CHAPTER I - INTRODUCTION
Introduction

Luminescence has been an active field of scientific investigation for a period which encompasses the present century. Luminescence is well known to us by its applications in fluorescent lighting, fluorescent paints and pigments, electroluminescent panels, radar and cathode ray tube screens, nucleon and radiation detectors. It also has its important application in nuclear scintillation counters and in the recently developed varieties of solid state 'Lasers' which give coherent source of very high intensity.

Luminescence is now known to comprise of important optical properties of matter in the solid state, being directly connected with it through 'defects' or an imperfect crystal lattice. It is a very convenient and sensitive indicator of changes of composition, structure and atomic interactions in many solids. It is luminescence which has led to the realization of the extreme importance of small concentrations of impurities on the detailed electronic processes taking place in solids and throws light on related phenomena such as photoconductivity and colour centres.

1.1 Basic Concepts

(a) Luminescence: When a substance absorbs energy in some form or the other, a fraction of the
absorbed energy may be re-emitted in the form of electromagnetic waves in the visible or near visible region of the spectrum\(^1\). This phenomenon is called 'Luminescence'. It is distinguished from thermal radiation in that it does not follow Kirchoff's law. A time delay in emission of the order of \(10^{-9}\) sec. distinguishes it from the Raman and Compton effects which are completed in a time of about \(10^{-14}\) sec. or less\(^2\).

Luminescence may also be defined more specifically by pre-fixing the mode of excitation\(^3,4\) as follows:

(i) Photoluminescence – that produced by absorption of photons of energies from a few to several electron volts;

(ii) Radioluminescence – that produced by bombardment with high energy particles or radiation such as X-rays and \(\gamma\)-rays;

(iii) Cathodoluminescence – a specific case of radioluminescence produced by cathode rays;

(iv) Electroluminescence – that produced by an electric field;

(v) Triboluminescence – emission resulting from mechanical strain;

(vi) Chemiluminescence and Bioluminescence – emission produced by chemical or biological reactions;

(vii) Sonoluminescence – emission produced by ultrasonic waves;
Thermoluminescence — this is a particular case of photoluminescence. If the phosphor is cooled and excited and then the temperature is raised in the dark at a constant rate, a sudden burst of luminescent radiation is observed. This phenomenon is known as 'thermoluminescence' although the term is misleading in that the prefix suggests that heat is the primary excitant. Leverenz suggested a more appropriate term 'thermostimulation' for the phenomenon.

The excitation process resulting due to charged particles, X-rays and γ-rays has been explained by Goldberg\(^5\). The energetic charged particles ionize electrons which in turn excite and ionize additional electrons. The energy loss of a primary beam of electrons in traversing inorganic solids is of considerable interest. The empirical law for the energy loss of an electron in passing through matter is known as Thomson-Whiddington law.

\[ E_0^2 - E^2 = bx \]

where \( E_0 \) is the initial energy of the incident electron, \( E \) is the energy after traversing the path \( x \) and \( b \) is a constant characteristic of the material.

X-rays and γ-rays incident on a luminescent material create energetic secondary electrons, which excite luminescence by the same process involved in cathodoluminescence.
(b) Fluorescence and Phosphorescence: A distinction between the two has been made on the basis of the physical processes involved and also the physical conditions of the experiment. According to Curie\(^6\) and others, fluorescence is the luminescence emission during excitation, whereas phosphorescence is the emission after \(10^{-8}\) sec. of removing the excitation source. Some authors also define fluorescence as the emission of light for which decay time is temperature independent and phosphorescence as the temperature dependent part\(^7,8\). Moreover, fluorescence is produced due to transitions between excited and ground states of an activator whereas phosphorescence is due to a delayed return of electrons from a metastable level via the excited state (Fig. 1.1).

(c) Phosphors: Phosphors are structure and impurity sensitive solid crystalline materials capable of absorbing energy from various sources at certain frequencies and re-emitting it as visible or near visible radiation of other frequency during or after cessation of excitation\(^9\). These are strongly influenced by chemical composition, crystal structure, presence of impurities in small amounts and other physical conditions such as temperature and type of excitation.

(d) Host Materials: These form the vehicles for carrying imperfections. They are normally
Fig. 1.1  Schematic diagram of the process of \( \text{phosphorescence} \ (\text{HE}T_{1}\text{S}_{1}\text{L}) \) and \( \text{fluorescence} \ (\text{HE}S_{1}\text{L}) \)

\( C \) - Conduction band;  \( F \) - Filled band  
\( H \) - Hole; \( E \) - Electron  
\( T_{1} \) - Electron traps; \( T_{2} \) - Hole traps  
\( S_{1} \) - Excited state; \( S_{2} \) - Ground state  

\( L \) - Luminescence centre
colourless or light coloured compounds possessing high melting points. These materials have high solubility for foreign atoms. The sulphides, selenides, phosphates, tungstates, oxides, molybdates and silicates mainly of Zn, Cd and the alkaline earths are used as host materials\(^{(10)}\).

(e) Activators : Activators are elements introduced deliberately in a host lattice in small amounts or occurring naturally in them, which give rise to localised levels in the forbidden gap of the host material permitting radiative transitions\(^{(11)}\). The activator atoms may occupy a regular lattice site in the host or may be incorporated interstitially. In some cases a second foreign element is added to the phosphor to enhance the emission produced by the primary activator. The second activator is called a sensitizer.

(f) Fluxes \(^{(12-15)}\) : These are readily fusible inorganic salts acting as recrystallizing media. With the use of flux the firing temperature is lowered and the efficiency of the phosphor is often increased. The most popular fluxes are alkali and alkaline earth halides, borates and sulphates.

