1.1 SOLID STATE LUMINESCENCE

Solid-state physics is concerned with the physical properties of solids, particularly the special properties exhibited by atoms and molecules because of their association and regular periodic arrangement in crystals. The structure sensitive properties of inorganic crystalline substances have recently attracted large attention as these provide a sensitive way of investigating the fundamental processes involved in solid-state phenomena and also due to their commercial applications. A large part of the research work in this branch is, however, on the problem of 'imperfections', i.e. deviations from a perfect crystal lattice or structure. The phenomenon of luminescence also arises in an imperfect crystal lattice, mostly because of the presence of impurities.

During recent years, there have been important advances in many branches of solid-state physics. Semi-conducting solids and junction concepts came of age, the laser was born, and with that event, interest in the luminescence research increased dramatically. The phenomenon of Electro-luminescence— which involves both the optical and the electrical properties of solids, was discovered. Since, it provides the direct
conversion of electrical energy into light by the action of an electric field, it became fascinating research subject with attractive possibilities for illuminating devices.

1.2 DEFINITIONS

(a) Luminescence

Luminescence, in general, is used for the emission of light from a substance in the visible or near visible region during or following the absorption of energy such as ultra-violet radiations, X-rays or high energy particles (1, 2). Leverenz (3), however, defines luminescence as 'Emission of radiation of subatomic origin, in excess of thermal radiation'. Since the luminescence does not follow Kirchhoff's Law, it can be defined as 'cold light' (4) to distinguish it from thermal radiations. 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 (5).

According to mode of excitation, the phenomenon of luminescence can further be subclassified as follows:

(i) Photoluminescence

That produced by absorption of photons of several electron-volts e.g. ultra-violet radiations.

(ii) Radioluminescence

That produced by bombardment with high energy particles or radiations e.g. gamma rays.
(iii) Cathodoluminescence:
    A specific case of radioluminescence produced by cathode rays.

(iv) Electroluminescence:
    That produced by an electric field.

(v) Electrophotoluminescence:
    That excited by optical means and modified by electric field.

(vi) Triboluminescence(6):
    Emission produced during grinding and pulverising of certain solids due to mechanical strain and fracture.

(vii) Chemiluminescence(7):
    Emission produced by chemical reactions.

(viii) Bioluminescence(3):
    A specific case of chemiluminescence in biological processes.

(b) Fluorescence and Phosphorescence:
    These are the two important aspects of luminescence and are distinguished on the basis of physical conditions of experiment and the physical process involved.

    On the basis of physical conditions of experiment, Garlick(8) defines fluorescence as the luminescence emitted during excitation and phosphorescence as that emitted after cessation of excitation. The division between the two may
be fixed at $10^{-8}$ sec. after excitation ceases, as this is the time of relaxation of an ionised gaseous ion.

In terms of physical process involved, Perrin[8] defines fluorescence as the emission that takes place by one or more spontaneous transitions and phosphorescence as that which occurs with the intervention of a metastable state followed by the return to the excited state due to addition of energy. This definition is preferred by many workers (9,10,11).

(c) Phosphors[12]:

Substances which show luminescence are called phosphors. They may be crystalline or amorphous, organic or inorganic or even in the form of a supercooled liquid[13]. These substances are called Luminor or Luminophor. Mostly inorganic structure sensitive materials have been studied at length as phosphors. Phosphorescence of long duration is usually confined to those phosphors which are specially prepared by heat treatment and whose luminescence is due to traces of impurity (14,15). There are some substances such as manganous halides, salts of rare earths, tungstates, molybdates etc. which show luminescence in pure state. Randall (16) suggests that these materials contain groups, which function like foreign molecules in the matrix crystal from which they are separated by screening.

Mott and Gurney[17] have classified phosphors into two main groups:
(i) Photoconducting Phosphors: in which an electron is raised to the conduction band during luminescence process e.g. ZnS:Cu; CdS:Ag.

(ii) Non-photoconducting Phosphors: in which the photoconductivity is negligible under usual conditions of luminescence excitation. The emitting system is 'quasi-atomic'. KCl:Tl and NaI:Tl belong to this class.

Leverenz(18) has classified phosphors in terms of sites occupied by activator ions in the matrix as follows:

(i) Substitutional Phosphors: Those in which the activator ions occupy a substitutional site. These are characterised by exponential decay law.

(ii) Interstitial Phosphors: in which the activator ions are in an interstitial site. These are characterised by predominantly power-law decay.

(iii) Substitutional-Interstitial Phosphors: in which both the sites are occupied simultaneously. These are characterised by initial exponential decay followed by power-law decay.

