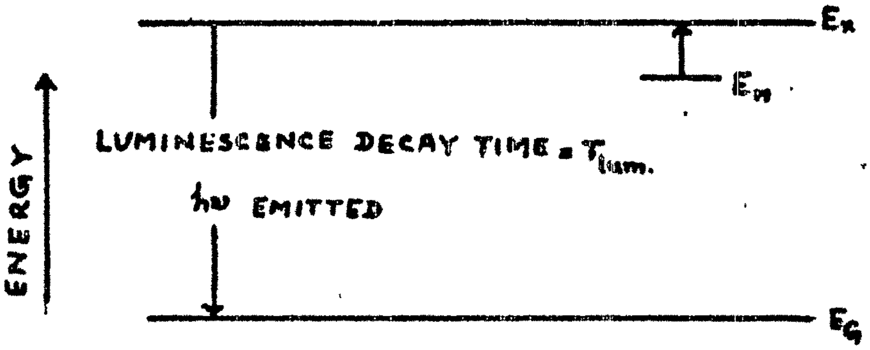
(b) the subsequent emission of photons of appropriate energy after the lapse of some period of time.

b) FLUORESCENCE AND PHOSPHORESCENCE :

The general phenomena of luminescence have been classified, according to the duration of the emission following removal of excitation; viz, fluorescence and phosphorescence. In the old literature fluorescence and phosphorescence were distinguished only by the criterion of an observable "afterglow",("persistance", "decay-time"). If the luminescence did not last longer than the irradiation, it was called fluorescence ; if it was visible for an appreciable length of time after the excitation ceases, it was called phosphorescence. Modern experimental techniques, however, permit the measurement of the finite duration of any emission process, even if it is as short as 10^{-9} sec. and on the other hand, the spontaneous transition probabilities, even in atomic processes, correspond to lifetimes which may continuously vary from 10^{-8} sec. to several seconds. Thus in the present state of knowledge and experimental technique, the duration of the emission process does not supply an unequivocal method of distinction between fluorescence and phosphorescence.

Thus the demarcation between fluorescence and phosphorescence according to old literature is quite arbitrary. The two terms can be distinguished more significantly by considering the temperature - - dependence of the luminescence decay - time , T_{lum}. Thus if luminescence is due to the spontaneous transition of a system from the excited state E_x to the ground state E_G (Fig. I), the luminescence will decay exponentially, the decay time depending on the transition probability. If it is an allowed electric dipole transition, the decay time is of the order of 10^{-8} to 10^{-9} sec. If the probability of transition $E_x \rightarrow E_G$ is of many orders of magnitude lower as in the case of electric quadrapole transition, magnetic dipole transition etc., the decay time increases. Here again the luminescence decays exponentially with time and is independent of temperature (in the range of temperature where the luminescence efficiency remains high). All the above cases are properly characterised as fluorescence, the "allowed" transition producing "fast" fluorescence" while the relatively "forbidden" transitions producing "slow" fluorescence. When the luminescence decay time depends upon the temperature

ENERGY LEVELS OF A SYSTEM



E_X = AN EXCITED STATE FROM WHICH SPONTANEOUS RADIATIVE TRANSITION CAN OCCUR WITH HIGH PROBABILITY

E_M = AN EXCITED STATE FROM WHICH A RADIATIVE TRANSITION IS "FORBIDDEN"

E_G = GROUND STATE

FIG. I

even in the temperature range where the luminescence efficiency is high, the luminescence can be most properly termed as "phosphorescence". This situation can arise on an atomic scale, (Fig. I), when an atom, molecule or centre is somehow excited to an energy level E_M (metastable) from which the transition $E_M \rightarrow E_G$ is completely or largly forbidden by the selection rules. Let us suppose that E_x is a higher excited level. The system can be raised to E_x by the absorption of energy ΔE, where $\Delta E = E_x - E_M$. The radiative transition $E_x \rightarrow E_G$ is an allowed one, (Fig. I). In such a case, if the energy $\Delta E_{absorbed} = E_x - E_M$ is provided to the centre the energy $\Delta E_{emitted} = E_x - E_G$ will be emitted. $\Delta E_{absorbed}$ can be provided by thermal means at room temperature, for example, in the case of a crystalline system, by absorption of phonons from the lattice, or by photons, for example absorption of infra - red light. In the above cases, a continuing luminescence can be observed even after the excitation source is removed. This emission will continue with diminishing intensity until there are no longer any centres in the E_M state. If the system is raised to higher temperature, the energy $\Delta E_{absorbed} = E_x - E_M$ will be provided at a more rapid rate. Consequently, the phosphorescence will be brighter and the decay time will be shorter due to the faster depopulation of the metastable state via the path

