CHAPTER-I

INTRODUCTION

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INTRODUCTION :

In ancient days Indians were believing that the universe is constituted by five elements and light is one of them. In Vedas there is a mention of significance of light at several places, meaning thereby light is life. There are many legends and stories which are being told from generation to generation about the production of light. A snake like cobra, possesses a stone known as "Nagmani", in its head. The stone emits light during night time, and is being used by the cobra to attract the insects as prey, by putting it on ground. It is also said that there is a cave in Himalaya, the walls of which emit light after ringing a big bell. During olden days these and such other facts were believed to be divinely but the phenomena behind these facts is 'luminescence' - the emission of 'Cold light'.

In nature luminescence has also been observed since long time and it is exhibited by fireflies, glowwarms, seabacterias, animals like fishes, trees, decay matters etc. However, the study of luminescence initiated in 1603 by vicenzo cascariolo, who synthesized firstever luminescent material by heating barium sulphate with coal which emitted fible blue glow at night after exposure to-day light. In 1889 Wiedemann(2) gave the first, although not accurate, definition of luminescence. The first law in this field was formulated by Stoke in 1852. Later, Mott and Gurney(3) (1940) and Randall and Wilkins (4) (1940) proposed theories to explain the phenomena and much theoretical contribution was made by Garlick and Gibson (5) (1948). Since then there has been a dramatic progress in the field of luminescence. The novel methods are being divised for synthesis of Phosphors and new phosphor...phosphor materials with improved properties are continuously being added to the list.

Now there are fortyeight phorphors (P_1 to P_{48}) which have been indexed and are being used in colour T.V. black and white T.V., television kinescope (efficiency about 10^2 millilamberts), radar tubes, flourescent lamps (efficiency 10^3 millilamberts), image intensifier tubes, voltage dependent colour display, flying spot pickup, beam indexing tubes, projection systems and infrared stimulation (6). The youngest branch of luminescence is the electroluminescence(El). There is a wide variety of applications of El and are summarised by Lowry (7). A few important ones are El lamps, LED's, colour display panels, image intensifiers and semiconductor lasers. Very recently Semi conductor lasers have received great attention because of production of laser diodes which are being increasingly used in photonics - a new branch of science parallel to electronics.

This rapid development of the luminescence field is not entirely due to technological utility of the phosphors but also due to their importance in basic research. Various theoretical models proposed so far to account the phenomenon are helpful in understanding the electronic processes involved in solids at the atomic levels. Not only that, but these are being used to refine and to test the validity of varies theories proposed in other branches of science.

1-2.1 CLASSIFICATION OF LUMINESCENCE PHENOMENON :

In literature, the term luminescence has been defined in different ways (2,10,11). 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 (11) and is to be distinguished from Raman, Compton and Rayleigh scattering and Cherenkov radiation in that, the time delay in luminescence after excitation is longer than 10^{-9} Sec.; whereas in the later it is of the order of 10^{-14} Sec. (12).

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

(a) Photoluminescence : Produced by absorption of ultraviolet or visible radiations.

(b) Radioluminescence : Caused by bombardment with high energy particles or radiations such as X-Rays, γ rays etc.

(c) Cathodoluminescence : A special case of radioluminescence, produced by cathode rays.

(d) Electroluminescence : Caused by application of electric field.

(e) Sonoluminescence : Produced by sound waves usually of ultrasonic variety.

(f) Triboluminescence : Produced by utilization of mechanical energy.

(g) Chemiluminescence : Occurs as a product of chemical reaction.

(h) Bioluminescence : A chemiluminescence in living organisms.

(i) Galvanoluminescence : Produced during electrolysis in galvanic cell.

(j) Thermoluminescence : Thermoluminescence, however, do not refers to the thermal excitation but rather to the thermal stimulation of luminescent emission when the sample is excited by other means.

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

(k) Photo-electroluminescence : Refers to radiation moduleted electroluminescence.

(l) Electro-photoluminescence : Refers to enhancement of light intensity by the applied field.

(m) Electro-thermoluminescence : Refers to thermoluminescence enhanced by the applied field.

(n) Photo-transferred thermoluminescence : Refers to thermoluminescence stimulated by radiation dose at high temperature, usually beyond 400° c.

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

The general term of luminescence is categorised either as flourescence or phosphorescence depending on the duration of emission following removal of excitation. Garlick (10) defines flourescence as emission of light during excitation and phosphorescence after excitation is removed. According to Leverenz (13) and Kroger (14), a luminescence emission which lasts upto the initial 10^{-8} sec. after excitation, is to be called flourescence, while the subsequent is to be referred to as phosphorescence. Phosphorescence may be of short duration or long duration according to the over-lasting time of 10^{-8} sec. to a minute and above respectively (15).

1-3 PHOSPHORS AND RELATED TERMS :

1-3.1 Definition :

Phosphor is a term applied in industrial technology to a luminescent material, particularly one artificially produced for use in various appliances such as television tubes, radar screens and flourescent lamps etc. They may be either organic or inorganic but most of interesting and commercially important ones are inorganic (16).

Conventional phosphors, consisting of one and sometimes more of the following components : (i) the host which is the major component, (ii) one or more activators (acceptors) and (iii) a co-achivator or charge compensator (donor), are classified as : (a) phosphors in pure form and (b) impurity activated phosphors.

1-3.2 Classification of Phosphors:

(i) 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 diamand (10, 17).

(ii) Impurity activated phorsphors :

Impurity activated phosphors usually exhibit better luminescence than the pure ones. For activation small amounts of foreign ions are added into the crystal lattice of the base compound; called host lattice or matrix material. The impurity or foreign ion, which causes luminescence is called activator. The second impurity introduced in addition to the first, to enhance the luminescence, is called co-activator or sensitizer. Due to presence of some impurities (e.g. Fe, Co, Ni etc.) the luminescence intensity decreases. These are termed as killers or poisons.

(iii) Other well known phosphor systems :

Leverenz (18) has divided all phosphors into two major groups on the basis of the site occupied by the activator in the matrix, as follows :

(a) Substitutional Phosphors, which are characterised by an exponential decay law.

(b) Interstitial phosphors, which are characterised by power law decay.

Zwikker (19) divided the phosphors into four groups, viz.

(a) Sidot phosphors : ZnS, CdS etc.

(b) Manganese phosphors : ZnS : Mn

(c) Lenard phosphors : CaS, SrS etc.