(d) Activators:

The luminescence in many phosphors is due to the presence of certain impurities, called activators. These impurities provide localized energy levels in the forbidden energy gap of an insulator or semiconductor and permit radiative transitions(19). The activator atoms may lodge themselves into the interstitial site or may substitute for
the cations of the host crystals. The variety of impurity molecules able to activate a phosphor is generally very large and probably largest in the case of alkaline earth sulphides (20).

(e) Fluxes:

These are readily fusible salts acting as a readily recrystallizing medium used in the preparation of phosphors.

(f) Centres:

Garlick (5) and many other workers (21) call the impurity atoms or ions as centres. If the emission improves on their inclusion, that is, the probability for radiative transition is much greater than that for the non-radiative transition, such a centre is called a 'luminescence centre' (11). On the other hand, if the emission is suppressed, that is, the probability for non-radiative transitions is greater than that for the radiative transitions, such a centre is called a 'killer centre'.

(g) Traps: (22, 23, 24, 25)

These are the metastable levels or states in the forbidden gap capable of capturing 'electrons' or 'holes'. These may be due to added impurity or other defects in the crystal. An empty energy level close to the bottom of conduction band can act as an electron trap. Free electrons may come in the neighbourhood of such a trap and be captured with release of energy. Similarly, a filled localized energy level close to the valence band may act as a hole trap. A free hole coming
in the neighbourhood of a hole trap may disappear because the electron in that occupied energy level may make a transition to the hole with the release of energy. A normally occupied electron trap is called 'donor level' while a normally occupied hole trap is known as an 'acceptor level'.

1.3 ELECTROLUMINESCENCE:

The phenomenon of electroluminescence i.e. the conversion of electric energy from the applied voltage into visible or near-visible radiation — excluding the phenomenon of incandescence, gas discharge and cathode-ray excitation, has been the subject of various investigations during the last decades.

The earliest indication that an electric field could influence the light emitted by a phosphor was the work of Gudden and Pohl(26), who, in 1920 showed that application of electric field leads to a momentary enhancement of the afterglow from a phosphor previously irradiated by ultraviolet radiations. In 1924, Lossew(27) observed light emission from silicon-carbide in an electric field while studying the properties of silicon-carbide detectors. The light emission was localized to regions near the anode and the cathode. A number of papers have been published since then by various authors (28,29). 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 have confirmed this view (29). There was little work on the effect of a.c. fields until the pioneer work of
Destriau(30) was started in 1936. Results of this have been reported in Phil. Mag. (31). Destriau observed that there was a 'provocation of luminescence in certain substances by varying electric fields of high intensity'.

The various electroluminescence effects known to date in the case of crystalline solids can be divided into two main categories as follows:

(a) Pure or intrinsic electroluminescence:
(The Destriau effect)

It is the result of the sole action of the applied alternating electric field on a phosphor powder embedded in a suitable dielectric medium. Only this type of electroluminescence is investigated in the present investigation.

(b) Carrier-injection electroluminescence:

It covers the emission produced by injection of charge carriers either through the surface of the crystal or across a P-N junction. A current passes and the luminescence intensity is approximately proportional to this current. The main characteristics of this type of electroluminescence are as follows:

(i) High electric field is not required to excite emission.

(ii) The fundamental controlling quantity is the injected current and not the voltage producing this current.

(iii) The charge carriers of importance are minority carriers.
(iv) Once these carriers are injected, they are able immediately to recombine with carriers of the opposite sign to produce radiation without the necessity of gaining further energy from the field.

1.4 BACKGROUND THEORY

Electroluminescence involves electronic states and transitions in crystalline solids. Materials which exhibit electroluminescence are relatively transparent to the emitted radiation and may be insulators or semiconductors depending on the magnitude of the electronic conductivity. Certain aspects of electroluminescence involve local electric fields approaching or equalling the fields encountered in dielectric breakdown. Therefore, the electronic theory of insulators and semiconductors and also the current theories of dielectric breakdown are briefly reviewed below.

(a) Insulators and Semiconductors:

When atoms are brought together to form a crystalline lattice, the characteristic energy levels of the individual atoms are broadened into bands of allowed energies which may or may not overlap. If the constituent atoms furnish just enough electrons to fill the highest occupied band completely and if there is an energy gap between the top of this band and the bottom of the first empty band, then these bands are referred to as the valence band and the conduction band respectively and the perfect crystal is an insulator at absolute zero.
The magnitude of the forbidden gap is a characteristic property of the crystal and varies from a small fraction of an electron-volt to many electron-volts. The band gap increases with increasing polar character of the crystal (32–34).