(g) Centres : Impurities, lattice defects and other perturbations of the ideal crystal configuration give rise to discrete energy levels in the forbidden energy gap. These energy levels are responsible for different centres which are classified as follows :-
(i) Luminescent Centres \(^{16,17}\) - These are discrete energy levels which have a high electron capture cross-section and greater probability for radiative transitions than for non-radiative ones. The nature of the luminescence centre generally determines the luminescence spectrum.

(ii) Killer Centres - These are also discrete energy levels which have a large electron capture cross-section, but a low probability for radiative transitions \(^{18}\).

(h) Traps \(^{19-24}\) : Trapping is the fundamental process for energy storage in the case of phosphors. The sites in the host lattice where the absorbed energy is stored temporarily are called trapping centres. Trap is a restricted region in the crystal where an electron or hole may be captured and is no longer free to move through the crystal unless an optimum quantity of optical or thermal energy is supplied which is necessary to release it. After liberation from the trap the electron or the hole may migrate through the crystal to recombine with the luminescent centre or killer centre or may be retrapped. A normally occupied electron trap is called a 'donor' level while a normally occupied 'hole trap' is known as an 'acceptor' level.

1.2 Electroluminescence

(a) Early Investigations : Electroluminescence is the conversion of electrical energy
from the applied voltage into visible or near visible radiation (excluding the phenomenon of incandescence, gas discharge and cathode ray excitation). It has been the subject of various investigators during the present century. It is hoped that one day it may be possible to light a room by applying a voltage to the electrodes on a sheet covered with an appropriate semiconductor. There may also be its application to wall television.

Gudden and Pohl (25) have shown in 1920 that application of an electric field produces a momentary enhancement of the afterglow from a previously irradiated phosphor. In this case, the electric field fulfils only a modulating function. In 1940, Lossew discovered that the light emission from silicon-carbide was due to the presence of p-n junctions in this material. Lehovec, Accardo and Jamgohian (26) have confirmed this view. Pioneer work on electroluminescence was started by Destriau (27,28) in 1936. Destriau observed that light was emitted from certain substances by the application of a variable electric field of high intensity. Normally only the solids are electroluminescent; however, some of the liquids like selenium also show electroluminescence. A few oils with some impurities may emit light under high dc field excitation (29).

Electrically stimulated light emission can be brought about in several ways (30). It is therefore necessary to prove in a given case that electroluminescence is the primary phenomenon
arising from application of an electric field.

The electroluminescent and photoluminescent phosphors can be distinguished from one another in a number of ways. In electroluminescence, the emission originates from distinct spots within each phosphor grain whereas in photoluminescence the emission is too uniform to be resolved optically. Moreover, some phosphors which are photoluminescent may not at all be excited by an electric field^{27}. The difference between the colours produced by gas discharge and electroluminescence emission have been shown photographically by Wendel^{31} using colour films. The electroluminescence can also be distinguished from air discharge as its intensity increases with the frequency provided that other parameters are constant, but this is not the case with silent air discharge.

(b) Classification of Electroluminescence: Electroluminescence can be classified into the three following categories^{32,33}.

(1) 'Pure' or 'Intrinsic' Electroluminescence - This is also known as Destriau effect. It includes mainly light emission by a phosphor powder embedded in a suitable insulator, due to an alternating electric field. The same effect may also be observed in a phosphor without any contact with the electrodes.
(ii) 'Carrier - Injection' Electroluminescence - It includes the emission originating by injection of charge carriers. The excited carriers can arise in three ways in the absence of external radiation and at ordinary temperatures.

(a) by electrical ionization processes within the crystal;
(b) by their introduction from outside through some boundary (carrier injection); and
(c) by their increased concentration at some points within the crystal under the influence of the field (carrier accumulation).

In this type of electroluminescence (EL) a current passes and the luminescence intensity is approximately proportional to this current. The main features of this EL can be summarized as follow:-

(a) High electric field is not necessary for emission.
(b) The basic controlling parameter is the injected current and not the voltage which produces this current.
(c) Minority carriers are the important charge carriers.
(d) Once these carriers are injected they are able to recombine immediately with the carriers of opposite sign to produce radiation without the necessity of gaining further energy from the field.

(iii) Electro-photoluminescence - Luminescence associated with the application of an electric field during or after photo excitation is referred to as electro-photoluminescence. This phenomenon is also known as Gudden-Pohl effect.
1.3 Background Theory

The phenomenon of electroluminescence involves electronic states and transitions in crystalline solids. The substances showing electroluminescence are comparatively transparent to the emission and may be insulators or semiconductors. Certain aspects of electroluminescence involve local electric fields approaching or equalling the fields encountered in dielectric breakdown.

