CHAPTER I

INTRODUCTION

1-1 LUMINESCENCE PHENOMENON:

Phenomenon of liminescence was first observed by Casciarolo in 1603. However, a systematic study of luminescence began in 1887, with the work of E.Becquerrel (1). Weidmann (2), in 1889, gave the first definition of luminescence while Stokes,in 1852, formulated the first law in this field. In the begining of this century, Mott and Gurney (3) proposed theories to explain the phenomenon. However, a novel interest in the field arosed with the theoretical contributions of Randall and Wilkins (4) and Garlick and Gibson (5). Since then there has been a spectracular growth of phosphor studies and novel methods are being devised for their synthesis and new phosphor materials with improved properties are continually being added to the list.

The rapid development of the luminescence field owes entirely to the technological utility of phosphos. They are used in fluoresent screens for T.V., cathode ray tubes, and electron microscopes, in fluoresent lamps, picture display panels, image tubes and in many other solid-state opto-electronic devices.

1-2 Definitions:

1-2.1 Luminescence:

In the literature the term luminescence has been defined in different ways (2,6,7). In general it denotes the absorption of energy in matter and its re-emission as visible or near visible radiation. The emitted radiation is non-thermal in origin (7) and is to be distinguished from Raman, Comption, and Raleigh scattering and Cherenkov radiation in that, the time delay in luminescence emission after excitation is longer than 10^{-9} sec; whereas in the latter it is of the order of 10^{-14} Sec. (8).

The luminescence phenomenon may be distinguished in accordance with the source of input energy as follows.

a) Photoluminescence: Produced by optical radiation.

b) Radioluminescence: Produced by bombardment with high energy particles or high energy radiation (x-rays, γ-rays etc.)

c) Electroluminescence: Caused by application of an electric field or current to matter.

d) Cathodoluminescence: Produced by electron beam or cathode ray.

e) Triboluminescence: Produced by utilization of mechanical energy.

f) Chemiluminescence: Caused by chemical reaction.

g) Bioluminescence: Caused by biological reaction.

1-2.2 Fluorescence and Phosphorescence:

Fluorescence and phosphorescence are particular cases of luminescence. Garlik (6) define fluorescence as emission of light during execitation and phosphorescence after excitation is removed. According to Leverenz (9) and Kroger (10), a luminescence emission which lasts upto the initial 10^{-8} Sec. after excitation is to be called fluorescence, while the subsequent is to be referred to as phosphorescence.

1-3. PHOSPHORS:

Material exhibiting luminescence are known as ' Luminophors'. When they are prepared in laboratory for practical applications they are termed as 'Phosphors' (11,12). 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. (6,13).

1-3.2 Impurity Activated Phosphors:

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

1-4. THE TERMS:

1-4.1 Luminescence Centre: It is an atom or imperfection in the crystal where excitation and emission take place.

1-4.2 Trap: A trap is an atom or imperfection in the crystal capable of capturing an electron or hole.

1-4.3 Metastable Levels: These are the levels, corresponding to the defect states which can be excited by electron bumbardment but not by photoexcitation. A transition from these levels to normal state is forbidden. Representative life times of metastable levels are of the order of 10^{-2} to 10^{-4} Sec. (14).

1-5. MECHANISM OF PHOTOLUMINESCENCE:

The mechanism of photoluminescence involves four processes: (i) excitation, (ii) emission, (iii) transfer of energy during excitation and emission, and (iv) storage of part of the absorbed energy during excitation.

