

CHAPTER ONE

SOLID STATE LUMINESCENCE

CHAPTER ONESOLID STATE LUMINESCENCE1-1 INTRODUCTION:

The first luminescent material was synthesised by Casciarola in 1603 by heating barium sulphate with coal. However, the actual systematic study of luminescence began in 1887, with the work of E. Becquerel (1). In 1889, Weidmann (2) gave the first definition of luminescence while Stokes in 1852, gave the first law in this field. Later Mott and Gurney (3) proposed theories to explain the phenomenon. However, a novel interest in the field arose with the theoretical contributions of Randall and Wilkins (4) and Garlick and Gibson (5). After that there has been a dramatic progress in the field of luminescence. Now there are forty eight phosphors, which have been indexed (7) and are being used in colour TV, black and white TV, radar tubes, image intensifier tubes, voltage dependent colour displays, flying spot pick-up, beam indexing tubes, projection systems, printing systems and infra red stimulation. The youngest branch of luminescence is electroluminescence (EL). There is a wide variety of applications of EL and are summarised by Lowry (8). A few important of them are EL lamps, colour display panels light emitting diodes, semiconductor lasers, and image intensifiers.

The rapid development of the luminescence field is not entirely due to the technological utility of the phosphors but also due to its importance in the basic research. Various

theoretical models so far proposed in the field of luminescence are helpful in understanding the electronic processes involved in solids at the atomic levels. Not only that, but these are being used to refine and to test the validity of various theories proposed in other branches of science.

1-2 DEFINITIONS:

1-2.1 Luminescence:

In the literature, the term luminescence has been defined in different ways (2,6,9). In general, the absorption of energy in matter and its re-emission as visible or near visible radiation is called luminescence. The emitted radiation is non-thermal in origin (9) and is to be distinguished from Raman, Compton, Raleigh Scattering and Cherenkov radiation in that, the time delay in luminescence emission after excitation is longer than 10^{-9} second; whereas in the latter it is of the order of 10^{-14} second (10).

The luminescence phenomenon is classified according to the mode of excitation used, as follows:

- A) **Photoluminescence:** produced by absorption of ultraviolet or visible radiation.
- B) **Radioluminescence:** caused by bombardment with high energy particles or radiation as X-rays, r-rays etc.
- C) **Cathodo Luminescence:** a special case of radio - luminescence, produced by cathode rays.
- D) **Electroluminescence:** caused by application of electric field.

1-2.2 Fluorescence and Phosphorescence: (Fig.1.1):

The general term, luminescence, is categorised either as fluorescence or phosphorescence depending on duration of emission after removal of excitation. Garlick (6) defines fluorescence as emission of light during excitation and phosphorescence after excitation is removed. According to Leverenz (11) and Kroger (12), a luminescence emission which lasts upto the initial 10^{-8} second after excitation is to be called fluorescence, while the subsequent is to be referred to as phosphorescence.

1-3 PHOSPHORS:

Material exhibiting luminescence are called 'luminophosphors'. When they are prepared in laboratory for practical applications they are termed as 'phosphors' (13,14). Most of the phosphors which have more practical utility are inorganic in origin.

1-3.1 Phosphors in Pure Form:

Certain phosphors even when they are well purified show luminescence and they are known as self activated phosphors. Heat treatments usually necessary to make them luminescent. The examples are ZnO, ZnS, molybdates, diamond etc (6,15).

1-3.2 Impurity Activated Phosphors:

The frequent ability of a material to exhibit luminescence is associated with the presence of 'activators'. These activators may be impurity atoms occurring in relatively small concentration in the host material.

- E) Sonoluminescence: produced by sound waves, usually of ultrasonic variety.
- F) Triboluminescence: produced by utilisation of mechanical energy.
- G) Chemiluminescence: occurs as a product of chemical reaction.
- H) Bioluminescence: a chemiluminescence in living organisms.
- I) Galvanoluminescence: produced during electrolysis in galvanic cells.
- J) Thermoluminescence: Thermoluminescence, however, do not refers to the thermal excitation but rather to the thermal stimulation of luminescent emission when the sample is excited by other means.

Often, the combinations of above types are in use and are as follows:

- A) Photo-electroluminescence: refers to radiation modulated electroluminescence.
- B) Electro-photoluminescence: refers to enhancement of light intensity by the applied field.
- C) Electro-thermoluminescence: refers to thermoluminescence enhanced by the applied field.
- D) Photo-transferred thermoluminescence: refers to thermoluminescence stimulated by radiation dose at high temperatures, usually beyond 400°C .

1-4 LOCALISED ENERGY LEVELS IN FORBIDDEN GAP:

Impurities, lattice defects or other perturbations in an ideal crystal lattice of a phosphor can give rise to discrete energy levels in the forbidden energy region. These have been classified as follows:

1-4.1 Luminescence Centres:

These are the energy levels responsible for the spectrum of emitted luminescence. The absorption and emission properties of these centres are the characteristic of the activator ion and the base material. These centres possess high capture cross-section for excited electrons and much greater probability for radiative transitions than for non radiative transitions(16,17).

1-4.2 Killer Centres:

These are the discrete localised energy levels which possess a small capture cross-section for excited electrons and much greater probability for non-radiative transitions than for the radiative ones.

1-4.3 Electron Traps:

A localised level which can capture an excited electron, produced in the centre or elsewhere in the crystal, without allowing an electron to fall directly in to a normally filled level, is called an electron trap or just a trap.

1-4.4 Hole Traps:

These are the localised levels just above the valence band capable for capturing a positive hole.

1-4.5 Metastable States:

Energy states existing within the forbidden region which can be excited by electron bombardment but not by photo-excitation are termed as metastable states. A transition from metastable level to normal state with emission of radiation has very low probability i.e. the transitions from these levels are forbidden. The transition from higher level to metastable state are permitted. The mean life time of metastable state is found to be much longer than the life time of radiating level. Representative times are 10^2 to 10^4 second for metastable states and 10^7 to 10^9 second for radiating level (18).

1-5 CRITERION FOR OCCURANCE OF LUMINESCENCE:

A crystal wherein transition of an atom or ion into an excited state has occurred by absorption of radiation or otherwise, can return to the ground state by ridding itself off the energy absorbed. The latter is usually dissipated in the form of heat. In some cases, however, it is re-emitted in the form of light radiation; and the crystal exhibits luminescent properties. It is seldom that these are exhibited by pure (physically and chemically) substances. Randall (19) suggested that a pure substance is fluorescent if each elementary cell of the crystal contains an ion or complex group with an unfilled valence electron layer entirely shielded by the surrounding medium.

From theoretical point of view, absorption of a radiation quantum by a pure crystal gives rise to a free electron and a

hole. These may recombine without emission, when are subjected to the effect of crystal lattice vibrations and transfer their energy to the lattice in the form of heat. Hence it results that the electron transitions responsible for emission should be well shielded off by the surrounding atomic configuration from intersections with crystal lattice vibrations for radiative recombination to occur (20). However, when defects are present in the lattice, the probability of recombination of electron and hole with the emission of radiation increases. The reason being that the electron and hole are better shielded off at the counters than elsewhere from the effect of lattice vibrations and thus probability for them to transfer their energy to the surrounding atoms or ions in the form of heat is lesser. The necessary defects may be created due to self activation (local defects) or may be produced by incorporating the foreign impurities (foreign defects).

