CHAPTER - 2

GENERAL CONCEPTS OF LUMINESCENCE AND THERMOLUMINESCENCE

GENERAL ASPECTS OF LUMINESCENCE

The emission of light from material has been a subject of interest to the scientists for many centuries. However, it was only in the 17th century that science came to their rescue to solve this mistery. Emission of light from liquids and solids thus became a topic of interest.

According to Widemann(1) and Garlick(2), luminescence is the phenomenon involving the absorption of energy by a substance and its reemission in the visible or near visible region. Luminescence is however, different than the thermal radiation. The phenomenon of luminescence doesn't follow Kirchoff's law for absorpotion and emission, and on the basis of time decay, it also differs from physical processes like Raman effect and Compton effect. In the case of Luminescence emission, this time delay is greater than 10^{-9} second. While Raman and Compton effects are completed in a time around 10^{-14} Second or less.

TYPES OF LUMINESCENCE

The prerequisite to luminescence emission is the excitation of the luminescent substance, since the energy radiated by the system must be provided in some way. Various types of luminescence are often distinguished by a prefix denoting the nature of the source of energy exciting the substance. If luminescence is produced by the absorpotion of electromagnetic radiations, then it is known as photoluminescence.

Cathodoluminescence is produced by energetic electrons or cathode rays. Electroluminescence is produced by an electric field applied to luiminescent substance. Triboluminescence is the phenomenon where visible light released during grinding and pulverizing of the substance. Chemiluminescence utilizes the energy of a chemical reaction. Bioluminescence is the biological process and Sonoluminescence depends on the ultrasonic irradiation of materials.

The features common to all forms of luminescence are

1) Occurence of some processes whereby an atom, molecule is excited to a higher energy state by the source of energy.

2) Its radiative de-excitation to ground state, i.e. having the emission of a photon with appropriate energy after the lapse of some period of time. Some of the better general reference in luminescence are reviewed in books(3-17).

PHOTOLUMINESCENCE : FLUORESCENCE AND PHOSPHORESCENCE

When luminescent material is excited by radiation or cathode rays, emission occurs during the excitation and in some of the solids for considerably longer period, even after the excitation has ceased.

Fluorescence and Phosphorescence have been defined in different ways by different workers. A further distinction between the types of luminescence is made on the basis of time dependance of the emission. Initially, the term 'fluorescence' was applied to luminescence which persisted only as long as the excitation was continued. If the luminescence was observable after the excitation has stoppd, the phenomenon was called 'Phosphorescence'. But this is not a meaningful distinction, because with instrumental techniques one can really observe a luminescence glow after the excitation has stopped (persistence, decay time). If the decay time is of the order of $10^{-8} - 10^{-9}$ s, it would have to be classified as 'fluorescent'. Using a visual persistence, system would therefore have to be called 'phosphorescence based'; on the instrumental measurement of after glow.

A more meaningful distinction between fluorescence and phosphorescence is based on the dependence of luminescence decay time on its absolute magnitude. Thus, if the emission is due to the spontaneous transition of the system from the excited energy level E to ground energy level Eg (Fig 2.1), the luminescence will decay exponentially with a decay time determined by the probability of the transition between these states. If this is an allowed electric dipole transition, with emission of a photon in the visible region of the spectrum, the decay time willbe in the range of $10^{-8} - 10^{-9}$ s. If the transition $E \rightarrow Eg$ is of different type,(Electric quadrupole, magnetic dipole etc.) the transition probability is many orders of magnitude low, with corresponding increase in decay time. The transition probability in all cases is however, an intrinsic characteristics of the luminescence centre, the luminescence decays exponentially with time and the decay time is independent of the temperature in the range, where luminescence efficiency remains high. All the above cases are properly characterized as fluorescence. The 'allowed' transitions producing a 'fast' fluorescence whereas the 'forbidden' transitions, the slow fluorescence.

When the luminescence decay time depends on the temperature range where luminescence efficiency is high, the term phosphorescence is applied. On atomic scale this situation can arise when an atom, molecule or a centre is somehow excited to an energy level Em, from which it cannot return to ground level with photon emission, the transition $Em \rightarrow Eg$ is completely forbidden according to the selection rules. Let us suppose that the system can be raised by absorption of energy $\Delta E = E \rightarrow Em$ to a higher excited level E such that the radiative transition $E \rightarrow Eg$ is an allowed one. Hence, if the energy $\Delta E_{ab} = E - Em$ is provided to the centre, the energy $\Delta Eem = E - Eg$ will be emitted. If ΔE absorbed can be provided by thermal means at room temperature, a continuous luminescene (phosphorescence) can be observed even after the removal of excitation source. This emission will continue with diminishing intensity, there being no longer the occupancy of the metastable centres.

If the system is raised to a higher temperature the energy $\Delta Eab = E - Em$ will be provided at a more rapid rate, the phosphorescence thus will be brighter and the decay time will be shorter due to faster depopulation of metastable state via the path.

$$E_M + \text{Heat} \longrightarrow E^* \longrightarrow E_G + h\nu_{\text{emitted}}$$

Consequently, with lowering of the temperature there will be a decrease in phosphorecence brightness and an increase in decay time. Thus, the important difference between fluorescence and phosphorescence is the temperature dependence of the decay time.

THEORIES OF LUMINESCENCE

The configurational co-ordinate model and energy band model provide all the interpretations of luminescence phenomena. The two models are exclusive and complement to each other in explaining luminescence phenomena and are in no way incompatible.

The energy band model neglects the atomic rearrangement that occurs during luminescence, while cofigurational co-ordinate model ignores the charge transport through the lattice.

Configuration Co-ordinate Model

In contrast to the absorption and luminescence spectra of dilute gaseous atomic systems, which consist of sharp lines, the corresponding spectra in solid phosphors generally consist of rather broad bands having widths of a few tenths of an electron volt. In photoluminsenence of solid system, the emitted light generally is of longer wavelength than exciting light; a condition first experimentally noted in 1851 by G. Stokes and is known as Stoke's law. These spectral characteristics as well as other properties connected with the temperature dependence of the luminescence efficiency of phosphors, may be understood by considering the 'Configurational Coordinate diagram'.

