CHAPTER I

INTRODUCTION

CHAPTER-I

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1.1 LUMINESCENCE:HISTORICAL

The study of luminescence is an important branch of physics. It has extended our knoweldge of the structure of solids and mechanism of light emission. The term luminescence includes various excitation processes and emission of light either as fluorescence or phosphorescence.

The first ever luminescent material, barium sulphate heated with coal, emits feeble blue glow at night, after exposure to day light. It was observed in 1603 by Cascierolo of Bologna, Ital~~g~~y. He named it as Lapis Soleris i.e. sunstone. Later in 1768, Catston found a brighter luminescent material by heating calcium carbonate with sulphur. It was then followed by the contributions of Lenard and his School (1) and J. Becquerel, who studied phosphors doped with various impurities.

The oldest record of luminescence is the bio-luminescence observed in living organisms which is beacause of chemical reaction in the living organism. This was observed in fire-flies and glow worms. The reference is found in Shih Ching, the "Book of Odes" well before 3000 B.C.

The TL was first reported by Robert Boyle to the Royal Society, London in 1663. He observed a glimmering light when a diamond is heated in the dark.

The phenomenon of light emission by solids after excitation was not subjected to systematic study until the middle of nineteenth century. The first law in this study was proposed by Stokes (2) in 1852, stating that emitted wavelength is greater tha the wavelength of excitation radiation. At the same time A.H.Becquerel (3) laid the foundations for the experimental investigations of the emission spectrum and duration of after glow by undertaking the study of luminescence. The German

Physicist Wiedemann in 1889, introduced the term 'luminescence' (4) as emission of electro magnetic radiation in excess of thermal radiation. After this, a theoretical explanation for luminescence was given by Randall and Wilkins (5) in 1910 and then Garlick and Gibson (6) since then there is a spectacular growth of phosphor studies.

At the beginning, the luminescence was associated with the sulphides. But improved calcium sulphide among the activators manganese was one of the activators was made by Friedrich Hoffman (7) in 1700. Afterwards many methods are developed and synthesised for new ~~phosphors~~ phosphor materials with improved properties. These luminescent materials are used in many solid state opto-electronic devices.

The importance of luminescence is due to its application in basic research. Thus from both theoretical and practical point of view, luminescence continues to be an active field of scientific research.

1.2. DEFINITIONS

1.2.1 Luminescence :- Luminescence is a phenomenon in which the material absorbs energy and reemits the energy at visible or near visible frequency radiation. The time delay in luminescence emission after excitation is longer than 10^{-9} sec. whereas in Raman etc. later it is of the order of 10^{-14} sec. (8). The emitted radiations are nonthermal in origin (9) and it is distinguished from Raman, Compton, Rayleigh Scattering and Cherenkov radiations.

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

a) Bioluminescence :- a chemiluminescence in a living organism.

b) Chemiluminescence :- It is a product of chemical reaction. 9

c) Radioluminescence :- It is caused due to bombardment with high energy particles or radiations such as x-ray, gamma rays etc.

d) Galvanoluminescence :- produced during electrolysis in galvanic cell.

e) Triboluminescence :- produced by utilization of mechanical energy.

f) Sonoluminescence :- produced by sound waves usually of ultrasonic variety.

g) Electroluminescence :- It is due to an electric field.

h) Photoluminescence :- produced by the absorption of uv or UV visible radiations,

i) Catho-doluminescence :- a special case of radioluminescence, produced by cathode rays.

j) Thermoluminescence :- it does not refer to the thermal excitation but rather to the thermal stimulation of luminescent emission when the material is excited by other means.

Many times combinations of the above luminescence processes are also used.

1.2.2 :- Fluorescence and phosphorescence :

Depending upon the duration of emission after the removal of an excitation, the luminescence is classified as fluorescence or phosphoreseence. Fluorescence is defined as emission of light during excitation (6) and phosphorescence, after excitation is removed.

According to Levereng and Kroger(35) a luminescence emission which lasts up to the inetial 10^{-8}sec after excitation is fluorescence, while the subsequent is to be referred as pho~~r~~sphorescence.

1.3 : Phosphors :

The luminescent material, which is artificially produced for use in various applications is known as phosphor. The phosphor is used for TV-tubes, fluorescent lamps, radar screens etc. They are inorganic or organic in nature but inorganic phosphors are more important. (10)

Phosphors are classified as :

1) Phosphor in pure form
2) Impurity activated phosphors

The phosphors consists of following components.

a) the host,
b) one or more activators (acceptors)
c) a co-activator or a charge comp~~a~~ensator (donor)

1.3.1 :- Phosphor in pure form :

The self activated phosphors shows luminescence when they are in pure form. (11, 6)

1.3.2 :- Impurity activated phosphors :

These are showing better luminescence than pure one. For activation, small amount of impurity is added to the base compound called host lattice or matrix material. The impurity which causes the luminscence is called activator. The impurity which is added along with the first impurity is called as co-activator, which will increase the luminescence. There are some impurities in the presence of which the luminescence intensity decreases. Such impurities are known as killers or poisons.

e.g. fe, Co, Ni, etc.

1.4 :- Localised energy levels in Forbidden gap :

The lattice defects or the impurities added give rise to decrete energy levels in the forbidden energy gap in an insulator or a semiconductor. These energy levels are classified as -

A) Meta-stable states :-

These are the energy states adjusting with in the forbidden region, which can be excited by electron bombardment and not by photo excitation. A transition from meta stable state to normal state is forbidden. The transition from higher level to a meta stable state is allowed. The life times of meta-stable levels are of the order of 10^{-2} to 10^{-4} sec.

B) Luminescence centres :-

These are the energy levels which are responsible for spectrum of emitted luminescence. These centers possess high capture cross-section for excited electrons and much greater probability for radioactive transition than for non-radioactive transition. (12) The absorption and emission properties of these centres are the characteristics of activator ions and the host material.

C) Electron and hole traps:

The excited electrons are captured by a localised energy level produced in the centres or else where in the crystal, without allowing an electron to fall directly into a normally filled level is called an electron trap or just a trap.

Hole traps are localised energy levels just above valence band, capable of capturing a hole.