$$E_M + \Delta E_{\text{absorbed}} \rightarrow E_X \rightarrow E_G + h\nu_{\text{emitted}} .$$

On the other hand, on lowering the temperature, opposite effects will be produced, namely, a decrease in phosphorescence brightness and an increase in the decay-time. Thus the temperature dependence of the decay-time is the important difference between fluorescence and phosphorescence.

In attempts to classify luminescence with respect to temperature, the term "thermoluminescence" or temperature stimulated light emission following removal of excitation is used to denote merely phosphorescence obtained at various temperatures. In the usual thermoluminescence experiment the system is excited at a temperature at which the phosphorescence intensity is low (long decay time); then heated through a temperature range where the phosphorescence is bright (very short decay time), until a temperature is reached at which all the centres have been thermally excited out of their metastable level and the luminescence completely disappears.

If the energy $\Delta E_{absorbed} = (E_X - E_M)$ is provided by light absorption, the system exhibits the phenomenon of "optically stimulated" luminescence. This terminology is not to be confused with the stimulated emission involved in laser action. In the optically stimulated emission referred to here, the stimulated light is of different frequency.

$$\left(\nu_{stimulated} = \frac{E_X - E_M}{h} \right)$$

from that of

$$\left(\nu_{emitted} = \frac{E_X - E_G}{h} \right), \text{ and}$$

the emission is incoherent.

c) TRAPS AND TRAPPING MECHANISM :

Trapping is a fundamental process for energy storage. Those regions of crystals which are able to capture electrons and holes and detain them in a restricted locality are called traps(24-26). By absorption of an optimum amount of thermal or optical energy, a trapped electron or hole is released and it is free to move until it is either captured by a centre or re-trapped. Capture by a centre is followed by a transition to ground state by either a radiative or non-radiative process releasing the stored energy. Traps may be classified into two main types :

i) Traps associated with particular impurities : In this case trapping involves a change in the effective valence of the impurity ion.

ii) Traps associated with defects in the crystal. It is the result of the formation of regions with an excess positive charge (electron traps) or negative charge (hole traps) surrounding the defects.

Production of traps in a given phosphor depends on (i) Presence of impurities(27, 28) (ii) Temperature of preparation(27) (iii) Atmosphere during preparation(29).

d) LUMINESCENCE CENTRE :

The localities in a phosphor where energy is re-emitted after absorption are called luminescence centres(30, 31). These localities contain ions or groups of ions which possess levels in which luminescence transitions take place. Crystal lattice defects such as vacancies and impurities act as luminescence centre. The impurity centres are created in phosphors as a result of inclusion of some foreign constituent known as "activator". In most of the luminescent systems the activators are incorporated by heat treatment(32). The activators are supposed to provided necessary shielding for the absorbed energy which would otherwise be dissipated in the form of thermal vibrations(33).

In the luminescence centre, the probability of radiative transition is more. If the probability of non-radiative transition is more, then it is known as a "killer-centre".

e) IMPERFECTIONS IN CRYSTALS :

Imperfections present in crystals profoundly affect their luminescent properties. The most important defects are interstitial ions, vacant lattice sites, impurities and dislocations. The concentrations of various imperfections are independent of each other. In the case of pure stoichiometric compounds like MX, where M stands for alkali metal and X for halogen, usually five types of disorders can be distinguished(34-36).

i) Interstitial sites occupied by atoms M (or ion M_i) together with equal concentration of vacancies from where M atom has been removed.

ii) Interstitial sites occupied by atoms X (or ion X_i) together with equal concentration of vacancies from where X atom has been removed.

iii) Vacant M sites together with equal concentration of vacant X sites.

iv) Interstitial M_i together with equal concentration of X_i .

v) Part of atoms M occupy X position and an equal number of X atoms occupy M position.