Fig. 2.2 shows the curves representing potential energies of the normal and excited states of the luminescence centres in relation to the variation of one of its configuration co-ordination. Absorption of radiation raises the centre from the state A to state B. Electronic transition (due to energy absorbed) may be represented by a vertical line AB according to Franck-Condon principle, which states that when an electron is excited optically, the nucles of ions may be considered to remain at rest during the process. The system is not in equilibrium in the state B, somehow trying to adjust itself so as to reach to C, giving off the energy difference BC in the form of lattice vibrations or phonons. Further, the centre returns to the ground state by emission of luminescence CD and finally loses more energy DA by vibrational interchange. Seitz (fig. 2.3) and Dexter et al(18) (fig 2.4) proposed a modified model to show how a radiationless transision can take place from the excited state to the ground state by an internal conversion process. This model with few quantum mechanical modification explain (a) Stoke's shift (b) Width of absorption and emission bands at low temperature (c) Monomolecular decay (d) F-centre luminescence and (e) Thermal quenching of luminescence. Its limitations are : (a) it cannot explain processes occuring between absorption and final emission e.g. photoconductivity and (b) in most cases(19), precise configuration co-ordinate diagram have not been possible. Some workers (20,21) also suggested a multidimensional model as against the one dimensional model.

ENERGY BAND MODEL

The collective electron model by Bloch has been modified by Mott & Gurney (22) and Seitz (23) to explain luminescence mechanism of phosphors. The energy states of an eletron in a crystal may be derived from the state of the individual atoms and ions which compose the crystal. The discrete energy levels in atoms and ions are broadened into bands are separated by "forbidden regions" and they are either unoccupied or filled. Thus, instead of the discrete energy states, there are discrete energy bands for the electrons inside the crystal. The uppermost completely filled band is called "Valence band" and the next higher allowed band is called "Conduction band". These energy levels in an allowed band are so closely spaced that effectively they form continuum. The energy level diagram indicating different electronic processes occuring in a crystalline solid is shown in figure 2.4.

When the activator atom is incorporated in a crystalline solid, it will give rise to localized energy levels in the normally forbidden energy gap. The localized energy levels may be classified into two categories.

1) Levels belonging to the host atoms which are under the perturbing influence of activators.

2) Levels which belong to activator atoms themselves.

Suppose G and A are two levels corresponding to say, an activator atom, represented in fig 2.5 in terms of energy band picture when activator atom is in the ground state, level G is occupied by electrons and level A is empty while reverse is true in the excited state. The excitation from G to A may be accomplished in at least three following ways.

1) It is possible that the incident photon of proper frequency is absorbed directly by the electron in level G whereupon it arrives in A (fig. 2.5)

2) The optical properties of alkali halides indicate that in the band picture of solids, they are to be described as typical insulators with a forbidden gap of the order

the excited state. Thus, the energy can be transferred from the exciting source to the impurity via host crystal, when the electron returns from the excited state to the ground state, luminescent emission is observed.

C) EFFECT OF TEMPERATURE ON LUMINESCENCE

There are two outstanding processes by which a material can become a generator or originator of light (radiation), after absorbing suitable extraneous primary energy. In one process, the absorbed energy is converted into low quantum energy, heat that diffuses through the material which then emits radiation called the thermal radiation. In the other process an appreciable part of the absorbed energy is temporarily localized relatively high quantum energy excitation of atoms or small group of atoms. Which then emit radiation called luminescence radiation. Strictly speaking, luminescence is a process whereby matter generates non-thermal radiation, which is the characteristic of the particular luminescent material. Very often, however the radiation so generated is called luminescence. To avoid the misinterpretations that can arise when luminescence and other radiations are used synonymously. We shall use the term luminescence to denote either the luminescence process as a whole or just the final emission part of the process.

Luminescence then is distinguished by emission of radiation, e.g. light and ultraviolet, in excess of the thermal radiation produced by heat in a given material. Examples of luminescence emission are the narrow spectral lines and bands of radiation emitted by (a) Electronically excited gases, such as in lightning and neon lamps, (b) Certain oxidizing organic matter in liquids exposed to air, for example in glow norms and fireflies and (c) Coating of tiny phosphor crystals excited by invisible alpha particles, electrons, and ultraviolet, as in luminescent watch dials, Television picture tubes and fluorescent lamps. In all these cases of luminescence, the temperature of luminescing material is best maintained near or below room temperature. Also the quality and quantity of luminescence radiations, especially infrared, which is emitted in the increasing order as the temperature of the solid is increased.

Examples of thermal radiation is the emission of infrared and light from electrically heated incandescent filaments in common lamps. The quality and quantity of thermal radiation depends chiefly on the temperature rather than on the nature of the emitting solid material.

FLUORESCENCE IN COUMARIN:

Coumarin (24) has a very low fluorescence quantum yield, but its derivatives (24) are highly fluorescent and have high quantum yield. The fluorescence of a large number of coumarin are studied for their dependance on enviornmental factor (24,25). Extensive study of luminescence of different coumarin was made by several workers (26,27,28). Fluorescence of coumarin has been employed for their detection in chromatography to detect the spots (29). Fluorescence characteristics of 7,4 sustituted coumarin was studied by S.S. Rathi et al (30). Fluorescence efficiency of coumarins depends on the nature and position of substituents. Efficiency can also be changed by changing surrounding media. Substituents which enhance electron mobility increases the intensity (24). It has been observed that electron attracting group at 3-position and electron repelling group at 7-position enhance the fluorescence intensity (31,32). The study of fluorescence spectra of different coumarins in different solvent has been reported by many worker (27,28,30,33,34).

APPLICATIONS OF LUMINESCENCE

The various applications of luminescence are fluorescent screens, Paints, Luminescent dyes for fibers, Optical brightning agents, Scintillators, Lasers, Flaw detection, Analytical chemistry, Biology and Medicine, Temperature indicator, dosimetry, etc.

(1) FLUORESCENT SCREENS

The different luminescent materials under the exposure of ionizing radiations, display visible emission of different colours. If the screen is prepared with luminescent materials, it can be used to give the visible image of an irradiated object. This property is used in T.V. Screens, watch dials and luminescent lamps.

(2) PAINTS

The unusual brightness of fluorescent paints is due to the presence of organic luminophores in them. The brilliancy observed in luminescent paints is due to the light reflected from painted surface and also the light due to luminescence. Enamels, decorative paints and printing inks belongs to the category of luminescent paints, and are by combining luminescent pigments and various binder. The different patents on the luminescent paints were reported (35,36,37).

(3) LUMINESCENT DYES FOR FIBERS

The rapid strides in the chemistry of polymer materials over the past several years have prompted to find solutions to the problems involved in the dyeing of fibers. Dyeing is generally done at high temperature so the dyes should be stable at high temperature and also, should be stable to the process of dyeing. Different classes of colouring materials have been reported in the patents (38,39,40).

(4) OPTICAL BRIGHTENING AGENTS

The yellowness inherent in textile material was eliminated by optical brightening agent. Derivatives of stilbene (41,42), compounds with benzazole group (43,44), Derivatives of coumarin and carbostyryl (45,46) are the popular optical brightening agents. One of the coumarin derivatives is used as brightner for photographic paper (47).