(d) Pohl phosphors : KCl, NaI etc.

According to White (20) luminescent materials can be divided into three broad classes in terms of the degree of localization of excitation and luminescence process.

(a) Molecular phosphors :

Characteristics :

i) Intra - molecular excitation and emission.
ii) Energetics determined largely by structure of molecule and molecular orbitals.

Molecular phosphors are mainly organic; although compounds activated by the Uranyl ion (UO_2^{2+}) would fall into this group. The materials include diazo-dyes, aromatic compounds, and many biological materials.

Excitation, relaxation and emission take place entirely within the molecular orbitals of the organic molecules. There is little or no momentum transfer. The energetic of the luminescence depends on the molecular rather than crystal structure.

(b) Insulator phosphors :

Characteristics :

i) Localised excitation and emission.
ii) Energetics determined largely by energy levels of activator.

Insulator phosphors are defined as those in which the excitation-relaxation-emission process take place in a localised region of the crystal. The details of the energetics are determined to a large extent by electronic structure of the activator and sensitizer ions that make up the localised centre, as modified by the local fields generated by the crystal host. Insulator phosphors ought to have wide band gaps because the activator electronic levels must fit into the gap with energy differences corresponding to visible light.

(c) Semiconductor phosphors :

Characteristics :

i) Delocalised excitation and emission

ii) Energetics determined by band structure or crystal and defect states.

Semiconductor phosphors are those in which excitation transfer is a fundamental part of process. These may be intrinsic as in edge emission, or extrinsic with modified luminescence due to impurities. The luminescence behaviour of extrinsic phosphors is not determined so much by the electronic structure of the impurity itself as by the way in which the impurity modifies the band structure of the host crystal, semi-conductor phosphors, however, need not have narrow gaps. Further, in terms of photoconductivity associated with luminescence while in the other photoconductivity does not accompany luminescence (21).

1-3.3 Localised Energy Levels in Forbidden Gap :

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

(a) Luminescence Centres and Absorption Centres :

These are the energy levels responsible for the spectrum of emitted luminescence. The absorption and emission properties of these centres are the characteristic of the activator ion and the base material. These centres possess high capture cross-section for excited electrons and much greater probability for radiative transitions than for non-radiative transitions (15, 22).

Absorption Centres : In many phosphors absorption and emission centres are the same but in some, the energy is absorbed in one of the centre and transferred in the lattice itself to the other centre where it gets emitted which forms the emission or luminescence centre. Thus the centre where energy is absorbed is called absorption centre.

(b) Killer Centres :

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

(c) Hole Traps :

These are the localized levels just above the valence band capable of capturing a positive hole.

(d) Electron Traps :

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

(e) Metastable States :

Energy states existing within the forbidden region which can be excited by electron bombardment but not by photo-excitation are termed as metastable states. A transition from metastable level to normal state with emission of radiation has very low probability i.e. the transitions from these levels are forbidden. The transition from higher level to metastable state are permitted. The mean life time of metastable state is found to be much longer than the life time of radiating level. Representative times are 10^{-2} to 10^{-4} sec. for metastable states and 10^{-7} to 10^{-9} sec. for radiating level (23).

1-4 CRITERION FOR OCCURANCE OF LUMINESCENCE :

A crystal wherein transition of an atom or ion into an excited state has occured by absorption of radiation or otherwise, can return to the ground state by ridding itself off the energy absorbed. The latter is usually dissipated in the form of heat. In some cases, however, it is re-emitted in the form of light radiation; and the crystal exhibits luminescent properties. It is seldom that these are exhibited by pure (physically and chemically) substances. Randall (24) suggested that a pure substance is flourescent if each elementary cell of the crystal contains an ion or complex group with an unfilled valence electron layer entirely shielded by the surrounding medium.

From theoretical point of view, absorption of a radiation quantum by a pure crystal gives rise to a free electron and a hole. These may recombine without emission, when are subjected to the effect of crystal lettice vibrations and transfer their energy to the lattice in the form of heat. Hence it results that the electron transitions responsible for emission should be well shielded off by the surrounding atomic configuration from interactions with the crystal lattice vibrations for radiative recombination to occur (25). However, when defects are present in the lattice, the probability of recombination of electron and hole with the emission of radiation increases. The reason being that the electron and hole are bettler shielded off at the counters than elsewhere from the effect of lattice vibrations and thus probability for them to transfer their energy to the surrounding atoms or ions in the form of heat is lesser. The necessary defects may be created due to self activation (local defects) or may be produced by incorporating the foreign impurities (foreign defects).

1-5 RECOMBINATION PROCESSES :

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

1-5.1 Radiative Recombination Processes :

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

(a) Band to band recombination : (Fig. 1.2(i)) :

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

(b) Recombination via shallow donor or acceptor levels : Fig. 1.2(ii) :

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

(c) Donor-acceptor recombination : Fig. 1.2(iii) :

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

$$hv = E_G - (E_D + E_A) + e^2 / ER \quad \ldots . \ (1.1)$$

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

(d) Recombinetion via deep levels : Fig. 1.2(iv) :

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

(e) Exciton transitions :

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

1-5.2 Non-radiative recombination processes :

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

(a) Multi-phonon processes : (Phonon emission) Fig.1-3(i):

An electron may lose energy by the production of a number of quanta of lattice vibrations (phonons). M.Lax(26) assumes that an electron in conduction band falls into excited state of large orbit associated with an impurity atom. The electron then falls into states of lower and lower energy by successive phenon emission until it reaches the impurity ground state. The energy released will raise the temperature of lattice.

(b) Auger recombination : Fig. 1-3(ii) :

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

(c) Surface recombination :

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

1-6.1 Mechanism of photoluminescence :

The mechanism of photoluminescence involves four processes : (A) Excitation and Emission, (B) Transfer of energy during excitation and emission and (C) storage of the part of energy absorbed during excitation.

(A) Excitation and Emission :

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

(a) Classical configuration co-ordinate curve model :

The configuration co-ordinate model is shown in Fig.1.4. It was first proposed by Von-Hippel (27) and later on F.seitz (28) considered is to explain the luminescence behaviour.

In the figure, the ordinate represents the energy of the system while absicissa represent a configuration co-ordinate which specifies the configuration of the ions around the centres. The ground and excited states of the centre represented resemble the para bolas. The equilibrium position of the centre in the ground state lies at A and the horizental energy levels drawn represent the vibrational states.