1-5.1 Excitation and Emission:

Several schemes have been proposed to explain these processes. Some of them are as follows:

(A) Classicial Configuration-Coordinate Curve Model:

The configuration co-ordinate curve model is represented in fig.1.1. It was introduced by Van-Hippel (15) and was applied by Seitz (16) to explain the luminescence behaviour. In figure, the ordinate represents the total energy of the system for the ground and excited states of the centre, while abscissa the ' configuration co-ordinate ' which specifies the configuration of the ions around the centre. The equillibrium position of the centre in the ground state is represented by the point **A**. If the centre absorbs the light energy, it is raised to the excited state at B. The transition is vertical in accordance with the Frank-Condon principle. From B the centre relaxes to new equilibrium state C, the state corresponding to the minimum energy of the excited state. The energy difference between B and C (See Fig.1.1) is given off as lattic vibrations. Having reached centre at this new equilibrium position it returns to the ground state at D by giving luminescence emission. The centre finally relaxes from D to **A** again giving up energy to the lattic vibrations.

(B) Energy Band Model:

The energy band model (17,18) is illustrated in Fig.1.2. According to this model, the phosphors which are usually semiconductors or insulators, are describable in terms of the valence band (f) and the conduction band (c), with localised energy levels in the forbidden region between the bands. These localised levels are associated with impurities or imperfections in the host lattic. In fig.1.2 such levels are shown. The level L represents the ground state of the luminescence centre, while the levels T_1 and T_2 represent the electron and hole traps respectively.

The act of excitation and emission takes place as follows:

Absorption of the light energy in the phosphor excites luminescence centre from its ground level (L) to the excited state (S_1) by raising the electron into the conduction band. Such excited centre then 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 separation between the valence and conduction band, it also excites electrons (E) from the valence band into the conduction band creating holes (H) in the valence band. This absorption is known as the fundamental absorption band. However, such electron and hole pairs normally do not recombine radiatively (19).

(C) Schon-Klasens' Model:

This model was proposed by Schon (20) and elaborated upon by Klasens and his co-workers (21,22,23). Fig.1.3 illustrates the model for the case of single luminescent centre. The ground level (L) of the luminescent centre is assumed close to the valence band. On absorption of light in the fundamental absorption band, a free electron and a hole are created. The electron moves to the conduction band while the hole diffuses through the valence band and captures an electron from the luminescent centre. This excites the luminescent centre. The free electron after migrating in the conduction band falls into the empty centre which gives emission of light.

(D) Lambe-Klick's Model:

In this model (24) the ground state of the luminescent centre (L) is assumed close to the conduction band (Fig.1.4). 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 centre. This transition gives rise to luminescente. Subsequently the electron from conduction band diffueses to the centre and gets captured there, thus completing the cycle.

(E) Williams and Prener's Model:

In the model proposed by Williams (25) and Prener (26) two centres are involved (Fig.1.5). The ground level (I) of the first centre is assumed close to the valence 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 in the valence band captures on electron from the ground level I and thus leaves it empty. The emission then takes place by the transition from the level II to the I (See.Fig.1.5).

1-5.2 Energy Transfer:

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

(A) Energy Transfer with no Movement of Charge Carriers:

There are three mechanisms for transfer of energy in such cases.

(i) Cascade Mechanism:

In this type of mechanism (27) one centre on absorbing excitation energy emits radiation (Primary emission). This emitted radiation in then absorbed by the second centre, which finally emits luminescence (secondary emission). This mechanism is most effective in those cases where the primary emission overlaps the absorption spectrum of the secondary emission system.

(ii) Resonance Transfer:

Here the transfer of energy from absorbing system to the emitting system is accomplished by a quantum mechanical resonace process (27,28) such as electric dipole field overlap, electric dipole-quadrupole field overlap or by exchange interaction. The efficiency of processes depends upon the distance over which the energy is transferred.

(iii) Exciton Migration:

The nonconducting 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 process the excitons transfer excitation energy from one point to another by moving quickly through the lattice without contributing to the electrical conductivity (29).

(B) Energy Transfer with Movement of Charge Carriers:

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

1-5.3 Energy Storage:

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

(A) Phosphoresence Decay:

Phosphorescence decay is diminishing after-glow under isothermal conditions, observed from 10^{-8} seconds, after removal of excitation. It arises due to the release of trapped electrons in trapping levels during excitation.