(5) ORGANIC SCINTILLATORS

Luminescent materials capable of emitting light when exposed to ionizing radiation, allow the use of them as scintillators. Luminescent scintillators are usually in the form of single crystal or luminophore in organic solvent, or solid solution in plastic single crystals of anthracene (48), stilbens (49) and tetracene(50) were reported for their use as scintillators. Liquid scintillators(51,52) are also reported with good efficiency. Plastic scintillators are more stable under varying temperature conditions and can be used in broader temperature range than other organic scintillator. Reported Plastic scintillators are polyvinylxylene, polymethyl styrene(53). Plastic scintillators are widely employed in cosmic ray research, detection of short particle, neutron detection and other applications(54).

(6) LASERS

In recent years, lasers based on organic luminophores have been gaining in importance, their main advantage being the possibility of frequency tuning in a broad range of wavelengths.

(7) FLAW DETECTION

One of the major areas of application of organic luminophore is inspection of various materials for defects. Advances in aviation, rocketry, building of spacecraft and many other machines operating under heavy duty conditions impose increasingly stringent requirements on the strength of individual components and assemblies. It is therefore, extremely necessary the timely and reliable detection of all kinds of defects, including superficial one arising in course manufacture and operation machines. It is known that surface microcracks tend to draw the wetting liquid by dint of intermolecular forces. This principle underlies luminescent dye penetrant testing used primarily for detecting surface cracks in the articles made up of metals, alloys, glass etc. The physical aspect of this method have been discussed elsewhere(55). Luminescence flaw detection technique is used to detect fine cracks in refractories, transverse defects, leaks through vessels.

(8) LUMINOPHORES IN ANALYTICAL CHEMISTRY

One of the practical appplications of luminophores is fluorimetric determination of traces of inorganic substances present in metal alloys, soil, air, biological samples(56-57). The most frequently used technique of fluorescence analysis based on luminophores include fluorimetry.

Different luminophores used for fluorimetric determination are Aminoxanthene dyes, Hydroxyxanthene dyes, Hydroxyanthroquinone dyes. Fluorescent indicators are used to determine end point in titrations.

(9) BIOLOGY AND MEDICINE

Luminescence is used to investigate structure of various biological molecules, bearing in mind, that the luminescence properties are extremely sensitive to structural changes and environment. This provides valuable information on the structure of complex biopolymers. Lumiphores are also used to determine charge on the membrane surface, lipid phase velocity, membrane fluidity. Many pathological processes in the body are linked with structural rearrangement in biomembrane. To investigate the pathological process, fluorescent probes are found to be useful.

(10)TEMPERATURE INDICATOR

Organic luminophores sensitive to temperature changes have found applications as temperature indicators. Reversible and irreversible indicators are widely used in Modern Technology. Reversible indicators permit timely detection of overheating in moving parts of various mechanisms, heating due to overloading of electrical equipment. Irreversible indicators used to sense the highest temperature inside complex mechanism during the operation. Solid solution of pyrene in Polymethylmethacrylate, 1-4 distyryl benzene are used as luminescent temperature indicators.

(11) DOSIMETRY

A great deal of interest has been displayed in the use of organic luminophores in the dosimetry of ionizing radiation by a method based on the relationship between the degrees of damage substainted by luminophore and radiation dose. The operation of dosimeter is based on the changes in luminescence properties under the effect of radiation. Advantages of fluorescent dosimeters are the small size, low cost but low thermal stability is the disadvantage.

THERMOLUMINESCENCE (TL)

GENERAL CONCEPT OF THERMOLUMINESCENCE

Themoluminescence (TL) or Thermally stimulated Luminescence (TSL) appears when a solid is heated with uniform heating rate, after being irradiated at a low temperature, by a certain radiation, viz. X-rays, γ-rays, β-rays, particle beams, UV light etc. Part of the energy absorbed by the specimen during the radiation may be released in the form of light, when the specimen is heated to high temp with uniform rate. The TL from the material is found to be sensitive to (i) the amount and nature of the impurity (ii) the thermal history (iii) Prethermal, mechanical and/or radiation effects (iv) the size of material particle (v) the crystallization history and (vi) defects present in the material.

The phenomenon of the Thermoluminescence might have observed or far back as the stone age. However, it was not until 1603 when the investigations with a synthetic material were carried out. In 1738, Du Fay while explaining his experiments on natural quartz showed that TL could be reactivated by the exposure of the specimen to light. Heat only stimulated the emission and was not its cause. The 'glimmering light' that was observed then was named 'thermoluminescence' in 1903 by a German Scientict E. Wiedemann during his explanations on the properties of some minerals. In 1904, Madam Curie(58) referred in her doctoral thesis, that "certain bodies such as fluorite become luminous when heated, they are thermoluminescent." The first theoretical model for the TL phenomenon however appeared in late 1940's. Randall and Wilkins (59,60) suggested the model which is now associated with "first order Kinetics" while Garlic and Gibson (61) developed another model, more suitable for some TL curves known as "the second order kinetics". Halperin and Braner(62), May and Partridge(63), then developed the "General order Kinetics" model.

The phenomena of Thermoluminescence is qualitatively explained with the help of the band structure of solids with respect to the electronic energy levels(64,65,66).

The forbidden gap is imagined to contain some acceptor or doner metastable levels which are basicallly responsible for the observed thermoluminescence. Metastable level known as trap, is characterised by the energy E, which, an electron must acquire from the lattice vibrations in order to escape from it and diffuse around the crystal in the conduction band. Before the irradiation of the specimen, it is in the valence band (V.B.). The traps and centres provided by defects are represented as energy levels intermediate between the valence and the conduction band, called the forbidden gap.

When the material is excited by any ionizing radiation, some electrons from valence band are excited to conduction band (fig. 2.6a).

Generally these electrons cannot remain excited indefinitely; that means the life time of an electron in the conduction band is very short and the electron attains its ground state immediately accompanied with photon and/or phonon emission. However, an impurity atom present in the material energy state in the forbidden band. An excited electron can find itself in this state, (i.e. trapped), rather getting back to its normal valence band, this trapped electron will remain in the trap for a period. If now, the material is heated, the thermal energy supplied enables the stimulation of the electron out of the trap (detrapping) which then returns to the ground state with the emission of light (fig.2.6b). Alternatively, a hole may be excited into the valence band where it wanders until it recombines with an electron at the trapped counter part emitting the light (fig.2.6c). In many cases, it is possible that the electrons and holes are detrapped more or less simultaneously and they recombine at an entirely new sites called luminescence centres or recombination centres (fig.2.6d).

In reality, a trapped charge carrier when detrapped, has a finite probability of getting retrapped (fig. 2.6e). When this retrappng is significant, the shape of the glow curve is different from the case when it is absent. There are also practical situations where the trapped charge carrier recombines directly without being excited into the conduction band or valence band. This is a case of TL involving isolated luminescence centre (fig.2.6f).