The difference between an insulator and a semiconductor cannot be defined precisely, for the distinction depends not only on the host crystal, but also upon the temperature of the crystal and the impurities which are present. When the number of free charge carriers present in either the valence band or the conduction band is sufficient to influence a physical measurement such as the electrical resistance, the crystal is usually referred to as a semiconductor.

If the pure crystal which is described above as an insulator is at a temperature other than absolute zero, a certain concentration of 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 intrinsic semiconductor. The intrinsic concentration of electrons or holes is temperature dependent and in a simple semiconductor with spherical energy surfaces is given by

\[ n_i = 2 \left( \frac{\sqrt{m_e m_h}}{2\hbar^2} \right)^{3/2} \frac{e^{-E_g/2kT}}{e^{3/2}} \]

where \( E_g \) is the width of the forbidden band, \( m_e \) is the effective mass of electrons in the conduction band, and \( m_h \) is the effective mass of holes in the valence 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 provide 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

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

where $N_i$ - 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 $E_i$. Equation (1.2) is then replaced by

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

where $N$ is the concentration of the impurity acting as a 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:
\[ \sigma = e \left( n_c \mu_c + n_v \mu_v \right) \quad \ldots \quad (1.4) \]

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. For intrinsic conductivity the concentrations of holes and electrons are equal, and in the simple extrinsic case discussed the equilibrium concentration of minority carriers may be neglected.

Detailed treatments of the properties of semiconductors have been given by many authors (35,36).

(b) Dielectric Breakdown

Zener (37) proposed that breakdown occurs 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.

A quite different theory of dielectric breakdown was proposed by von Hippel (38). He conceived that a conduction electron in an electrostatic field is accelerated by the field and retarded by the interaction with the vibrational modes of the lattice. He 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 illustrated in Fig. 1.1 yields an avalanche.

Regardless of whether the low- or the high-energy criterion for breakdown is used, the avalanche theory yields somewhat high but roughly correct breakdown fields for crystalline polar insulators and also predicts an increase in breakdown field with temperature and impurity content which is observed. Seitz(39) 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:

\[
P = \exp \left[-\frac{\sqrt{2mE}}{3eF} s \right]
\]  \hspace{1cm} \text{(1.5)}

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

Wolff(40) has taken account of 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 and has the following approximate form:

\[
P = \exp \left[-\frac{4\hbar \nu}{e^2 \lambda^2} \cdot \frac{E_0}{F^2} \right]
\]  \hspace{1cm} \text{(1.6)}

where \( \nu \) is the optical phonon frequency and \( \lambda \) is the mean
Fig. 1.2 Energy level diagrams 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 carrier.
free path for phonon scattering. In general, $E_o$ is larger than the band gap $E_g$.

To account for the breakdown characteristics observed at high temperatures when collisions among the conduction electrons becomes important, Frolich (41) introduced the concept that conduction electrons in a strong field are characterized by an electronic temperature greater than the lattice temperature. His model also involves equilibrium between conduction and trapped electrons, as well as between the conduction electrons (42, 43).

1.5 Basic Mechanisms of Electroluminescence

Several mechanisms for electroluminescence excitation have been proposed and extensively discussed by many workers (44-47). The major mechanisms which have been advanced for the explanation of this phenomenon are summarized below:

(a) Carrier-Injection Mechanism,
(b) Acceleration-Collision Mechanism, and
(c) Direct Field Ionization Mechanism,
    (i) Valence Band Ionisation,
    (ii) Direct Field Ionisation of Impurities.

(a) Carrier-Injection Mechanism:

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 (48,49), some of these do not lead to luminescence. Radiative recombinations only result in injection electroluminescence (See Fig.1.2).

Fig. 1.2(A) shows the energy-level diagram for a P-N junction in the absence of an applied voltage. 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 holes the minority carriers. 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. Radiative recombinations, in this case, contribute to the normal thermal (black-body) radiations of the material.

When a voltage is applied in the forward direction (Fig. 1.2B) 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, the injection electroluminescence takes place.

Shockley (50) analysed the injection characteristics of P-N junctions by using quasi-Fermi levels for the two types of carriers while Hall (51) and Shockley and Read (52) 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.1.3. If the junction
Figure 13

In the diagram, there are two bands labeled 'Conduction Band' and 'Valence Band'. Between these bands, there is a dashed line labeled 'Quasi-Fermi Level'. The diagram also indicates 'N-Type' and 'P-Type' categories.
is biased in the forward direction by a potential difference \( V \), the injected hole current \( I \) is given by

\[
I = e n \left( \frac{D}{T} \right)^{1/2} \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right]
\]  .. (1.7)

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

\[
D = \frac{kT}{e} \mu
\]  .. (1.8)

At higher applied voltages the carrier motion is determined by the electric field, not by diffusion and equation (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 levels for the electrons and holes become sufficiently separated, as noted by Bernard and Duraffourg(53), so that populations are inverted and laser action is possible.