The mechanism of phosphoresence decay can be followed from the energy band model of fig.1.2. An electron raised into the conduction band by absorbing light energy may-according to minimum energy principle-fall into a trap (T_1) instead of immediately recombining with a centre. After some time the trapped electron returns to ground state via a conduction band giving rise to phosphorescence (Process HE T_1 S_1 L).

(i) Effect of Trap Distribution on Phosphoresence Decay:

The intensity and form of the 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 great distance from the conduction band. The intensity of the phosphorsence decay is a function of population of traps at particular depth. More the population higher is the intensity and vice versa.

(B) Thermoluminescence:

If previously excited and decayed phospher is heated with a uniform heating rate, the luminescent intensity varies with temperature. This variation of luminescence intensity with temperature gives what is known as the glow curve and the phenomenon is termed as 'Thermoluminescence' (TL).

the electrons released from the shallow traps, during early stage of thermoluminescence, are retrapped in the deeper ones. These electrons are then released at high temperature and enhance the TL emission.

(D) Kinetics of Luminescence:

Kinetics of luminescence is concerned with the mechanism involved in recombination of electrons with luminescence centres. It may be either monomolecular (first order), bimolecular (second order) or intermediate.

(i) Monomolecular Kinetics:

If traps are situated close to the luminescence centres (less than 10^{-6} cms.away) and if a very small movement of electrons is made to recombine with luminescence centres,the kinetics of luminescence process is said to be monomolecular (7). Under such a situation, according to minimum energy principle, there is negligible probability for an electron to be retrapped in the deeper empty traps. Thus in the monomolecular kinetics, the probability of retrapping is negligible or, in other words, the process of recombination is dominant (30,31).

(ii) Bimolecular Kinetics:

In this case the traps are located away from the luminescence centres (at distance greater than 10^{-5} cms.) and the electrons have to go through large displacements for recombination with luminescence centres. Under such circumstances, 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 (30,31).

(iii) Intermediate Kinetics: (32):

Kinetics of luminescence is said to be intermediate when it is neither monomolecular nor bimolecular. Under this situation the relative location of traps from luminescence centres is an intermediate case and similar is the condition with the processes of recombination and retrapping.

1-6. Statement of the Problem:

Despite considerable work that has been done on other phosphor systems such as ZnS. and Cds, very little attension has been paid to SrS phosphar. Recently, studies on SrS phosphers, doped with one or more impurity elements, have been reported by some workers (33,34,35). However, these studies are mainly devoted to the determination of trap depths and spectral distribution of emitted radiation, and very little is known about the nature and origin of trap. Moreover, the kinetics of luminescence process and distribution of trapping states in these phosphors is not unambiguously known. As regards their luminescence behaviour with and without flux, they have been little investigated and mechanism of energy transfer is not completely clear.

In the present investigation SrS phospher doped with varying concentration of Zn have been prepared in microcrystalline form and their photo and thermoluminescence are studied systematically. The measurements of photoluminescence are carried out at room temperature while that of thermoluminescence in the temperature range of 300° to 400°K.

(i) Photoluminescence:

Photoluminescence involves the study of phosphoresence decay. The decay curves have been analysed to infer the decay law as well as the kinetics of luminescence process. The trap depths have been calculated by 'peeling off' procedure. Finally an attempt has been made to infer the distribution of trapping states.

(ii) Thermoluminescence:

The results of thermoluminescence have been examined in terms of some of the resent theoretical models. Using glow curves, the activation energy and order of kinetics have been estimated. The effect of addition of Zn and a flux NaCl on general features of glow curves and on E values have been discussed and conclusions have been drawn about the nature and origin of trap and mechanism of energy transfer.