People have also explained the TL on the basis of configurational co-ordinate model (67,68).

Scientists have investigated and established that the material in any condition contains impurities, defects (deviation from the regular array of atoms in Crystals). High energy irradiation by X-ray, β-ray etc. for example remove electrons from ions in their normal structural positions. While most of the electrons fall back to a position of lower energy. Some of the displaced electrons may become trapped at the sites of structural imperfections, which will cause an increase in the potential energy of the structure. The trapped electrons remain in the traps at higher energies for long period of time, being unable to escape unless supplied energy is sufficient enough to enable them to penetrate the energy barrier surrounding the traps and to return to their normal lowest energy state in the structure. Hence, when the material is heated at the uniform heating rate, the trapped electrons escape from their various metastable energy levels and fall back into their normal positions. During this transition the excess energy frozen in the structure is released partly in the form of light (photons) thereby accounting for the phenomenon of Thermoluminescence.

A plot of the measured intensity of TL from material heated at constant rate in a specified temperature range, appears in the form of characteristic curve which exhibits a great variety of pattern and is called the "glow curve" or "TL curve". The energy required to release the electrons of the various types of traps is variable and consequently, the temperature required to exhibit TL curves depends on the type of the trap. Thus peak will appear on the TL curve and each of the maxima will represent a particular structural electron trap.

The applications of TL in various field are progressing. TL finds favour in much diverse scientific disciplines as radiation protection and control, Health Physics, Archaeology, Geology, Environment and Space monitoring, Solid State Physics, Biology, Agriculture Forensic science etc. (69-74).

THERMOLUMINESCENCE IN POLYMERS

Though the Thermoluminescence has been known since the seventeenth century, it was not reported for the organic polymer till 1955(75). Most of the discussion regarding TL is pertinent to crystalline solids. The organic polymers are used usually in amorphous or at the most partially crystalline forms. Therefore, TL observed in polymers cannot be interpreted on the basis of 'lattice defects'. Traps, Luminescence Processes, Luminescence Centers etc., are of totally different nature in the polymers. The characteristics of TL in polymers has been reviewed by Fleming and Hagekyriakou (76) and Potridge et al (77).

CHARACTERISTICS OF TL IN POLYMERS

TL in a polymer results from the sequence of events. Thermoluminescence in polymers is observed by exposing the polymer specimen to some form of ionizing radiation and then heating the same. The plot of TL intensity vs temperature is called a 'glow curve', which is a complex form of TL data. TL can be observed after delays of hours or days between the end of irradiation and the commencement of heating. Most of the workers assume that TL emission in polymers result from the sequence of events as mentioned here. When polymer is exposed to ionising radiation , immobile positive ions are produced, which exists before irradiation in the form of impurity molecules and trapped electrons. When specimen is heated, the electrons escape from their traps; by thermal excitation or disruption of traps through the onset of chain motion or by tunneling through the potential barrier associated with the traps. The electrons move various distances in order to recombine with the positive ions. This recombination results into an excited state which subsequently decays to the ground state; wherein the decay involves a radiative transition.

TL intensity in polymers falls to unworkably weak levels at temperatures greater than about 250°K (78, 79, 80). Hence, generally the sample is irradiated at 77° K. The absence of TL above 250°K is probably due to the deexcitation of luminescence centre molecules occuring through collisional processes at such temperatures rather than by radiative transitions. While the quenching in organic compounds has been explained by Brisk (81) & Boustead(82). They described four different mechanisms for quenching in polyethylene.

The glow curves in case of polymers frequently consist of a single broad peak with a poorly defined 'shoulder' on one side. The spectrum of the emission is very broad, typically covering the range 300-600nm (79,83). Though, most of the auothers assume that the spectrum, will not alter significantly during either the glow or the isothermal decay, it may not be true for polyethylene, polystyrene and polypropylene, the emission results from the electronic transition due to the presence of the inherent carbonyl group.

The time dependence of isothermal decay in intensity has been reported by several workers (78, 84, 85, 86, 87). Hama et al have suggested a relationship of the form $I(t) = Io/ (1+\alpha t)^{m}$ for polymer. I(t) is the intensity at time 't' Io is the intensity immediately after irradiation. α and m are the constants dependent on dose rate.

In some polymers, like polyethylene and polystyrene TL output considerably reduces, if the polymer is exposed to

UV, visible or IR after irradiation(78, 88). This type of disappearance of TL is known as bleaching. In the polyethylene , the bleaching increases with decreasing wavelength of light(88). This effect can give the information about nature of traps and the release mechanism. It is observed that D.C. Voltage across the thickness during TL emission increases the intensity immediately(78, 89). Results have been analysed in terms of field assisted thermal detrapping of electrons (90,91) and Electrons tunneling from traps to luminescence centre(89,92).

NATURE OF TRAPS

In crystalline material lattice defects are traps. The polymers are amorphous or partially crystalline. Hence, the nature of the traps is totally different. Patridge (77) suggested the four main types of traps.

CAVITY TRAPS

There are voids with irregular shapes defined by the local spatial configuration of the local chain. Such traps would eventually be broken up by the motin of pendant group or backbone segments, but would be stable within limited temperature ranges. Presence of such traps are suggested in polyethylene by Nikolskii(88).

The estimated lower limit of energy is about 0.8 eV and upper limit is roughly 3.0 eV in contrast to the range 0.1-0.5 eV usually reported for the traps below 250°K. In polymers, the amorphous material, there is no sharply defined energy gap between valence and conduction band; instead they have "tails" consisting of continuous distribution (energywise) of localized state of traps(93). These traps are separated from the relevent band of extended states by a mobility gap. So, trapped electrons would probably need to be excited into conduction band in order to move and recombine with luminescence centre.

Many elaborate and elegant schemes(94,95) have been proposed to derive the activation energy, from the glow curve or isothermal decay, for the distribution traps. However, these schemes yield no meaningful results(96).

b) MOLECULES

Molecules with positive electron affinity for example oxygen, were found to be more effective traps in polyethylene, short chain of hydrocarbon (98), branched paraffin (99), squalane (100) and polytetrafluoroethylene (101). Charlesby et al (97) quotes the electron affinity of molecular oxygen as 0.8 eV, while Phelp and Pack(134) quotes the same as 0.43 eV.

The later one is computed from the approximate relationship of E= Tm(k)/500 which relates trap depth E and temperature Tm of the associated glow curve peak. Above equation yields estimation of Tm which is somewhat higher than the experimental Tm value for the oxygen peaks in polyethylene and hydrocabons. Boustead (98) suggests that the depth of the oxygen molecule traps in the saturated hydrocarbons is less than the electron affinity of molecular oxygen because of an interaction of the molecule with polymer matrix via hydrogen bonding forces. He also suggested that molecular, oxygen ion will fit into triclinic structure but not into the orthorhombic one. Patridge from the calculations suggested that the escape of electrons from oxygen traps is indeed a thermally activated process.