The first and the second types are called Frenkel disorder, the third type is called Schottky disorder, fourth is rare and fifth is antistructure disorder.

f) CONCENTRATION QUENCHING :

The increase in activator concentration usually increases the luminescence efficiency until an optimum concentration is reached. Any further increase in the concentration of activator may decrease the luminescence efficiency until the emission is quenched. This phenomenon of concentration quenching has been explained by assuming that an activator centre is non-luminescent if there is another centre at the nearest point of the surrounding lattice(37-39). The value of the parameter differs from one phosphor to another. It is defined as the number of lattice positions (whether substitutional or interstitial or both surrounding the given activator) such that if any of these sites is occupied by another activator, the luminescence is quenched.

According to the assumption of Dexter and Schulman(40), the degradation of energy occurs at special quenching sites in the crystal. Quenching has been attributed to resonance transfer of energy from one activator to another until it arrives at an activator near one of the energy sinks. Activator quencher transfer then occurs and the energy is lost. Dexter and Schulman also proposed that the absence of luminescence in most unactivated pure crystals is the result of rapid resonance transfer of excitation energy to imperfections and impurity quenchers.

2.2 THEORETICAL MODELS FOR INTERPRETATION OF LUMINESCENCE PHENOMENA :

To explain the phenomenon of luminescence different models have been proposed. A short resume of these models is given below : 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 to each other in explaining the 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.

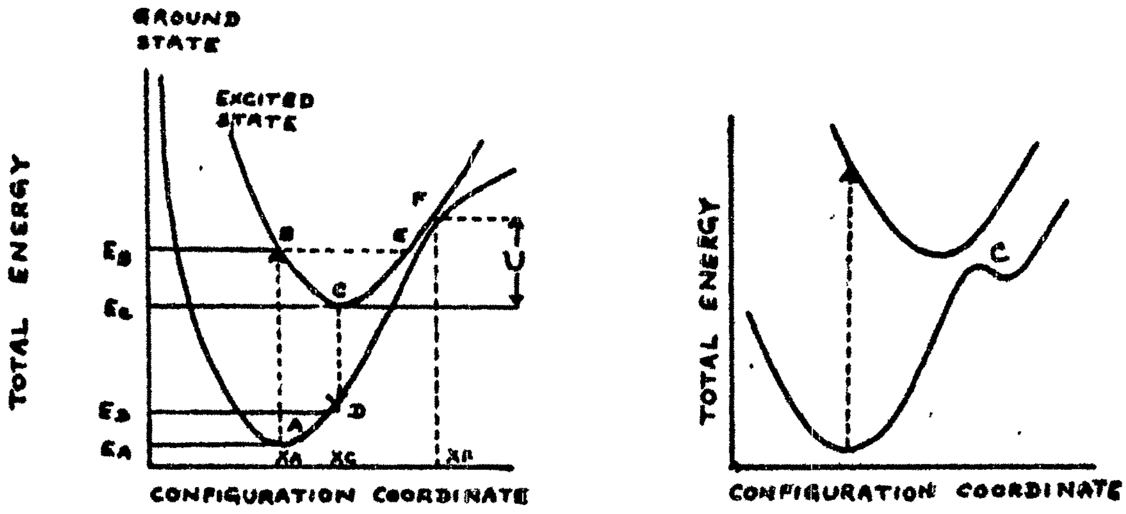
a) CONFIGURATION COORDINATE MODEL :

In the photoluminescence of solid systems, the emitted light generally is of longer wavelength (lower energy) than the exciting light. This condition was first experimentally noted in 1852 by G.Stokes and is known as Stoke's law. Moreover, the luminescence spectra of solid phosphors generally consist of broad bands (having widths of a few tenths of an electron-volt) in contrast with those of dilute gaseous atomic systems which consist of sharp lines. These properties together with other properties connected with the temperature dependence of luminescence efficiency of phosphors, may be understood by consideration of so-called "configuration coordinate diagrams" .

The configuration coordinate model was originally proposed by von Hippel(41), but Seitz(42) applied this model to explain the characteristic luminescence processes.