1-6 RECOMBINATION PROCESS:

The processes by which free carriers recombine can be classified into radiative and non-radiative process.

1-6.1 Radiative Recombination Process:

In this process the released energy is emitted either wholly or partially as the emission of radiation. The process may take place in either of the following basic ways as illustrated in fig.1.2.

A) Band-to-band Recombination: (Fig.1.2(i)):

If an electron in the conduction band recombines directly with a hole in the valence band, a photon of energy equal to or greater than the band gap energy of the semiconductor is emitted. The electron and hole will recombine from the states close to the band edges, but the thermal distribution of carriers among these states will give an appreciable width to the emission spectrum. The process being observed in pure materials.

B) Recombination via Shallow Donor or Acceptor Levels (Fig.1.2(ii)):

In this case the energy of transition can be somewhat smaller than the band gap energy. However, donor and acceptor levels can be very close to conduction and valence band often being separated from them by only a few millielectron volts. Thus it may only be possible to differentiate between shallow impurity transitions and band-to-band transitions by sophisticated spectral measurements at low temperatures.

C) Donor-Acceptor Recombination: (21) (Fig.1.2(iii)):

An electron trapped on a donor can recombine with a hole trapped on an acceptor that is several lattice spacings away. Donors and acceptors tend to associate into pairs. The coulomb interaction between a donor and an acceptor is a strong function of the overlap of electron and hole wave functions. The coulomb interaction increases the energy of the excited state and is inversely proportional to donor acceptor spatial

separation (R). The energy of photon resulting from donor-acceptor transition is given by

$$h\nu = E_G - (E_D + E_A) + e^2/\epsilon R \quad - - - - \quad (1.1)$$

where E_D and E_A are the donor and acceptor binding energies respectively; ϵ is the dielectric constant of the host material. This gives rise to line spectrum with the wavelength of the lines separated by a few angstroms. A distinguishing character of donor-acceptor transition is their time resolved spectra; a change in the spectrum as emission decays after the excitation is removed. Most light emitting diodes use this mechanism.

D) Recombination via Deep Levels: (Fig.1.2(iv)):

In this case the photon energy is considerably smaller than the band gap energy; and the emission wavelength may be so long as to lie outside the region of the visible spectrum which is of interest.

E) Exciton Transitions:

An electron and a hole can interact to form a state whose energy is less than that of a free electron and a hole. This system is called an exciton and is analogous to an excited electronic state of an atom. In this situation one must consider that the electron and the hole have a spatial association. Furthermore, if one of these charges is localised at a centre the exciton will be bound to this centre. For example, a free electron can become associated with positively

charged centre to form a bound exciton. This exciton then decays with emission of radiation.

1-6.2 Non-radiative Recombination Processes:

Recombination processes in which the energy released does not appear as a photon are also possible. The recombination energy being dissipated as heat by various mechanisms.

A) Multi-phonon Process: (Phonon emission): (Fig.1-3(i)):

An electron may lose energy by the production of a number of quanta of ^glattice vibrations (phonons). M.Lax (22) assumed that an electron in conduction band falls into excited state of large orbit associated with an impurity atom. The electron then falls into states of lower and lower energy by successive phonon emission until it reaches the impurity ground state. The energy released will raise the temperature of lattice.

B) Auger Recombination: (Fig.1-3(ii)):

It is possible for an electron to recombine with a hole and to give up the excess energy to a second conduction band electron. The second electron will thus be raised to higher energy state in the conduction band and subsequently lose energy by a thermalization process. Since the second electron stays within the continuum of states in the conduction band, no defined energy transitions are involved in thermalization process and Auger recombination is thus a non-radiative process.

C) Surface Recombinations:

It is well known that surface recombination is non-radiative, possibly because a continuum (or quasicontinuum) of states may join the conduction band to valence band. The recombination at surface states dissipates the excess energy by phonon emission. Defects in surface such as pores, grain boundaries and dislocations may provide regions where a localised continuum of states bridges the energy gap and allows non-radiative recombination.

1-7 MECHANISM OF LUMINESCENCE:

Basic processes involved in the mechanism of luminescence are explained in Fig. (1.1). A luminescence centre in the ground state absorbs the energy, goes to the excited state and returns to the ground state with emission of energy in the visible region. Many times, there is delay in the emission which is caused by the metastable level in between ground state and the excited state. The delayed emission is termed as phosphorescence.

1-7.1 Mechanism of Thermoluminescence:

If a previously excited and sufficiently decayed phosphor is heated with a uniform heating rate; it is found to give luminescence; the intensity of which varies with temperature. The phenomenon is treated as "thermoluminescence (TL)".

In thermoluminescence, electrons (or holes) trapped during excitation are released from traps by thermal activation.

Such released electrons get combined with luminescence centres and give rise to TL emission.

A) Glow Curve:

The variation of TL intensity with temperature is known as a 'glow curve'. A glow curve may have one or more glow peaks, depending upon the presence of trapping levels of different depths. A particular glow peak belongs to the traps of one depth and is characterised by its own peak temperature and height. These are the functions of position of trapping levels below the conduction band and the number of electrons trapped in the level. The peak height is also a function of rate of heating. This is because, at higher heating rate, the rate of release of electrons from the traps increases and hence the TL intensity. The glow curve can be used to estimate the activation energy E for thermal release of trapped electrons or holes and provides means of determining the escape frequency factors. As both E and S depend sensitively upon the trapping centres, glow curve can yield valuable information about the role of various impurities present in the sample.

B) Kinetics of Luminescence:

The kinetics of luminescence is concerned with the mechanism involved in the recombination of electrons with the luminescence centres and owes its origin to the probability of retrapping of electrons in deeper empty traps. There are three modes of kinetics involved in a luminescence process viz.

- i) monomolecular kinetics: (Order of kinetics = 1)
- ii) bimolecular kinetics: (Order of kinetics = 2)
- iii) intermediate kinetics: (Order of kinetics lying between 1 and 2).

i) Monomolecular Kinetics: (First order kinetics):

If the traps are situated close to the luminescence centres (less than 10^6 cm. apart) and if a very small movement of electrons is needed to recombine with luminescence centres, then the kinetics of luminescence process is said to be monomolecular (23). Under such a situation, according to minimum energy principle, there is negligible probability for an electron to be retrapped in deeper empty traps. Thus in the monomolecular kinetics, the probability of retrapping is negligible or in other words, the process of recombination is dominant (24,25).

ii) Bimolecular Kinetics: (Second order kinetics):

In this case, the traps are localised away from the luminescence centres (at distance greater than 10^5 cm.) and the electrons have to go large displacement for recombination with luminescence centres. Under such circumstances, according to the minimum energy principles, there is greater probability for an electron to be retrapped in the deeper empty traps. Thus in bimolecular kinetics, the process of retrapping is dominant (24,25).

iii) Intermediate Kinetics:

When the order of kinetics is neither uniquely monomolecular nor uniquely bimolecular, then one is left with an idea of intermediate kinetics. In this case, the traps are supposed to be distributed in the vicinity of luminescence centres in such a way that the probability of retrapping of electrons in deeper traps is small but not negligible. The occurrence of such an intermediate order of kinetics is shown to be feasible by several workers (26,27).