D) Killer center :

These are the energy levels which are having small capture cross-section for excited electron and much greater probability for non-radiative transition than for the radiative transtion.

E) Colour centres :

A colour centre is a lattice defect that absorbs visible light. The set of defects, which results from charge compensation are called the colour centres. If some crystals are irradiated with electrons, neutrons, x-rays or Gamma rays, a colour change is produced e.g. diamond is coloured ~~xxxproduced~~ blue by electron bombardment and quartz is coloured brown. After irradiation damages the crystal lattice and various types of point defects are produced. The usual place to find colour centres is in ionic crystals.

F F-centres- the most extensively studied and the simplest colour centre is the F-centre (13), its origin is alkali halides.

1.5 :- Mechanism of photoluminescence :

The photoluminescence mechanism involves the following processes -

i) Excitation

ii) Emission

iii) Transfer of an energy during excitation and emission and,

iv) Storage of the part of absorbed energy during excitation.

1.5.1 : Excitation and Emission :

Several models have been proposed to explain the processes involved in the mechanism of photoluminescence. Some of them are as follows :

i) Energy band model :

The energy band model (10, 14) is explained by the fig 1.2. According to this model, the phosphors which are semiconductors or insulators are described interms of valence band (f) and conduction band (c) with localised energy levels in the forbidden gap. The localised energy levels are associated with impurities or imperfections in the host lattice. as shown in fig. 1.2 The level 'L' represents ground state of the luminescence centre, while levels T_1 and T_2 represent electrons and hole traps respectively.

The excitation and emission takes place as follows : Absorption of light energy in the phosphor excites luminescence centres from ground state (L) to the excited state (g) by raising the electron into the conduction band. Such an excited centre then captures an electron from the conduction band and returns to its ground state by giving luminescence emission. If the energy absorbed in the phosphor is equal to the separation between the valance and conduction bands it also excites electrons (e) from valance band to conduction band creating holes (H) in the valance band. This is known as fundamental absorption band. However, such electron and hole pairs normally donot recombine radiatively (15, 16)

ii) Classical configuration co-ordinate curve model :

This model is explained in fig. 1.3. It was introduced by Van-Hippel (17) and was applied by Seitz (18) to explain the luminescence behaviour. In fig. along the ordinate total energy of the system for the ground and excited states of the center, while the abscissa the 'confrguration co-ordinate' which specifies the configuration of the ions around the center. Point A represents the equilibrium position of the center in the ground state. If the light is absorbed by the centre, it is raised to the excepted state B. According to the Frank Condon principle the transtion is vertical. From B, the centre relaxes to new equlibrium state C, the state corresponding to the minimum energy excited state. The energy difference between B & C is given off as lattice vibration. Having reached the centre at this new equilibrium position it returns to the ground state 'D' by giving luminescence emission. The center finally relaxes from D to A. again giving up energy to the lattice vibration. Thus the emitted energy is smaller than the absorbed one and explains the stokes shift.

(iii) Lambe-Klick's Model :

In this model (19) the ground state of luminescent center (L) is assumed close to the conduction band fig 1.5. With absorption of light photon, a free hole and electron are produced. The hole diffuses to the centre where it captures the electron from the center. This transition gives rise to luminescence. Subsequently the electrons from conduction band diffuse to the center and gets captured there, thus completing the cycle.

iv) Schon-Klasen's Model :

This model was proposed by Schon (20) and elaborated by Klasen and his co-workers (21, 22, 23). ~~The~~ Fig. 1.5 illustrates the model for the case of single luminescence centre. The ground level 'L' of the luminescence centre is assumed close to the valance band. On absorption of light in the fundamental absorption band, free electron and holes are created. The electron moves to the conduction band while the hole diffuses through the valance band and captures an electron from the lumenscence centre. This excites the luminscence center. The free electron after migrating in the conduction band falls into the empty center which gives emission of light.

v) Williams and Prener's Model :

In this model proposed by Williams (24) and Prener (25) two centres are involved as shown in fig 1.6.

The groundlevel (I) of the first centre is assumed close~~d~~ to the valance band while the excited level (II) of second is assumed close to the conduction band. After absorption of the energy in the fundamental absorption band a free hole and an electron are produced. The excited level (II) captures an electron from the conduction band while the hole~~s~~ in the valance band captures an electron from ground level (I) and thus leaves it empty, the emission then takes place by the transition from level II to the I.

1.5.2 :- Energy Transfer :

In the phosphor systems, where absorption and emission of light energy takes place at the same center, no energy transfer is involved. However, in the system in which absorption and emission are not confined to the same center, energy is transferred from absorption to the emission one. It occurs in two ways, (A) Energy transfer with no movement of charge carriers (B) Transport of energy by charge carrier.

(A) Energy transfer with no movement of charge carriers :

In this case there are three mechanisms for transfer of energy

1) Cascade Mechanism
2) Resonance Mechanism
3) Exciton Migration

1) Cascade Mechanism :

In this mechanism (26) one centre on absorbing excitation energy emits radiation.. This is known as primary emission. These emitted radiations are absorbed by second centre which finally emits luminescence, that is known as secondary emission. This mechanism is most effective in those cases where the primary emission overlaps the absorption spectrem at the secondary emission system.

(ii) Resonance Transfer :

Here the transfer of energy is accomplished by a quantum mechanical resonance process. (27, 28) from absorbing system to the emitting system, such as electrical dipole field over laps & electric dipole-quadrupole field overlap or by

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exchange interaction. The efficiency of process depends upon the distance over which the energy is transferred.

iii) Exciton Migration :

The non conducting excited electron/holepairs are known as excitons. Because of their interaction with phonons they do not remain localised but migrate through out the crystal transfering the energy. In such process the excitons transfer excit~~i~~ation energy from one point to the another by moving quickly through the lattice without contributing to the electrical conductivity. (29)

B) Energy Transfer with movement of charge carrier :

In this mechanism, energy is transfered by electron and hole migration. The process is same as that involved in Schon Klasen's and Lambe-Klick's models during excitation and emission.

