CHAPTER I

INTRODUCTION

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1.1 SOLID STATE LUMINESCENCE

"LUMINESCENCE is that phenomenon in which material absorbs energy and re-emitts it in the form of visible or near visible light". This material is called luminescent material or simply a phosphor.

The study of luminescence is an important branch in Physics, that extends the knowledge of structure of solids and the mechanism of light emission. Luminescence is a generic term, which includes various excitation processes and the emission of light either as fluorescence or phosphorescence.

1.2 HISTORICAL BACKGROUND

The discovery of luminescence dates back to even before 3000 B.C. Robert Boyle (1) observed the light emission from the gem that he was wearing.

The first and oldest record of luminescence is the bioluminescence, observed in living organisms like fireflies and glow worms. The effect is observed due to the chemical reactions in the living organism. The first written reference of bioluminescence is found in the book of Odes by Shih Ching well before 3000 B.C. Fig.1.1 shows an explanatory comments on bioluminescence given by famous Sung Dynansty Scholar Zhu Xi.

1603 is the most important year in the history of luminescnece. In this year Vincenzo Cascariolo of Bologna, Italy, synthesized the first ever luminescent material by heating barium sulphate with charcoal. It emitted feeble blue glow at night, after exposure to day light. For this reason it was called Lapis solaris i.e. sunstone. He, for the first time, used the word 'phosphor' (Greek-light emitter) to describe a complex preternatural luminescent material. This material was immediately investigated thoroughly by Mont albano (1634), Licetus (1640) and others. The first observation of TL recorded in literature is reported by Robert Boyle to the Royal Society, London in 1663. He observed a strange glimmering light, when diamond was warmed in the dark.

The first definition of luminescence as a non thermal light emission is found in the book of Licetus, written in 1640 (fig. 1.2). In 1669 the chemical element phosphorus was discovered by Henning Brandt It was called phosphorus for the reason that it too glowed in dark when exposed to moist air. Although, phosphorus is not a phosphor in the sense in which it is defined today, still the name is persisted in the present form.

Meanwhile, in 1740, using the Greek tittle 'Litheosphorus', meaning stony phosphors, Fortunio Liceti wrote the first monograph on the Bolognian stone. Since then, there began a chain of experimental studies to confirm the phenomenon of luminescence.

In 1768, Canton found a brighter luminescent material by heating calcium carbonate with sulphur.

A.H. Becquerel(2) in 1852 was the person to experimentally investigate the emission spectrum and made the systematic study of luminescence. Stokes(3) observed that the emitted wave length is greater than the excitation radiation. T.Sidot, discovered Zinc sulphide phosphor, which has emitted green light.

The term 'luminescence' was first introduced by German Physicist Wiedemann(4) in 1889 as emission of electromagnetic radiations in excess of thermal radiation. This definition however is not much accurate, because the Cherenkov emission for instance, is not considered as luminescence.(5) It was pointed out by 'Andirowitsch'(5) (1950), that luminescent emission may be distinguished from Raman, compton, and Rayleigh scatterings and Cherenkov radiations. In the former case the time delay in the emission is larger than 10^{-9} sec. while in the latter cases it is completed in 10^{-14} sec.(5,6)

The theoretical explanation for luminescence was given by Randall and Wilkins(7) in 1945 and then by Garlick and Gibson(8) in 1948.

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

Today, the research in luminescence is manyfold, in advanced technology and other fields. There are a large number of new trends in the field that, it is difficult to point out any one, which stands above all the others.

Various theoretical models so far proposed, to account the phenomenon are helpful, in understanding the electronic processes involved in solids at the atomic levels. Luminescence was studied basically as a use of phosphors in picture display screens, fluorescent screen for C.R.O., TV, Electron microscopes and many such devices.

Sulphides and associated properties were maximum studied Sulphates are also studied. Very good samples of calcium sulphide were made by fried rick Hoffmann (9) in 1700. Later it was observed by many that addition of impurities like Rare Earths, Manganese, Bismuth etc., improved the luminescent properties of the phosphors.

Applications of rare-earth doped (particularly Sm, Dy and Tm) CaSO$_4$ phosphors in radiation dosimetry is of recent origin and these are being increasingly used because of their better sensitivities than LiF or CaF$_2$(10, 11, 12) phosphors. The published work on TL of rare-earth doped CaSO$_4$ phosphors by Yamashita et al(13) deals with selection 9/ of a TL dosimeter phosphor with maximum sensitivity and does not enter into any detail regarding the nature of TL process in these phosphors. TL phenomenon of Borates is also studied by Dhayagude(14).

The effect of impurities on the thermoluminescent properties of the inorganic phosphor was soon realised and the natural multidoped phosphor went into background(15) .The emphasis firstly was on 'Mn' doped samples as this was known to be responsible for (16) TL emission in natural samples. Extensive work on alkali halides doped with TL and other impurities(17) ultimately led to well known phosphors of LiF:Mg, Ti (18) used in radiation dosimetry. CaSO$_4$:Dy phosphor is also found suitable in TL dosimetry

9 Thus both theoretically & practically, luminescence is an active field of research.

1.3 DEFINITIONS

1.3.1. LUMINESCENCE

Luminescence denotes means the absorpiton of energy in the matter and its re-emission as visible or near visible radiation. This emitted radiation is non thermal in origin.(19)

In case of luminescence it is essential for the exciting light to be absorbed, if it has to be re-emitted. In the Rayleigh effect, the exciting light is not absorbed, but scattered by the particles of the medium. The amount of scattering being inversely proportional to the fourth power of the wave length. The intensity of the scattered light is proportional to the density fluctuations in the medium, due to thermal agitation. The Rayleigh effect can be completely explained in terms of classical physics. Its intensity is independent of state of order of the molecules and depends only on the number of particles present and on the rules which define the transitions between quantum states in a molecule.

In case of luminescence, it is necessary for the exciting light to be absorbed. Thus, the intensity of the emitted light will be proportional to the number of atoms or molecules capable of absorbing the particular incident wave length and will be subject also to the quantum rules of absorption. According to the law of conservation of energy, the emitted light must have the same energy as or smaller energy than the incident radiation. It must have longer wave length.

According to the mode of excitation the luminescence phenomenon is classified as follows :

1. Bioluminescence :

   It is produced by bio-chemical reactions.

2. Cathodo-luminescence

   It is produced due to excitatin of cathode rays.

3. Chemi-luminescence

   It is produced due to chemical reactions,

4. Galvano-luminescence

   It is produced at electrodes of an electrolytic solution during electrolysis.

5. Cando-luminescence

   It is produced by non-black body radiation at high temperature.

6. Electroluminescence

It is produced due to high frequency field and even due to ac / d-c field and not due to heating effect produced by electric field.

7. Effuvio-luminescence

It is produced under the influence of electric discharge in rerefied gases enclosed in vacuum tubes.

8. Iono-luminescence

It is produced due to bombardment of material particles.

9. Photo-luminescence

It is produced by irradiation with high energy photons usually ultra-violet rays.

10 Radio-luminescence

It is produced by irradiation with radio acitve rays i.e. by α rays, β rays and γ rays.

11. Sonoluminescence

It is produced by irradiating with high energy ultra sonic waves.

12 Thermo-luminescence

It is produced by heating the irradiated phosphor. This luminescence is due to release of electrons from the traps due to thermal excitation and return to luminescence centres. It is not heat radiation.

Thermoluminescence is also termed as Calori-luminescence.

13 Tribo-luminescence

It is produced by crushing, fracturing, grinding or by mechanical strain of the crystals. Thus tribo-luminescence is produced by mechanical disruption of crystals. There are other types of luminescence in which two factors are responsible for luminescence phenomenon, the first prefix denotes the controlling factor and the second, the source of power which stimulates luminescence.

14 Electro-Cathodo-luminescence

It is produced by cathodo-luminescence stimulated by electric field.