(i) Insulators and Semiconductors: If an insulator is at a temperature other than absolute zero, a certain concentration of the electrons will occupy states at the bottom of the conduction band and will leave in the valence band an equal number of empty states which are called positive holes. In this case the crystal is described as an intrinsic semiconductor. The intrinsic concentration of electrons or holes is temperature dependent and in a simple semiconductor with spherical energy surfaces is given by

\[ n_i = 2 \left( \frac{\sqrt{m_e}}{m_h} \right) \frac{K T}{2 \pi \hbar^2} \exp \left( -\frac{E_g}{2 K T} \right) \]

(1.1)

where \( m_e \) is the effective mass of electrons in the conduction band, \( m_h \) is the effective mass of holes and \( E_g \) is the width of the forbidden band.
Suitable impurities are an additional source of charge carriers. When both donor and acceptor impurities are present in equal concentrations, the electrons from the donors will be acquired by the acceptors and the impurities are thereby compensated electrically. When these impurities are not present in equal concentrations, extrinsic conduction may result. The presence of excess donors may provide conduction electrons; the presence of excess acceptors provides positive holes in the valence band. For uncompensated donor or acceptor levels which are mostly unionized and which lie $E_i$ away from the edge of the conduction or the valence band, the concentration of the free carriers is given by

$$n = N_i \left( \frac{m^* KT}{2\pi \hbar^2} \right)^{3/4} e^{-1/2 \frac{E_i}{kT}}$$ (1.2)

where $N_i$ is the concentration of uncompensated donors or acceptors and $m^*$ is the effective mass of a free carrier. In practice there almost always is a sufficient concentration of compensating impurities to cause the Fermi level to drop to $E_i$. Equ. (1.2) is then replaced by

$$n = \frac{N_i}{N - N_i} \left( \frac{m^* KT}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_i}{kT}}$$ (1.3)

where $N$ is the concentration of the impurity providing the majority carrier.
The electronic conductivity $\sigma$ in semiconductors is determined by the concentrations of charge carriers $n$ and by their mobilities $\mu$, according to the relation:

$$\sigma = e \left( n_c \mu_c + n_v \mu_v \right)$$ \hspace{1cm} (1.4)

where $e$ is the magnitude of the electronic charge and the subscripts $c$ and $v$ refer to charge carriers in the conduction band and the valence band respectively.

(ii) Dielectric Breakdown: It was suggested by Zener$^{(34)}$ that breakdown takes place when the intensity of the electrostatic field becomes great enough for transitions to take place from the valence band to the conduction band by a process related to quantum-mechanical tunnelling. Von Hippel$^{(35)}$ suggested a quite different theory of dielectric breakdown. According to him, a conduction electron in an electrostatic field is accelerated by the field and retarded by the interaction with the vibrational mode of the lattice. He further postulated that breakdown occurs when on an average the conduction electron gains energy from the field more rapidly than it loses energy to the vibrational modes for all velocities up to the velocity required for ionization of a valence electron by an inelastic collision. These collisions create additional charge carriers which are also accelerated. The exponential growth of charge carriers (Fig. 1.2) yields an avalanche.
Fig. 1.3 Energy level diagram for a $p-n$ barrier.

(A) in the absence of an applied field and
(B) for current flow in the forward direction with consequent injection of minority charge carriers.
Seitz (36) has emphasized that statistical fluctuations in which conduction electrons suffer unusually few collisions with lattice vibrations initiate breakdown. The probability per particle of attaining the energy \( E \) in an electric field of intensity \( F \) is of the following form:

\[
P = \exp \left[ -\frac{2mE}{3eF} S \right]
\]

(1.5)

where \( S \) is the average frequency of collisions with phonons.

Wolff (37) has considered the effect of the ionizing collisions on the distribution function in an analysis of electron multiplication in \( p-n \) junctions of silicon and germanium. The probability of attaining \( E_0 \), the minimum energy for ionizing collisions, is obtained numerically by the following approximate form:

\[
P = \exp \left[ -\frac{4\hbar \bar{\omega}}{e^2 \lambda^2} \frac{E_0}{F^2} \right]
\]

(1.6)

where \( \bar{\omega} \) is the optical phonon frequency and \( \lambda \) is the mean free path for phonon scattering. In general, \( E_0 \) is larger than the band gap \( E_g \).

1.4 Basic Mechanism of Electroluminescence

Piper, Williams and others (38-41) have proposed and extensively discussed the mechanisms for EL excitation. The important mechanisms are as follow: -
(i) Carrier - injection mechanism

(ii) Acceleration - collision mechanism, and

(iii) Direct field ionization mechanism.

(i) Carrier - injection mechanism\(^{(42)}\) - The injection of minority charge carriers in a semiconductor may occur either at an electrode contact, a defect or an adjacent region of opposite type (a p-n junction). Once the minority charge carriers are injected, a variety of recombination mechanisms are possible,\(^{(43,44)}\) some of which do not lead to luminescence. Only radiative recombinations result in injection electroluminescence (Fig. 1.3).

The energy-level diagram for a p-n junction in the absence of an applied voltage has been shown in Fig. 1.3A. In the n-type region the density of negatively charged carriers (electrons in the 'empty' conduction band) exceeds that of positively charged carriers (positive holes in the 'filled' valence band); here electrons are the majority carriers and the holes are minority carriers. Whereas, in the P-type region the situation is reversed. At such a junction, there is a state of dynamic equilibrium between the processes of thermal production and subsequent recombination of electron-hole pairs. In this case, radiative transitions contribute to the normal thermal (blackbody) radiations of the material.
As shown in Fig. 1.3B, when a voltage is applied in the forward direction and additional carriers are injected, this equilibrium is upset and the rate of recombination is increased. If some of these recombinations occur with emission of radiation, electroluminescence takes place.