A configuration coordinate diagram represents the potential energy of the various electronic states of the centre in terms of a single coordinate that characterizes the centre. For example, if the centres were vibrating diatomic molecule, the configuration coordiante diagram would be identical with the ordinary potential energy diagram, in which the potential energy of the molecule in the ground state and in the various electronically excited states is plotted as a function of the intranuclear distance. In this case the intranuclear distance would be the "configuration coordinate".

Consider the case of a more complex centre, e.g. a centre consisting of a central positively charged impurity ion and its nearest shell of anion neighbours in a solid. There are several modes of vibration of the centre. If it is assumed that one of these modes is one which has the greatest influence on the energy of the centre, the configuration coordinate can be taken as the distance between the central ion and one of its equidistant anion neighbours. Fig. II(a) shows the configuration coordinate diagram of such a centre. The potential energy of the system in its electronic ground state is represented by the minimum of the lower curve. The minima occurs at the equil~~l~~ibrium separation between the central ion and its neighbours. Above absolute zero temperature, thermal vibrations will cause displacements from the equil~~l~~ibrium positions (of the order of KT) The upper curve shows the potential energy of the first electronically excited state of the centre. The top curve has comparatively less curvature, because the interatomic forces in the excited state are generally weaker than those in the ground state. Its minimum is also generally displaced with respect to the minimum of the ground state curve.

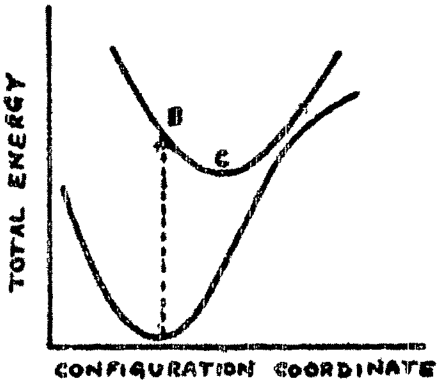


CONFIGURATION - COORDINTE MODEL

(a)

SEITZ - MODEL

(b)



DEXTER, KLICK AND RUSSEL MODEL

(c)

FIG. II

It is assumed that there also exist discrete quantum states of the lattice (vibrational states) when the electronic system is in its ground state or in its excited state. Such an assumption is justified within the framework of Born-Oppenheimer or adiabatic approximation. Physically one assumes that the electrons move in a potential well determined by the actual positions of the neighbouring ions, whereas the equilibrium positions and vibrational states of the nuclei are determined by the average positions of the electrons and so depend only upon the electronic state. The construction of different shapes and equilibrium positions of the configuration coordinate curves merely reflects these assumptions.

With the aid of these features, one can describe the luminescence process as follows : When the centre is excited by the absorption of a photon, the average electronic distribution is changed and after sufficent time the ions move to new equilibrium positions. According to the Frank-Condon principle an electronic transition occurs in a time interval so short that the ions are unable to move, i.e. the transition occurs with no change in the configuration coordinate of the ions.

In Fig. II(a) absorption will occur between point A, the ground state equilibrium position and point B, the point on the excited state curve with the same configuration coordinate X_A . A photon must have the energy ($E_B - E_A$) to produce this excitation. The system at B is now in a state of excitation with energy ($E_B - E_C$) in excess of the equilibrium energy E_C . The nuclei then move to new equilibrium coordinate X_C with the loss of an amount of energy ($E_B - E_C$). This energy appears as heat, i.e. as lattice vibrations. From point C the system can jump to D with the emission of a photon of energy ($E_C - E_D$) . The centre then loses an amount of energy ($E_D - E_A$) in the form of heat as it relaxes from D to A . Since energy is lost as heat, it is obvious that ($E_B - E_A$) is greater than ($E_C - E_D$) (Stoke's Shift).