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1-7 REFERENCES:

1. Becqueral, E., "La Lumiere, Ses Causes et Ses Effects", Gautheir- Villars, Paris (1867).
2. Wiedmann, E., Weidmann's Ann., 37, 177 (1889).
3. Mott, N.F. and Gurney, R.W., Electronic Processes in Ionic Crystals (Oxford University Press, 1940).
4. Randall, J.T. and Wilkins, M.H.F., Proc.Roy.Soc., A184, 366 (1945).
5. Garlick, G.F.J. and Gibson, A.F., Proc.Roy.Soc., 60, 574 (1948).
6. Garlick, G.F.J., "Luminescent Materials," (Oxford, Clarendon Press, 1949).
7. Curie, D., "Luminescent in Crystals" (Methuen and Co. Ltd., London, 1963).
8. Williams, F.E., Luminescence of Inorganic Solids, Edited by P.Goldberg, New York, P.2 (1966).
9. Leverenz, H.W., Science (London), 109, 188 (1943).
10. Kroger, F.A., Physica, 14, 425 (1948).
11. Matossi, F.R. and Nudelman, S., Methods of Experimental Physics, Vol.6, Part-B, Page 293 (1959).
12. The Harper Encyclopedia of Science, Edited by Jomes R.Newman.Vol.III, M through R.P.910.
13. Symposia on Diamond, Proc.Indian Acad.Sci., A19, 189 (1944).
14. Milman J and Halkias C.S., Electronic devices and circuits Tata Mcgrow Hill, 1967.

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

16. Seitz, F.,Trans.Faraday Soc.,35,79 (1939).

17. Bloch,F.,Z.Physik,52,555 (1923).

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

19. Abhyankar,M.D.,Ph.D.thesis,University of Sougar, Sagar (1968).

20. Schon,M.,Z.Physik,119,463 (1942).

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

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

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

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

25. Williams,F.Z.,J.Phys.Chem.Soc.Solids,12,265 (1960).

26. Prener,J.S.and Williams,F.E.,J.Phys.Rad.,17, 667 (1959).

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

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

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

30. Halperin,A. and Braner,A.A.,Phys.Rev.,117,408 (1960).

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

32. Chen,R.J.Electro Chem.Soc.116,1254,(1969).

33. Sharma, D. and Singh, A., Indian J. Pure and Applied Physics, Vol. 7, 310 (1969).

34. Singh, A., Indian J. Pure and Applied Physics, Vol. 7, 367 (1969).

35. Keller, S., J. Chem. Phys., 29, 180 (1958).

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CONFIGURATION COORDINATE MODEL