An absorption of radiation raises the centre from ground state A to excited state at A : resulting in the transition A A' which is vertical in accordance with Frank-Condon principle. At A: the centre is in a non-equilibrium high vibrational state and so by vibrational interchange with its surroundings relaxes to new equilibrium state at B; the point corresponding to minimum energy of the excited state. Having reacted centre to B, it may return to the ground at B' with emission of luminescence (vertical transition BB'). The centre finally relaxes from B' to A again giving up energy to the lattice by vibratiohal interchange. Thus the emitted energy being smaller than the absorbed one and explains the Stoke's shift.

In addition to Stoke's shift, the model can explain the decrease in luminescence efficiency at elevated temperature and thermal quenching.

(b) Energy band model :

This model is based on the collective electron model of Bloch (29) for crystelline solids which was subsequently developed by Riehl and Sch, on (30), Johnson (31), Mott and

Gurney (3) and a few other workers (4,5,14,32). The model is illustrated in Fig. 1.5. According to this model, the phosphors which are usually semiconductors or insulators, are describable in terms of valence band (F) and conduction band (C), with localised energy levels in the forbidden region between the bands. These localized levels are associated with impurities or imperfections in the host lattice. In Fig. 1.5 such levels are shown. The level L represents the ground state of luminescence centre, while the levels T_1 and T_2 represents the electron and hole traps respectively.

The act of excitation and emission takes place as follows : Absorption of 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 an 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 band and the 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. However, such electron and hole pairs normally do not recombine radiatively, (33). Various workers have been modified the energy band model to explain the luminescence characteristics of specific phosphors. Some, which are well-known, are being Schon klasen's model (34), Lambe-kliek's model (35) and William and Premer's model (36, 37). These are illustrated in Figs. 1.6 to 1.8.

(B) Energy Transfer During Excitation and Emission :

An phasphor systems, where absorption and emission of light energy taken place at the same centre, no energy transfer is involved. However, in systems in which absorption and emission are not contained to the same centre, energy is transferred from absorption centre to the emission one. It may occur in two ways : a) Energy transfer with no movement, (b) Energy transfer with movement of charge carriers.

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

In this model, there are three mechanisms for energy, nemely, (i) Cascade mechanism, (ii) Resonance transfer and (iii) Exciton migration.

(i) Cascade Mechanism :

In this type of mechanism (38) one centre on absorbing energy emits radiation (Primary emission). This emitted radiation is then absorbed by the second centre, which finally emits luminescence (secondary emission). This process of radiative transfer through the emission and reabsorption of photons is known as "Cascade mechanism." This mechanism is most effective in those cases whdre the emitting systems are efficient activators and spectral distribution of primary emission overlaps the absorption spectrum of the emitting systems. The process is useful for the activators in inorganic phosphors which have forbidden transitions (38, 39).

(ii) Resonance Transfer :

In this process, the emitting system is an activator and the absorbing system which transfers energy is called sensitiser, and the phenomenon of transfers energy is called sensitised luminescence. The significance of sensitised luminescence in inorganic solids resides or the fact that resonance energy transfer can take place between an allowed transition in the sonsitiser and a forbidden transition in the activator. The entire process of resonant transfer of enerty has been given by Dexter (A) in the following five stages :

1. Absorption of photon of energy E by the sensitiser.
2. Relaxation of the crystal lattice around the sensitiser ion to such an exten that the available electroy energy in radiative transfer from sensitiser shall be $E_1 < E_0$
3. Transfer of energy D_1 to the activator.
4. Relaxation of the crystal lattice around the activator ion to such an extent that the available energy emitted in radiation shall be $E_2 < E_1$

5. Emission of energy E_2

Stages 3 and 4 requires 10^{-13} sec. each or more for excess of energy to be dissiated by the phonons over the crystal lattice, leading to stoke's low. Stage 4 takea a time, that depends on the distance of the surrounding activator ions. Stage 5 requires 10^{-8} sec. or more depending on the degree of forbiddences of transition. Since Stoke's law is obeyed, the activator represents a kind of 'trap' for the electron excitation energy i.e. the excited activator cannot enter into resonance with the sensitiser $A(E_2 < E_0)$ and no energy transfer can take place activator to sensitiser.

Transfer of energy is accomplished by quantom mechanical resonance process (38, 39) such as electric dipole-quadrapole field overlap, electric dipole-quadrapole field overlap or by exchange interaction. The efficiency of processes depends upon the distance overwhich the energy is transferred.

(iii) Exciton Migration :

Absorption of energy near the fundamental band leads to the formation of bound electron-hole pairs. Wannier, in 1937, proposed the existance of excitons i.e. associated electron - hole pair held together by coulomb attraction and not combining to emit radiation. Because of their interaction with phonons, they do not remain localised but wander throughout the crystal transferring the energy. In such a process, the excitors transfer excitation energy from one point to another by moving quickly through the lattice without contributing to the electrical conductivily (40). However, they do contribute to luminescent emission both in exciation mechanism and in radiative recombination, processes.

Broser and Balanskii have shown experimentally the possibility of the action of excitons at large distances from their point of creation. However, excition migration over large distances is only possible in very pure and defect free crystals. It is specifically sensitive to the presence of surface states.

(b) Energy transfer with movement of charge carriers :

In this mode, the energy is transferred by migration of excited electrons or holes through the crystal. The process is the same as that involved in Schen-Klasen's and Lambe-Klick's models during exciation and emission.

(c) Energy Storage :

Many phosphors store the part of absorbed energy during exciatation. This temporary storage of energy is due to trapping of excited electrons in trap levels. The energy required (thermal) to liborate a trapped electron is known as the activation energy, E, and is measured in electron volts (eV). It is also a measure of depth of trapping state and hence referred toas trap depth and is the difference between the trapping level and the corresponding excited level.

1-6.2 Photoluminescence Decay :

Photoluminescence decay is a diminishing after glow under isothermal condition, observed from 10^{-8} sec. after removal of exciatation. It arises due to the release of trapped electrons is trapping levels during exitation. The recombination of those with luminescence centres given rise to two modes of decay, namely, emponential and hyperbolic.

1-6.3 Kinetics of Luminescence :

Kinetics of luminescence is concerned with the mechanism involved in recombination of electrons with luminescence centres.