C) Theories of Thermoluminescence:

Urbach (28) gave the first practical approach for the thermoluminescence study. However, the first theoretical treatment for the thermoluminescence on the basis of energy band model was due to Randall and Wilkins (29). According to them the impurities and the lattice defects which give rise to localised levels in the forbidden region, constitute the electron traps, hole traps and metastable states. Amongst these the electron traps are just below the conduction band of energies say E_1, E_2, E_3 --- and hole traps of energies W_1, W_2, W_3 --- above the valence band. The situation is illustrated in Fig.1.4. In a fully compensated phosphor, the hole traps W_1 contain electrons before irradiation, while the electron traps E_1 are empty. Irradiation removes electrons from either the hole traps or valence band and lifts them into conduction band; from which they may later be trapped at sites of E_1 and corresponding holes at the sites of W_1 . As heating beings, the traps begin to be empty.

If $E_i \leq W_i$, electrons are liberated and recombine with hole centres emitting radiation during the transition. In this case the hole centres are generally referred to as luminescence centres. Emission occurs by hole excitation if $E_i \gg W_i$ and electron traps correspond to the luminescence centres. Based on the consideration of retrapping of electron or holes during luminescence process, there are two different theories: one proposed by Randall and Wilkins and other by Garlick and Gibson.

i) Randall and Wilkins Theory:

Randall and Wilkins (29) made the following assumptions in analysing the glow curves: (a) an ejection of electrons is the only rate determining process, (b) radiationless transitions and probability of retrapping is negligible, (c) the lifetime τ for recombination is so small that $\frac{dn}{dt} \ll \frac{n}{\tau}$ with n as the concentration of electrons in conduction band, and (d) glow peaks arising from the traps of different depths do not overlap. With these assumptions, they obtained an expression for variation of TL intensity with temperature.

Let n be the number of electrons at any time t in trap located at a depth E below the conduction band. The electrons in the traps have Maxwellian distribution of thermal energies. Hence the probability P per unit time that an electron at temperature T may escape from a trap of depth E is given by the Arrhenius function i.e.

$$P = S \exp. \left(- \frac{E}{KT} \right) \quad \text{-----} \quad (1.2)$$

where K is the Boltzmann constant and S is the escape frequency factor.

The rate of electron escape from the trap is given by

$$\begin{aligned} \frac{dn}{dt} &= -np \\ &= -nS \exp. \left(-\frac{E}{KT} \right) \quad \text{---} \quad (1.3) \end{aligned}$$

on reannealing

$$\frac{dn}{n} = -S \exp. \left(-\frac{E}{KT} \right) dt \quad \text{---} \quad (1.4)$$

At an uniform heating rate β , $\beta = \frac{dT}{dt}$ and therefore $dt = \frac{dT}{\beta}$. Substituting this in equation (1.4) and on integrating we get,

$$\begin{aligned} \log \left(\frac{n}{n_0} \right) &= - \int_{T_0}^T \frac{S}{\beta} \exp. \left(-\frac{E}{KT} \right) dT. \\ \text{or } n &= n_0 \exp. \left[- \frac{S}{\beta} \int_{T_0}^T \exp. \left(-\frac{E}{KT} \right) dT \right] \quad (1.5) \end{aligned}$$

Where n_0 is the number of electrons trapped initially at temperature $T = T_0$.

The TL intensity I is given by

$$\begin{aligned} I &= -\frac{dn}{dt} \\ &= nS \exp. \left(-\frac{E}{KT} \right). \\ &= n_0S \exp. \left(-\frac{E}{KT} \right) \\ &\quad \exp. \left[- \frac{S}{\beta} \int_{T_0}^T \exp. \left(-\frac{E}{KT} \right) dT \right] \\ &\quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad (1.6) \end{aligned}$$

ii) Garlick and Gibson's Theory:

Considering the equal probabilities for the retrapping and recombination of released electrons (assuming bimolecular process), Garlick and Gibson (5) extended the theory given by Randall and Wilkins and obtained an expression for the variation of TL intensity with temperature. Let N be the total number of electron traps of which n are filled at any time t . Thus there will be $(N - n)$ empty traps and n empty centres. An electron (excited) can be retrapped in one of the $(N - n)$ empty electron traps or can recombine with one of the n empty luminescence centres with equal probability. The probability that an escaping electron will recombine with an empty luminescence centre and not getting trapped is given by

$$\frac{n}{[(N - n) + n]} = \frac{n}{N} \quad \text{---} \quad (1.7)$$

The rate of escape of electrons from the traps will be,

$$\frac{dn}{dt} = \frac{n^2}{N} S \exp. (-E/KT) \quad \text{---} \quad (1.8)$$

The thermoluminescence intensity I is given by the solution of equation (1.8), which is

$$I = \frac{n_0^2 S \exp. (-E/KT)}{N \left[1 + \frac{n_0}{N} \int_{T_0}^T \frac{S}{\beta} \exp. (-E/KT') dT' \right]^2} \quad (1.9)$$

where n_0 is the value of n at $t = 0$.

The theoretical glow curves for monomolecular and bimolecular processes plotted according to the equations

(1.6) and (1.9) respectively are shown in Fig.1.5. It may be seen from the figure that for given values of E , S and β ; the curve for bimolecular process has greater half width than that for monomolecular (30).

1-7.2 Mechanism of Electroluminescence:

Electroluminescence is the light generated in a phosphor by conversion of electrical energy supplied by electrical contacts; in the absence of incandescence, cathodo-, or photoluminescence. The direct conversion of electrical energy into visible or near visible radiation takes place by the following three processes; (i) excitation, (ii) emission, (iii) energy transfer during excitation and emission.

Several possible modes have been proposed to explain these processes and various stages of development could be thought to follow the sequence as shown in the flow chart (of Fig.1.6). However, the general mechanism consists of the three main stages:

Stage 1: Excitation of charge carries,

Stage 2: Acceleration of charge carriers, and;

Stage 3: Energy transport and radiative de-excitation.

(Stages III, IV, and V in the flow chart combined together).

A) Excitation of Charge Carriers:

There are three mechanisms of excitation and each is shown to be theoretically fessible in appropriate solids with suitable local field conditions.

- i) Field ionization of valence electrons,
- ii) Field ionization of impurity ions, and;
- iii) Injection of minority charge carriers.

i) Field ionization of Valence Electrons:

The possibility and probability of exciting an insulator with an intense electric field in such a way as to excite valence electrons into the conduction band was first pointed out by Zener (31). The transfer^{of} valence electron may take place by quantum mechanical tunneling process (32) producing a free electron and a free hole simultaneously. The requisite of very high local field (about 10^5 to 10^7 volts/cm), Sometimes; may lead to breakdown of the crystal (Zener breakdown and is rarely observed).