15 Photo-electro-luminescence

It is produced by electro-luminescence stimulated by photon radiation.

16 Cathodoelectro-luminescence

It is produced by electro-luminescence stimulated by (cathode rays) electrons

17 Electro-thermo-luminescence

It is produced by thermo-luminescence stimulated by electric field.

18 Thermo-tribo-luminescence

It is produced by heating the phosphor and subsequently grinding it or fracturing it.

19 Electro-photo-luminescence

It is produced when the photo-luminescence is stimulated with electric field.

1.3.2 FLUORESCENCE AND PHOSPHORESCENCE (FIG.1.4)

The general term of luminescence is classified either as fluorescence or phosphorescence depending on the duration of emission after the removal of exciation. Carlick(8) defined fluorescence as 'emission' of light during excitation and phosphorescence, after excitatin is removed

According to' Leverenz(20) and Kroger(21) a luminescence emission which lasts up to the 10^{-8} seconds after excitation is fluorescence while the subsequent is to be referred as phosphorescence. Fig.1.4 shows energy states in fluorescence and phosphorescence.

1.4 PHOSPHORS AND THEIR CLASSIFICATION

The term 'Phosphor' is used for 'luminescent material', particularly the ones that are artificially produced for use in different appliances such as television tubes, radar screens, fluorescent lamps etc. They may be either organic or inoranic. But the inorganic phosphors have more importance commercially.

Conventional phosphors consist of one or sometimes more of the folliwing components.

i) the host, which is the major component,

ii) one or more activators (acceptors)

iii) a co-activator or charge compensator (donor).

These phosphors can further be divided as -

a] phosphors in pure form

b] Impurity activated phosphors,

1.4.1 PHOSPHORS IN PURE FORM

Certain phosphors show luminescence even when they are not intentionally activated but well purified. These are known as self activated phosphors. Heat treatments are usually necessary to make them luminescent. Some notable examples of this type are ZnO, many tungstates and molybdates and diamond (8,22)

1.4.2 IMPURITY ACTIVATED PHOSPHORS

Impurity activited phosphors show usually better luminescence than pure ones. For activation small amounts of foreign ions are added into the crystal lattice of the base compound, called the host lattice or matrix material.

The added impurity may -

1) enhance the luminescence intensity of the host in different ways-

a] the intensity at the output may be increased the wavelength remaining the same, (intensifier) (b) new wave lengths of emission may be observed (originator).

2) causes reduction in the intensity Killer(23).

1.5 EXPLANATION OF LUMINESCENCE IN TERMS OF CRYSTAL STRUCTURE

An ideal crystal is a regular array of equally spaced atoms. This structure of the atoms depends on the crystal that is considered. But many times there are certain imperfections developed in a crystal -point defect, surface defect and volume defect.

Defects can also be purposefully created in a solid by external addition of impurities.

The external impurities may occupy certain lattice positions of the atoms or lie in the interstitial positions. Many times this is without disturbing the charge neutrality(24)

The defects (usually point defects) or impurities giving rise to discrete energy levels in the forbidden energy gap in the insulators may be one of the following :

1] Luminescent Centre

2] Killer centre

3] Electron traps

4] Hole traps

5] Metastable state

1] LUMINESCENT CENTRE (fig. 1.3)

The emission spectrum is due to these centres. These centres have high capture cross-section for excited electron and greater probability of radiative transition than non-radiative transition(24) .These are characteristic of the host as well as the added impurity.

2] KILLER CENTRE

The centres that have a small capture cross section and greater probability of non radiative transition than radiative transition are called Killer Centres. These are usually characteristic of the added impurity.

3) ELECTRON TRAPS

These are the discrete energy levels that have a large capture-cross section for an electron before it falls into already filled level.

4) HOLE TRAPS

These are energy levels just above the valence band that can capture a hole.

5) METASTABLE STATES

These are discrete energy levels which have life time (10^{-2} to 10^{-4} secs) greater than that of a radiating level (10^{-7} to 10^{-9} secs). Transitions from any other level to a metastable state are not allowed. Thus, an electron does not give luminescent output by a transition from a radiating level to a Metastable level.

The absorbed energy may be in uv region but the output is in visible region. This is because many a times the excited level itself shifts its energy to a lower level in an adiabatic way(25).

1.6 MECHANISM OF PHOTOLUMINESCENCE

The actual mechanism of photoluminescence can be studied under four processes :

1] excitation

2] emission

3] transfer of energy during excitation and emission

4] Storage of the part of absorbed energy during excitation.

1.6.1 EXCITATION AND EMISSION

Excitation and emission can be explained on the basis of different models

1) Classical configuration curve model. Fig (1.5) shows two energy levels. This model was introduced byVan-Hippl (26) and applied by Scitz (27).

The x-axis shows the 'configuration coordinate' 'r'. It specifies the configuration of ions around the centre. The y-axis represents the total energy of the system for the ground and excited states of centre. 'A' represents the equilibrium position of the lower level and 'C' represents the equilibrium position of the higher level. When the centre absorbs energy it is raised to the excited state 'B'. From 'B' the centre relaxes to the position 'C' (the minimum energy). (The energy difference between B and C is given off as lattice vibrations) From this position 'C' it returns to the ground state at 'D' and then relaxes back to 'A'.

The transition from 'C' to 'D' is responsible for the luminescent output.

All the transitions are vertical and in accordance with the Frank-Condon principle.

2) Energy Band Model

The energy band model (28,29) is shown in fig. (1.6) Insulators and semiconductor phosphors can be described using this model in terms of the valence band (F) and the conduction band(C), with localised energy levels in the forbidden region between the bands.

The level 'L' represents the ground state of the luminescence centre 'T_1 ' represents an electron trap and 'T_2 ' represents a hole trap.

When light is absorbed the luminescence centre is excited from its ground level (L) to the excited states (S1) by raising the electron into the conduction band. This excited centre captures an electron from the conduction band and returns to its ground state by giving luminescence emission. If the absorbed energy in the phosphor is equal to the energy difference between the conduction band and valence band. an electron (E) from the valence band goes to conduction band creating a hole (H) in its place. Such electron and hole pairs do not normally combine radiatively.

Such absorbption is known as fundamental absorption band.

3) Schon-Klassen's Model :

This model was proposed by Schon(30) and elaborated upon by Klassen and his co-workers(31, 32, 33) .Fig.(1.7) shows the model for the case of a single luminescent centre. The ground level (L) of the luminescence centre is assumed closed to the valence band When light is absorbed in the fundamental absorption band, a free electon and a hole are created. The electron moves to the conduction band. and the hole diffuses through the valence band and captures an electron from the luminescent centre. The free electron after migration in the conduction band falls into the empty centre which gives emission of light.

4) Lambe Klick's Model(fig. 1.8)

In this model (34) the ground state of the luminescent centre (L) is assumed close to the conduction band. When light is absorbed, a free electron and hole are produced. The hole diffuses to the centre where it captures the electron from the centre. This transition gives rise to luminescence.The electron from the conduction band diffuses to the centre and gets captured there and thus the cycle is completed.

5) Williams and Prener's Model (Fig. 1.9)

This model was proposed by Williams (35) and Prener (36) .Two centres are involved. The ground level of the first centre is assumed close to the valence band and the excited level (II) of the second is assumed close to the conduction band. When energy is absorbed a free hole and electron are produced. The excited level II captures an electron from the conduction band and the hole in the valence band captures an electron from the ground level (I) and thus leaves it empty. The emission then takes place by the transition from the level (II) to (I).

1.6.2 ENERGY TRANSFER

In phosphor systems where absorption and emission of light energy takes place at the same centre, no energy transfer is involved. However, in systems in which absorption and emission arenot confined to the same centre, energy is transferred from absorption centre to the emission one. It occurs in two ways :-

1] Energy transfer with no movement of charge carriers and

2] Transport of energy by charge carriers.