Shockley\(^{(45)}\) analysed the injection characteristics of p-n junctions by using quasi-Fermi levels for the two types of carriers while Hall\(^{(46)}\) and Shockley and Read\(^{(47)}\) investigated the statistics of recombination of electrons and positive holes. The band theory model of a p-n junction biased in the forward direction is shown in Fig. 1.4. If the junction is biased in the forward direction by a potential difference \(V\), the injected hole current\(^{(38)}\) is given by

\[
I = en \left( \frac{D}{\tau} \right)^{1/2} \left[ \exp \left( \frac{eV}{KT} \right) - 1 \right] \tag{1.7}
\]

where \(n\) is the density of excess minority carriers, \(\tau\) is their life-time, and \(D\) is the diffusion constant, which is related to the drift mobility \(\mu\),

\[
D = \frac{KT}{e} \mu \tag{1.8}
\]

At higher applied voltages the carrier motion is determined by the electric field, and not by diffusion and so Equ. (1.7) does not apply. Luminescent emission may occur in or near the p-n junction by either intrinsic or extrinsic radiative recombination. At very high injection densities the quasi-Fermi
Injection Electroluminescence in Forward biased p-n junctions

Carrier Acceleration Electroluminescence in Reversed biased junctions
levels for the electrons and holes become sufficiently separated, as noted by Bernard and Duraffourg\textsuperscript{(48)}, so that populations are inverted and laser action is possible.

(ii) Acceleration-Collision Mechanism - The charge carriers are accelerated out of equilibrium with the lattice and to optical energies in this mechanism, so that they have inelastic collisions with the impurity or valence band electrons and excite them to states from which radiative de-excitation results. A simplified form of this mechanism occurs with high field reverse biased junctions (Fig. 1.5). The carriers tunnel through the forbidden gap and are accelerated to high kinetic energies. The emission is a combination of interband and intraband transitions.

Piper and Williams\textsuperscript{(39)} and Curie\textsuperscript{(49)} have proposed a mechanism for the Destriau type of EL, in which the excitation process for the luminescence centres involves three steps: (a) the raising of electrons for acceleration into conduction band under the action of electric field; (b) acceleration of some of these electrons by the field and (c) collision of these electrons with the centres causing the excitation or ionization of the latter. In the end, the radiative or non-radiative recombination of electron with the centres will occur. These processes have been considered below:
(a) Raising of electrons into conduction band - These electrons come from donor levels which are deeper than traps but not as deep as centre levels. The donor levels are emptied by the action of electric field and not by thermal activation as in that case the electroluminescence would be temperature dependent and involve a high activation energy. Piper and Williams\(^{39}\) have shown that for such emptying of the donor levels an electric field of about \(2\times10^5\) volts/cm would be necessary. Such a field could not occur throughout the interior of the crystal but would probably exist in the potential barrier of the Mott-Schottky type. Frenkel et al. proposed that in producing the ionization of the levels, the field and the phonons assist each other in the following way:

If \(E\) is the depth of the level in the absence of the field, the probability of ionization per second is given by

\[
P = S \exp \left( - \frac{E}{KT} \right)
\]

(1.9)

which is very small if \(E\) is large. In the presence of the field \(F\) the depth is reduced to

\[
E' = E - f(F)
\]

(1.10)

and the probability of ionization becomes

\[
P = S \exp \left[ - \frac{E - f(F)}{KT} \right]
\]

(1.11)

where \(f(F)\) is a function of the field. Different expressions are proposed\(^{51}\) for \(f(F)\).
During the first few cycles of the applied field on the cell the brightness is very low. Gradually the electrons fall into the traps which at the beginning are empty and the ionization of the latter by the same process as above soon plays a dominant role in the supply of electrons to the conduction band.

(b) Acceleration of the electrons by the field — The application of high electric fields is a must to accelerate charge carriers to optical energies. The electrons or holes must be injected or created in the high field region. Many investigators have studied the behaviour of the conduction electrons in high electric fields in connection with the dielectric breakdown of solids. For acceleration of the electron the condition is that it must gain energy more rapidly in the field than it loses by interaction with phonons; if $\mathcal{E}$ is the energy of such an electron, then

$$\left( \frac{d\mathcal{E}}{dt} \right)_{\text{field}} > \left( \frac{d\mathcal{E}}{dt} \right)_{\text{phonons}}$$

(1.12)

If $\omega$ is the length of path between two phonon encounters, at the end of path $\omega$, the electron exchanges with the phonon an energy $h\mathcal{J}$. Then the condition for acceleration can be written in the form given by Fröhlich and Mott as follows:

$$eF\omega > h\mathcal{J} \left[ 1 + \frac{2}{\exp \left( \frac{h\mathcal{J}}{kT} \right) - 1} \right]$$

(1.13)
The mean free path in the ionic crystal rises gradually and is proportional to the energy of the electrons (Fig. 1.6). Thus, an electron which begins to be accelerated and crosses the critical zone at about a tenth of an electron-volt has a mean free path greater than $10^{-6}$ cm, and the process of acceleration continues even in fields of the order of $2 \times 10^4$ volts/cm.

(c) Excitation of the centres by impact of a fast electron

The conduction electrons which experience unusually few collisions with lattice phonons will attain sufficient energy to ionize activator centres by inelastic collisions. If a conduction electron which is in an elastic field of intensity $F$ acquires energy $E$, which is necessary for excitation of an activator system by an inelastic collision and if it traverses a path length $l$ without being scattered, the relation between $E$ and $l$ is given by

$$ E = e F l \quad (1.14) $$

and the probability of an electron traversing a path greater than $l$ is

$$ p = e^{-l/\lambda} \quad (1.15) $$

where $\lambda$ is the mean free path. The probability, therefore, of acceleration of a conduction electron to sufficient
Fig. 1.6

The Trajectory of a Field-accelerating Electron in the Conduction Band

Fig. 1.7

Excitation mechanism for Electroluminescence due to impact of an accelerated electron.