It may be of first order or monomoleculer in which traps are situated close to the luminescence centres (less than 10^{-6} cm away), resulting these by the more probability of recombination of an electron then retrapping which is almost neglisible or it may be of second order (41, 42) or Bimolucular in which traps are located away from the luminescence centre (distance greater than 10^{-5} cm) so that the probability of recombination is neglisible and the electrons gets trapped in deeper empty traps (41, 42). And if the traps are supposed to be distributed in the vicinity of luminescence centres in such a way that the probability is small but not neglisible, which has been reported by several workers (43, 46).

1-7 ABSORPTION SPECTRA :

Apart from emitting radiation materials can also absorb the energy in amounts which depend upon the structure of material and wavelength of radiation and the spectra obtained is known as absorption spectra. Thus, the spectra obtained by spectroscopic analysis of the light emitted through an absorbing medium, which lies between the source of excitation and a detector is the absorption spectra.

1-8 EMISSION SPECTRA :

The radiations consisting of visible wavelengths plus some invisible radiation constitute a spectrum of emission. Emission spectra are obtained when materials are heated or subjected to exciation from an electric arc or discharge of some kind. The spectra obtained by analysing radiative emitted from luminous source is called as emission spectra.

Phosphors owe their practical importance due to their property of absorbing incident energy and converting it into visible radiations. In general, impurity activation of the crystal is needed for this phenomenon to occur, though vacancy may also be very useful. The impurities and imperfections present invariably in the solid perturb the periodic potential of the solid produce localized levels. Thus each impurity or lattice defect gives rise to a new absorption band on longer wavelength side of the fundamental absorption band. Since such impurities or lattice defects govern the luminescence emission characteristic of a phosphor, emission studies are advantageous in knowing about their defects and energy levels involved in electronic transitions leading to a particular emission. The absorption studies are being complementary to the emission studies.

If the phosphor is excited by optical source, only certain wavelengths are absorbed by the phosphor. In general, absorption of short wavelength is associated with matrix material and absorption of long wavelength is associated with activator. Absorption and emission are intimately related processes. The emission characteristics of the phosphor are also determined by the nature of the base material, the activator and its concentration. The positions and intensities of the emission bonds are the characteristics features of a phosphor under study. The emitted radiation has invariably longer wavelength than the exciting radiation since the energy difference being manifested as thermal loss.

According to the means used for excitation, the emission spectra are further called to be as electroluminescent spectra. thermoluminescent spectra, cathodoluminescent spectra etc.

The emission characteristics of phosphor exhibit, in general, one or more broad spectral bands situated at different positions in the spectrum, and are characteristic of particular luminescence Centre.

1-9 POINT DEFECTS, COLOUR CENTRES, LUMINESCENCE AND EPR :

Any deviation in a crystal from a perfect periodic lattice or structure is an imperfection. The common point imperfections are chemical impurities, vacant lattice sites, and extra atoms not in regular lattice positions. Many important properties are controlled as much by imperfections as by the nature of the host crystal, which may act only as a vehicle for imperfections. The luminescence of crystals is nearly always connected with the presence of impurities or imperfections.

The simplest imperfection is a lattice vacancy, which is a missing atom or ion, also known as a Schottky defect, in which an atom is transferred from a lattice site in the interior to a lattice site on the surface of the crystal, and in another, namely, Frenkel defect, an atom is transferred from lattice site to an interstitial position, a position not normally occupied by an atom.

The hyperfine splitting of the electron spin resonance furnishes valuable structural information about paramagnetic point defects, such as F centres in alkali halide crystals and the donor atom in semiconductor crystals.

The effect of magnetic field (EPR) over the unpaired electron gives the information about the defects in crystals. The luminescence centres, the traps (hole or electron) can in general be studied with these measurements.

1-10 Statement of Problem:

Despite considerable work that has been done on sulphide phosphor systems such as ZnS, CdS, CaS, BaS and SrS (47-51); very little attention has been paid to oxide phosphors. Recently, studies on CaO, MgO and ZnO phosphors, doped with one or more impurity elements have been reported by some workers (52-56). Although these studies are mainly devoted to the determination of spectral distribution of emitted radiation, absorption spectra, electroluminescence studies and to the thermoluminescence, very little is known about the nature and origin of luminescence centres. Moreover, the mechanism of energy transfer in these phosphors is not unambiguously known. As regards to their luminescence behaviour with and without flux, they have been little investigated and role of flux in these phosphors is not completely clear.

In the present investigation CaO phosphors doped with varying concentrations of Bi^{3+} and Sm^{3+} have been prepared in microcrystalline powder form and their absorption and emission spectral characteristics are studied systematically in co-relation with the structural properties. The structural properties have been investigated using the XRD and EPR techniques.

A) Optical Absorption Spectra:

The optical absorption spectra have been studied in the wavelength range of 3500 A° to 6000 A°. The data obtained have been used to know the nature and origin of absorption centers and to infer the mechanism of energy transfer in co-relation with the results of emission spectra. Attempt has also been made to elucidate the effect of changing concentration of activators and addition of flux.

B) Optical Emission Spectra:

The optical emission spectra have been studied using interference filters in the wavelength range of 4000 A° to 62500 A° with 3650 A° excitation. The results obtained have been used to infer the nature and origin of luminescence centres and defects responsible for the emission bands. The conclusions have been drawn about the role of impurities Bi^{3+} and Sm^{3+} and of flux in luminescence behaviour of studied samples.

c) X-Ray Diffraction & EPR Studies:

X-ray diffraction studies have been carried out with a view to gain the information about the crystalline structure and formation of CaO phosphors. The attempt have been also made to interprete the data in the light of effect of addition of activators and flux. The EPR measurements have been carried out to elucidate the nature and origin of defect centers acting as luminescence centres and absorption centres.