An experimental fact that some systems luminesce only at low temperatures can be understood with this model. When the system in the ground state or excited state can be characterized by a high vibrational quantum number, it is easy to show that the nuclei will be localized in the vicinity of the end points of the oscillations. For example, these points are at B and E in the excited state. If the ground and excited state curves have the same energy E_F at some configuration coordinate X_F, the system can go from the excited state to the ground state by a radiationless transition as it loses energy towards E_C. This transition will occur at the configuration coordinate X_F. Such a situation is indicated in Fig. II(a). Increase of temperature provides the activation energy U ($= E_F - E_C$) required for a radiationless transition of the system from the excited state to the ground state of X_F. This decreases the efficiency of luminescence and is the so called "thermal quenching" of luminescence. The probability of such a transition P_{diss} is proportional to $e^{-U/kT}$, while the radiative transition probability, P_{lum} is independent of temperature. The quantum effeciency of luminescence is

$$\eta_{lum} = (1 + const\ e^{-U/kT})^{-1}$$

Thus the non-radiative transition is favoured by an increase and the radiative transition by a decrease of temperature. From the measurement of quantum efficiency as a function of temperature one can obtain the activation energy U. A good activator has a high value of U. When the doping agent or defect has a low value of the activation energy the absorbed energy is easily degraded as heat, and the centre is called a "Killer - - centre" or poison.

Seitz(42) modified the model which helps to explain the radiationless transition. According to him, the system after excitation relaxes to such an extent (Fig. II(b)) that its minimum C lies outside the ground state curve and this increases the probability of non-radiative transition.

The other model (Fig. II(c)) was proposed by Dexter et al(43). In this model the energy dissipated during relaxation is less than that dissipated according to the Seitz model and systems come quite close to the ground state from where the radiative transfer is not possible. In fact this model along with its few quantum mechanical modifications successfully explains : (i) Stoke's Shift (ii) Width of absorption and emission bands at low temperature (iii) Thermal quenching of luminescence and other temperature effects (iv) Mono-

-molecular decay (v) F-centre luminescence (vi) sensitization processes in doubly activated solids(44). Its limitations are : (a) It can not be applied to the processes occuring between absorption and final emission, e.g. photoconductivity (b) Because of the configurational difficulties, it is difficult to have precise configuration coordinate diagrams in most cases(13,45) on theoretical considerations only.

b) CONTINUOUS DIELECTRIC MODEL :

This model removes the defects of the above model by considering the interactions between the centre and the lattice as of a short-range type. Huang and Rhys(46) have proposed a theory where they treated the lattice as a continuous dielectric in which the centre is embedded and considered long range interactions, electrical in nature. In absorption, the centre experiences a difference in charge distribution resulting in a change in lattice polarisation which is accompanied by the creation of lattice phonons. Extension and refinement of this work has been carried out by Lax and Burstein(47), Pekar(48), O'Rourke(49) and Meyer(50).

c) ENERGY BAND MODEL :

Bloch's(51) collective electron model for the energy state of a perfect crystal lattice was extended to explain the long duration phosphorescence of sulphide and silicate phosphors by Riehl and Schon(52) and independently by Johnson(53). According to this model, when atoms are arranged in an orderly way to form a crystal lattice, its closely packed atoms interact with one another. Thus one must think of electrons as occupying a band of energy levels, instead of the single, sharply defined energy level of an electron in an isolated atom. Nevertheless, just as a single electron in an atom is permitted only certain energy levels and is forbidden any intermediate energies, so there is a forbidden band of energy values which cannot be occupied by any electrons(54). When the crystal is unexcited, the lowest energy band is completely filled with electrons. If exciting energy is supplied to the crystal, some of the electrons will jump this band across the forbidden band just above it into a permissible higher band. Now if an electron jumps back to thelowest band, it will emit energy, but not in the form of light. The quantum of energy required for a jump from one level to another depends on the width of the gap, and the size of the quantum determines the frequency, or wavelength, of the radiation emitted : the bigger the quantum, the higher the frequency. In this case the gap across the forbidden band is so wide that an electron jumping back to the lower band emits its energy at a frequency in the ultraviolet region rather than in the lower frequency region of visible light.

But one can narrow the gap. Suppose one inserts a new rung within the forbidden zone to shorten the step for the jumping electrons. This can be accomplished by introducing a few activator atoms into the crystalline solid. An energy level permissible to activator electrons lies within the normally forbidden gap. If an activator electron is excited to a higher energy level, it leaves a vacancy which can be filled by an electron droping from the higher band. The drop to this level is short enough - - that is, the quantum is of the right size - to produce emission of light. The electron berths provided by the activator atoms are therefore called luminescence centres.