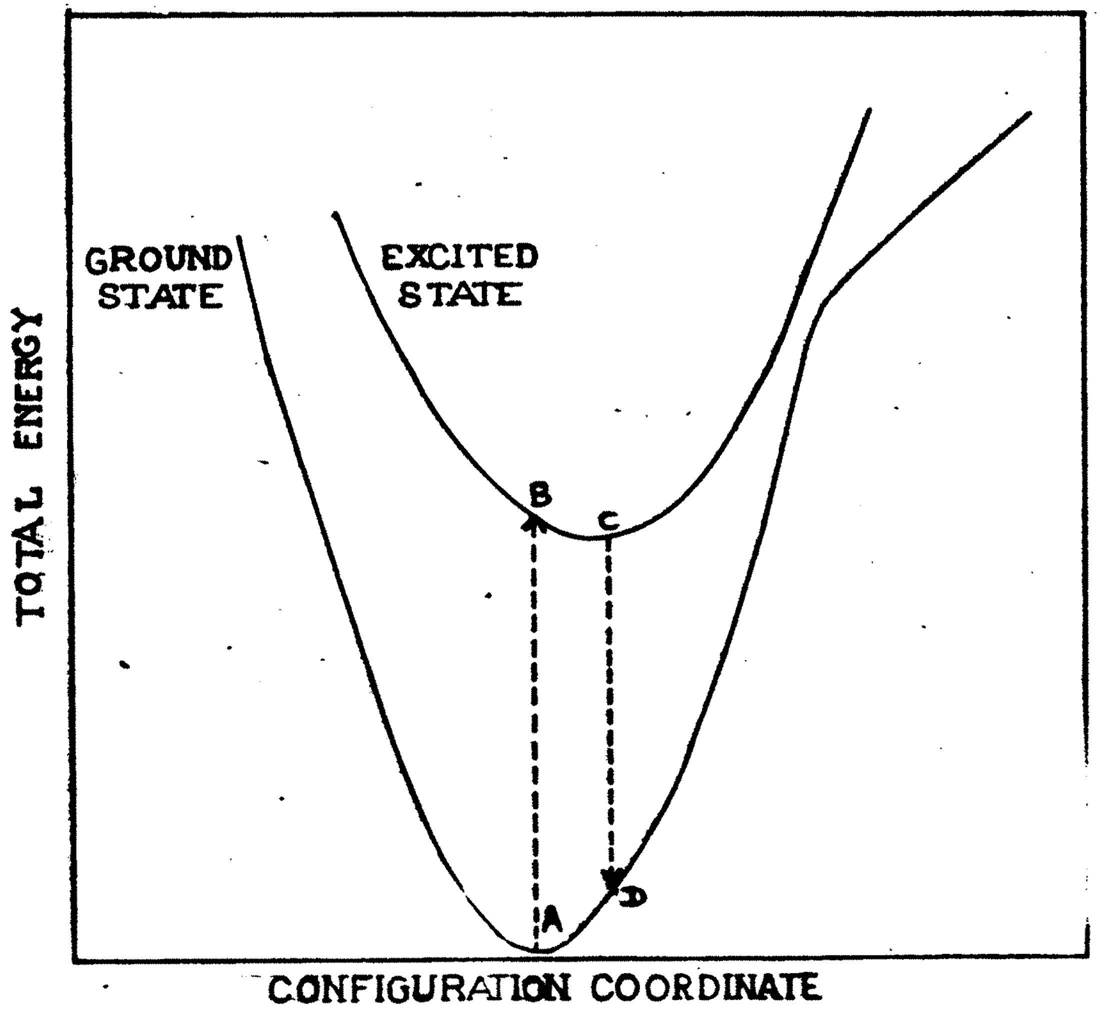

Fig. 1·1

ENERGY BAND MODEL.