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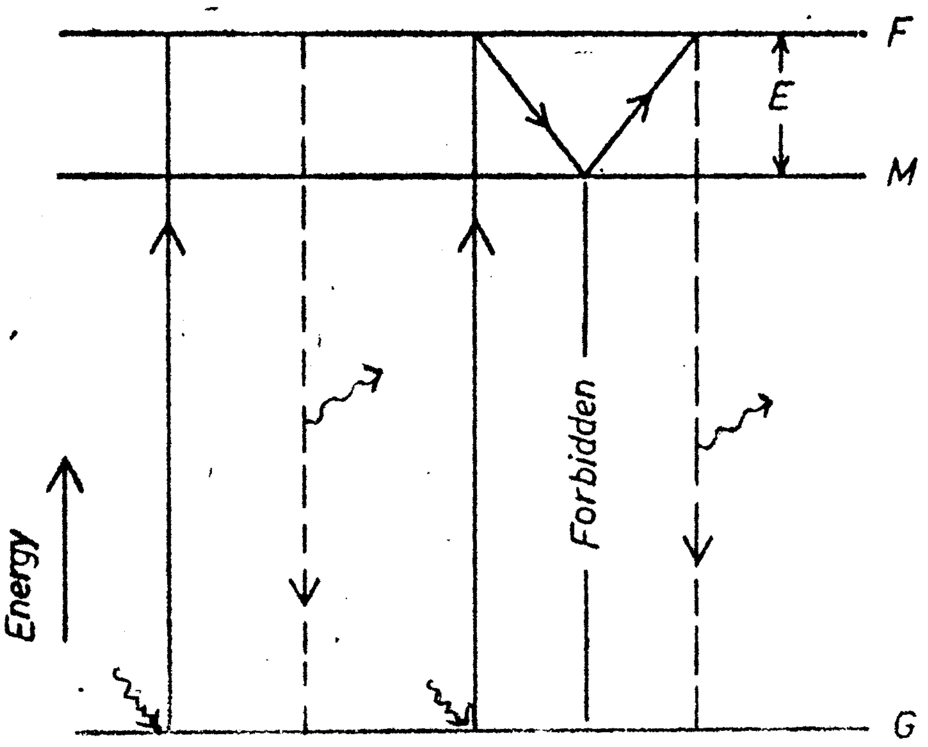
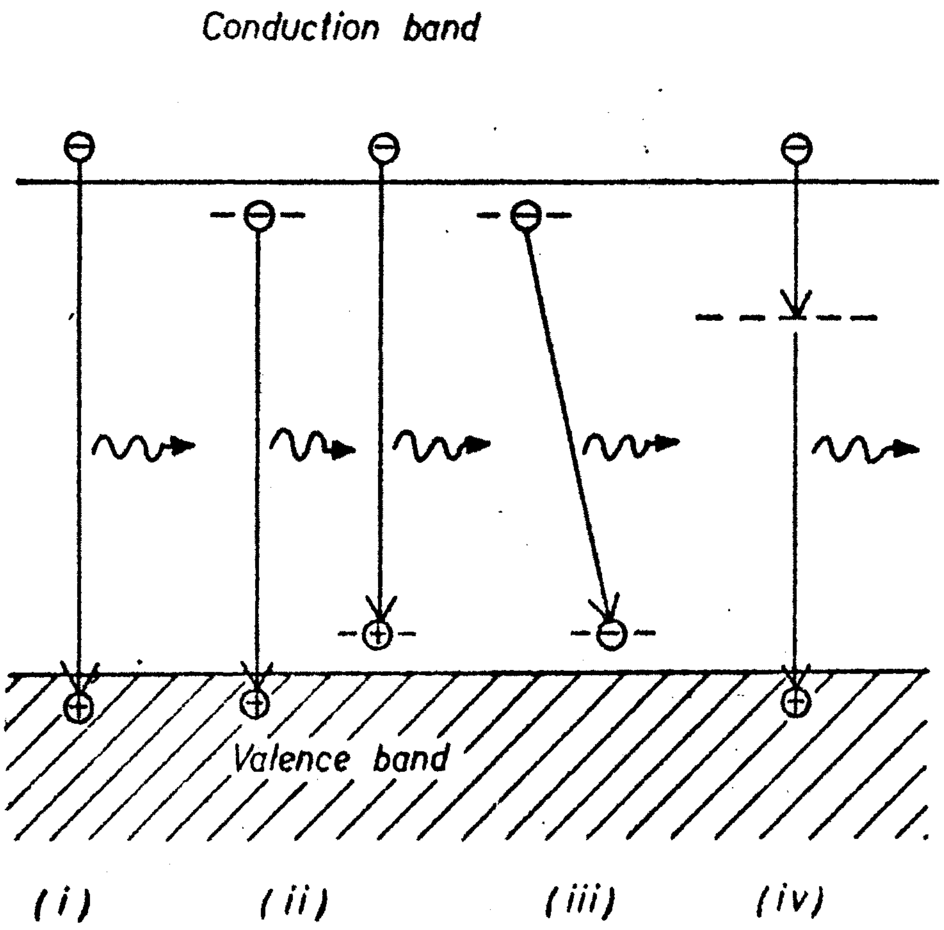


G — Ground state
F — Excited state
M — Metastable state
E — Activation energy

G → F : Excitation
F → G : Fluorescence
F → M : Fall in metastable state
M → F : Thermal or optical activation
F → M → F → G : Phosphorescence

Fluorescence and phosphorescence phenomena (after Jablonski, 1935).