The probability that an electron will penetrate into the conduction band per unit time is given by (33).

$$P = \frac{ea}{2\pi\hbar} F \exp. \left(- \frac{\pi \sqrt{2m^*}}{4\hbar e} \frac{E_g^{3/2}}{F} \right) \quad \text{--- (1.10)}$$

Where m^* is the effective mass, F is the local electrical field, E_g is the band gap and a is the unit cell dimension.

Normally, it turns out that a dielectric breakdown of substance would take place much before any significant number of electrons are promoted. If, however, the applied field have very high values in a very narrow region and low values elsewhere, a breakdown is avoided, because carrier multiplication

which leads to breakdown, does not have high probability in a thin region. Thus in such a case, the carrier excitation by this mechanism appears to be a possibility.

ii) Direct Field Ionization of Impurities:

It is well known that solid state luminescence usually originates from excited impurity systems called activators having dimensions of interatomic distances. Due to difference either in charge or of atomic size as compared to base matrix, perturbed states or discrete levels are created within the energy gap of the semiconductor. To radiate in the visible portion of the spectrum, the activator system must have an excited state, atleast 2 eV higher than the ground state. Ionization of activator centre is also a permissible mechanism, provided conduction electrons are available or made available subsequently. The field strength necessary to ionize these centres at a reasonable rate would normally be in excess of dielectric breakdown strength of crystal matrix. Breakdown in materials with suitable band gap for luminescence, normally occurs by an avalanche mechanism, rather than by field ionization of valence electrons. Piper and Williams have shown that an electric field of about 2×10^5 volts/cm. is necessary. Mc Afee et.al (31) and Franz (34,35) made calculations and obtained an expression for probability of field emission per unit time and is

$$P = 17 \times 10^{12} \left(\frac{m^*}{m} \right)^{1/2} \left(\frac{F}{k} \right)^{1/4} \exp. \left(- \frac{7 \times 10^7 (m^*/m)^{1/2} E_i^{3/2}}{F} \right)$$

- - - (1.11)

Where K is the dielectric constant and E_i is the depth of the impurity level from the bottom of the conduction band.

iii) Injection of Minority Charge Carriers:

A third method of excitation is the introduction of both types of free carriers into a particular region of a crystal. The introduction may occur from a surface, a defect or an adjacent region of opposite type. The last one constitutes a p-n junction which we shall consider in detail.

Shockley (36) analysed, the injection characteristics of p-n junction by using quasi-fermi levels for two types of carriers. Hall (37), Shockley and Read (38) investigated the statistics of recombination of electrons and positive holes.

Fig.1.7 (a) shows an energy level diagram for a p-n junction in the absence of an applied voltage. By definition in n-type region the density of negatively charged carriers (electrons in empty conduction band) exceeds that of positively charged carriers (holes in valence band). Here the electrons and holes referred to as the majority and minority carriers respectively. In p-region, reverse is the situation. In each region there is continual thermal production and subsequent recombination of electron hole pairs and the system is said to be in dynamical equilibrium.

Fig.1.7 (b) shows the energy level diagram for a p-n junction with the applied voltage in the forward direction. Here electrons are injected into p-type region and holes into n-type region, which corresponds to minority carrier injection. The excess minority carriers produced in this way, diffuse

away from the junction **biased** in the forward direction, decaying with lifetime τ . The mean diffusion length L is related to the drift mobility μ by the relation $D = (KT/e)\mu$. If V represents the potential difference and n , the hole density on n-type region, then the injected hole current will be given by

$$I = q n e \left(\frac{D}{\tau} \right)^{1/2} \left[\exp. \left(\frac{eV}{KT} \right)^{-1} \right] \quad \text{---} \quad (1.12)$$

Where D is the diffusion constant.

At higher applied voltages, the carrier motion is determined by the electric field. Luminescent emission may occur in or near the P-n junction by either intrinsic or extrinsic recombination, resulting in 'P-n junction electroluminescence'. At very high current densities, the quasi-ferrmi level for the electron and the hole become sufficiently separated so that their populations are inverted and laser action is possible.

B) Stage II: Acceleration of Charge Carriers in the Crystal Bands:

In order to produce electroluminescence by inelastic collisions of high velocity electrons and activator systems, atleast three conditions must exist. High field region capable of accelerating charge carriers to large kinetic energies must be produced; electrons and holes must be injected into this high field region and activator atoms must be suitably located to absorb by collision a significant fraction of energy from

the field by the charge carriers. The carriers (electrons or holes) are created in the crystal bands by any one of the already illustrated excitation processes. The conduction electrons (or holes) experience an accelerating force as a result of applied field and retarding force resulting from interactions with phonons. With a moderately strong field condition ($10^5 - 10^6$ Volts/cm.) electrons will attain sufficient energy to ionise impurities or valence electrons by inelastic collisions with lattice phonons. The probability (P) of acceleration of a conduction electron to sufficient kinetic energy, for the inelastic collision excitation of an activator system is given by,

$$P = \exp (E_g / eF\lambda) \quad - - - - \quad (1.13)$$

where λ is mean free path.

In facilitating the acceleration mechanism of excitation of electroluminescence, the catastrophic consequences of dielectric breakdown can be avoided by an inhomogeneous field distribution in crystals, for example, a narrow high field region in series with an extensive low field region. Such configuration can exist if we have a Mott-Schottky exhaustion type barrier, a thin intervening intrinsic region or a p-n junction biased in the reverse direction. In high field reverse biased junction, the carriers tunnel through the forbidden gap and are accelerated to high kinetic energies. The emission is the combination of interband and intraband transitions.

C) State III: Transport of Energy to Radiating Site and Radiative de-excitation:

The excess energy available with the conduction electrons or holes must be transported to the agent which it eventually going to take part in the radiative transition leading to electroluminescent emission. The transport is achieved by the movement of charge carriers or by collision process or by movement of excitons.

i) Transport and Capture of Charge Carriers:

A well known means of energy transport within a crystalline powder is migration of minority charge carriers. In n-type materials, in which fermi level is close to the conduction band, a free hole represents an amount^{of} stored energy almost equal to band gap. If this hole is captured by an activator which then captures an electron from conduction band, a photon is emitted. Sometime a hole may be captured at another centre where at it recombines with conduction electron and excitation energy is dissipated in lattice vibrations. The flow of energy represented by transport of charge carriers depends on concentration gradient, on the electric field intensity and on concentration of trapping stages.

ii) Collision Process: (Fig.1.8):

An electron in conduction band or a hole in valence band may be accelerated to large values of kinetic energy.

In this energy range, in addition to exciting phonons, a charge carrier is able to create an electron hole pair or to excite a localised impurity system by an inelastic collision. The efficiency of electron-hole pair^y production in terms of path length L and mean free path λ is given by

$$n = \frac{L}{\lambda} = \frac{A^{-1}}{F^2} \exp. \left(- \frac{B}{P} \right) \quad - - - \quad (1.13)$$

Where F is the applied field and A and B are the constants. There is a threshold value for the energy of an electron below which it cannot create an electron-hole pair, and is approximately calculated to be one and half times the band gap (39).

iii) Movement of Excitons:

An electron in an excited state and a hole left behind in the filled band form a coupled pair^y called an excitation. An excitation may be thought of, as resulting from an electronic transition from a negative ion to a nearest neighbouring positive ion. The excitation of a radiating centre by direct interaction with an exciton is also probable but this does not involve any movement of charge carriers. Exciton diffusion has been suggested as the mechanism of energy transfer in cathodoluminescence of ZnS (40).