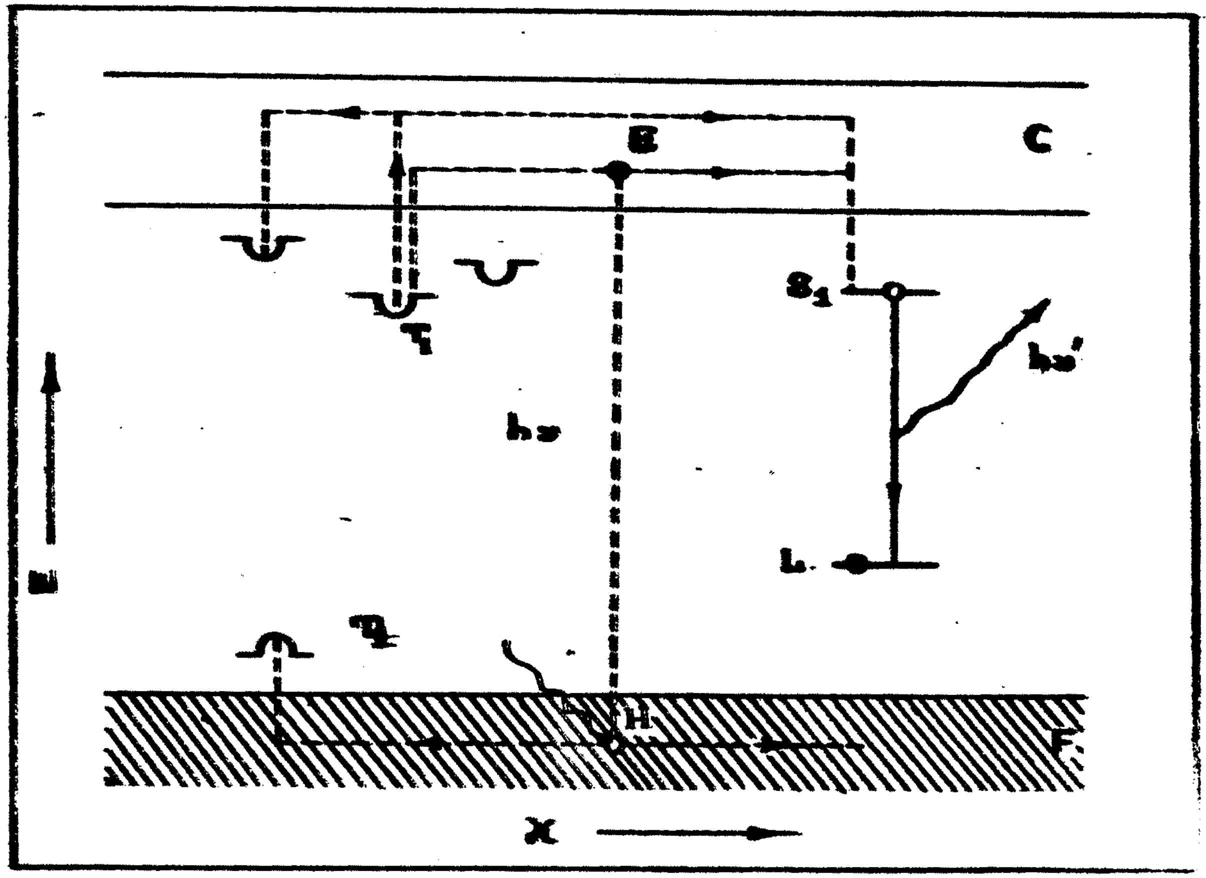

Fig. 1·2

SCHÖN AND KLASENS' MODEL.