B - Conduction band

\( d \) - Shallow donor level

\( C \) - Luminescence centre

(i) - Ionization of donor by electric field

(ii) - Possible acceleration of the ejected electron

\( (t) \) - trajectory of an electron which remains thermal

(iii) - Ejection of electron initially in the centre, due to impact of an accelerated electron.
kinetic energy for inelastic collision excitation of an activator system is

\[ P = \exp \frac{E}{eF\Lambda} \]  

(1.16)

Impact of a fast electron with a luminescence centre involves the loss of the whole or part of its energy and release of an electron from the centre into the conduction band (Fig. 1.7). Both electrons will have after impact some residual motion in the field direction. They will be in the same state as an electron beginning its acceleration and will be moved far from the original centre by the action of the field.

(iii) Direct Field Ionization Mechanism: This mechanism may be discussed in two parts.

(a) Valence band ionization – Zener\(^{(34)}\) was the first to point out the possibility of exciting an insulator with an intense electric field in such a way as to excite valence electrons into the conduction band. He calculated the probability of excitation for an insulator with a small band gap. Mc Afee et al.\(^{(55)}\) and Franz\(^{(56)}\) have modified Zener's result to include materials with larger band gaps. The probability per unit time, \( P_i \), for ionization from the valence band in a field \( F \), is given by

\[ P_i = \frac{e\alpha}{\hbar} F \exp \left[ - \frac{\pi \sqrt{2m^*}}{4\hbar e} \cdot \frac{E_g^{3/2}}{F} \right] \]  

(1.17)
where, \(m^*\) is the effective mass, \(F\) the local electric field intensity, \(E_g\) the band gap and \('a'\) the unit cell dimension. Thus, the total current density from a region of constant field intensity of thickness \(t\) and with a total potential difference \(V\), is

\[
I_v = 4 \times 10^{11} \rho aV \exp \left[ -\frac{4 \times 10^7 \left( \frac{m^*}{m} \right)^{1/2}}{F} \cdot E_g^{3/2} \right]
\]  

(1.18)

where \(V\) is expressed in volts, \(F\) in volts/cm, \(E_g\) in eV, \('a'\) in angstroms, \(\rho\) in valence electrons per \(\AA^3\), and \(I_v\) in amp/cm\(^2\). Thus to a good approximation the field required to induce a current of one amp/cm\(^2\) is given by

\[
F_v = \frac{4 \times 10^7 \left( \frac{m^*}{m} \right)^{1/2}}{\log \left( 4 \times 10^{11} \rho aV \right)} \cdot E_g^{3/2}
\]  

(1.19)

where \(V\) determines the thickness of the high field region.

(b) **Direct field Ionization of Impurities**: Burns (57) has suggested that in this mechanism a strong electric field is required so that the electron from activator centres may escape to the conduction band by the well known quantum mechanical tunnelling process.

Franz et al. made calculations not only for the field ionization of valence electrons, but also for the ionization of an electron into the conduction band from a localized state in the forbidden band. (56, 58) This state is assumed to be bound by an
energy $E_i$ in a square-well potential. For a well with a radius of 3 Å, the probability of escape per unit time $P_i$ in a field of intensity $F$ is approximated by the expression

$$P_i = \frac{2 \times 10^7 F}{(m^*E_i/m_0)^{1/2}} \exp \left[ - \frac{7 \times 10^7 (m^*/m)^{1/2}}{7 \times 10^7 (m^*/m)^{1/2}} \cdot \frac{E_i}{F} \right]^{3/2}$$

(1.20)

where $P_i$ is measured in sec$^{-1}$, $F$ in volts/cm and $E_i$ in eV.

Piper and Williams (59) have shown that the results of Franz reduce in typical cases to

$$F_z = \frac{6 \times 10^6 E_g^2}{7 + \log_{10}(F_{zT})}$$

(1.21)

and

$$F_i = \frac{10^7 E_g^{1/2} E_i^{3/2}}{8 + \log_{10}(F_{iT})}$$

(1.22)

where $F_z$ and $F_i$ are the field strengths in volts/cm, required to produce a mean transition time $\tau$ for the case of Zener (band to band) tunnelling or field ionization of centres respectively and where $E_g$ is the band gap and $E_i$ the ionization energy of the centres in eV.

1.5 Mott-Schottky Exhaustion Barrier

It is an experimental fact (38-41,60) that the energy required to excite the luminescence centre is usually higher
than that supplied by the applied field. A barrier, has therefore been suggested so that the local field in a particular part of the crystal will be increased to a value close to the breakdown field. An exhaustion barrier similar to the Mott-Schottky barrier (61) is, generally, assumed because the dependence of the barrier height and width on the work function of the electrode material is in accord with the characteristics of an exhaustion barrier. This type of barrier was proposed by Piper and Williams (40) in connection with the acceleration-collision mechanism. Most of the applied potential appears across the barrier. The field in the barrier region, even for moderate applied electric fields, will be sufficient to produce ionization of deep donors and subsequent acceleration and collision can lead to luminescence. This process has been shown in Fig. 1.8.

If the crystal lies between two similar electrodes at different potentials, electrons will move across the crystal and into the anode easily, but a potential barrier at the cathode equal in height to the difference in work functions will prevent the movement of electrons from the cathode into the crystal. The exhaustion layer next to the cathode will broaden until the entire potential difference is across the exhausted region of the crystal. As the applied potential is increased the magnitude of the field next to the cathode increases until the potential barrier arising from the difference in work-functions is so thin that it can be
Fig. 1.8  Schematic representation of the acceleration-collision mechanism of electroluminescence. Electrons from traps in the localized high field region are liberated by the action of the field and/or temperature (1) or are injected from a "contact", are then accelerated by the field (2) to acquire kinetic energy above the bottom of the conduction band, and collide with activator centres whereby they lose their energy (3) and the activator centre is ionized (4) or excited. Emission usually occurs later in the cycle when the alternating potential is reversing.
penetrated by electrons from the cathode. A direct current will flow through the crystal above this critical voltage.