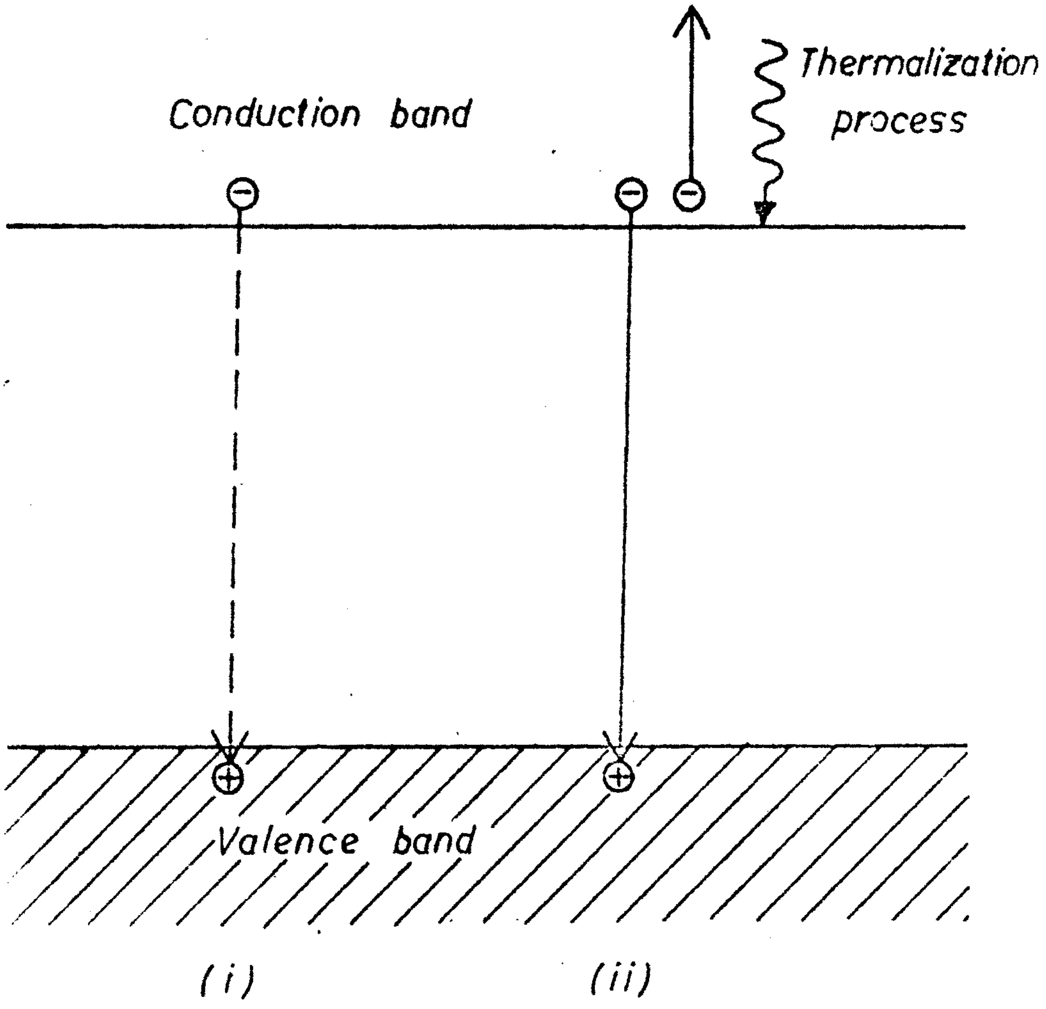
FIG. 1·1



Radiative transitions:

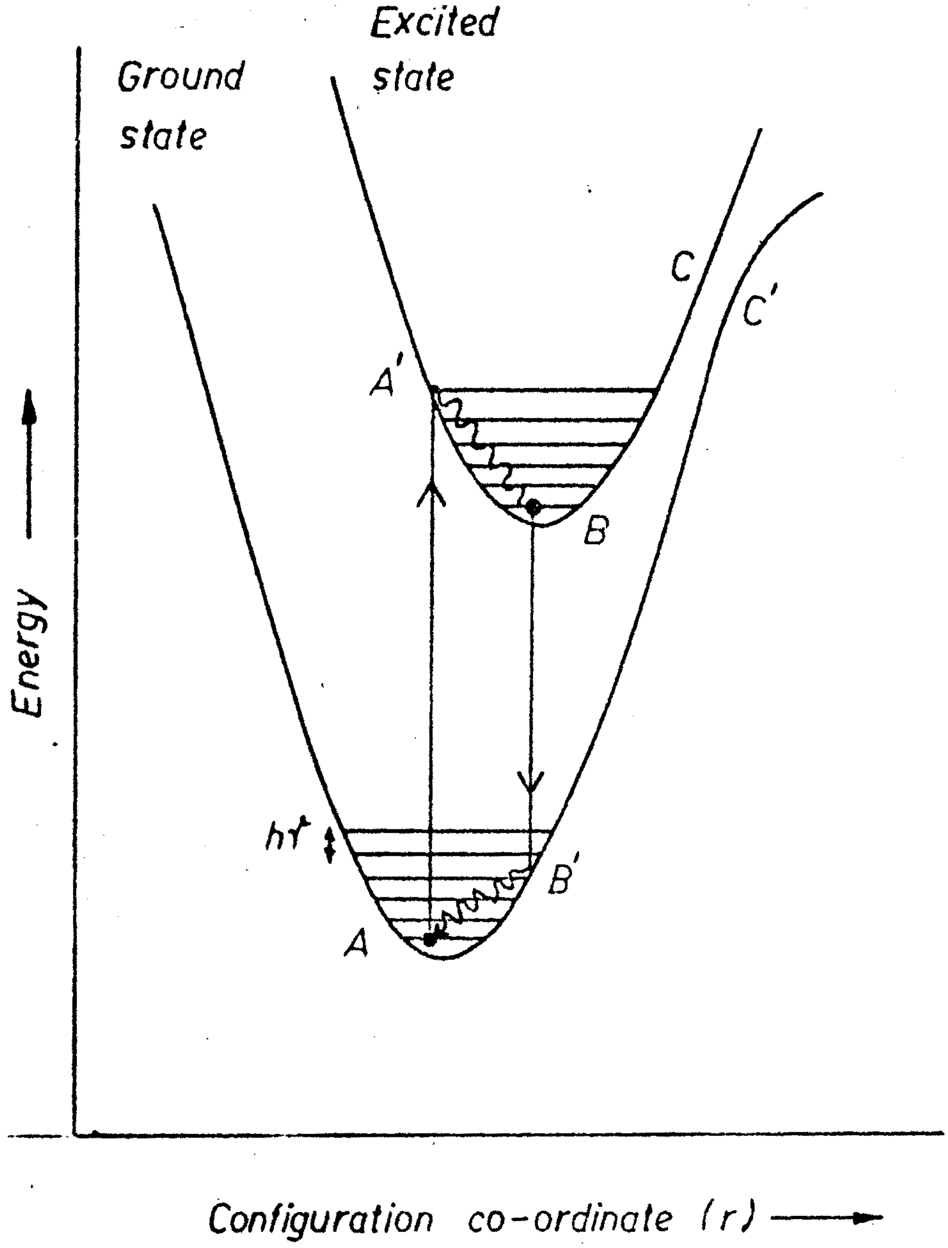
(i) band — band
(ii) via shallow donor or acceptor levels
(iii) donor — acceptor
(iv) via deep levels.

FIG.1·2



Non radiative transitions
(i) multiphonon,
(ii) Auger.