1) Energy Transfer with no movement of charge carriers:

a)Cascade Mechanism

In this type of mechanism(37) one centre on absorbing energy emits radiation. (Primary emission). This emitted radiation is then absorbed by the second centre which finally emits luminesce (Secondary emission). This mechanism is most effective in those cases where the primary emission overlaps the absorption spectrum of the secondary emission system.

b]Resonance Transfer

In this case, the transfer of energy from absorbing system to the emitting system is accomplished by a quantum mechanical process(37,3 such as electric dipole field overlap, electric dipole quadrupole field overlap or by exchange interaction. The efficiency of the process depends upon the distance over which the energy is tranferred.

c) Excitation Migration

The non-conducting excited electron hole pairs are known as excitons. Because of their interaction with phonons they do not remain localised but migrate throughout the crystal transferring the energy. In such processes the excitons transfer exciation energy from one point to another by moving quickly through the lattice without contributing to the electrical conductivity.(39)

2] Energy Transfer with Movement of charge carriers :

In this mechanism, energy is tranferred by electron andhole migration. The process is the same as that involved in Schon-Klassens and Lambe-Klick's models during exciation and emission.

1.6.3 ENERGY STORAGE

In many cases a part of the absorbed energy is stored during excitation. This is due to trapping of the excited electrons in trap levels. The energy required to release a trapped electron is known as "Activation Energy". It is also referred to as 'trap depth' as it is the energy difference between the trapping level and the corresponding excited level.

This stored energy may be liberated in two ways - Phosphorescnece or Thermoluminescence.

a) Phosphorescence

When the excitation of the phosphor is stopped an after glow called phosphorescence is observed. This is due to the releaseof the energy stored during excitation. Electrons from the trapped levels giving phosphorescence are liberated. It is observed from 10^{-8} secs. after removal of excitation source.

The mechanism of phosphorescence decay can be followed from the energy band model in fig. (1.6).An electron raised into the conduction band by absorbing light energy may according to the minimum energy principle fall into a trap (T1) instead of immediately recombining with a centre. After some time the trapped electron returns to the ground state via conduction band giving rise to phosphorescence (H E $T_1 S_1$ L).

Effect of Trap Distribution on phosphorescence decay :

The intensity and form of decay depend upon the distribution of traps. If traps are located close to the conduction band the resulting decay is faster and hence it is of short duration. On the other hand, it is of long duration if traps are situated at a great distance from the conduction band. The intensity of phosphorescnece decay is a function of the population of traps of particular depth. More the population, higher is the intensity and vice versa.

b) Thermoluminescence

If a previously excited and sufficiently decayed phosphor is heated at constant rate then light is emitted. This phenomenon is known as thermoluminescence. Here heat is not the excitation agent but it only acts as a stimulant. Hence it is more correctly called as Thermally stimulated Luminescence (TSL). The exciting agent may be any one of uv, ionising radiations, mechanical vibration etc.Phosphorescence at any temperature after the removal of excitation is nothing but isothermal decay of TL at that temperature.

Actually any decrease in the thermal energy of the electrons retards the luminescence process until the temperature of the crystal is raised so that it appears that the luminescence is thermally produced(40) The electrons trapped during exciation are released by thermal activation.

The variation of the total light output with temperature is known as 'Glow Curve'. The temperature at which the TL output is maximum is called peak temperature. It is a measure of the trap depth. The position of the trapping levels below the conduction band and the number of electrons trapped in these level decide the peak temperature and peak intensity.

The release of electrons from the traps depends on the rate of heating. Thus, the peak intensity also in turn depends on the heating rate.

Finally, the TL glow curve may exhibit many peaks depending on the nature of the material. These peaks will correspond to traps of different depths.

A band pass filter or monochromator can be kept between the sample and the photomultiplier tube (used to record TL output): the TL glow curve of a particular emission wavelength can be recorded. This is known as monochromatic TL glow curve(41). Such a glow curve depends on the emission properties and thus the energy gap between the two levels involved during the emission.

The glow peak temperature is a measure of thermal activation energy needed for the detrapping.

The rate of heating affects the glow peak temperatures, intensities and the shape of glow curve but not the emission spectrum.

Thus, TL characteristics of any material can be specified by the TL glow curve (heating rate specified) and TL emission spectrum (with temperature specified) - both related to specific initial excitation of the material.

1.7 MECHANISM OF ELECTROLUMINESCENCE

It is possible to produce luminescence by exciting electrons electrically. The substances which emit light (in the visible or nearly visible region) due to the application of an electric field (AC or DC) are called electroluminescent materials. The phenomenon involved is called electroluminescence.

The mechanism consists of three stages;

i] excitation.

ii] transfer of energy from the site of excitation to the site of emission, and,

iii] recombination.

1.7.1 EXCITATION

The excitation of EL takes place by a supply of energy to the charge carriers. The different mechanisms proposed are :

i) Field ionization of valence electrons and impurities :

The possibility of exciting an insulator with an intense electric field was first pointed out by Zener(42). The transfer of valence electrons may take place by quantum mechanical tunneling process (41) producing a free electron and free hole simultaneously.

ii) Injection EL :

Minority carriers may be injected either at an electrode contact or at P N Junction. The difference in work functions, the position of the Fermi level in the semiconductor, nature of the intermediate chemical or physical barrier layer, surface states and the concentration of the donor and acceptor are the governing factors of the behaviour of the surface of contact.The barrier formed in the rectifying contact is known as Mott Schottky barrier. In this type, minority carriers can be injected into the interior of the semiconductor. Injection EL occurs by the following methods.

a] P-N injection :- As shown in fig. (1.10) the potential energy of electrons in the Nregion is raisedunder the forward bias condition. Due to thisthere is free flow of electrons into the P-region and holes into the N-region. When an electron and a hole overlap, they combine radiatively.' In LED's one side of the junction is more heavily doped and the carries on this side experience a reduction in the barrier height.

b] Heterojunctions :- Materials with small band gap act as a source of luminescent region and that with large band gap act as a source of injected charge carriers. (shown in fig. 1.11).

c] Schottky barriers :- Fig. 1.12 shows the inversion layer in an N-type material. When forward bias is applied the bands are flattened and minority carriers are injected into the bulk matrix where they recombine rediatively.

d] Metal-Insulator-Semiconductor (MIS) structure :- An applied voltage can control band bending and an inversion layer can be introduced by one polarity. Such carriers accumulated at the surface can be injected by reversing the polarity of the metal electrode (shown in fig. 1.13). The holes accumulated at the surface are injected and recombination takes place. Injection of electrons can take place by tunneling if the insulator is made thin.

iii) Radiative Tunneling

Electrons from the conduction band tunnel into the gap where they make radiative transitions to the valence band or an emptystate in the band gap. The semiconductor should be degenerately doped on both sides for this process to occur (fig.1.4)

iv) Acceleration-Collision EL

This process is found in most materials like ZnS. It is based on the acceleration of the electrons in the conduction band followed by a collision excitatin of the luminescent centre. The different stages are shown in fig. (1.15). The field strength at which EL excriation takes place depends upon the Mott Schottky exhaustion barrier (Piper et al. 1958). The field in the barrier and the thickness of thebarrier increases with the square root of the voltage.

v) Breakdown Luminescence

This occurs due to avalanche breakdown, i.e. multiplication of electrons and holes by gaining sufficient energy from the electric field. Such pairs recombine radiatively.

1.7.2 TRANSFER OF ENERGY

Movement of charge carriers helps the transfer of energy from the point of excitation to the site of emission. The concentration gradient, the electric field intensity and the concentration of trap depths decide the flow of energy due to the transport of charge carriers.

This transport of energy can also occur by mechanisms not involving electronic charge carriers, i.e. by

i]Cascade transfer mechanism .
ii] Resonance transfer mechanism.
iii] Excitation migrating mechanism.