Below this threshold, conduction electrons must originate within the crystal. An alternating potential applied between the electrodes will alternately deplete and replenish exhaustion layers at the electrodes. After the first few voltage cycles electron traps will behave in many respects like donors. If the donor levels lie at different depths below the conduction band, the deeper ones will be field-ionized. The necessary field to excite the electron from a deep donor will vary with the depth of the donor. The conduction electrons from sufficiently deep donors will be in a strong enough field to be successfully accelerated to large kinetic energy, i.e., they will gain energy from the field more rapidly than they will lose it to the lattice by phonon emission. At energies above 3 eV these electrons will be capable of exciting activator atoms by impact (which can then be thermally or field ionized) and above 3.7 eV these electrons can begin to excite valency electrons to the conduction band. Some of the holes created by the excitation of valency electrons will be captured by activator centres, which become ionized. Subsequent capture of electrons from the conduction band leaves the activator systems in the emitting state.

The thickness of the barrier can also be calculated by considering a single crystal phosphor in close contact with plane parallel electrodes. The thickness of the crystal is small in
comparison with the dimensions of the electrode so that edge-effect may be neglected. If an electric potential difference is applied between the electrodes, an exhaustion layer will form next to the cathode as described above.

Let \( V_0 \) be the applied potential, which is large compared to the difference of work functions,
\[
N = \text{be the density of electron donors,}
\]
\[
\varepsilon = \text{be the dielectric constant of the crystal,}
\]
\[
d = \text{be the width of the exhaustion layer, and}
\]
\[
x = \text{be the distance into the crystal from the cathode.}
\]

In the exhaustion region, the positive space charge density will be \( \text{Ne} \); no space charge exists in the bulk of the crystal. Substituting in Poisson's equation:
\[
\frac{dE}{dx} = \left( \frac{4\pi Ne}{\varepsilon} \right) \tag{1.23}
\]

Integrating, we get
\[
E(x) = \left( \frac{4\pi Ne}{\varepsilon} \right) x + C \tag{1.24}
\]

Substituting the boundary conditions at \( x = d \), \( E(x) = 0 \); in Eqn. (1.24) and defining
\[
A = \left( \frac{8\pi Ne}{\varepsilon} \right)^{1/2}
\]

We have
\[
E(x) = \frac{1}{2} A^2 (x - d) \tag{1.25}
\]
If an electron at the cathode has the potential energy of $V_0$, with respect to the anode, then
\[ V(x) = - \int_x^d E(x) \, dx \]
\[ = \frac{1}{4} A^2 (d - x)^2 \]  
(1.26)

On squaring Eqn. (1.25), we get,
\[ \left[ E(x) \right]^2 = \frac{1}{4} A^2 \cdot A^2 (d - x)^2 \]
Or
\[ \left[ E(x) \right]^2 = V(x) \cdot A^2 \]  
from Eqn. (1.26)
Or
\[ E(x) = A \sqrt{V(x)} \]

but at $x = 0$, $V(x) = V_0$

Hence,
\[ V_0 = \frac{1}{4} A^2 d^2 \]  
from Eqn. (1.26)
Or
\[ d = \frac{2 \sqrt{V_0}}{A} \]

Substituting the value of $A$
\[ d = \frac{2 \sqrt{V_0 \varepsilon}}{\sqrt{8 \pi N e}} \]
\[ d = \frac{V_0 \varepsilon}{2 \pi N e} \]  
(1.27)

This gives the width of the exhaustion layer.
1.6 Recombination Processes

The processes by which free carriers recombine can be classified in several ways. The first major division is into radiative and non-radiative processes. In the former the released energy is emitted, either wholly or partially, as radiation. Such a process can lead to electroluminescence. In non-radiative processes the recombination energy is dissipated ultimately as heat by various mechanisms. The radiative processes are as follow:

(i) The recombination of an electron hole pair by 'collision': There are two possibilities here. The 'direct' process with no phonons taking part and the 'indirect' process which requires phonon participation.

The process of recombination is shown in terms of the energy band diagram in Fig. 1.9A. A free electron falls into a hole, the difference in energy between the initial and final states being emitted as radiation. The processes shown in Fig. 1.9B involve what can loosely be described as 3-body collisions, i.e., coupling between an electron, a hole and a phonon is required. This is essentially a rarer process than that shown in Fig. 1.9A. This 'phonon participation' leads to another difference between the 'indirect' process and the 'direct' process shown in Fig. 1.9A. If the
(A) Direct transitions with no phonon participation.

(B) Indirect transitions requiring phonon participation to conserve momentum.
difference in electron momentum is taken up by the creation of a phonon of energy $\Theta$, then the frequency of the emitted light will be given by $\varepsilon_1 - \varepsilon_2 - \Theta = h\nu$, i.e., the photon energy is less than that corresponding to the difference between the electron energy states, the difference, $\Theta$, being used to create the phonon.