D) Radiative de-excitation:

The radiative de-excitation takes place with appreciable radiative transition probability. The transitions may be from one state to another within the same band (10) (intraband),

band to band (inter band) or from one band to impurity state and vice versa, or from impurity state to impurity state (41). This has been illustrated in Fig.(1.2) vide section 1-6.1.

1-7.3 Mechanism of Electrothermoluminescence:

The light output during thermoluminescence can be affected by the application of a constant electric field. However, one should not believe that these two processes are linearly additive in any strict sense. At low temperatures, e.g. below -150°C the effect amounts to a slight quenching, while at higher temperatures, e.g. -150°C to 50°C , there is more or less pronounced enhancement depending upon strength and frequency of the applied field (42). As usual, the emission intensity sensitively depends upon the rate of heating. At any rate, electrons released from traps in the course of thermoluminescence take part in the electroluminescent process and produced additional light. Thus whenever thermoluminescence shows a brightness peak, the combined effect is expected to show a similar but greatly enhanced peak.

Hahn (43) showed the mechanism of trap filling by electric field, is similar to thermoluminescence, Rabotkin (44) has shown that the mechanism of thermal extinction is similar to that of photoluminescence.

1-8 STATEMENT OF THE PROBLEM:

The alkaline earth sulphide phosphors are amongst the earliest known impurity activated phosphors (45,46). These phosphors have gained significance since the discovery of their utility for sensitized luminescence and infra red stimulation (47,48). However, they are less investigated as compared to ZnS and CdS. In recent years, it has been shown that the CaS phosphors can be obtained of the qualities so as to replace other commercial phosphors (49,50). For instance, their photo and cathodoluminescence efficiencies are about 80% and 20% respectively. Thus CaS phosphors are important in view point of commercial applications as well as for fundamental phosphor research.

A survey of phosphor literature (49,57) presents that in the last two decades there has been some interest grown in activated CaS phosphors. However, most studies made so far on CaS phosphor system have been largely confined to interpretation of fluorescence and phosphorescence spectra and to the determination of trap depths. A systematic investigation of their electroluminescence behaviour is lacking. Although a few workers (58-67) have recently reported such studies, the mechanism of electroluminescence is not completely clear. In this investigation, CaS phosphors activated with varying concentrations of Zn have been prepared and systematic study of their electroluminescence and electrothermoluminescence have been undertaken.

A) Electroluminescence:

A. C. electroluminescence measurements have been carried out to investigate the possible relationship between brightness-voltage and brightness-frequency. The brightness-current and current-voltage characteristics are equally important in understanding the mechanism of electroluminescence.

B) Electro-Thermoluminescence:

The observations of electro-thermoluminescence have been carried out by applying an A. C. voltage to a phosphor and simultaneously heating it with a uniform heating rate. Such measurements are supposed to throw light on the release of electrons from traps and their recombination with luminescence centres under the action of electric field. Moreover, the study will provide the information to correlate the electrothermoluminescence and thermoluminescence.

In addition to these aspects, the concentration quenching effect, dependance of the electroluminescence efficiency on concentration of activator have been studied.

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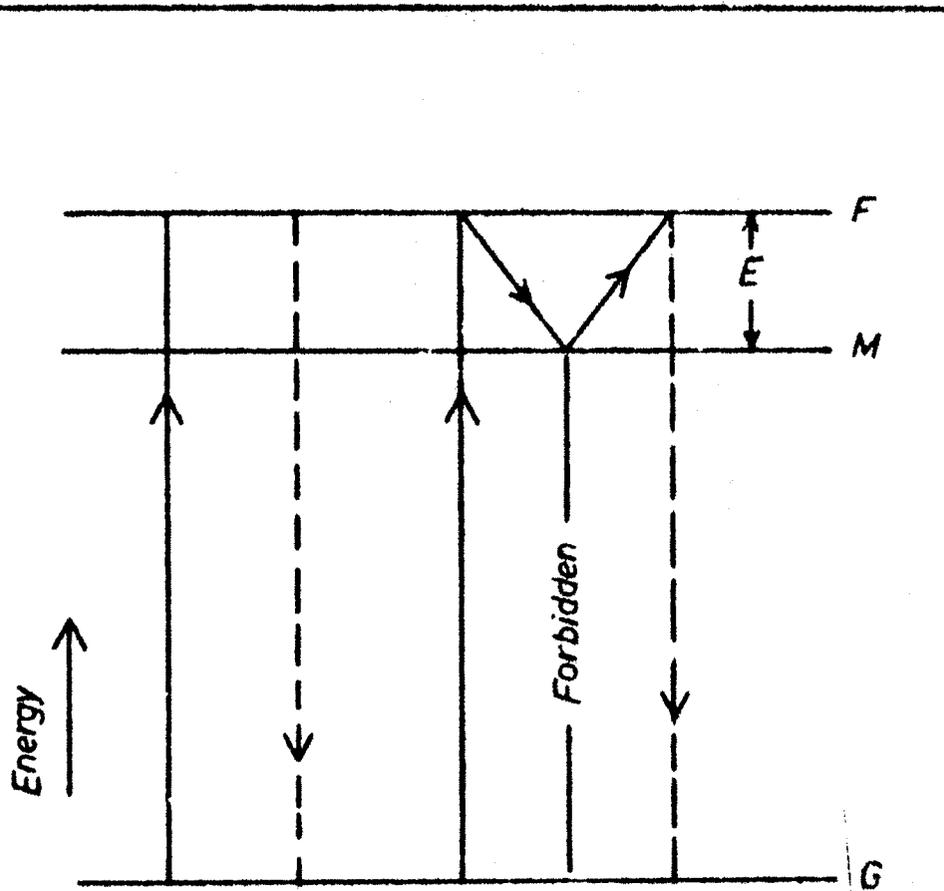
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G — Ground state