(b) Acceleration-Collision Mechanism

In this mechanism, the charge-carriers are accelerated out of equilibrium with the lattice and to optical energies, so that they have inelastic collisions with 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,
as shown in fig.1.4. The carriers tunnel through the forbidden gap and are accelerated to high kinetic energies. The emission is a combination of inter- and intraband transitions.

Curie(54) and Piper and Williams (45) have suggested a mechanism for the Destriau type of electroluminescence. The excitation process for the luminescence centres involves three steps:

(i) The raising of electrons for acceleration into the conduction band under the action of electric field.

(ii) Acceleration of some of these electrons by the field.

(iii) Collision of these electrons with centres causing the excitation or ionization of the latter.

Finally, the radiative or non-radiative recombination of electron with centres will occur.

We now consider in turn these different processes:

(i) Raising of Electrons into conduction band:

These electrons come from donor levels which are deeper than traps but not as deep as the 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 (45) have shown that for such emptying of the donor levels an electric field of about 2,00,000 volts/cm would be necessary. Such a field could not
Carrier acceleration electroluminescence in reversed biased junctions

**FIGURE 1.4**
occur throughout the interior of the crystal but would probably exist in the potential barrier of the Mott-Schottky type.

Frenkel(55) proposed that in producing the ionization of the levels, the field and the phonons assist each other in the following way:

If $\epsilon$ is the depth of the level in the absence of the field, the probability of ionization per second is given by

$$p = s \exp\left(-\frac{\epsilon}{kT}\right)$$  \hspace{1cm} \ldots (1.9)

which is very small if $\epsilon$ is large. In the presence of the field $F$ the depth is reduced to

$$\epsilon^* = \epsilon - f(F)$$  \hspace{1cm} \ldots (1.10)

and the probability of ionization becomes

$$p = s \exp\left[-\frac{\epsilon - f(F)}{kT}\right]$$  \hspace{1cm} \ldots (1.11)

where $f(F)$ is the function of the field. Different analytical expressions are suggested (56) for $f(F)$.

During the first few cycles of the applied field on the cell the brightness is very low (57). 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.
(11) Acceleration of the electrons by the field:

High electric fields are necessary to accelerate charge carriers to optical energies. The electrons or holes must be injected or created in the high field region. The behavior of the conduction electrons in high electric fields has been studied extensively by many investigators (40,41,58) in connection with the dielectric breakdown of solids. The condition for an electron to accelerate is that it must gain energy more rapidly in the field than it loses by interaction with phonons, if $E$ is the energy of such an electron, then

$$\left( \frac{dE}{dt} \right)_{\text{field}} > \left( \frac{dE}{dt} \right)_{\text{phonons}} \quad \cdots (1.12)$$

If $\omega$ is the length of path between two phonon encounters, at the end of path $w$, the electron exchanges with the phonon an energy $h\omega$. We can then write the condition for acceleration in the form due to Frolich and Mott:

$$eF\omega > h\nu \left[ 1 + \frac{2}{\exp \left( \frac{h\nu}{kT} \right) - 1} \right] \quad \cdots (1.13)$$

In ionic crystals the mean free path rises gradually and is proportional to the energy of the electrons (Fig.1.5). 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 20,000 volts/cm.
The trajectory of a field-accelerating electron in the conduction band.
On the other hand the interactions, which are sensibly isotropic at low energies, only occur with low-angle scattering at higher energies and the path finishes by being a straight line effectively in the direction of the field.

(iii) 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 ionise activator centres by inelastic collisions. If a conduction electron which is in an electric 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 $\ell$ without being scattered, the relation between $E$ and $\ell$ is given by

$$E = eF\ell \quad \ldots (1.14)$$

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

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

where $\lambda$ is the mean free path. The probability, therefore, of acceleration of a conduction electron to sufficient kinetic energy for the inelastic collision excitation of an activator system is

$$p = e^{-E/eF\lambda} \quad \ldots (1.16)$$
Impact of a fast electron with 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.1.6). 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.