1.5.3 :- Energy Storage :

After removal of excitation, many phosphors store part of absorbed energy during excitation. This is due to trapping of excited electrons, in trap levels. The energy required to librate a trapped electron is known as the 'activation energy' and is always denoted by E. This is also known as 'trap depth' as it is the energy difference between the traping level and corresponding excited level.

A) Phosphorescnce Decay :

It is diminishing after glow under isothemal conditions, observed from 10^{-8} seconds after removal of excitation.

It arises due to the release of traped electrons in trapping levels during excitation.

The mechanism of phosphorescence decay can be followed from the energy band model of fig 1.2. An electron raised into conduction band by absorbing light energy may according to minimum energy principle fall into trap (T_1) instead of immediately recombining with a centre. After some time the trapped electron returns to ground state via conduction band giving rise to phosphorescence.

B) Thermoluminescence :

If a previously excited and sufficiently decayed phosphor is heated with uniform heating rate, it is found that luminescence intensity varies with temperature. The phenomenon is termed as 'Thermoluminescence' (TL)' or more correctly ~~as~~ Thermally Stimulated Luminescence (TSL).

In thermoluminescence, electrons or holes trapped during excitation are released from traps by thermal activation. Such released electrons gets combined with luminescence centres and give rise to TL emission.

Glow Curves :

The variation of TL intensity with temperature is known as 'glow curve'. A glow curve may have one or more glow peakes, depending upon the presence of the trapping level at 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 the trapping level 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 TL intensity also increases.

The TL glow curves may exhibit many peaks depending upon the nature of the material. These peaks will correspond to traps of different depths.

1.6 :- Mechanism of electroluminescence :

Due to the application of electric field (A.C. or D.C.) substance which emits electromagnetic radiations, visible or near visible, are called electroluminescence materials, and the phenomenon involved in the emission of light is termed as electroluminescence (EL). The mechanism of EL consists of following stages :

i) excitation,

ii) Transfer of energy from the site of excitation to the site of emission and,

iii) recombination. (33)

i) Excitation :

1.6.1 : The excitation takes place by a supply of energy to the charge carriers, generally charge carriers are electrons and the type of energy supplied will be either potential ~~and~~ or kinetic or both.

The different excitation mechanisms proposed are -

a) Field ionisation of valence electrons and impurities.

b) Acceleration - Collosion EL :

c) Injuction EL.

d) Radiative tunnelling

e) Break down luminescence

a) Field ionisation of valence electrons and impurities. The possibilty of exciting an insulator with an intense electric field in such a way as to excite valence electrons into conduction band was first pointed and by Zener (34). The transfer valence electron may take place by tunneling process (35), producing free electron and hole. Simultaneously, as the breakdown field competes with both of these processes, an activator system having a low ionization energy in dielectric phosphors (large band gaps) should be more conductive to EL, by this process (piper et. al. 1955).

b) Acceleration - Collison EL :

In the phosphors like ZnS a process is found based on which ? the acceleration of electrons in the conduction band followed by a collison excitation of luminescence centres. Its various stages are shown in fig 1.7. A Mott Schottky exhaution barrier is suggested to account for the stability against breakdown at the field strength at which EL excitation takes place. (Piper et al, 1958). The field in the barrier and the thickness of the barrier increases as the square root of the voltage. The source of charge carriers may be deep donors, acceptors or traps which are field ionised.

C) Injuction EL :- Injuction of minority carriers may occurs either at an electrode contact or a P.N. junction.

In a surface contact, the interface may possess ohmic characteristics or is capable of rectification and thus, its behaviour is governed by factors like the difference in work function, the position of fermi level in the semiconductor, nature of the intermediate chemical or physical barrier layer, surface states and the concentration of donor and the acceptors. The barrier formed in the rectifying contact is known as Mott Schottky barrier. In this type of barrier minority carriers can be injected into the interior of the semiconductors.

The injuction EL occures in following structures.

1) P.N. junction
2) Hetero junction
3) Schottky barrier
4) Metal insulator semiconductors (MIS) structure.

d) Radiative TUNNELLING :

As shown in fig. 1.8 electrons from the conduction band tunnel into the gap where it makes a radiative trasition to the valance band or an empty state in the band gap. To occur this process the semiconductor should be degenerately doped on both sides.

e) BREAKDOWN LUMINESCENCE :

By gaining energy from the electric field electrons and holes are multiplied and there by ~~from~~ form an avalanche breakdown. The pairs created in this way, recombine radiatively.

1.6.2 : ENERGY TRANSFER :

The mode of energy transfer from point of excitation to the site of emission occurs via movement of charge carriers.

The flow of energy due to transport of charge carriers depends on the concentration gradient, the electricfield intensity and the concentration of the trapping states.

The transport of energy from the electrically excited system to the emitting system can also occur by the mechanisms not involving electric charge carriers i.e. by,

i) Cascade transfer mechanism.

2) Resonance transfer mechanism.

3) Excitation migration mechanism.

1.6.3 : RECOMBINATION :

In this process various transitions take place from upper to lower energy states. The transition can be radiative or non-radiative.

RADIATIVE TRANSITIONS :

i) Band to band transition

ii) Band to impurity transition

iii) Transitions of localised centres

iv) Transitions at isoelectronic centres.

v) Donor acceptor transitions.

i) BAND TO BAND TRANSITIONS :

This type of transition occurs in direct semiconductors from conduction and valance bands and in case of indirect semiconductor it requires emission or absorption of a phonon to complete the lowest energy transition across the energy gap.

ii) TRANSITION BETWEEN BAND TO IMPURITY :

This transition occurs between an impurity state and intrintic band and its probability is high, if the impurity state is deep.

iii) TRANSITIONS OF A LOCALISED CENTRE :

In large band gap materials impurities can be excited without ionising them i.e. without exciting their electrons to the conduction band.

iv) TRANSITIONS AT ISOELECTRONIC CENTRES :

Such centres are formed by replacing an atom of the host crystal by another but with the same valency. Radiative transitions can occur in the excitation band to an isoelectronic centre.

v) DONOR-ACCEPTOR TRANSITION :

Such transitions are found in LED's and in phosphors. This is also an efficient transition from donor to acceptor.