F — Excited state

M — Metastable state

E — Activation energy

G → *F* : Excitation

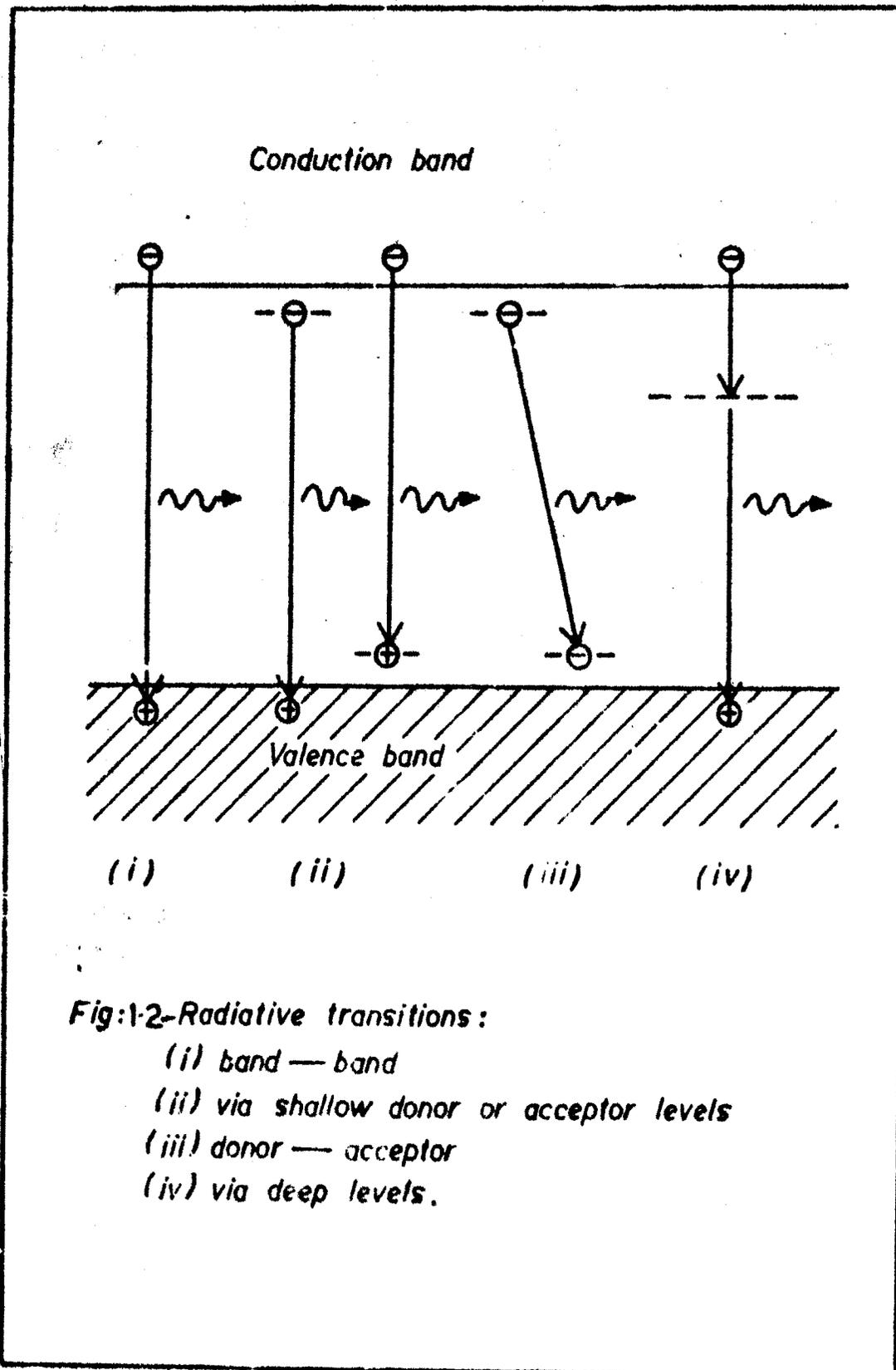
F → *G* : Fluorescence

F → *M* : Fall in metastable state

M → *F* : Thermal or optical activation

F → *M* → *F* → *G* : Phosphorescence

Fig : 11 — Fluorescence and phosphorescence phenomena
(after Jablonski, 1935).



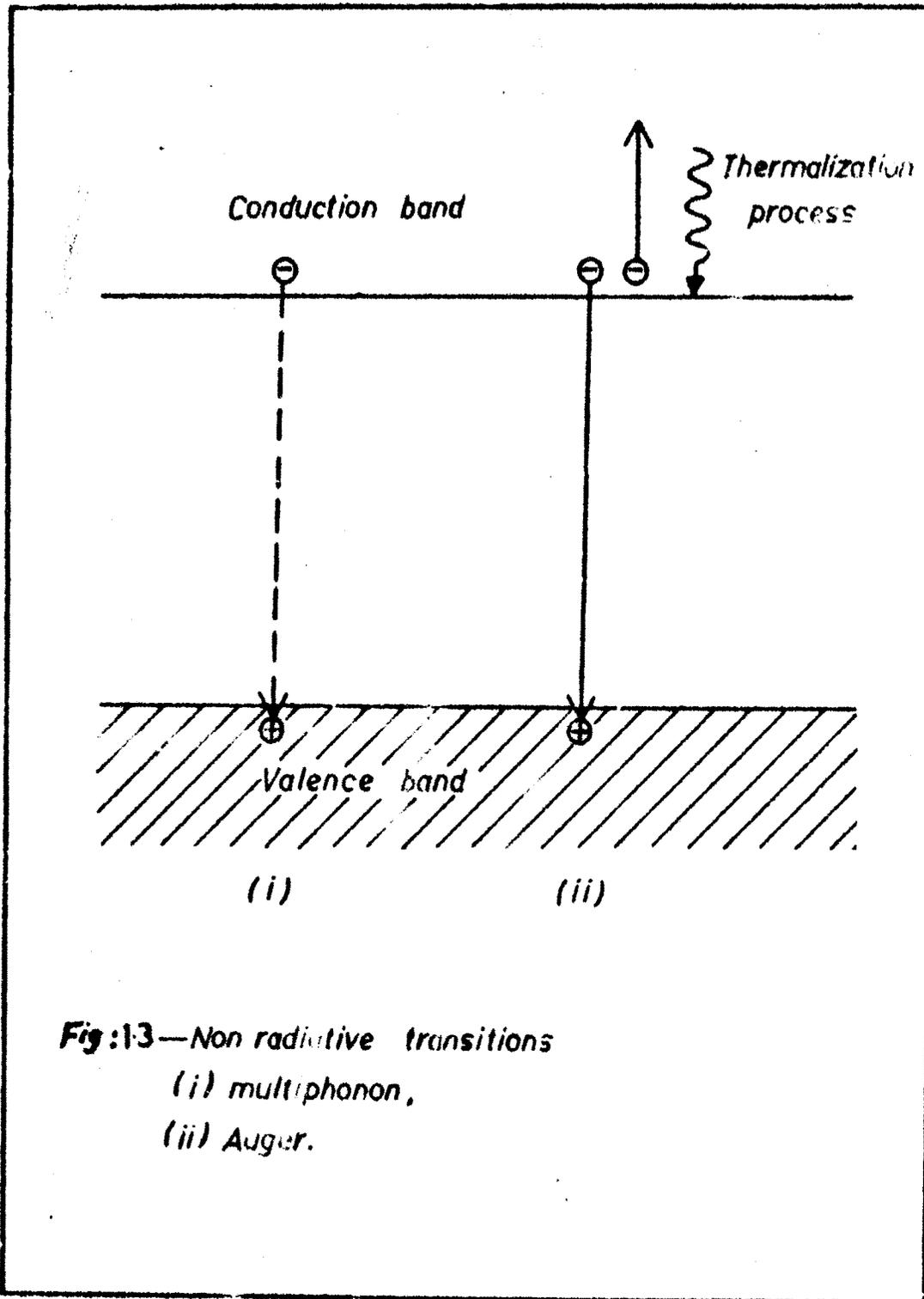


Fig:13—Non radiative transitions
(i) multiphonon,
(ii) Auger.