FREE RADICALS

A polymer exposed to the ionising radiation, can produce free radicals. These free radicals can capture the electrons. The electron affinity for free radicals is around 1 eV. Hence, they are unlikely to release electrons below the room temperature (102). Free radicals are shown to act as luminescence centres rather than traps (103, 104) in polymers. Such traps would be responsible for the glow peaks above room temperature but cannot account for the glow peaks appearing at lower temperature.

MOLECULAR GROUP

Molecular groups or molecules which do not have positive electron affinity may also capture electrons by distorting the polymer matrix in their neighbourhood. This leads to another type of cavity trap, examples of which have been found in TL emission from polytetrafluoroethylene and polytetrafluoroethylene-oxide irradiated in the presence of Helium(101). Fleming and Hagekyriakou (76) interpreted the above results in terms of weak electronic interaction of Helium with polymer matrix, mainly in the amorphous region of the sample. They also suggested a distribution of electron trap activation energies associated with an unspecified continuous structural change in the amorphous region as the samples are warmed.

LUMINESCENCE CENTRES

Distinction between the luminescence centres in polymers and those in crystalline solids is not clear. Not much information is known about the luminescence centres in polymers. During the exposure to ionizing radiations, positive sites in the chain can serve the role of luminescence centre. Frequently, the luminescence centres have been identified as the sites in the chain which have lost electrons during excitation.

ELECTRON DETRAPPING MECHANISMS

Three main mechanisms(76) have been proposed for the escape of electrons from the trap i.e. detrapping.

THERMAL EXCITATION OUT OF STABLE TRAPS

This is the escape mechanism envisaged by most authors and was first applied by Randall & Wilkins(59) considering the trap as a one dimensional potential well, the rate of escape R(t) of electrons at time 't' is given by

$$R(t) = n(t)\nu(t)(T)\ e^{-E/kT}$$

where $n(t)$: concentration of trapped electrons at time 't'
$\nu(t)$: frequency factor
E : trap activation energy
k : Boltzman constant
T : temperature in Kelvin

Above equation was given by Mott & Gurney(68) dealing with alkali halides. They assumed that (a) All the traps have same activation energy E, (b) The thermal energy of an electron in a trap has Maxwellian distribution and (c) the trapped electrons exchange energy with their surrounding by colliding with the walls of the trap. It follows from (c) that frequency factor $\nu(t)$ should be of the order of the phonon frequency of the lattice. This value is less for polymers than that for inorganic materials. Clearly this model envisages the escape of electrons from stable traps of fixed dimensions. Four main types of traps in polymers were suggested by Patridge(77). There traps have already been discussed in detail in the previous section.

TRAP BREAK-UP BY CHAIN MOTION

One would expect the onset of some particular form of motion within a given polymer matrix. The form of motion may be oscillation or rotation of the pendant group. The onset of motion would directly affect the trapping of electrons in the polymer(77). Cavity traps could be brokern up, electrons released from oxygen ions or free radicals, could be facilitated and distortion of the lattice could be effected. Many workers (80 , 105, 106) attempted to correlate the peaks in TL glow curve with particular type of molecular motions detected by the other techniques.

If a given TL glow peak originating from the electrons release triggered by chain motion, the measured activation energy is characteristic of motion and not of the trap.

Molecular motion may be affected by structural transition, so it is expected that structural transition causes TL through electron detrapping.

ELECTRON TUNNELLING

TL emission in polymer was explained by some workers(79, 89, 92) suggesting the electron tunnelling through a potential barrier of trap to luminescence centre. If electrons escape from the traps predominantly by tunnelling, then the TL intensity on returning to the original temperautre will be altered whereas in the case of thermal untrapping it will be significantly reduced. The assumptions commonly made in connection with electro-tunnelling process in organic solids are(107).

(1) All traps are of same shape and height, equivalent to a single activation energy in thermal excitation, some exceptions(108) are also reported.

(2) Luminescence centres are fixed and they do not interact with each other.

(3) Tunnelling process is 'resonant' i.e. the total energy of the electron does not alter during tunnelling.

(4) Electron executes some form of simple harmonic motion within the trap.

THERMAL STIMULATION AND KINETICS

May and Patridge(109) recognised the difference between stimulation of luminescence in crystalline solids and the polymers, when they found that the TL glow curves of polymers could not be fitted to 1st order or 2nd order kinetics. They suggested the empirical equation.

$$I = -c \frac{dn}{dt} = C\, S'\, n^{b}\, e^{-E/KT}$$

Where b is between 1 and 2 and is the 'order of kinetics.' S' has dimensions of frequency factor. Hama et al(79) also had to use an empirical relation to fit the data on isothermal decay.

Kinetics in polymers is different from that in the inorganic solids for more than one reasons. In amorphous materials there is no sharply defined energy gap between valence and conduction bands, they have 'tails' consisting essentially of a continuous distribution of localised traps. These traps are separated from the relevant band of extended states by mobility gap. The activation energy 'E' is thus not single as in most crystalline solids, but it extends over a range. Hagekyriakou and Fleming (110) have solved the kinetic equation resulting in such case.

In crystalline solids, it is assumed that the traps have Boltzman distribution for thermal energies, and hence, the probability of thermal release of electrons from the trap into conduction band is Exp(-E/kT). In polymers, the release of electrons may result from chain motion which could be thermally activated e.g cavity traps may be broken up and the electrons released due to the onset of a particular form of motion in a polymer matrix such as oscillation or rotation of a pendant group or small segments of the chain. Molecular chains themselves might be electron traps, the detrapping process is thus determined by unfreezing of chains. If a given TL glow peak originates in electron release triggered by chain moton, then the measured activation energy would be characteristic of that motion and not of the trap.

Charge carriers can be released from the traps during structural transition. Several transitions take place in polymers during heating and detrapping can occur due to molecular motions taking place during the transitions(111). The transitions are governed by equations totally different than the usual equation. If a glow peak corresponds to the charge carriers released during such transition, then it will be described more appropriately by the equation describing the transition. Direct thermal stimulation or that due to chain motion would increase with temperature. The transitions on the other hand, involve large changes in the detrapping probability within a narrow temperature range. Dalvi et al(133) have worked out kinetic equations by considering TL as a phase transition like process. According to them TL of 1st or 2nd order kinetics can be uniquely characterized by the transition temperature Tc, which is identified as the temperature at which rate of decay of luminescence is maximum under near isothermal conditions. The trap depth E, the frequency factor S, and transition temperature Tc are related by the equation.

$$2e^{E/kT_c} = S_o\ (\tau/\xi)$$

Where τ - characteristic electron hole recombination time and ξ is a constant of proportionality associated with electron hole recombination kinetics. This could be more appropriate for describing TL in polymers after defining the transition parameters.