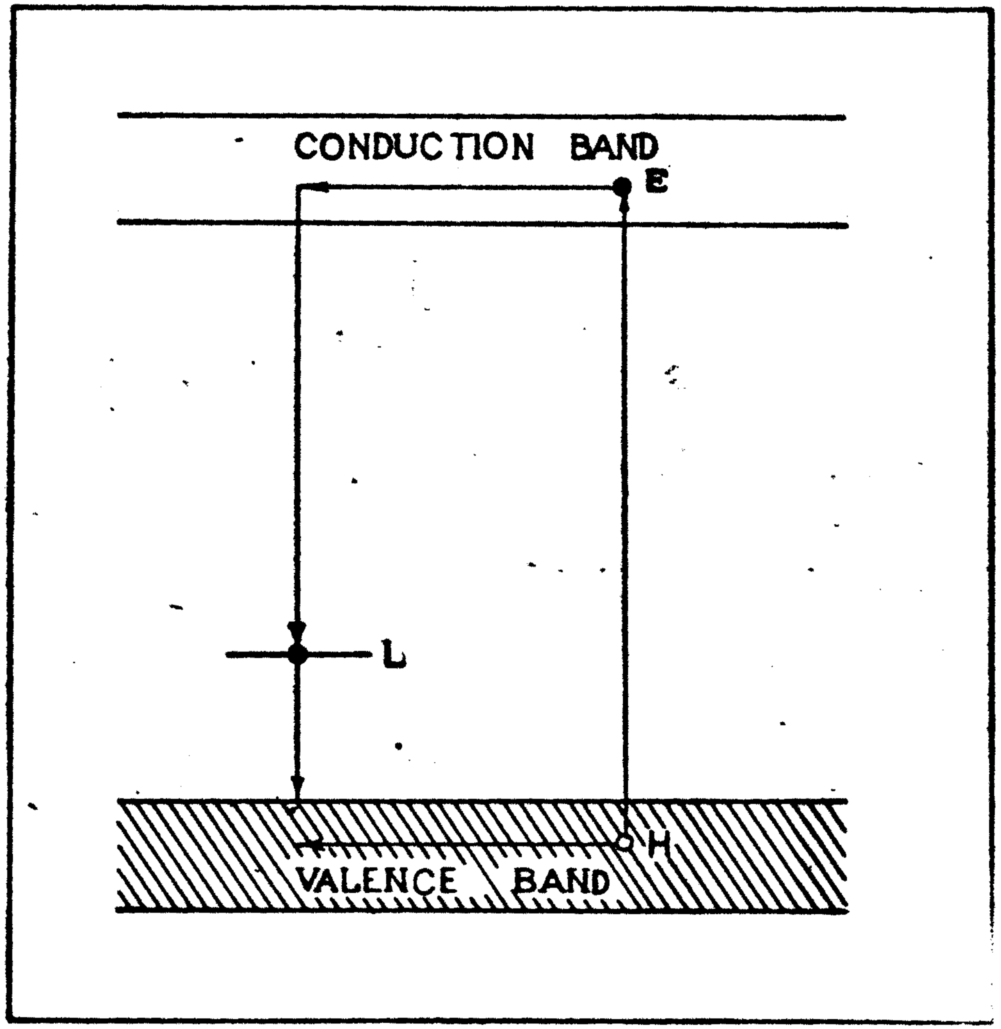

Fig. 1·3

LAMBE AND KLICKS MODEL

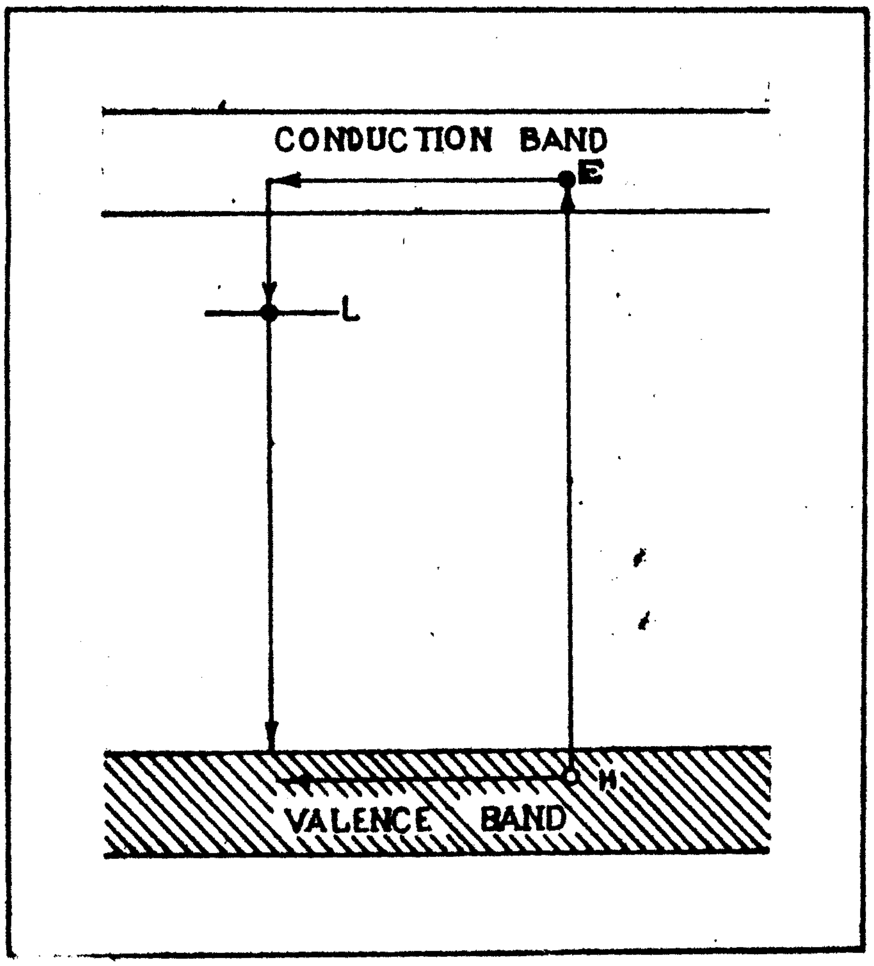

Fig. 1·4

WILLIAMS AND PRENER'S MODEL.