1.7.3 RECOMBINATION

Luminescent output can be got by the recombination of electron and hole.During this process a variety of transitions take place from upper energy states to lower energy states. The transition can be radiative or non-radiative.

A] Radiative Transition :

These are the transitions, that help in giving a luminescent output.

i) Band to band transitions :

Band to band transitions occur between the conduction band and the valence band in the case of direct semiconductors. In case of in direct semiconductors it requires emission or absorption of a phonon ? to complete the lowest energy transition across the energy gap.

photon

ii) Band to impurity Transitions

If the impurity state is deep, a radiative transition can occur between the impurity state and the valence band.

iii) Transitions of a localised centre :

In large bandgap materials impurities can be excited without ionising materials, i.e. without their electrons moving to the conduction band.

iv) Transitions at isoelectronic centres :

When an atom of the host is replaced by another but with the same valency an isoelectronic centre is formed.

v) Donor to Acceptor Transition :

Radiative transitions can take place between donor and acceptor levels. These transitions are observed in LEDs and phosphors.

Non-Radiative Recombination :

When a transition from an upper to a lower energy state occurs without emitting a photon, it is called a non-radiative transition or recombination. It can happen by several mechanisms.

i) Multiphonon Emission

Such emission takes place when an electron can escape the from excited state and return to its equilibrium position by generation of several phonons.

ii) Auger Effect

A recombining electron can transfer the energy to another electron in the excited state. This second electron goes to a still higher energy state and returns to lower energy state by multiphonon emission.

iii) Non-radiative defects :

In some cases a continuum of states may join the conduction band to the valence band. This results in non-radiative transition for surface recombination.

Some important requirements of a good EL phosphor are(43)

i) its electron traps should be shallow.

ii) its activation energy for the escape of holes from the ionised activator levels should be as large as possible and,

iii) should have a cubic structure which is more favourable for EL emission.

1.8 KINETICS OF LUMINESCENCE

The mechanism involved in the recombination of electrons with luminescent centres decides the kinetics of luminescence. There are three modes of Kinetics involved,

i) Monomolecular Kinetics (First Order).

ii) Bimolecular Kinetics (Second Order).

iii) Intermediate Kinetics (General Order).

i) Monomolecular Kinetics :

If traps are situated close to luminescence centres then a very small movement of electron is necessary to recombine the centre. The process is monomolecular or first order kinetics(19). In monomolecular kinetics,the process of recombination is dominant and probability of retrapping is negligible(42, 44).

ii) Biomolecular Kinetics

If traps are located away from the luminescence centres, then electrons have to undergo large displacements for recombination with luminescent centres. The kinetics involved is bimolecular or second order kinetics. In this case retrapping is dominant.(42,44).

iii) Intermediate Kinetics

In this case traps are distributed such that the probability of retrapping of electrons in deeper traps is small but not negligible Here the order of kinetics is neither uniquely monomolecular nor uniquely biomolecular and so it is called intermediate kinetics. Such kinetics is shown to be feasible by several workers.(45,46)

1.9 REVIEW OF PREVIOUS WORK

Luminescence of different materials has been studied to a great extent by different workers. Luminescent materials of special interst are activator doped materials rather than naturally existing ones. These include alkali halides, sulphates, borates, sulphides, carbonates etc. Extensive work done on alkali halides finally led to the well known phosphor LiF:Mg:Ti used in radiaton dosimetry. Detailed study of LiF crystal doped with various activators hasbeen carried out by Kathuria (47) The Mg and Ti doped LiF phosphor is manufactured by Harshaw Chemical Company under the trade names, TLD-100, TLD-600, TLD-700 M(18)

CaS phosphor with Mn, Bi, and rare earth doping has been studied by other workers(48, 49, 50, 51, 52) and are found to have good luminescent out put. Calcium sulphide and also Barium sulphide are good fluorescent materials for luminescent output. CaS phosphor is studied with Ag:Dy activator.(53).

7 Rare earths have been found to be efficient activator in Borates of the form $X_2Mg(BO_3)_2$:RE (X = Ca, Ba, Sr) as TL phosphor by Dhayagude(14).

Rare earth elements also have been found to be suitable activator in $CaSO_4$ host (54). $CaSO_4$:RE phosphor has better sensitivity than LiF, CaF_2 phosphor as reported by Nambi. This result agrees with that of other workers(15, 46, 47, 55).

Among the various activators Mn is proved to be a good activator in different phosphors (56).Mn can be used as a universal dopant in nearly all inorganic phosphors(15).Mn is almost exclusively responsible for the TL emission spectra of all types of natural calcite. It is one of the most efficient dopant for TL emission in CaF_2 and $CaSO_4$ (15). PL studies of Mn doped sulphate shows that it is not an efficient emitter of luminescnece unless a Co-dopant like Ce^{3+} is simultaneously used to sensitise it.(57)This isbecause Mn^{2+} ion recieves the excitation energy from co-dopant impurity ion (58) Mn doped phosphor showed a linear dose response within range of 10^{-2} to 10^4 radiation of gamma rays(57)

$CaSO_4$ phosphors are found to be popular because of their high sensitivity. $CaSO_4$:Mn phosphor is studied under uv irradiation for TL glow curve by Lyman(59). Nosenka(60) used $CaSO_4$:Mn phosphor for ionising radiation. Yamashita prepared a $CaSO_4$:Mn:Pb phosphor(61)which has good sensitivity as compared to $CaSO_4$:Mn phosphor.The chief disadvantage of $CaSO_4$ TL phosphor is the fast decay of the dosimetry peak which occurs at low temperature around 100°C (15).Bjarngard(62) developed $CaSO_4$:Sm to offset the fading characteristics experienced with $CaSO_4$:Mn phosphor. Yamashita(13) prepared $CaSO_4$ phosphor with various R E dopant and found that $CaSO_4$:Dy, $CaSO_4$:Tm have prominent TL peak at 200°c in radiation dosimetry (11) as these exhibited the best domestic characteristics along with maximum sensitivity. $CaSO_4$:Dy, TL phosphors and dosimeters are now available commercially from Harshaw Chemical CO, U.S.A. and Matsushita Electricals, Japan and these have found to favour among many radiation dosimetric investigators (12,63) CaF_2(64). $CaSO_4$(65,66) Mg_2SiO_4(67, (69) phosphors have proved to be more sensitive in comparison with LiF. $CaSO_4$:Mn is useful phosphor for radiaton dosimetry including uv radiation measurements. $CaSO_4$:Mn:Dy activation gives high TL sensitivity compared to Mn:Pb, Mn:Ag, Mn:Zr(70)

For $CaSO_4$:Dy phosphor three peaks are found at 110°c, 158°c, 235°c with heating rate 5.4°c/sec. 235°c peak is more sensitive to gamma rays. Activation energy is determined ~~be~~ by peak shape method, initial rise method, diff. heating rate method. Estimated activation energies are 1.23 ± 0.03 eV, 1.24 ± 0.03 eV, 1.23 eV. TL process is found to have II order. Frequency factor, 'S' is observed to be 3×10^{11} sec^{-1} (71).

ESR study of gamma irradiated sample of $CaSO_4$:Dy has been made. It is observed that in addition to usual intrinsic defects, four new paramagnetic centres are found to be present. These centres are related to sulphate ions. Two of these centres are proposed as holes trapped and shared between two adjacent sulphate ions.(72)

The spectra of thermoluminescence under x-irradiation in pure $CaSO_4$ have been studied by Tomita(73) to reveal the nature of luminescence centre.

In $CaSO_4$:Dy phosphor Ca^{2+} vacancies are involved in the formation of traps whichgive TL peaks.(74)

A lattice dynamics model for ionic crystals with complex anions is developed and applied to experimental phonon dispersion curves for orthorhombic $CaSO_4$. The model treats the suplphate as rigid unit and includes long range Coulomb interaction (75).