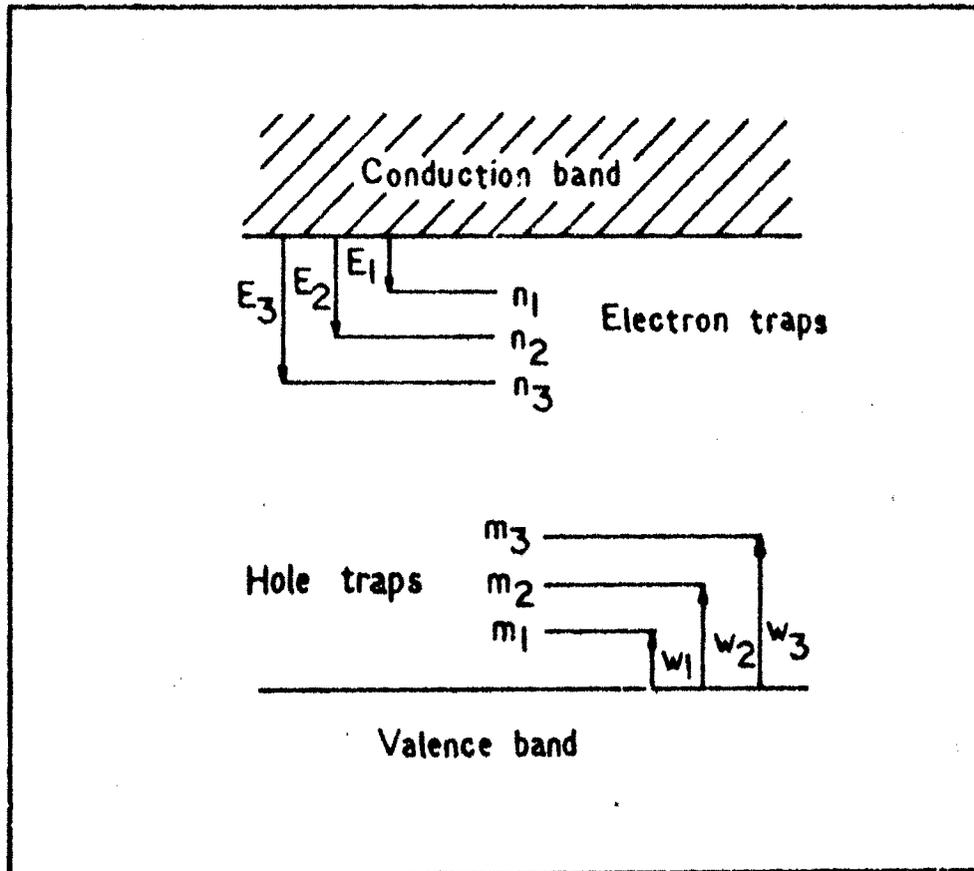


Fig.14: Energy levels for trapping centers in an insulator.

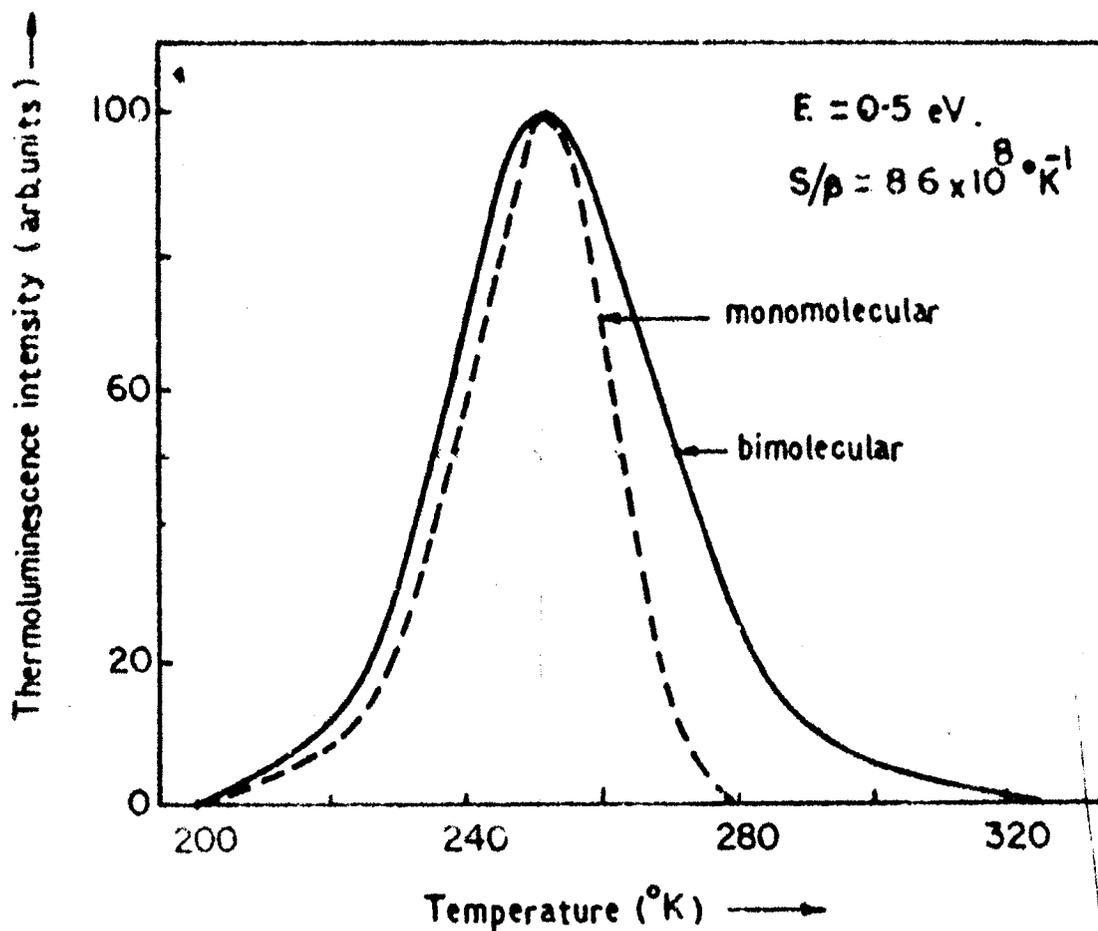


Fig. 1.5 - Theoretical monomolecular and bimolecular curves
 (after W. Hoogenstraaten, Philips Res. Repts, 1958).