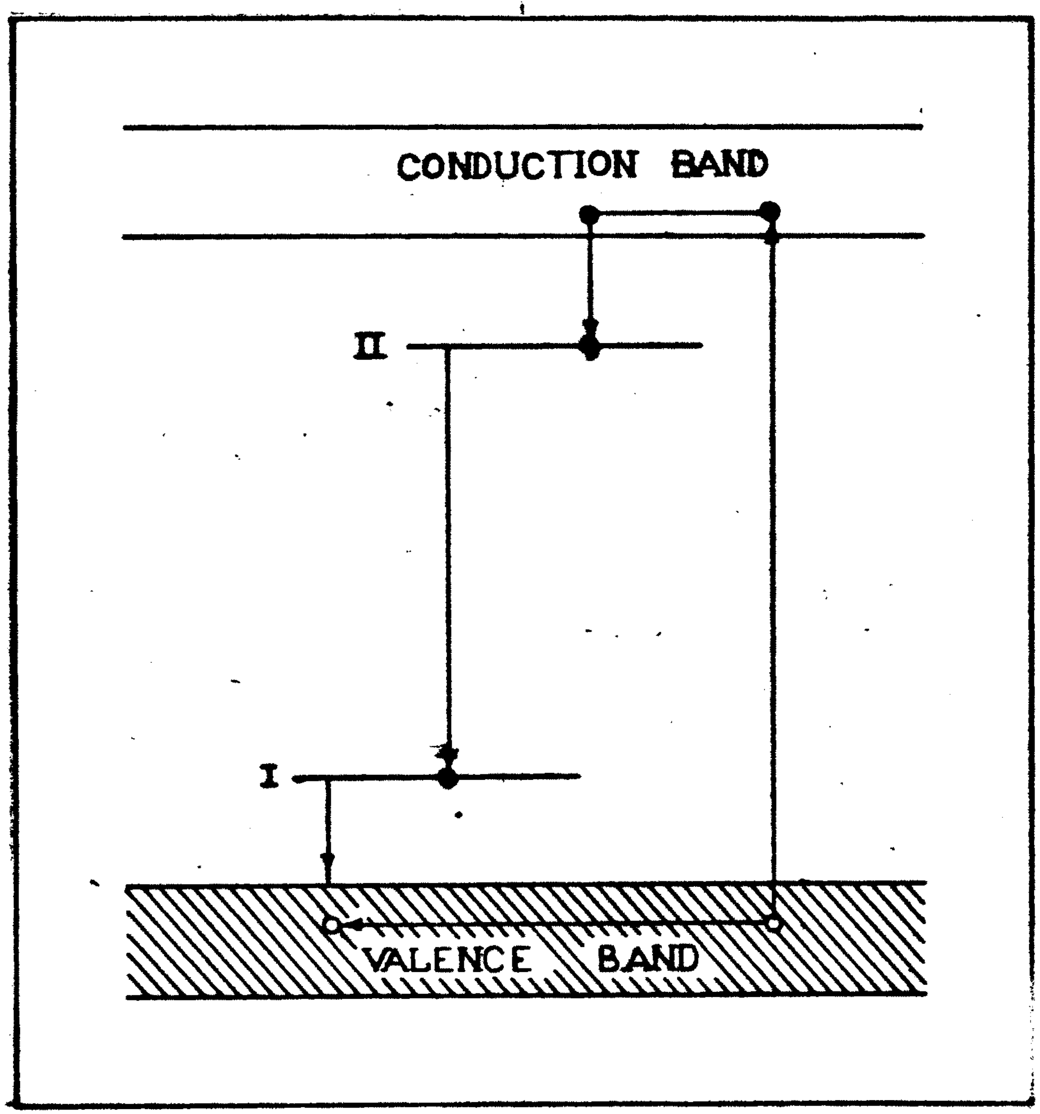

Fig. 15