PL and excitation spectra of various TLd phosphors were measured at 300°k. In Eu^{2+} spectra $4F^7 \longrightarrow 4F^7$ transition is observed near 360 nm in addition to broad band. No line emission due to Eu^{3+} centre was observed in any of the phosphors.

If $CaSO_4$: Eu^{2+} , cooled to low temperature, phonon structures are observed on emission bands and low energy excitation bands(76).

Short wavelength uv less than 250 nm causes Eu^{3+} to Eu^{2+} conversion. Eu^{2+} measurements were always prior to those Eu^{3+}. Intensities of Eu^{2+},Eu^{3+} spectra are weak under uv irradiation.(65,77)

The charge neutralityin the presence of $CaSO_4$:Dy phosphors without charge compensetor (Na_2SO_4), demands the removal of three Ca^{2+} to incorporate two Dy^{3+} ions. This mounts Ca^{2+} ion vacancies in the host lattice.The host lattice defects produced during the preparation phosphors due to such Ca^{2+} ion vacancies restrict the entry of Dy^{3+} activator ions in the lattice structure. However,the addition of Na_2SO_4 in $CaSO_4$:Dy phosphors wipes out the host lattice defects created by Ca^{2+} ion vacancies and brings about an appropriate charge compensation

$$2Ca^{2+} \text{ ——— } Dy^{3+} + Na^{+}$$

This is in accordance with the charge compensation theory of Kroger and Hellingmann.(78)

The role of Sm activator and the process of radiative energy transfer in $CaSO_4$ phosphors have been explained by Laitano and Martinelli (79). They have shown that, activators do not change appreciably glow peak temperature but their heights.

The survey of literature indicates that, thermoluminescence studies reported do not usually extend beyond 400°c, on account of the ever-increasing thermal noise signal at high temperatures. However, it is by no means certain that the trapping phenomenon is absent at high temperatures. Recently, Nagapal and Gangadharan (80) studied photo transferred thermoluminescence of $CaSO_4$: Dy phosphors with a view to investigate high temperature peaks in these phosphors. The analysis of their results shows that, the high temperature peak is responsible for the regeneration of the lower temperature TL peaks lying between 550°c and 570°c.

Mulla-Pawar (81) have studied the mechanism of EL in $CaSO_4$:Bi phosphors. They observed the type of radiative transitions involved in the phosphor system under study. The addition of Na_2SO_4 as a charge compensator in the preparation of some of the $CaSO_4$:Bi phosphors produced an enhancement of EL brightness at a lower voltage range and subsequent deterioration at a higher voltage range compare to the phosphors without it.

J.K.Srivastava and S.J.Supe (82) have studied the activation energies and frequency factors for $CaSO_4$: DY TL phosphor in 340°K - 740°K glow temperature region. They found activation energies in the range of 1.15 eV to 2.39 eV and frequency factor in the range of 8×10^{12} sec^{-1} to 2×10^{16} sec^{-1}.

The increasing importance of Calcium sulphate phosphors has motivated many workers to prepare them and to study their luminescence and spectral properties. The survey of literature indicates that although calcium sulphate phosphors are known to exhibit fluorescence, phosphorescence, thermoluminescence, it is hard to find much reference on the electroluminescence behaviour of these phosphors.

1.10 SCOPE AND OBJECT OF PRESENT WORK

The phenomenon of luminescence is complicated as it offers very large variety of behaviours of different phosphors. In the field, radiation dosimetry few phosphors such as LiF(83,84), CaF_2(85,86), $CaSO_4$ (doped samples)(87,88), Al_2O_3 (laboratory made)(89), $Li_2B_4O_7$, (doped samples)(90,91), Mg_2SiO_4 (doped samples)(14), $Sr_2Mg(BO_3)_2$:(doped phosphor)(14) have been successfully synthesized, studied and employed. In the last two decades; there has been a marked revival of interst in the alkaline earth sulphate phosphors.These phosphors have emerged as highly efficient luminescent materials for thermoluminescence dosimetry (TLD). These phosphors have been stuided for fluorescence and phosphorescence after x-ray irradiation and for TL after gamma irradiation(15,54).Gamma irradiation being high energetic may cause damage in the crystal structure, impregnating additional defects than originally present. Systematic study of these phosphors under uv excitation is not attended, possibally because uv radiation might have been thought insufficient to excite these phosphors. Moreover, the ability of these phosphors to prove their applicability in the luminescence process other than thermoluminescence is not tested in details so far.

In present investigation an attempt is made to synthesise a phosphor of composition $CaSO_4$:Mn:RE by double doping, which might find a place in uv dosimetry and other associated fields. Mn has been proved as an activator in a variety of phosphors(15), Rare earths (RE) like Tb, Dy have been successfully used as promising activator in $CaSO_4$(15,54,92). Energy transfer in $CaSO_4$:Mn:RE has been clearly brought out (15).

Keeping all this in view, efforts have been made in the present work to search for most suitable rare earth as second activator. Samples have been prepared by varying concentrations of both, Mn and best rare earth in the host $CaSO_4$ and are analysed for TL after uv exciation. A comparative study of TL phenomenon under different irradiation is also attempted. Estimation of parameters, like activation energy (Trap depth), frequency factor, size of traps, using available techniques and methods has been carried out to understand the nature and origin of traps and possible mechanism in various phenomena studied. Photoluminescence (PL), Thermoluminescence(TL), Electroluminescence (EL) and electrical conductivity measurement after irradiation are focii of the investigation. Structural characterisation of prepared phosphors has been done by XRD analysis. Study of the effect of dopants on TL glow curve, analysis of glow curve parameter, possible mechanism of electroluminescence, estimation of band gap are associated features of the present work.

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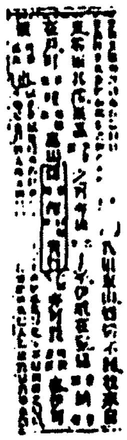
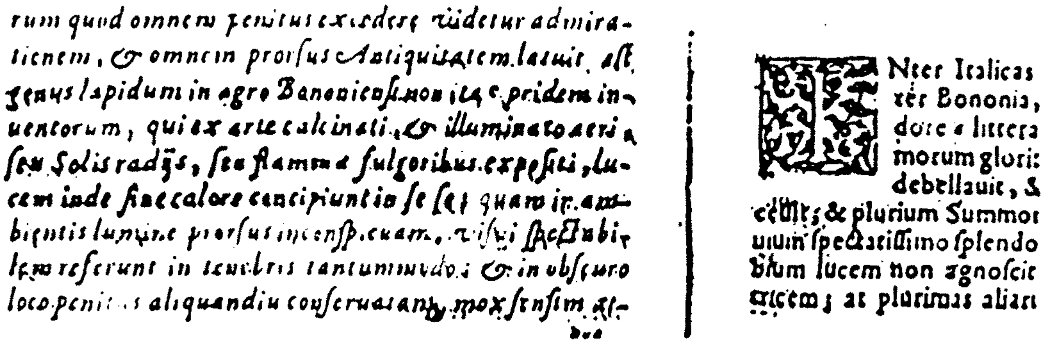


Reference to biolumines-
cence in the Chinese
"Book of Odes" with com-
mentaries

FIG. 1·1

" illuminato aeri seu solis radiis, seu flammae fulgoribus expositi,
lucem inde sine calore concipiunt in sase....."