In polymers, the electrons generated during the exposure to ionizing radiations may not travel far from its original position where it can recombine again, before it gets trapped. The spatial separation between the traps and recombination site may thus be of the order of hundred Angstroms. The recombination can then occur by 'tunnelling' which could be stimulated thermally(107).

TL IN SYNTHETIC POLYMER

Thermoluminescence has been studied much more in polyethylene than in any other polymer. Its glow curve contains four peaks, though not all these may be resolved under same experimental conditions. The effect of different warming rate was studied by Boustead (112), Charlesby & Patridge(113). Increased molecular mobility due to the increase in dose was studied by Nikolskii & Buben (114) & Aulov et al(115). The quenching of the peak by Oxygen molecule was explained by Patridge(116) with the help of 'exciton model' of alkane. Hirayama and Lipsky(135) used the above model to explain results for n-alkanes. Activation energy for polyethylene thermoluminescence have been measured by Nikolskii & Buben(117) using three different method.

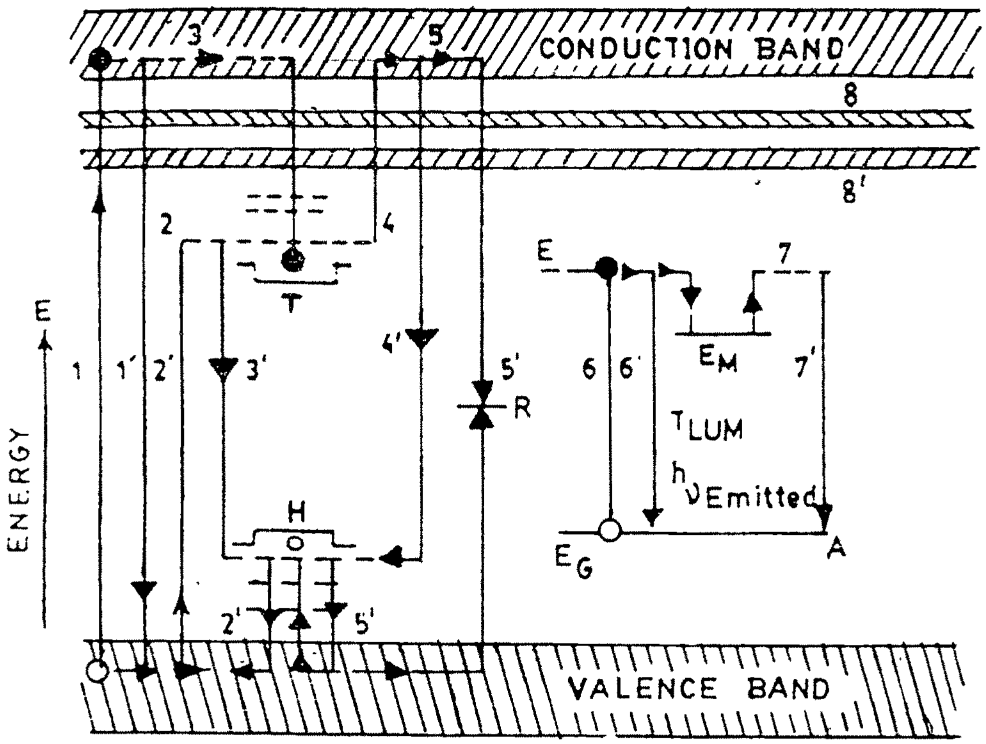
Thermoluminescence for extend chain crystals of polyethlene was studied by S.V. Moharil(118,119) Hashimoto (120). Many workers have studied thermoluminescence for polypropylene (112, 115) polyisobutylene(97, 121) dine polymers (122), polystyrene(123), Polymethylmethacrylate (124), Polytetrafluoroethylene (101) and many other synthetic polymers.

The TL of a considerable range of biological materials have been investigated by few workers(125, 126, 127).

APPLICATION OF THERMOLUMINESCENCE

During past two decades, very considerable progress has been made in the applications of the thermoluminescence for practical purposes(128, 129). The most widely developed application is its use in radiation dosimetry which spans area of Health Physics and bio-medical sciences, radiation protection and control. Thermoluminescence technique finds its aplication in dating of archeological (130) and geological materials. A recent application of TL concerns the dating of sand, dunes, which has implications in the study of their movement and some other aspects of the desert enviornment(131). This offers the possibility of looking into the mechanism of spread of desert areas in the past and its relationship with future predictions for the pattern of desert spared. Application of TL have been mentioned in forensic science which is concerned with characterisation of suspect materials and identification of forged objects. TL also finds application in solid state ionography, Enviornmental and space monitoring. The dose for rate in air due to terrestial source can be estimated by the formula given by lowder-de-planque(132).

The influence of enviornmental temperature, relative humidity, visible light etc. on TL was also reported. TL dosimeters have been used, for radiation moniotoring in manned spacecraft and satellites, Dentistry and clinical diagnosis, Agriculture for enhancing the storage life of grain and elimination of agricultural pests that infests food grains.



● - ELECTRON , O - HOLE , T - ELECTRON TRAP , H - HOLE TRAP
E_G - GROUND STATE OF IMPURITY A , R - RECOMBINATION SITE
E - EXCITED STATE OF IMPURITY A , ------- EXCITED STATE
E_M - METASTABLE STATE OF IMPURITY A

1, 1'	ELECRON HOLE RECOMBINATION IN THE VALENCE BAND.
2, 2'	RELEASED HOLE COMBINES WITH TRAPPED ELECTRON.
3, 3'	TRAPPED ELECTRON AND HOLE CENTRES INTERACT & ANNIHILATE.
4, 4'	RELEASED ELECTRON COMBINES WITH TRAPPED HOLE
5, 5'	ELECTRON & HOLE COMBINE AT A RECOMBINATION SITE R'.
6, 6'	EXCITED ELECTRON COMES BACK TO GROUND STATE.
7, 7'	RELEASED ELECTRON FROM META STABLE STATE E_M FALLS BACK TO GROUND STATE E_G.
8, 8'	EXCITON BANDS.