(ii) Recombination through an impurity centre. \textbf{(62)}

(iii) Recombination via associated defect states (Fig. 1.10):

So far the behaviour of impurities has been considered without regard to any interaction between the impurities themselves. This is a satisfactory approximation at low concentrations in materials of high dielectric constant. At high concentrations interactions occur. Donors and acceptors tend to associate into pairs. There is a coulombic interaction energy between the two which varies as $\frac{1}{r}$ where $r$ is the separation. As $r$ can have a whole range of values the result is a range of types of associated pairs. As the separation increases the number of coulombic states associated with the pair increases but the interaction energy decreases. Overlap of the wave function assists the electron in making transitions between donor and acceptor states. So we have a recombination process of the type shown in Fig. 1.10.
Recombination via associated donor-acceptor pairs

$\text{Ev} \quad \text{Ei}$

$h \gamma = \text{Ec} - \text{Ev} \cdot (\text{Ei} + \text{Em})$

$\text{OT - Ei}$
1.7 Electric field inside the phosphor particles

For electroluminescence studies, phosphor powders are generally used by embedding them in a dielectric medium. In connection with electroluminescence, Roberts\(^{(64)}\) suggested that the dielectric medium influences the relative field strength in the phosphor particles. The electric field inside the phosphor particles can be calculated by assuming them to be spheres and knowing the dielectric constants of phosphor particles and matrix material.

If \(d\) is the thickness of the cell and \(V\) is the applied voltage, then the average field inside the cell is given by:

\[
E_a = \frac{V}{d} \quad (1.28)
\]

If we consider a phosphor powder of dielectric constant \(K_1\) \(^{(64-66)}\) embedded in a medium of dielectric constant \(K_2\), it can be shown that the electric field strength \(E\) in the interior of the particles is given by:

\[
E = E_a \frac{3 K_2}{2 K_2 + K_1 - C (K_1 - K_2)} \quad (1.29)
\]

where \(C\) is the fraction of the total volume occupied by the particles. \(C = 0\) for no phosphor and \(C = 1\) for no embedding material.
Actually the phosphor particles are angular in form and their internal field is very far from homogeneous; even then the Equ. (1.29) gives a good working approximation for the electric field inside the phosphor particles.

1.8 Model Representation

These models are applicable to ZnS (embedded) type powders containing metal (Cu) as conducting phase. In the usual method for preparation of electroluminors the raw unfired base mixture contains a large concentration of Cu. This Cu is dissolved in the lattice of powder particles at a high firing temperature. During cooling, precipitation occurs due to decrease in solubility of Cu. This leads to dislocation and imperfection lines. The lattice faults serve as nucleation centres for the precipitation of copper. The copper is deposited as copper sulphide. The use of copper is very useful as:

(i) copper sulphide is very conductive; (ii) the limit of solubility of copper is less than the concentration at which quenching occurs. After the firing process, the particles are spiked with fine, conducting, needle-like precipitates. (67)

If such a particle is subjected to a strong alternating electric field, the field relaxes inside the conducting needles and concentrates at the tips. The field intensification can become hundred fold or higher. The experimental data may be most suitably explained by the two following models.
(i) The Bipolar Field - Emission Model

The end of the acicular precipitate that points towards the negative cell electrode field - emits holes into the surrounding insulating crystal. The other end that points towards the positive cell electrode field - emits electrons. The field-injected holes become immediately trapped in the deep luminescent centres (above the valence band), forming a sheath of excited luminescent material around the conducting needle. In contrast, the field-injected electrons remain relatively mobile since electron traps are shallow. They move to the far end of the embedded particle. The source of the carriers is an unlimited reservoir since it emits equal number of electrons and holes, hence it never charges up. No light is emitted during this first application of the field.

If the external field is removed, the internal polarization field exists alone. If the external field is reversed, the external field is actually momentarily added to the decaying internal polarization field. The tip of the needle that is surrounded by positively charged luminescent centres is now negative and field-emits electrons into the comet-shaped sheath of excited material. These electrons recombine with trapped holes, giving rise to the observed light. The loose electrons in the bulk of the crystal particles are swept back towards the residual
trapped holes, recombining with them and giving rise to the secondary light. New holes and electrons are now field-emitted from opposite ends, stored in the crystal and the cycle repeats as shown in Fig. 1.11.

(ii) The Impact Ionization Model

Destriau assumed that the externally applied fields of about $10^4$ V/cm are sufficient to cause impact ionization throughout the volume of the particles, a view later supported by Curie. Theories of dielectric breakdown and of 'hot' electrons suggest, however, that fields in excess of $10^6$ V/cm are necessary for pair creation by impact.

Impact ionization takes place in the high field region near the surface of the conducting line. The impact generated holes are trapped there in activator centres and the excess electrons flow into the conductor, from which they are field-emitted into the luminescent crystal at the other end of the line, where they recombine with holes trapped there since the previous half cycle (main light peak). Other field detrapped electrons do not get sucked up by the conductor but move through the bulk to recombine directly with trapped holes (secondary light peak). This model can explain all the findings, including the line shape of EL emission. Compared to the bipolar field emission model, it may require higher fields ($10^6$ V/cm). This mechanism may,
FIG. 1.11

ZnS PARTICLE

HOLE TRAPS

CONDUCTING LINE

ELECTRON TRAPS.

THE BIPOLAR FIELD EMISSION MODEL.

FIG. 1.12

ZnS PARTICLE

IMPACT IONIZATION

CONDUCTING LINE

ELECTRON TRAPS

LUMINESCENCE CENTRE

RECOMBINATION

VALANCE BAND

THE IMPACT IONIZATION MODEL.
however become significant at higher applied voltages. It is illustrated in Fig. 1.12.