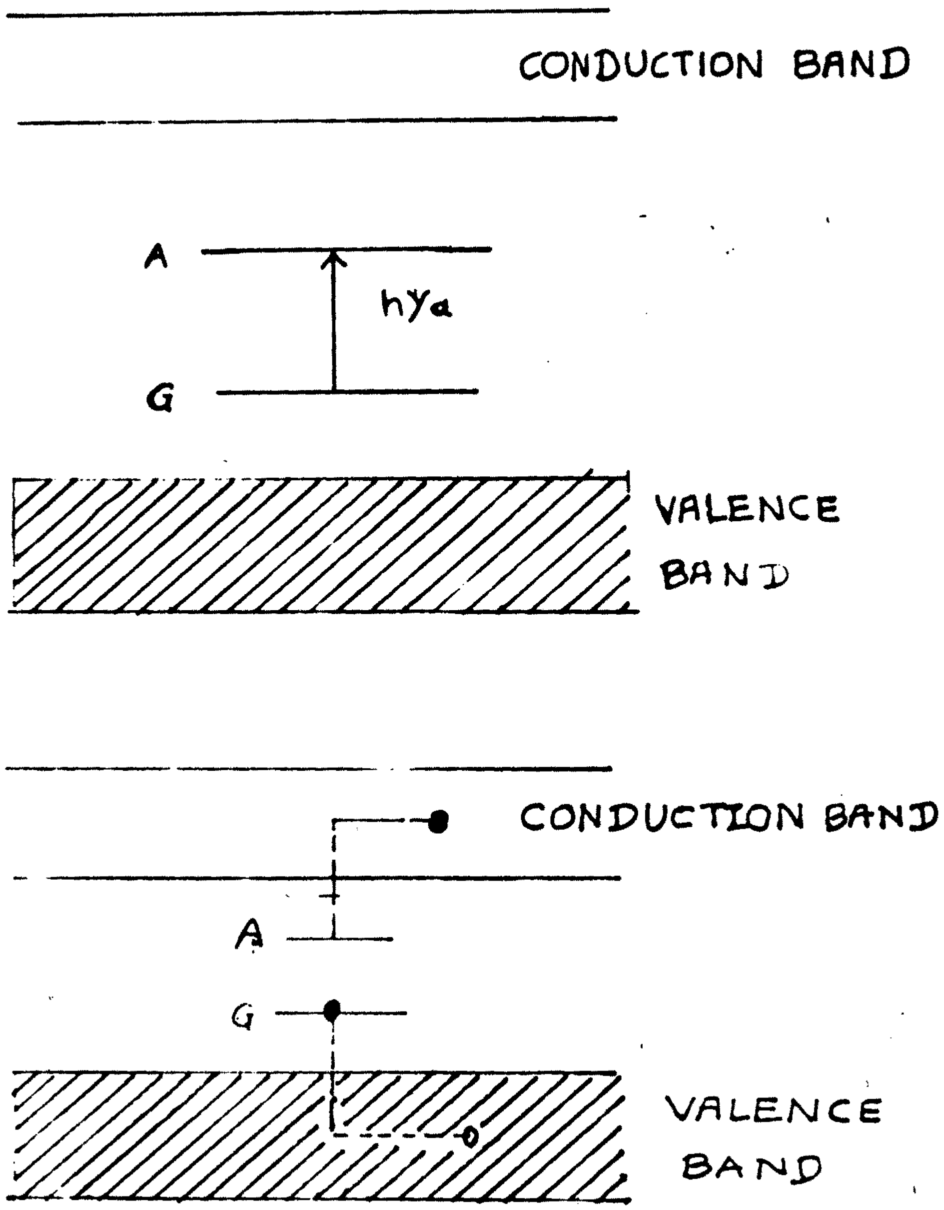


rum quod omnem penitus excedere videtur admira-
tionem, & omnem prorſus Antiquitatem latuit. eſt
genus lapidum in agro Bononienſi non ita pridem in-
uentorum, qui ex arte calcinati, & illuminato aeri,
ſeu Solis radijs, ſeu flammae fulgoribus expoſiti, lu-
cem inde ſine calore concipiunt in ſe ſe; quam in am-
bientis lumine prorſus inconſpicuam, viſui ſpectabi-
lem referunt in tenebris tantummodo; & in obſcuro
loco penitus aliquandiu conſeruatam, mox ſenſim at-

Nter Italicas
ter Bononia,
dore a littera
morum glori:
debellauit, &
celliis & plurium Summor
uium ſpectatiſſimo ſplendo
bium lucem non agnoſcit
cicem; at plurimas alias

Early definition of luminescence by Licetus, as it appears in his book of 1640. Photoluminescence of the Bologna stone; when properly calcinated and illuminated either by sunlight or flames, it conceives light without heat.

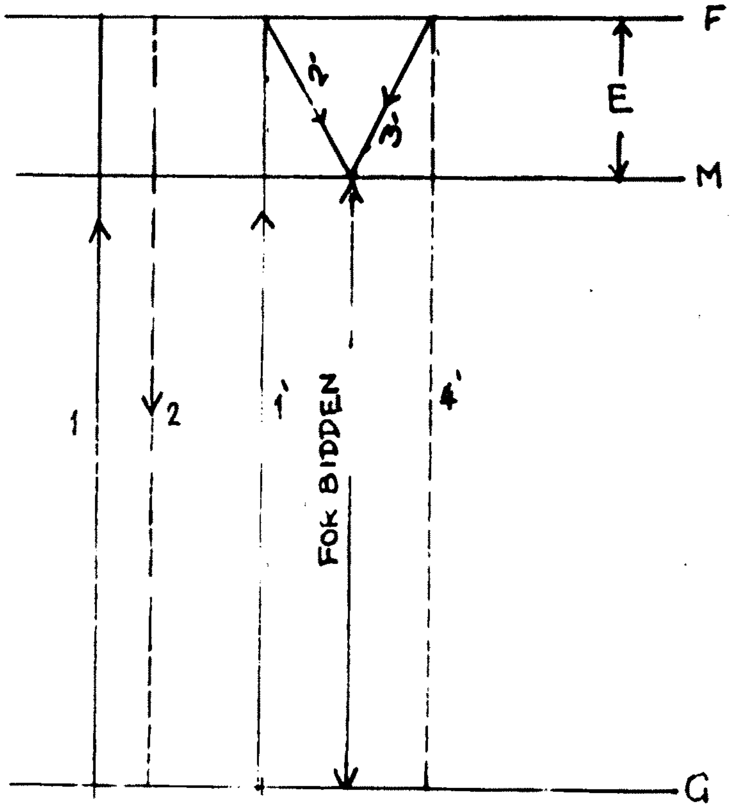
FIG. 1·2



THE LUMINESCENCE CENTER
AND
ITS EXCITATION

FIG.1·3

ENERGY STATES FOR FLUORESCENCE AND PHOSPHORESCENCE



G = GROUND STATE
F = EXCITED STATE
M = METASTABLE
E = ACTIVATION

1' = EXCITATION FLUORESCENCE
2 = FLUORESCENCE
2' = DROP IN METASTABLE STATE
3' = ACTIVATION THERMAL OR OPTICAL
4' = PHOSPHORESCENCE