FIG.1·3



AA' : absorption transition

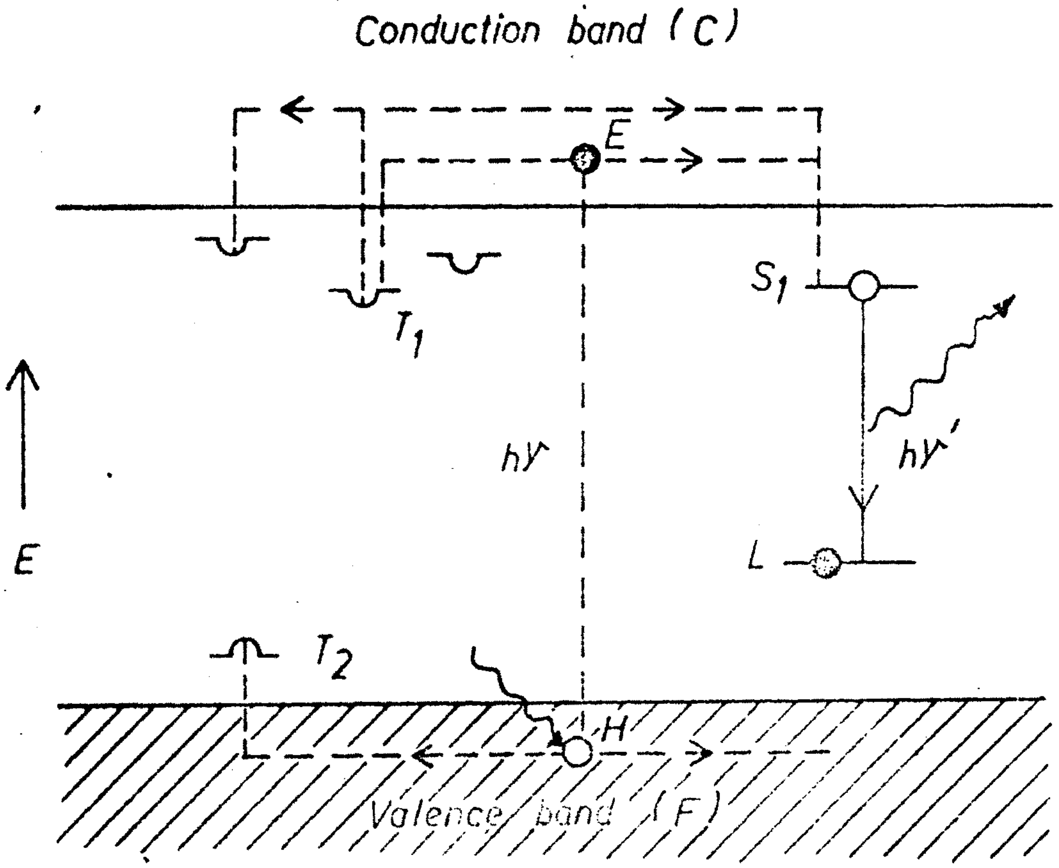
BB' : luminescence emission

$BCC'A$: non-radiative transition

$h\nu$: vibrational level separation

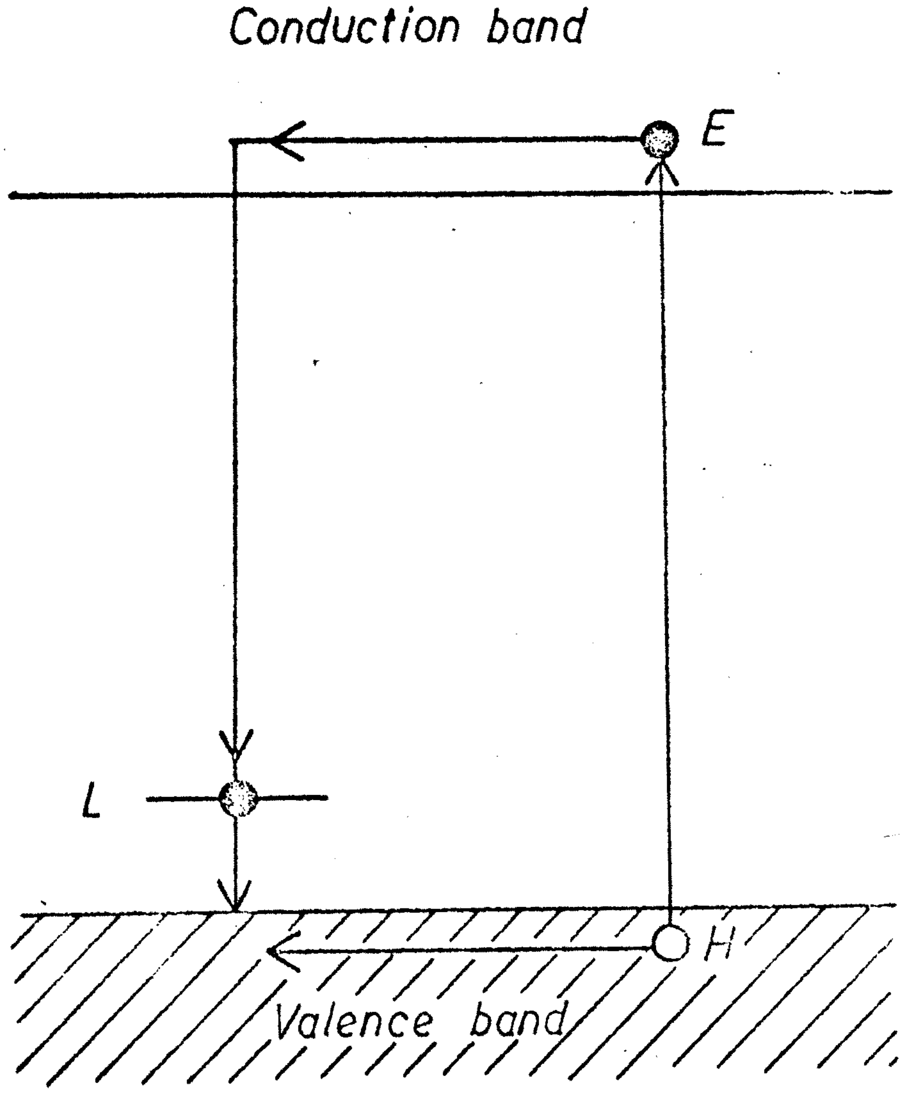
Configuration co-ordinate curve model.

FIG.1·4



Energy band model.

FIG.1·5



Schön - Klasen's model.