There are other holes, within the forbidden band and close to the higher energy band, into which electrons may fall. They are called traps. Electrons falling into traps generate only heat, but they are easily excited out of the traps and then can fall into empty luminescence centres, producing light.

The localized energy levels can be classified into two catagories : (i) the levels which belong to the activator itself (ii) the levels which belong to the host atoms which are under the perturbing influence of the activators. In terms of the energy band picture of Fig.III —Let G and A be two levels corresponding to an activator atom. In the ground state of the activator atom, level G is occupied, whereas in the excited state level A is occupied. The excitation from G to A may be accomplished in at least three ways as given below :

i) It is possible that the incident photon of proper frequency is absorbed directly by the electron in the level G, whereupon it arrives in A (Fig. III(a)).

ii) The study of the optical and electrical properties of solids like alkali halides indicate that they are to be described as typical insulators in the band picture of solids with a forbidden band gap of the order of 10 e.v. When an alkali halide crystal absorbs light in the far ultra-violet, an electron is liberated from the valence band into the conduction band. This corresponds to the removal of an electron from a halide ion, because the valence band arises from the valence electrons of the halide ions. This deficiency of an electron is called a hole. The freed electron and the resulting hole are both free to move in the crystal. If the centre AG is in the ground state, the level G may capture a hole from the valence band. In this way, excitation of the centre may be achieved (Fig. III(b)).

iii) If the radiation is not sufficiently energetic, it does not completely separate the electron and the hole, but they remain bound to each other by coulomb attraction. This situation arises when an alkali halide crystal absorbs light in the longest wavelength ultraviolet bands. The electrically neutral entity thus formed is an excited state of the crystal, transporting energy but no net electrical charge. The "mobile" particle consisting of an electron bound to a hole is called an "exciton" and the energy states corresponding to such a configuration are called exciton states. These states are shown in Fig. III(c). The exciton states can be considered to arise from a process wherein light absorption transfers an electron from a halogen ion to an adjecent alkali ion. The electron on the alkali ion and the hole on the halogen ion remain bound to each other by coulomb forces and the bound pair can migrate by the movement of the electron and hole to adjecent alkali and halogen ions respectively. During migration, if an exciton reaches an activator centre such as AG in Fig. III(a), it may give off its energy to the centre which would raise the electron of the activator from the ground state to the excited state. Thus the energy can be transferred from the exciting source to the impurity via the host crystal.

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

2.3 TYPES OF LUMINESCENT SYSTEMS :

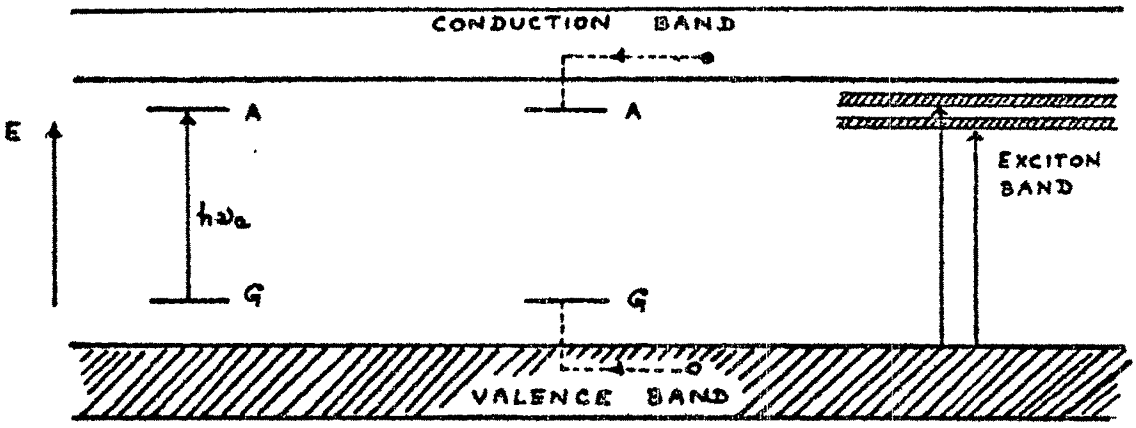
Luminescent systems have been classified into following catagories :