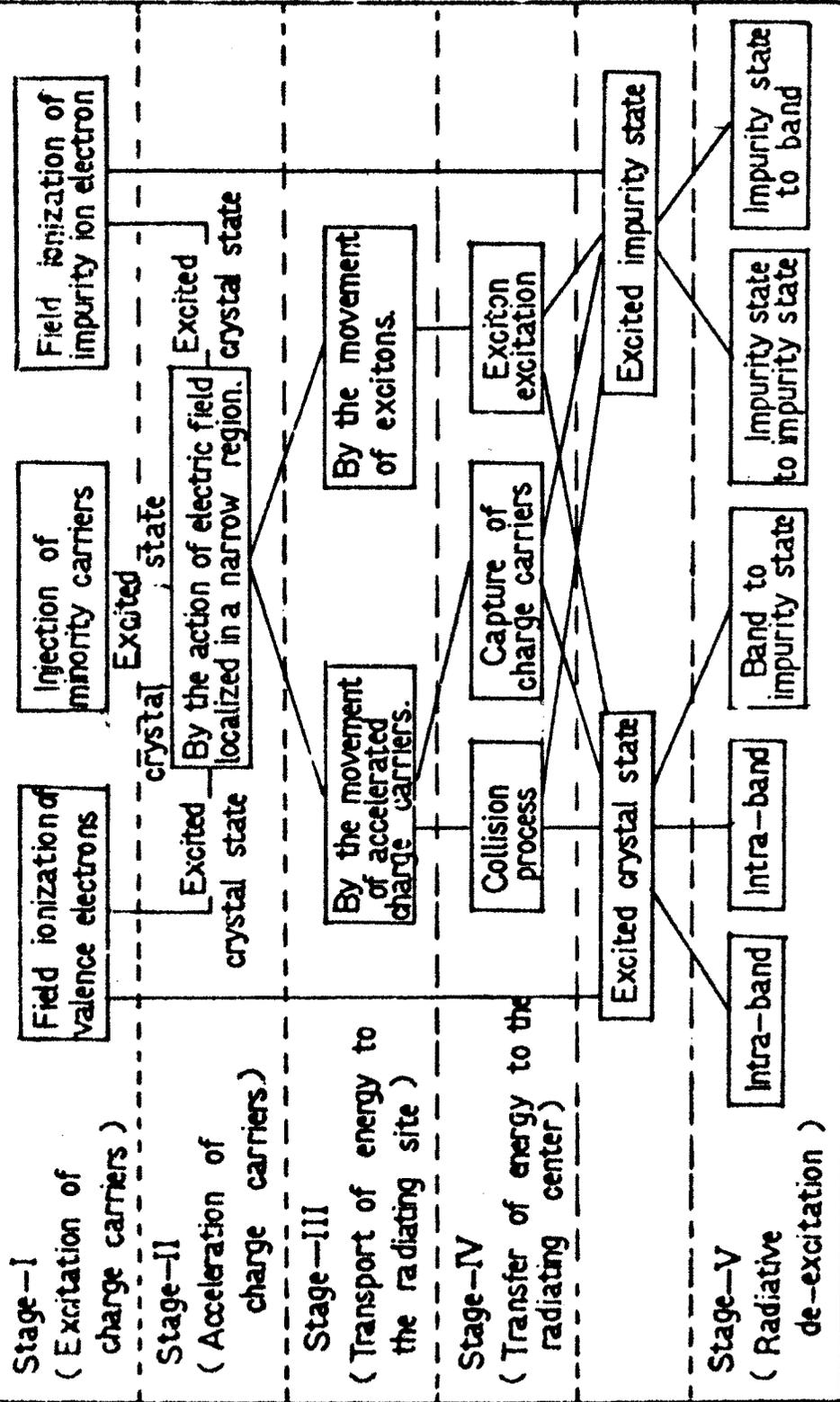
Handwritten notes:

1. 250 K
 0.5 eV
 86 x 10^8 °K^-1

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Fig. 1-6 — Flow chart showing the mechanism of electroluminescence.



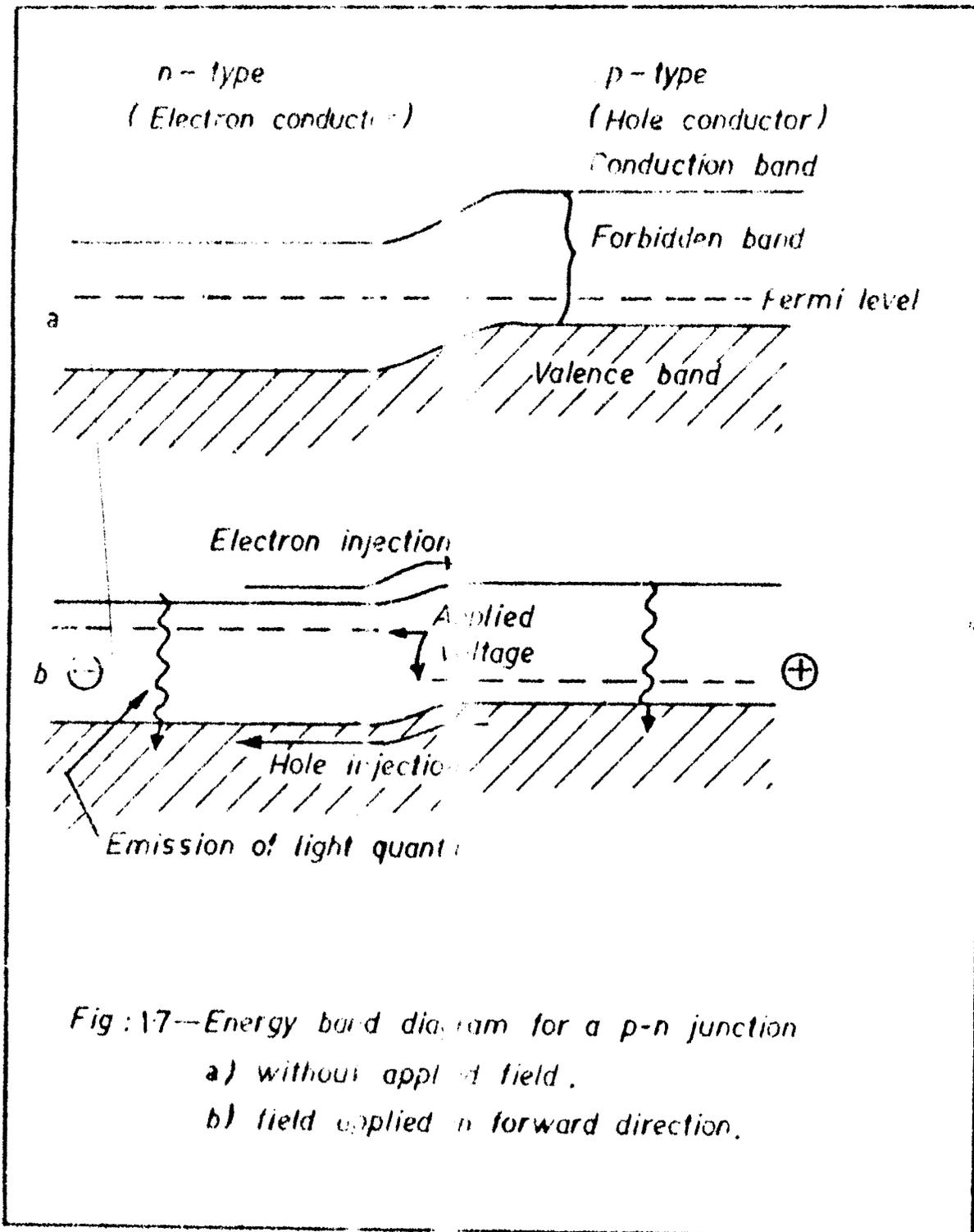


Fig : 17--Energy band diagram for a p-n junction

a) without applied field.

b) field applied in forward direction.