FIG. 2-1 ENERGY LEVEL DIAGRAM SHOWING VARIOUS ELECTRONIC PROCESSES CONNECTED WITH EMISSION IN A CRYSTALLINE SOLID CONTAINING IMPURITIES AND RADIATION INDUCED TRAPS

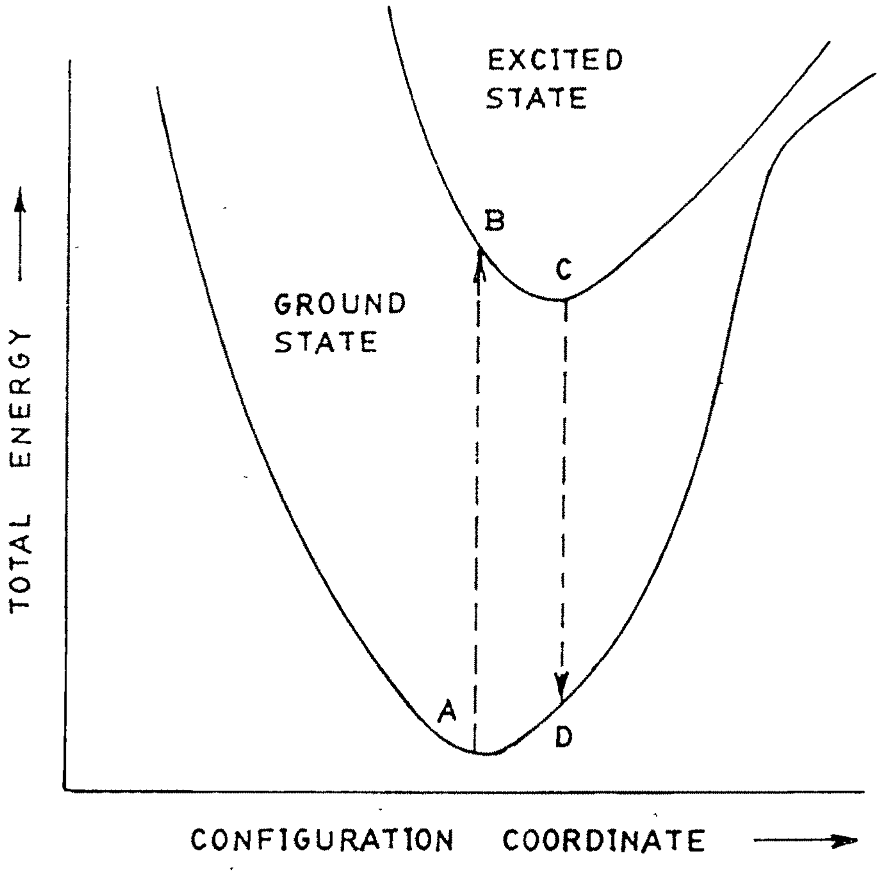


FIG. 2-2 SCHEMATIC CONFIGURATION CURVES

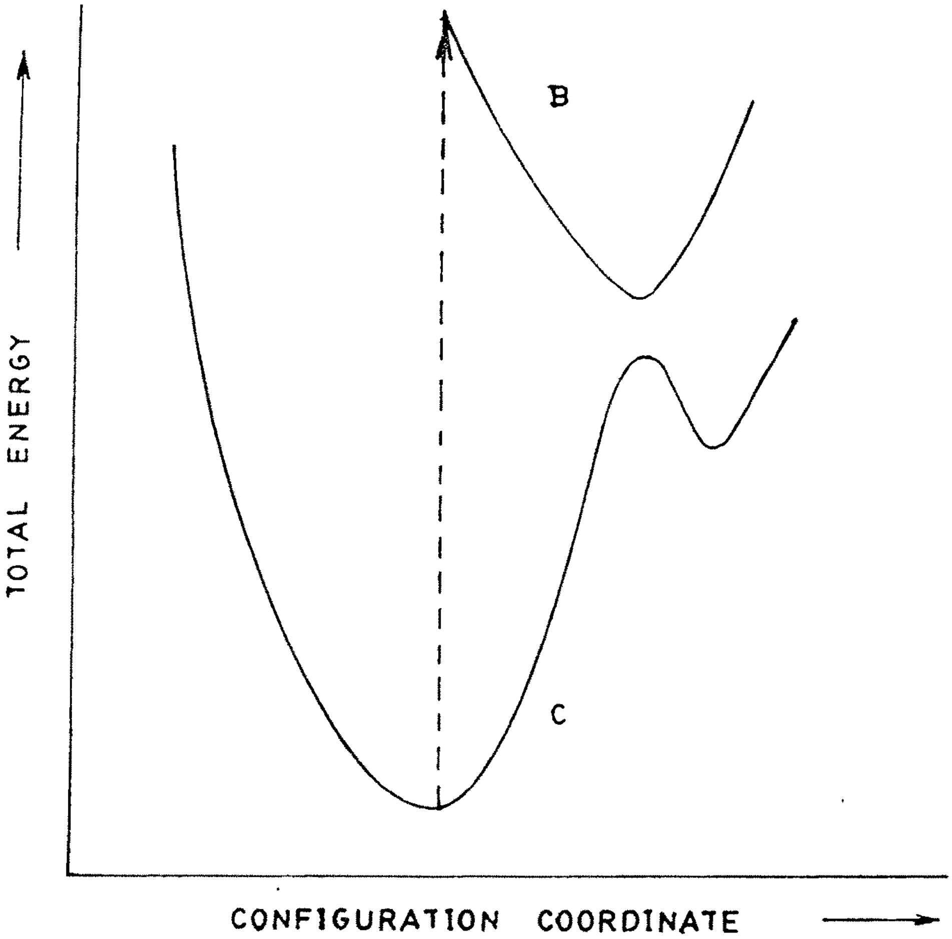


FIG. 2-3 CONFIGURATION COORDINATE DIAGRAM TO SHOW ABSENCE OF LUMINESCENCE (SEITZ)