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

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

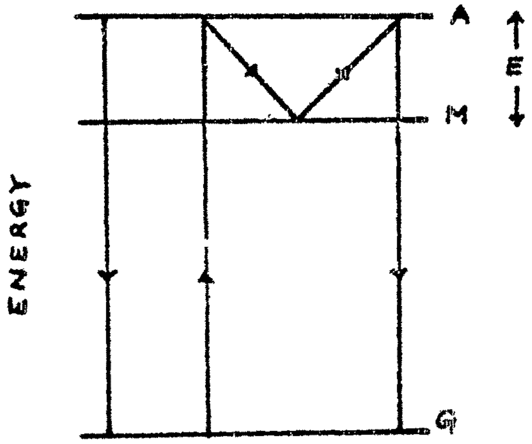
iii) Systems in which transfer of energy is predominently by the movement of charge carriers.

(i) Such systems are best treated by the configuration coordinate model and the continuous dielectric model. The centres involved are localized ones and the entire emission process is best represented by the simple diagram (Fig.. IV). The diagram was originally proposed by Jablonski. Absorption of exciting radiation by a luminescence centre raises an electron into the excited state A.. It may then either return directly to the ground state G with the emission of luminescence (fluorescence) or it may fall into the metastable state M lying just below A. In the latter case a rearrangement of the atoms of the centre takes place. The transition M → G is usually forbidden.. Thus electrons in metastable state can return to the ground state only if they are first raised into the excited state by receiving sufficient thermal energy or by absorption



(a) (b) (c)

FIG. III



JABLONSKI'S DIAGRAM

ILLUSTRATING FLUORESCENCE AND

PHOSPHORESCENCE MECHANISMS

FIG. IV

of long wavelength radiation. For the case of thermal excitation the probability of the transition M → A per unit time is given by

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

where S is a constant having the dimensions of frequency, E is the energy separation between the levels M and A , k is the Boltzmann's constant and T is the absolute temperature(55).

(ii) There are three different mechanisms of such a transfer :

a) 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. (3) The absorption band associated with Y must be of appreciable intensity. We shall then call X and Y as the sensitizer and activator respectively. If X is an impurity we speak of impurity sensitization and if it is the host lattice itself we speak of host sensitization.

The short-wave emission band determined by the sensitizer X may overlap the excitation band of Y which determines an emission band located at longer wavelength Under these circumstances, an internal cascade process may occur, whereby the luminescence emission associated with X is absorbed in the phosphor and excites luminescence emission associated with Y. In inorganic solids, one frequently deals with the activators having forbidden transitions where condition (3) is not usually satisfied.

b) RESONANCE TRANSFER :

Resonance transfer involves excitation, without ionization, of an atom which passes its excitation energy on to a neighbouring atom or centre when there is a sufficient overlap of the ψ's of the atoms (centres). Resonance transfer should occur without energy degradation for example, without energy loss as heat. 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 constant 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 radiation absorbed by X.

The efficiency of energy transfer from sensitizer to activator is not strongly dependent upon temperature, in general. The dependence of transfer efficiency on sensitizer 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(56,57,58).

c) EXCITON MIGRATION :

Another transfer process in which an electron on sensitizer X returns to its ground state, can be described in two stages : (1) The return of an electron on X creates an exciton which diffuses to Y. (2) The exciton is absorbed at Y and raises an electron into the excited state. This process being sensitive to the presence of surface states, transfer over large distances is possible only in the case of pure and defect-free crystals at low temperatures(59-62).

(iii) Energy can also be transferred from one point to another by the movement of charge carriers. Three different models have been proposed for such systems.

a) SCHON-KLASEN'S MODEL :