FIG. 1·4

CLASSICAL CONFIGURATION COORDINATE CURVE MODEL

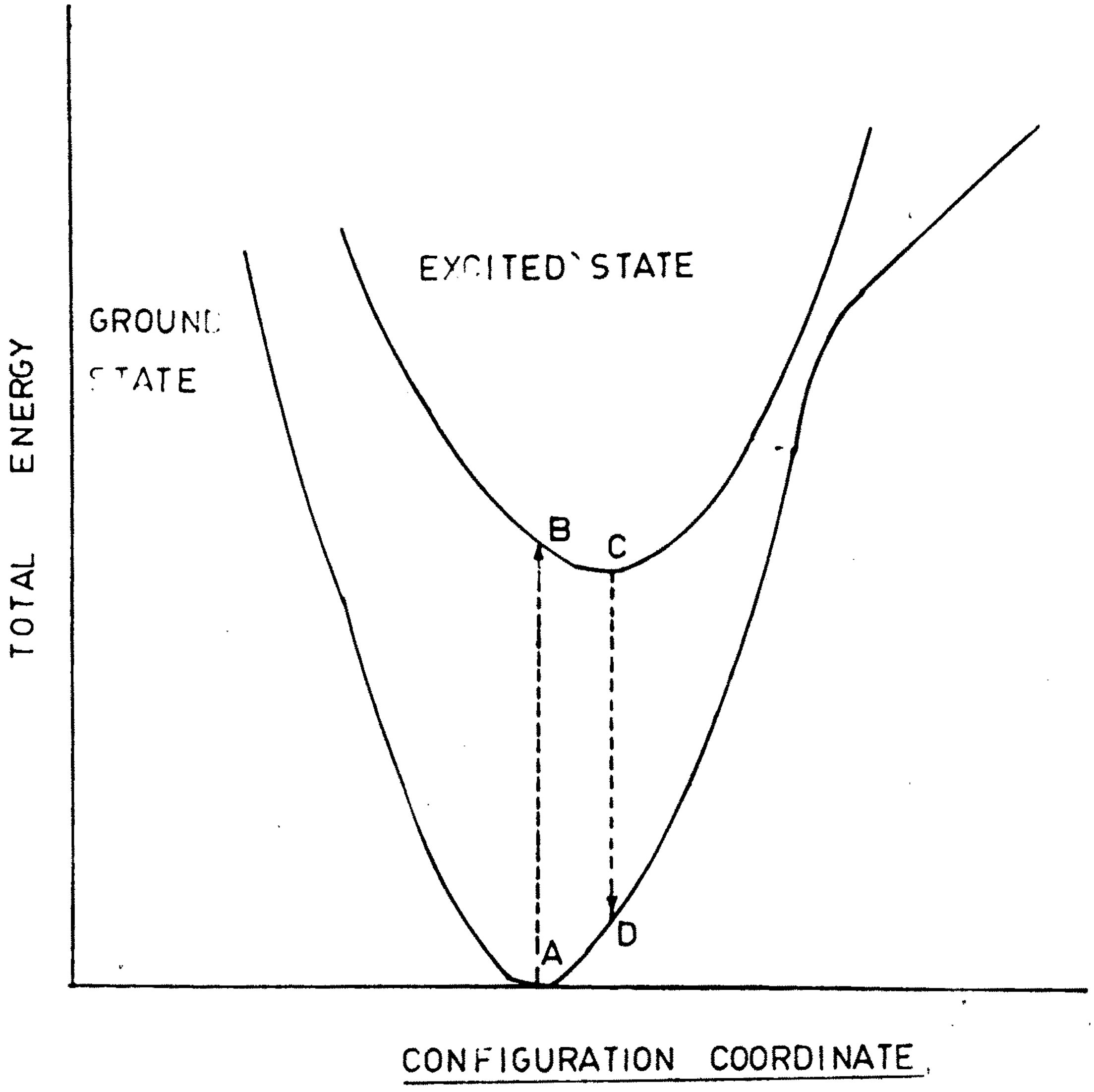


FIG. 1·5.