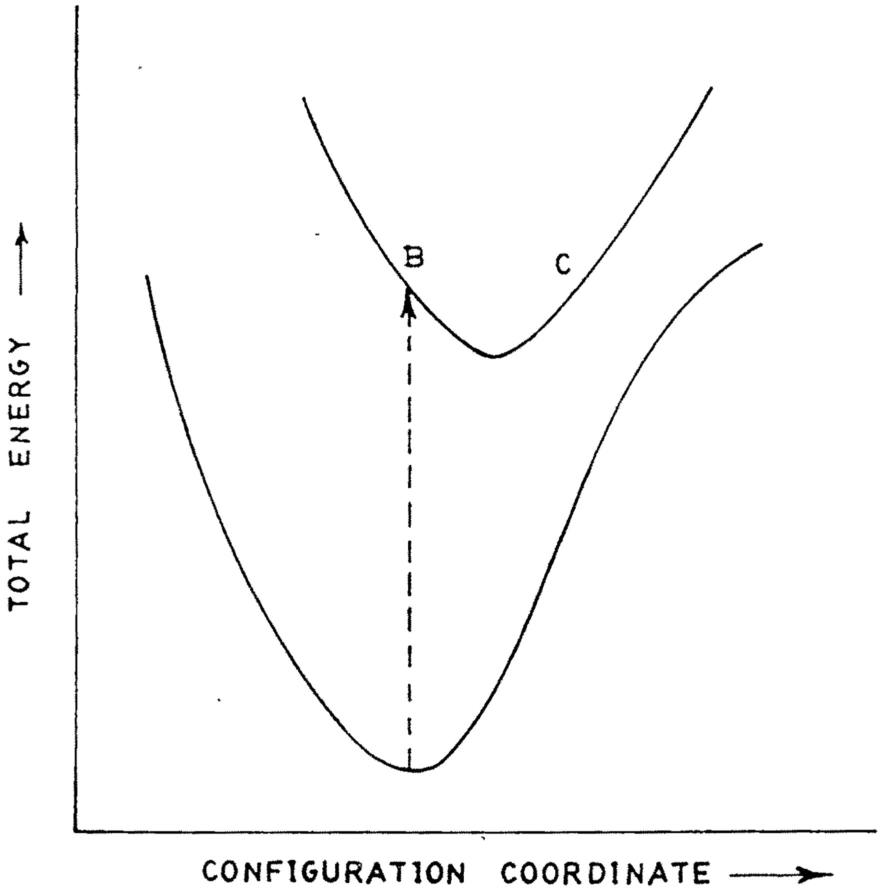
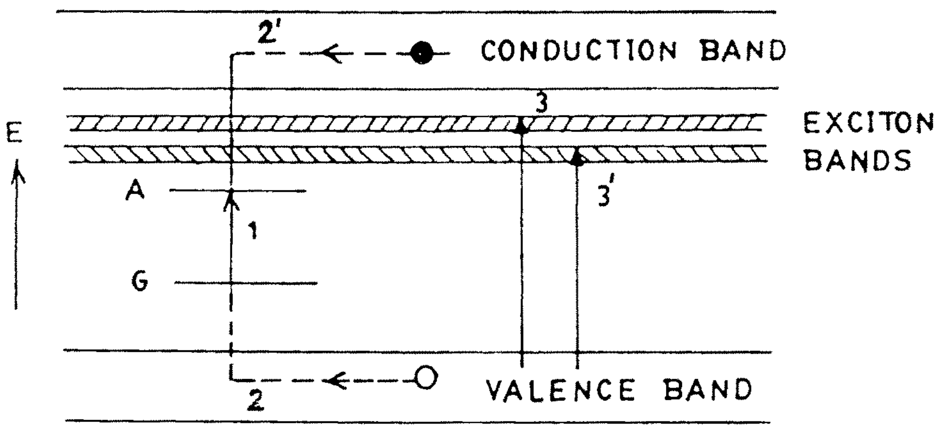


FIG. 2-4 CONFIGURATION COORDINATE DIAGRAM TO SHOW ABSENCE OF LUMINESCENCE AND CONDUCTION FOR LUMINESCENCE (DEXTER)



ENERGY BAND MODEL

FIG. 2-5

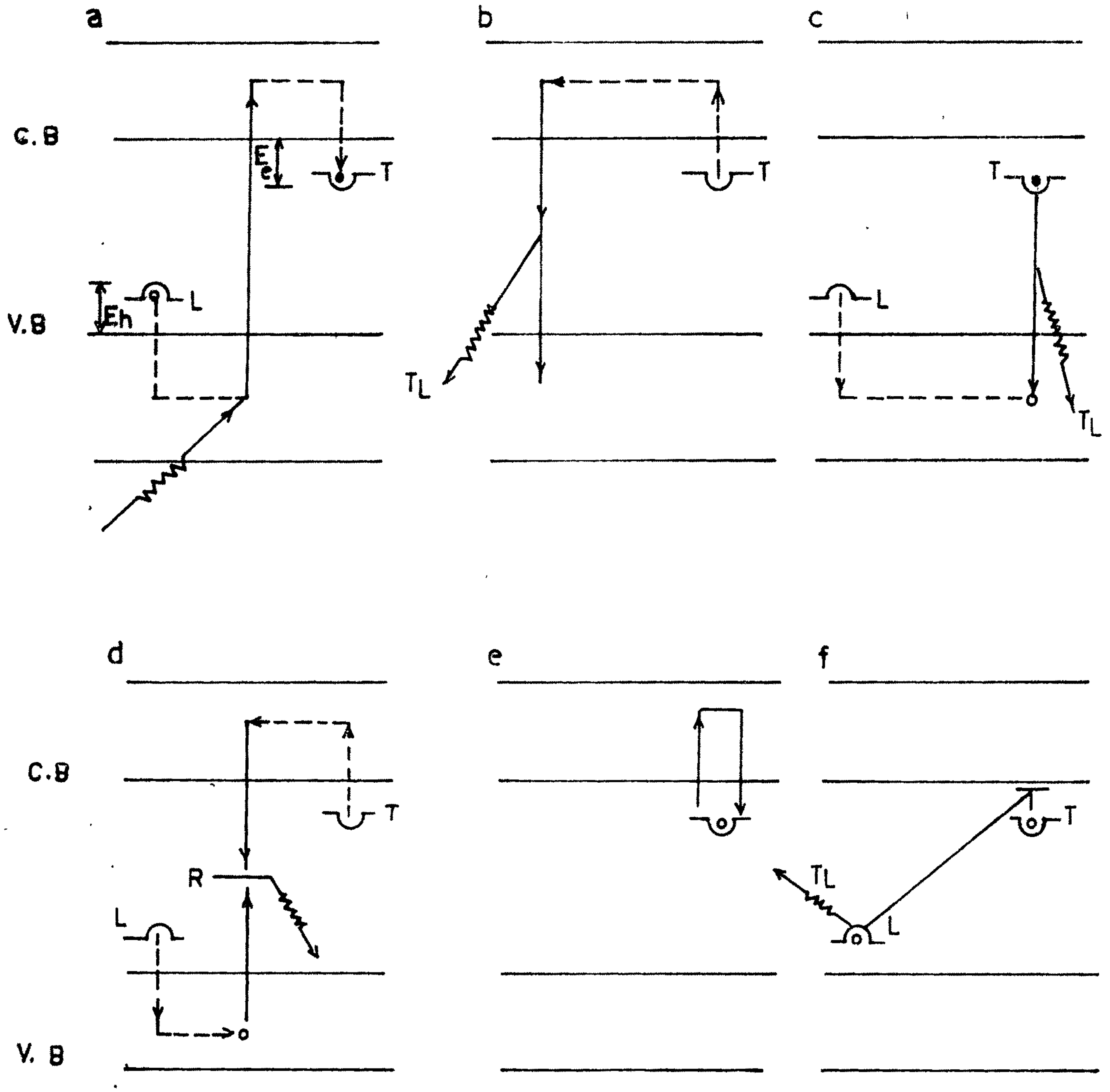


FIGURE 2·6

BAND THEORY MODEL

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