The obvious short-coming of this theory is that it has to assume conducting crystals. Whereas there is no doubt that this type of impact ionization EL in the cathodic depletion layer exists indeed in directly contacted conducting ZnS,\(^{(68)}\) ZnO,\(^{(69)}\) ZnSe and GaP crystals and in many semiconductors, even with DC current excitation, it is also certain that efficient, Destriau type powder particles do not fit into this model, since they are insulating.

1.9 Influence of Magnetic Field

Destriau\(^{(27)}\) suggested that a sufficiently intense magnetic field which is perpendicular to the electric field should quench electroluminescence. Assuming that no collisions with the crystal lattice occur, the maximum energy an electron can gain is

\[
E_{(\text{max})} = \frac{1}{2} m^* V_{(\text{max})}^2
\]

\[
= 2 m^* \left( \frac{E}{\mu H} \right)^2
\]

(1.30)

where \( m^* \) is the effective mass of the electron, \( E \) and \( H \) are the electric and magnetic field intensities respectively and \( \mu \) is the magnetic permeability. No quenching was observed by Destriau on application of a field of \( 6 \times 10^4 \) oersted.\(^{(70)}\)

Ince\(^{(70)}\) has applied magnetic fields of even greater
intensities to electroluminescent powder phosphors. No quenching effects were observed up to 13x10^4 oeresteds. The experimental results can be interpreted with the assumption that the effective mass of accelerated charge carriers is about 100 times that of a free electron.

1.10 Aging Effect of Electroluminescent Phosphor

There have been various reports indicating that electroluminescence devices gradually diminish in brightness as a result of continuous and prolonged operation. The rate of aging depends on the applied voltage and on the frequency.\(^{(71)}\) The aging is thought to result from physical changes taking place in the phosphor but not in the dielectric in which the phosphor is embedded. Roberts\(^{(72)}\) showed that this decrease is well determined by the relation

\[
B = \frac{B_0}{1 + t/t_c}
\]

(1.31)

where \(B_0\), \(B\) and \(t_c\) are initial light level, light level after time \(t\) and time required for the brightness to fall to \(B_0/2\) respectively.

The decrease in brightness is attributed principally to the decrease in the concentration of donors brought about by their small but finite ionic mobility, which supposedly permits irreversible recombination with activators at nearest neighbour sites.
1.11 Statement of The Problem

Although ZnO comes under the general classification of oxide phosphors, its properties are more like those of ZnS and other II - VI wide-band-gap semiconducting phosphors. However, the material, whose band gap (E_g > 3.4 eV) is only slightly less than that of ZnS (E_g > 3.9 eV) and has the same crystal structure, has not been as widely investigated. ZnO is known to exhibit edge emission in the near ultra-violet and also a more common green band whose origin is still a matter of some controversy. The fast decay of the edge emission has promoted the use of ZnO in flying-spot cathode ray tubes for television film scanning. Much work done on ZnO in recent years has been concerning cathodo-luminescence while the electroluminescence of these phosphors has been comparatively less studied.

The possibility of continuous laser action in rare earths activated phosphors and the phenomenon of sensitised luminescence have given a great impetus to the investigation of rare earths as activators. In rare earths the f - electron absorption transitions are weak and this permits the use of higher activator concentrations without complications of self-absorption or excitation depletion. Higher concentration of activator is useful in the study of electroluminescence. In some cases the rare earths show a broad band emission when the 5d state is excited and the transition takes place from this configuration to the ground state.
instead of decaying to one of the excited 4f levels. Cerium is one of the important activators showing such emission. The sensitisation of Mn and Tb emissions by Ce has been widely established in several host lattices. However, it has been noted that there is a kind of selectivity of the sensitisation effect with respect to the host material and the sensitisier. (73)

It was therefore proposed to study the electroluminescence of ZnO phosphors activated by cerium and samarium. The phosphors were accordingly prepared in which cerium and samarium occurred alone as well as in combination. Further it was proposed to study the visible emission from ZnO excited by ultra-violet radiation by preparing the unactivated phosphors from various starting materials.

(a) Emission Spectra : The emission spectra of unactivated zinc oxide phosphors, prepared by refiring the non-luminescent material with excess zinc, were studied under ultra-violet excitation. The cathodoluminescence of unactivated ZnO has also been studied. The study has been carried out at room temperature using a Bellingham and Stanley Spectrometer in conjunction with a photonmeter.

(b) Electroluminescence Spectra : The emission obtained from cerium and samarium activated zinc oxide phosphors as also the baked ZnO phosphors during the application of an a c field was analysed using the same set up as in the study of UV fluorescence.
(c) **Voltage Dependence of Electroluminescence (EL)** :

The electroluminescence brightness of activated ZnO phosphors has been studied as a function of the applied voltage (varied up to 480 V), the frequency being kept constant. Trap depths have been evaluated from the variation of the voltage dependence at different frequencies.

(d) **Frequency Dependence of EL Brightness** :

The dependence of brightness on the frequency of the applied field at various constant voltages has been studied.

(e) **Brightness Waves** :

The brightness waveforms at different voltages and frequencies were obtained using a C.R.O. and the patterns have been photographed.

(f) **Temperature Dependence of EL** :

The dependence of electroluminescence brightness on temperature has been investigated using a specially constructed EL cell and a photomultiplier in the temperature range 30 to 160°C. The study has been carried out at various frequencies and voltages keeping the other parameters unchanged. From the observed maxima in the brightness temperature curves trap depths have been calculated.

The results of the above studies have been reported and discussed in the light of existing theories.
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