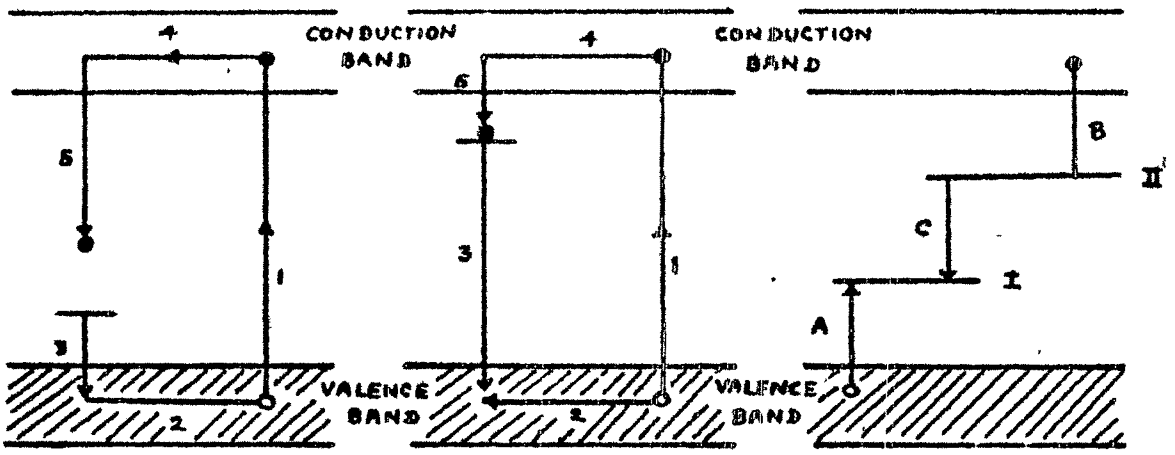
According to this model, the incorporation of an impurity produces a level in the forbidden energy band situated close to the valence band, which has a high probability for hole capture. The model is illustrated in Fig. (V(a)) for the case when excitation of luminescence is by absorption of light in the fundamental band of the host lattice. The sequence of events is as follows : (i) Light is absorbed in the fundamental absorption band producing a free electron and hole and leading to photoconductivity (ii) The hole diffusing through the valance band is immediately captured by the centre giving off a small amount of energy as infra-red radiation or as vibrational quanta. (iii) The electron wanders through the lattice until it finally comes near the centre . (iv) The electron is captured by the centre giving rise to luminescence. This model successfully explains the effect of poisons, variations of luminescence colour with temperature of some phosphors, the non-linear relationships between luminescent output and the exciting intensity and other similar phenomena(63,64,65).

b) LAMBE - KLICK MODEL :

Due to the failure of the Schon - Klasen's model to account for the difference in decay constants of phosphorescence and photoconductivity, Lambe and Klick proposed a somewhat different model which is illustrated in Fig. (V(b)). It differs from Schon - Klasen's model in that the trapping of the hole by the centre is considered to a large energy transition and is assumed to give rise to luminescence. Hole is captured near the impurity centre lying slightly below the conduction band and luminescent emission occurs leaving the centre now neutral in charge. The electron wandering through the lattice is finally captured by the centre, and in the capture only a small amount of energy is given off as infra-red radiation or as vibrational quanta. Increase in photoconductivity by infra-red radiation and stimulation of activator emission by radiation in the quenching band are also explained by this model(66-70).

c) WILLIAMS - PRENER MODEL :

Prener and Williams(71-77) pointed out that activators and co-activators are to be recognized as acceptors and donors respectively, the simultaneous incorporation of activator and cooactivator results in the transfer of an electron from donor to acceptor, giving rise to their compensated states. They considered that the association of activator and co-activator is necessary for the appearance of luminescence, and proposed that the luminescent transition is from the excited state (II) of the donor to the ground state (I) of the acceptor in an associated pair at second nearest or third nearest neighbour sites Fig. (V(c)). 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 the transition can take place. This model successfully explains the temperature dependence of fluorescence and photoconductivity and also the steady state luminescence.



SCHON-KLASEN'S MODEL

1 - EXCITATION
2 - HOLE MIGRATION
3 - HOLE CAPTURE
4 - ELECTRON MIGRATION (NON-RADIATIVE)
5 - ELECTRON CAPTURE RESULTING IN LUMINESCENCE

(a)

LAMBE-KLICK'S MODEL

1 - EXCITATION
2 - HOLE MIGRATION
3 - HOLE CAPTURE RESULTING IN LUMINESCENCE
4 - ELECTRON MIGRATION
5 - ELECTRON CAPTURE (NON-RADIATIVE)

(b)

WILLIAMS-PRENER MODEL

A - HOLE CAPTURE
B - ELECTRON CAPTURE
C - TRANSITION OF AN ELECTRON FROM LEVEL II TO LEVEL I GIVING EMISSION

(c)

FIG. V