ENERGY BAND MODEL

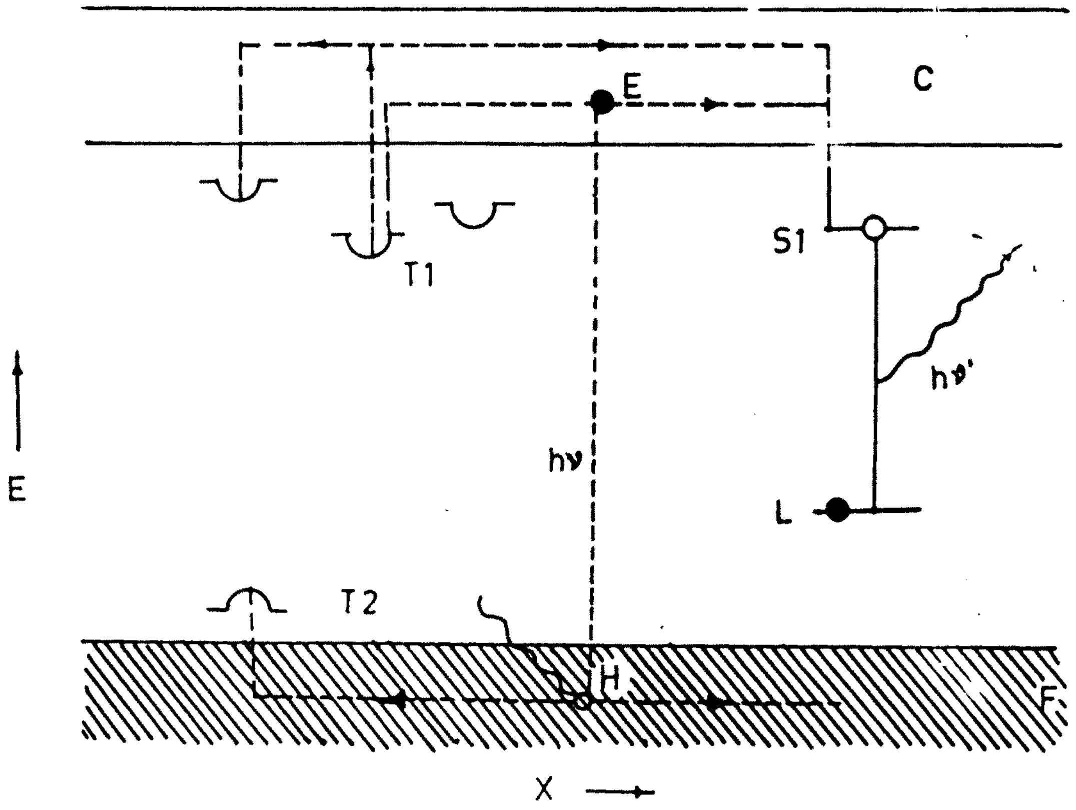


FIG. 1·6

SCHON - KLASSEN'S MODEL

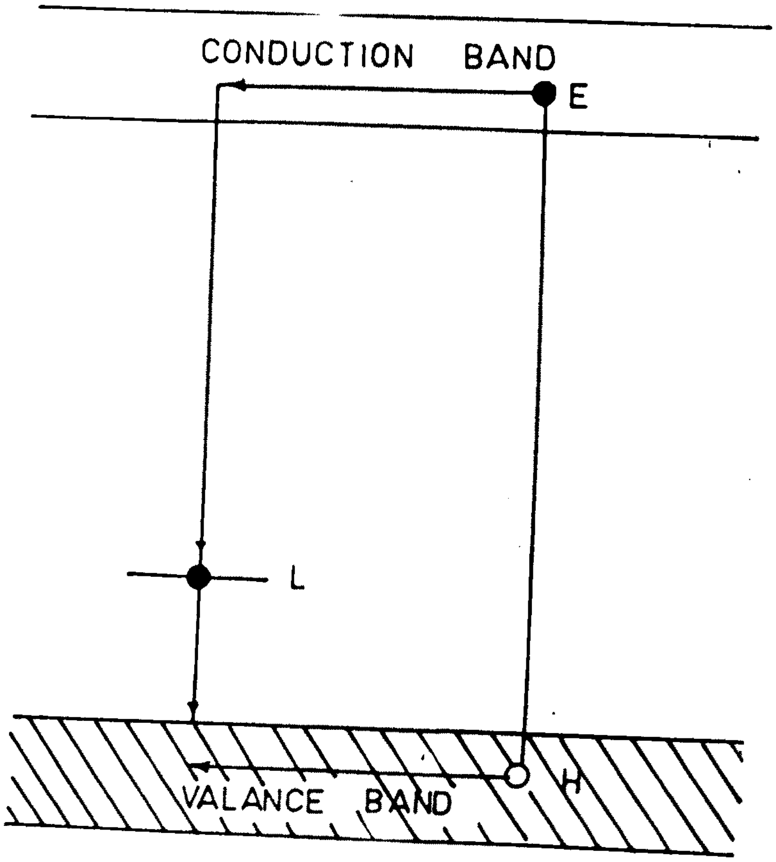


FIG. 1.7

LAMBE - KLICK'S MODEL

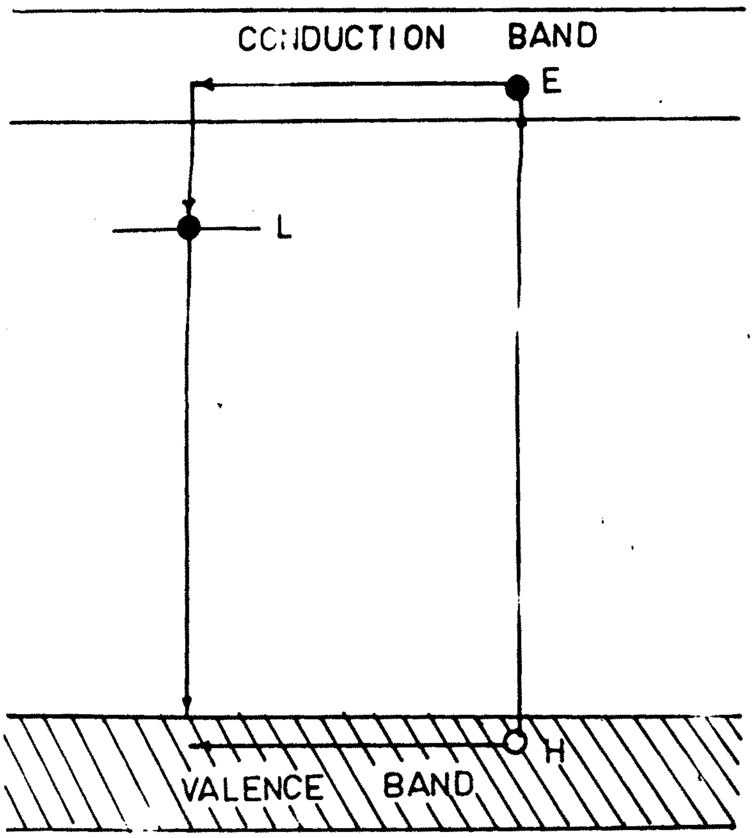


FIG. 1·8

WILLIAM'S AND PRENER'S MODEL

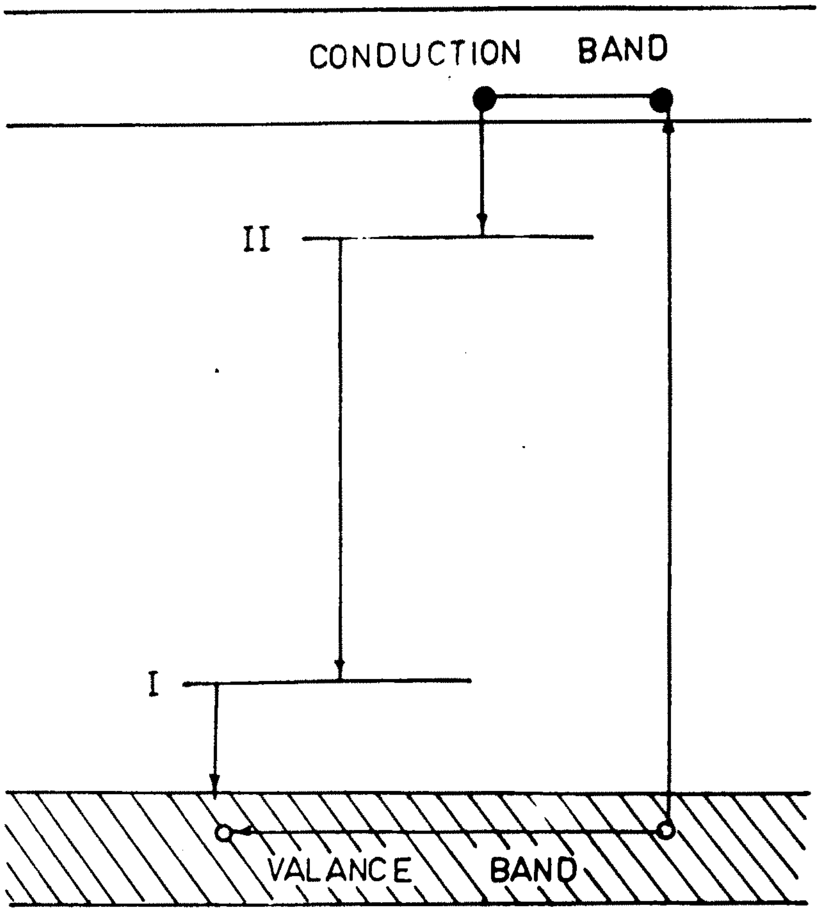


FIG. 1·9.

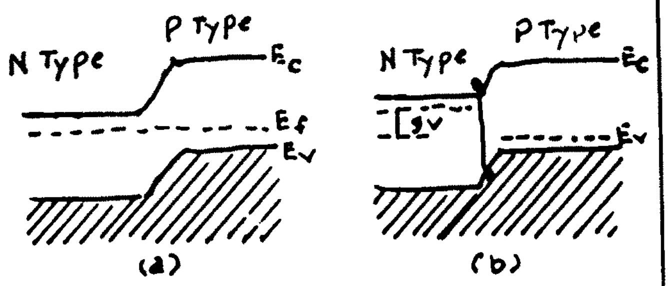


FIG. 1·10

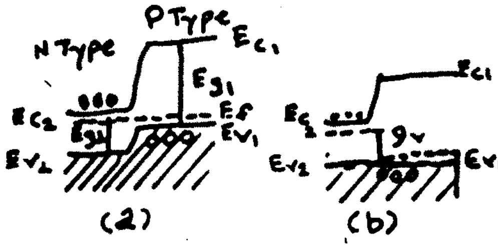


FIG. 1·11

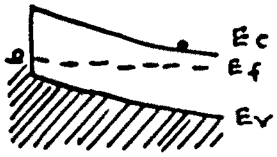


FIG. 1·12

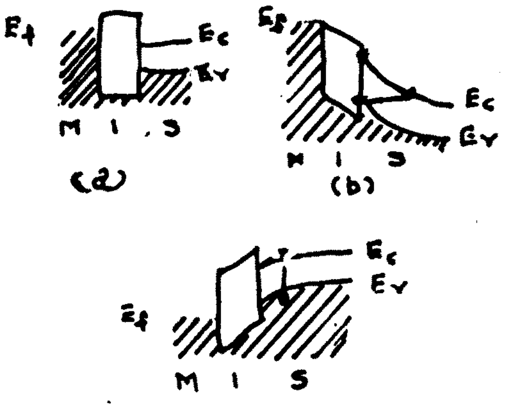


FIG. 1·13

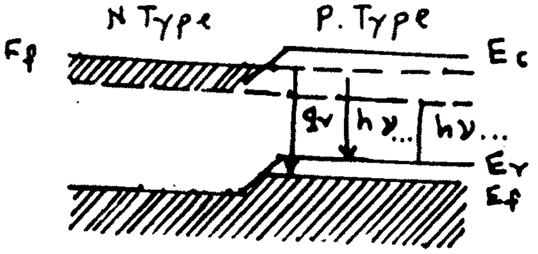


FIG. 1·14

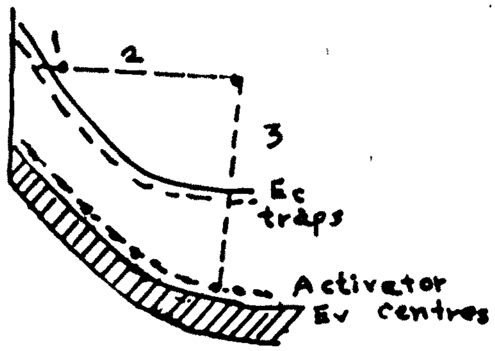


FIG. 1·15