The transition without emission of photon from upper to lower energy states are known as non-radiative transitions. This can occur through number of processes such as -

i) Multiphonon emission
ii) Auger effect
iii) Non radiative defects.

i) Multiphonon emission at the intersection of the ground and excited state configuration diagram. The electron can escape from excited state and returns to its equlibrium state by generation of several phonons.

ii) Auger effect : The 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 such as surface recombination crystal defects providing regions, where a localized continuum of states can bridge the energy gap and cluster of vacancies of impurities can form non-radiative centres.

For good EL-phosphors the important requirements are -

1) It's electron traps should be shallow.

2) Activation energy for escape of holes from the ionised activator levels should be as large as possible and

3) It should have cubic structure which is more favourable for EL emission.

1.7 Kinetics of Luminescnece

The kinetics of luminescence is concerned with the mechanism involved in the recombination of electrons with luminescence centres and owe its origin to the probability of retrapping of electrons, in deeper types of kinetics involved in luminescence process. It may be monomolecular (first order)bimolecular (second order), or intermediate (lying between first and second order).

Monomolecular kinetics (First Order)

If the traps are situated close to the luminescnece centres (less than 10^{-6} cm a part) 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 (29, 30) under such condition, according to ~~minimum~~ minimum energy principle, there is negligible probability for an electron to be retrapped in deeper empty traps. Thus in monomolecular kinetics, the probability of retrapping is negligible or in other words, the process of recombination is dominant (29).

Bimolecular Kinetics : (Second Order)

In this type, the traps are located away from the luminescence centres at a distance greater than 10^{-5} cm. and electrons have to go large displacements for recombination with luminescence centres. Under such conditions, according to the minimum energy principle, 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 (29).

Intermediate Kinetics :

When the order of kinetics is neither monomolecular nor bimolecular, then it is Intermediate Kinetics. Under this situation the traps are supposed to be distributed in the vicinity of luminescence centre in such a way that the probability of retrapping of electrons in deeper traps is small but not negligible. The occurance of such an intermediate order of kinetics is shown possible by some workers (31, 32).

1.8 Some Important Luminescent Materials Reported:

The phenomenon of luminescence is observed in a number of naturally existing materials. However, impurity activated luminescent materials have better luminescence out put and efficiency. The various phosphors investigated and now used in number of applications are alkali halides, sulphates, borates, sulphides, corbonates etc. The well known phosphor LiF:Mg,Ti is used in radiation dosimetry. This is manufactured by Harshaw Chemical Company under trade names TLD-100, TLD-600 and TLD-700

(36.) Study of LiF crystal doped with various activat~~ions~~ors has been carried out by Kathuria (37).

Nambi K.S.V.(38) has studied $CaSO_4$ phosphors doped with rare earths and found that these phosphors have better sensitivity than LiF or CaF_2 phosphors. He has also found that impurities having ionic radii close to radius of Ca^{2+}ion (Dy^{3+}, Tm^{3+}) have maximum TL out put, while La^{3+}, Yb^{3+} and Ly^{3+} whose ionic radii are largely different from that of Ca^{2+} do not yield any significant increase in TL out put. $CaSO_4$:Tm^{3+} can be used as radiation detector for measurement of environmental radiation in BARC.

Number of workers have studied the sulphide phosphors doped with various activators (16,39, 40, 41, 42, 43, 44, 47, 48). Among the various activators Mn is proved to be ~~good~~ the best activator in different phosphors. Mn can be used as universal dopant in nearly all inorganic phosphors (36). Mn is almost exclusively responsible for TL-emission spectra of all types of natural calcites. It is one of the most efficient dopant for TL-emission in CaF_2 and $CaSO_4$. It has been explained that Mn^{2+} ion receives the excitation energy from the codop~~p~~ant impurity ion (45).

The study of Mn along with rare earth in $CaSO_4$ phosphors have been studied (36), Rare earths are also found to be efficient activators in borates (46).

1.9 Statement of Problem~~s~~ :

Amongst the vast list of phosphors exhibiting variety of light emission~~s~~ under various conditions, sulphide phosphors have occupied their place even of historic importance apart from their utility in TV-Screens, as fluorescent material, Lamp, the nature posses a limitations in further applications. The quality of sulphide phosphor~~s~~ can be improved in the presence of impurities. Singly doped sulphides have been synthesised and have been studied by a number of research workers in last two decades and more. Double dop~~p~~ing has been found interesting from both theoretical and application point of view. Activated sulphide phosphors, are found to have better position in the list of phosphors from commercial point of view also. Since Mn and Bi in singly dop~~p~~ed sulphides have been found efficient activators, it was felt necessary to study the sulphide phosphor with double dop~~p~~ing.

To understand the role of Mn, Bi in CaS and various effects on doping of rare earths in presence of Mn or Bi independently, ~~effects~~ efforts are done in this dissertation. Since luminescence output of Mn doped or Bi doped phosphors in other hosts is found to increase in the presence of other activators, if is found proper to study. This aspect in presence of rare-earths. Since sulphides of composition CaS:Mn:RE and CaS:Bi:RE are not extensively studied. Many rare earths were earlier tried with the host material (CaS). Planning is channelised to prepare phosphors of the composition CaS:Mn:RE and CaS:Bi:RE and findout the suitable rare-earth amongst chosen i.e. Dy and Tb. These rare earths are found to increase luminescence output in the hosts. Optimum concentration of Mn:RE and Bi:RE in CaS with proper combination of them with rare-earth to gain the information about trap depth, mechanism of luminescence. Kinetics involved in luminescence, process and distribution of traps has been attended.

1.9.1 Phosphorescence Decay

Attempt has been made in present investigation to plot decay curves and find out nature of decay curve, nature of decay law, types of kinetics involved, distribution and population of traps at room temperature. Proper tools to analyse this are used from existing theories.

1.9.2 Thermoluminescence

An attempt has been made to investigate the effect of addition of impurities (Mn, Bi and RE) on glow curves. Using glow curves, the activation energy, the frequency factor and order of kinetics of luminescence process have been estimated.

1.9.3 Electroluminescence

A.C.electroluminescence measurements have been carried out to find out the possible relationship between brightness. Voltage and brightness, frequency. Effect of concentration of activators have been studied.