FIG.1·6

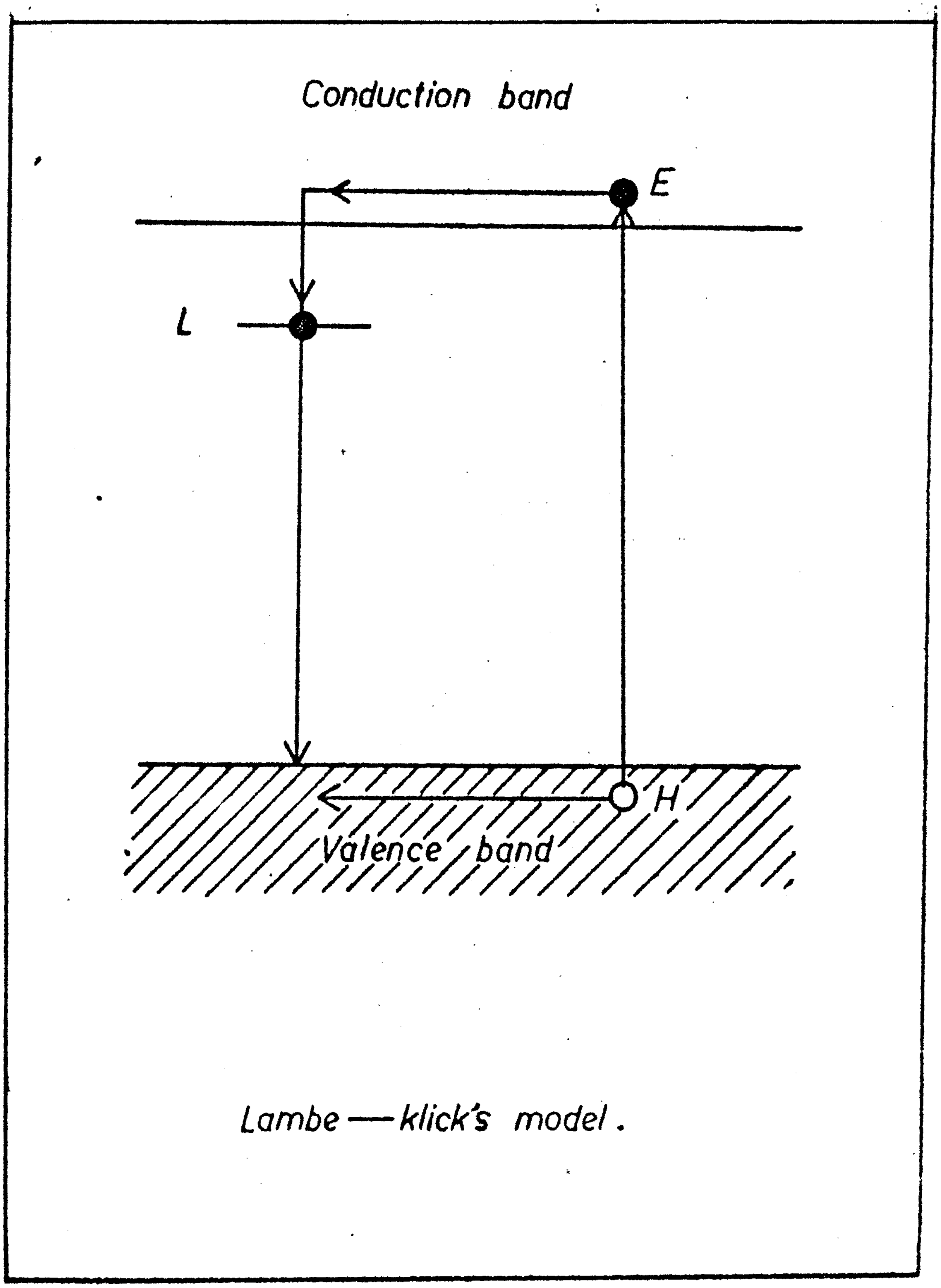
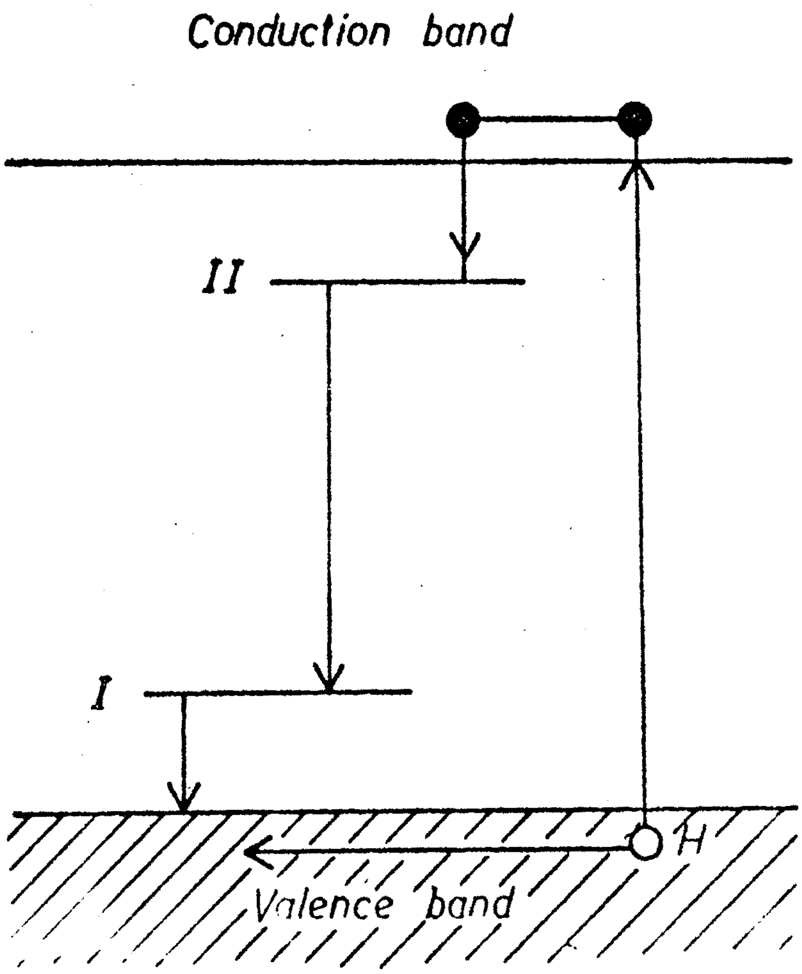


FIG.1·7



Williams and Prener's model.

FIG. 1·8