1.9.4 Thermally Stimulated Conductivity

An attempt is made to study the variation of conductivity with temperature. However attempts made to study conductivity under uv excitations have not given any significant results.

REFERENCES

1. Lenard, P., Schmidt, F and Tamaechek R., Handbuch der Expt. Phys., 23 Parts I and II, Aked, Vestagages, Leipzig(1928).

2. Stokes,G.G. "on the Refrangibility of Light" Phil. Trans. Roy. Soc. London, A. 142. II 463 (1852).

3. A.H.Becquerel, E. "La Lumiere, Ses Causes et sec Lffeets". Gautheier, Villars Paris (1867).

4. Wiedmaan E., Wied Ann. 37, 177 (1889)

5. Randall, J.J. and Wilkins, M.H.F. Proc. Roy SOC, A 184 366 (1945).

6. Garlick G.F.J. and Gibson, A.F., Proc. Roy.Soc. 60, 574(1948).

7. Haffmann, H., Chymia rationalis et experiments Berlin, (1784)

8. Williams F.E. 'Luminescnece of inorganic Solids edited by P. Goldberg, New York, P-2(1966).

9. Curie, D. Luminescnece in crystals. (Method and Col. Ltd., London, 1963).

10 Johnson, R.P.J.Opt. Soc. Amer 29, 387 (1939).

11. " Symposia on Diamond", Proc. Indian Prod.Sci-A. 19, 189 (1944).

12 Bube R.H.Phy. Rev. 80, 655 (1950)

13 C.M.Kachhava, "Solid State Physics", p. 164.

14 Bloch F.2, Physik 52, 555 (1928)

15 Abhyankar M.D., Ph.D.Thesis, Univ of Sagar (1968).

16 Lawangar R.D., Ph.D. Thesis, Shiv. Uni. (1974).

17 Von-Hippel A.Z., Physik, 101, 680 (1936).

18 Seitz, F. Trans, Farady Soc. 35, 79 (1939).

19 Lambe, J. and Klick C.C. Phys. Rev. 98, 909 (1955).

20 Schon, M.Z. Physik119, 463 (1942).

21 Klassens, H.A. Nature 158, 306 (1946).

22 Klasens H.A., Ramsden W. and Quanke, C.J. Opt. Soc. Amar, 38, 60 (1948).

23 Wise M.E. and Klasens, H.A. J.Opt. Soc. Amer 38, 226 (1948).

24 Wliliams E.E., T.Phys. Chem. Soc. Solids, 12, 65(1960).

25 Prener J.S. and William s F.C. J.Phys. Rad. 17, 667 (1956).

26 Klick C.C. and Schulman, J.H. Solid State Phys. Vol. 5, Academic Press, New York (1957).

27 Shulman J.H., Ginthner R.J. and Klick C.C.J.Electrochem. Soc. 97, 123 (1950).

28 Dexter D.L.J. Chem. 21, 836 (1953).

29 Halperin, A. and Braner, A.A. Phy. Rev. 117, 408 (1960)

30 Chen, R.J. Appl. Phys. 40, 570 (1969).

31 Chen R.J. Electr-Chem. Soci.116, 1254 (1969)

32 Kathuria, S.P. and Sunita C.M. J.Phy. D. Appl. Phy. 12,1 (1979)

33 Shashi Bhushan, Nucl. Tracks, Vol. 10 No 1/2 PP. 215-224(1985).

34 Zener C. M. Proc. Roy. Soc. (London) 145 A, 523 (1934).

35 Leverenz H.W. "An Introduction to Luminescence of solids", (Dover Publications Inc. New York, 1968).

36 Bapat, V.N.Ph.D.Thesis, Bombay Unit. 1977.

37 Kathuria, et al. "Gammarays induced Thermoluminescnece, and Phototransfered themoluminescence in Lithium fluoride " BARC (1979).

38 Nambi K.S.V. Ph.D.Theis, Gujrat Uni. 1974.

39 Patil M.G., Ph.D. Thesis, S.U.Kolhapur, 1981

40 Shalgaonkar C.S., Ph.D. Thesis, S.U.Kolhapur 1975.

41 Pawar S.H., Ph.D. Thesis, S.U.Kolhapur 1974.

42 Hadgal R.R.Ph.D. Thesis, S.U.Kolhapur 1982.

43 S.Bhushan and F.S.Chandra, Pramana, Vol. 24, No.4 PP. 575-582 (1985).

44 N.Singh et al., Phy. Status Solidi a (Germany) Vol.66, No.2 P-767-5 (1981)

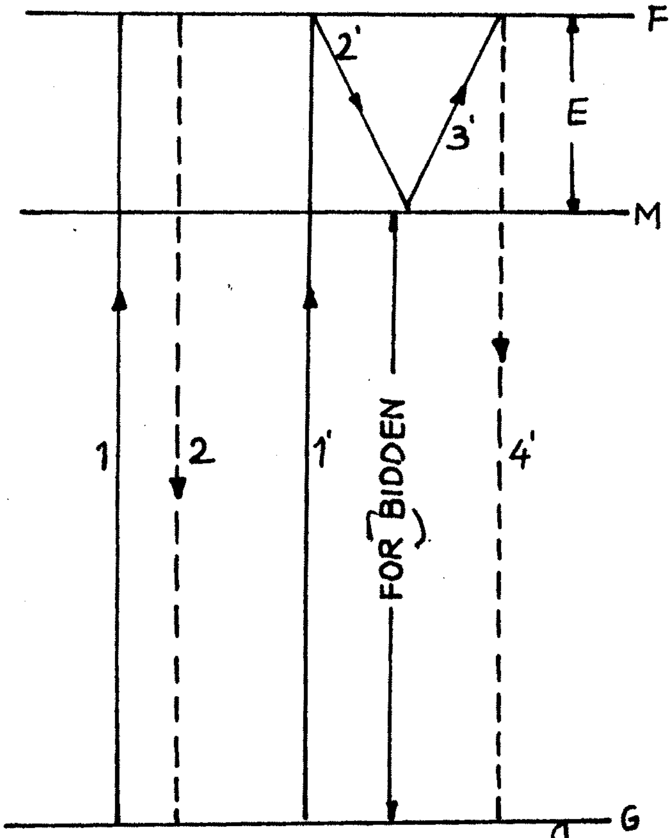
45 Sunta, C.M.Nucl. Track Vol. 10, No.1/2, pp. 47-53 (1985).

46 Dhayagude N.S.,Ph.D.Thesis, S.U.Kolhapur 1984

47 Shahane G.S.M.Phil. Thesis S.U.Kolhapur 1990

48 Kasture U.B., M.Phil. Thesis, S.U.Kolhapur 1990

ENERGY STATES FOR FLUORESCENCE AND PHOSPHORESCENCE.



G GROUND STATE.

F EXCITED STATE.

M METASTABLE STATE.

E ACTIVATION ENERGY.

1 1' EXITATION FLUORESCENCE.

2 FLUORESCENCE.

2' DROP IN METASTABLE LEVEL.

3' ACTIVATION THERMAL OR OPTICAL.

4' PHOSPHORESCENCE.

FIG. NO.: 1.1

ENERGY BAND MODEL

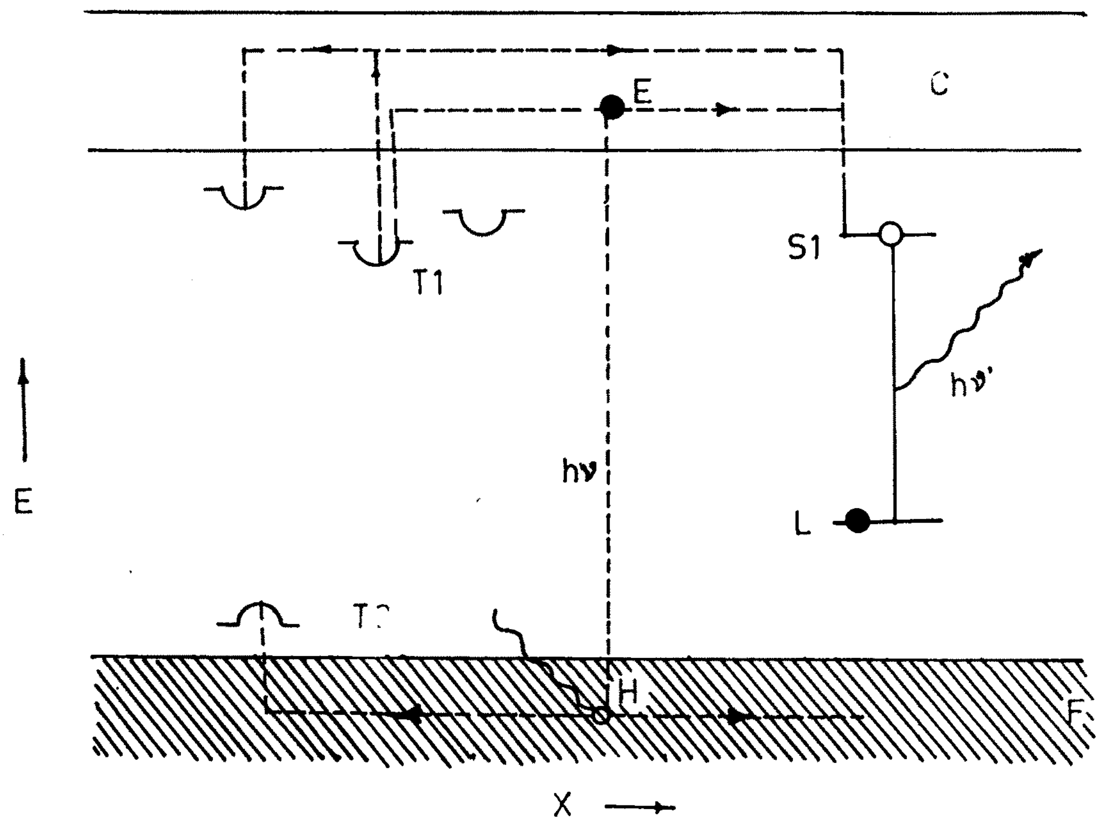


FIG. No.: 1.2

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CLASSICAL CONFIGURATION COORDINATE CURVE MODEL

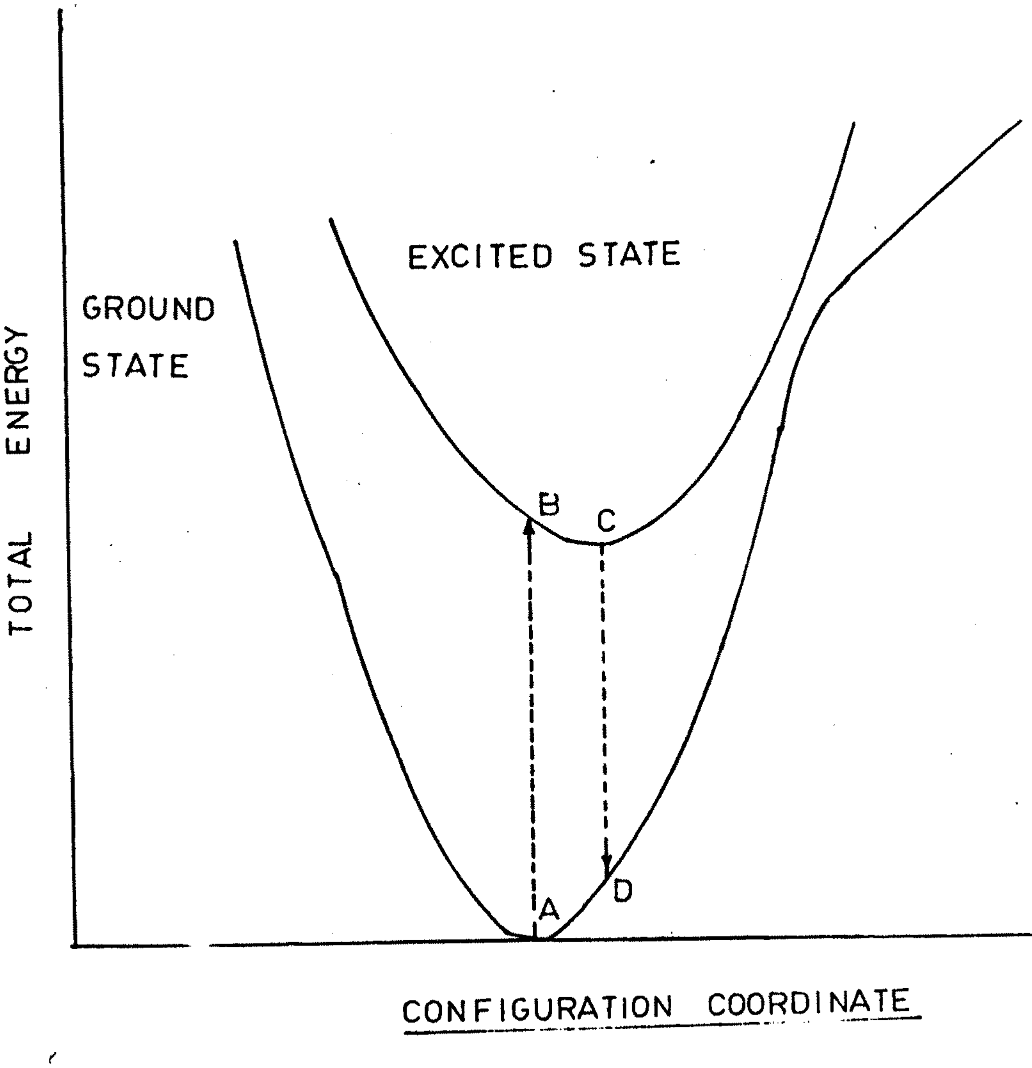

FIG.NO.: 1·3.

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LAMBE - KLICK'S MODEL

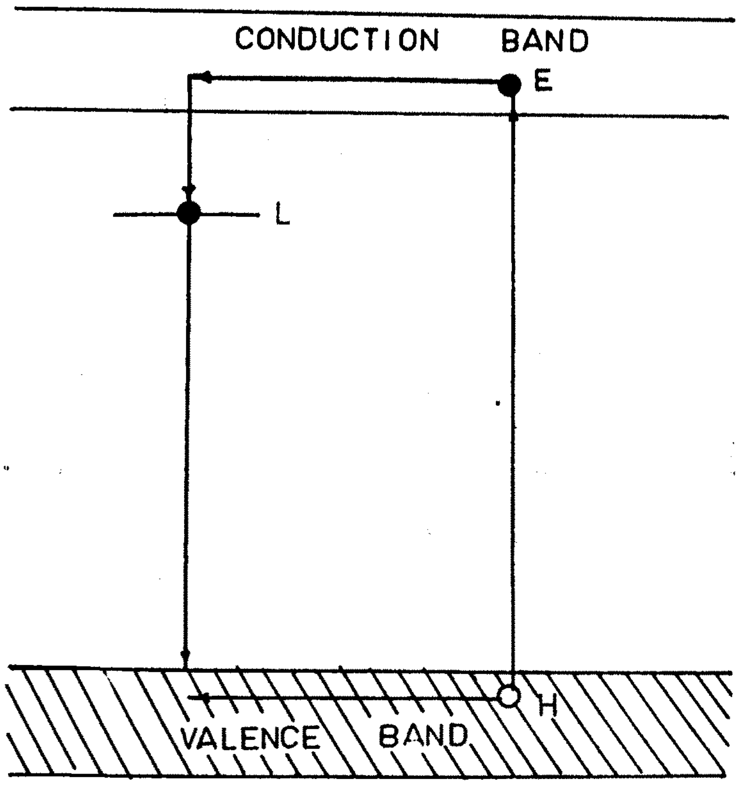

FIG.NO.: 1·4.

SCHON - KLASSEN'S MODEL

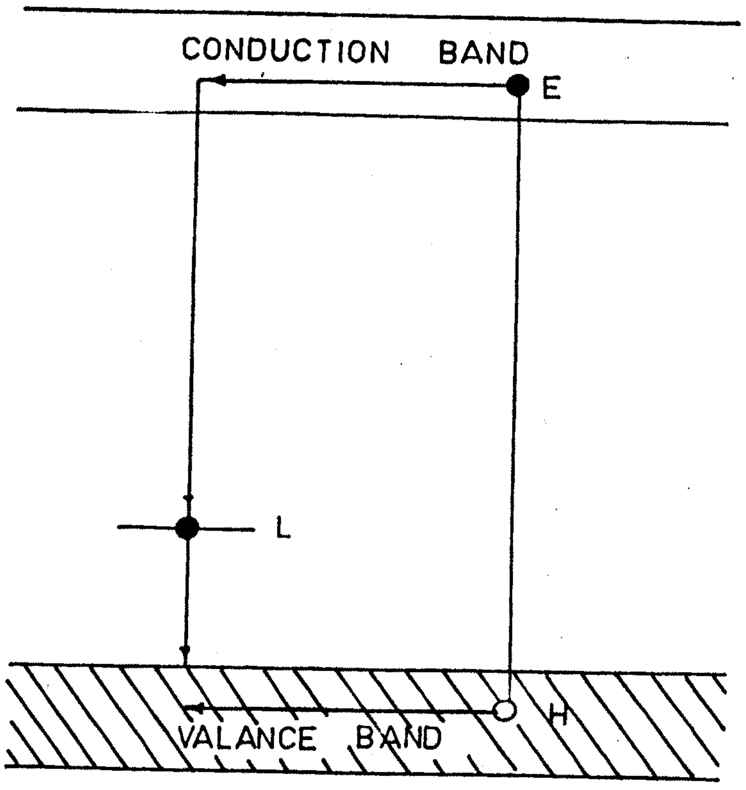

FIG. NO.: 1·5.

WILLIAM'S AND PRENER'S MODEL

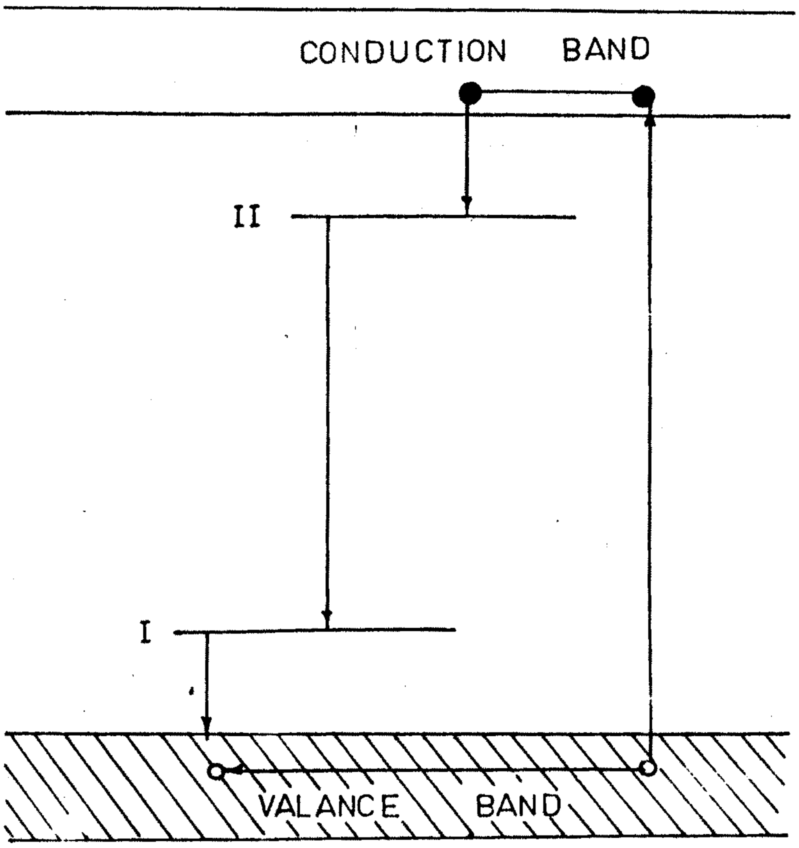

FIG.NO.:1·6.

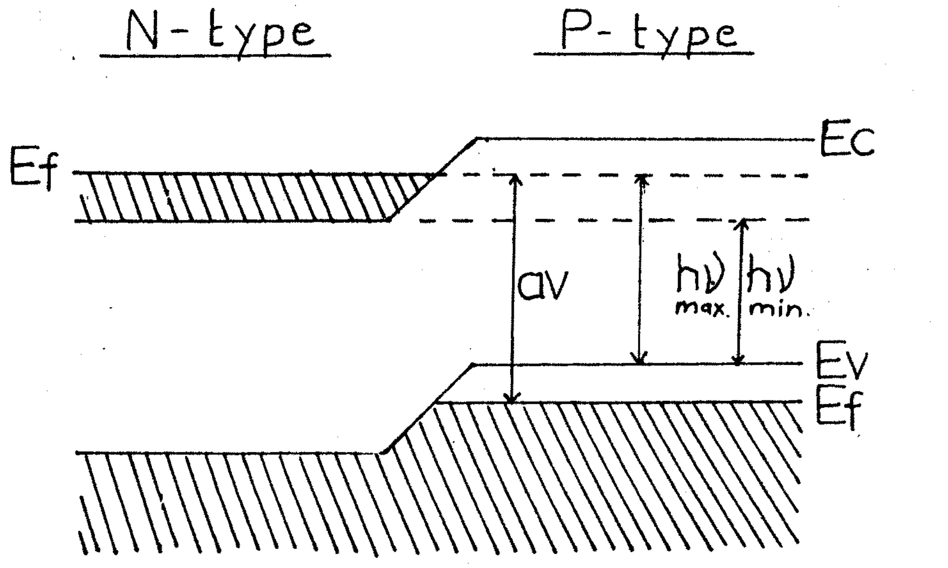

FIG. NO.: 1.8.

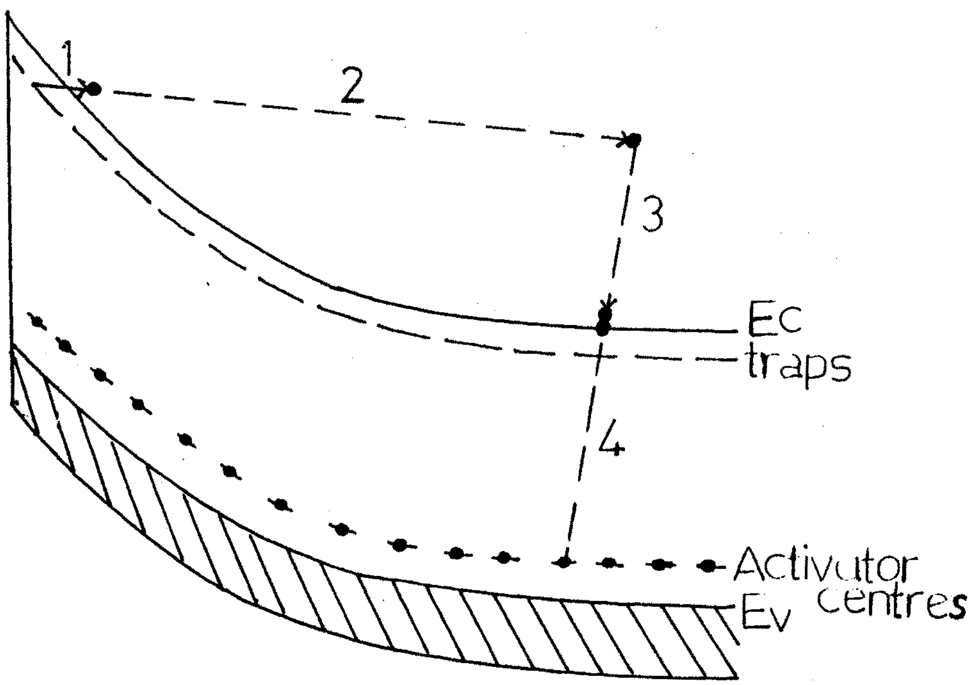

FIG. NO.: 1.7.