(c) Direct Field Ionization Mechanism

(1) Valence-band Ionization:

The possibility of exciting an insulator with an intense electric field in such a way as to excite valence electrons into the conduction band was first pointed out by Zener(37). He computed the probability of excitation for an insulator with a small band gap. This result was modified by McAlfee et al.(59) and Franz(60), to include materials with larger band gaps. The probability per unit time, \( P_1 \), for ionization from the valence band in a field \( F \), is given by

\[
P_1 = \frac{ea}{h} e^F \exp \left[ - \frac{\pi \sqrt{2m^*}}{4he} \frac{E_g^{3/2}}{F} \right]
\]

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
Fig. 1.6- 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.
total potential difference \( V \), is

\[
I_v = 4 \times 10^7 \varphi \, a \, V \, \exp \left( -\frac{4 \times 10^7 (m^*/m)^{1/2}}{F} E_g^{3/2} \right) \quad \ldots (1.18)
\]

where \( V \) is expressed in volts, \( F \) in volts/cm., \( E_g \) in eV, \( a \) in \( \text{Å} \), \( \varphi \) in valence electrons per \( \text{Å}^3 \), 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

\[
F_v = \frac{4 \times 10^7 (m^*/m)^{1/2}}{\ln(4 \times 10^7 \varphi \, a \, V)} E_g^{3/2} \quad \ldots (1.19)
\]

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

(ii) Direct Field Ionization of impurities

This mechanism requires a strong electric field so that the electrons from (filled) activator centres may escape to the conduction band by the well-known quantum mechanical tunnelling process. This process has been suggested by Burns (61).

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 (60, 62). 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\( \text{Å} \), the probability of escape per unit time \( P_i \) in a field of intensity \( F \) is approximated by the expression
\[ P_1 = \frac{2 \times 10^7 F}{(m^* E_1/m_0)^{1/2}} \exp\left[-\frac{7 \times 10^7 (m^*/m)^{1/2}}{F} E_1^{3/2}\right] \]

.. (1.20)

where \( P_1 \) is measured in sec\(^{-1} \), \( F \) in volts/cm and \( E_1 \) in e.v.

Piper and Williams (63) have shown that the results of Franz reduce in typical cases to

\[ F_z = \frac{6 \times 10^6 E_g^2}{7 + \log_{10}[F_z \tau]} \]

.. (1.21)

and \[ F_1 = \frac{10^7 E_g^{1/2} E_1^{3/2}}{8 + \log_{10}(F_1 \tau)} \]

.. (1.22)

where \( F_z \) and \( F_1 \) 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 \( E_1 \) the ionization energy of the centres in e.v.

1.6 MOTTSCHOTTKY EXHAUSTION BARRIER

It has been observed (44-47, 64) that the energy required to excite the luminescence centre is usually higher than that supplied by the applied field. A barrier is, therefore, suggested so that the local field in a particular part of the crystal will be increased to near the breakdown field. An exhaustion barrier similar to the Mott-Shottky barrier (65) 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 first proposed by Piper and Williams(46) in connection with 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. 1.7.

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 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
Fig. 1.7- 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 ionised (4) or excited. Emission usually occurs later in the cycle when the alternating potential is reversing.
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 by impact activator atoms (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.

(a) Thickness of the barrier:

Let us consider a single crystal phosphor in intimate 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,

\[ N \]

be the density of electron donors,

\[ \varepsilon \]

be the dielectric constant of the crystal,

\[ d \]

be the width of the exhaustion layer, and

\[ x \]

be the distance into the crystal from the cathode.

In exhaustion region, the positive space charge density will be \( \varepsilon N \varepsilon \); no space charge exists in the bulk of the crystal. Substituting in Poisson's equation

\[
\frac{d\varepsilon}{dx} = \left( \frac{4\pi \varepsilon N \varepsilon}{\varepsilon} \right)
\] .. (1.23)

Integrating, we get

\[
E(x) = \left( \frac{4\pi N \varepsilon}{\varepsilon} \right) x + C
\] .. (1.24)

Substituting the boundary conditions i.e. at \( x = d \),

\( E(x) = 0 \); in equation (1.24) and defining

\[ A = \left( \frac{8\pi N \varepsilon}{\varepsilon} \right)^{1/2} \]

We have

\[
E(x) = \frac{1}{2} A^2 (x-d)
\] .. (1.25)

If an electron at the cathode has a P.E. of \( V_0 \), with respect to anode, then
\[
V(x) = -\int_{x}^{d} E(x) \, dx \\
= \frac{1}{4} A^2 (d - x)^2
\]  \hspace{1cm} \text{(1.26)}

On squaring equation (1.25) we get
\[
\left[ E(x) \right]^2 = \frac{1}{4} A^2 A^2 (d - x)^2
\]
or
\[
\left[ E(x) \right]^2 = V(x) A^2 \hspace{1cm} \text{from eq. (1.26)}
\]
or
\[
E(x) = A \sqrt{V(x)}
\]
but at \( x = 0 \), \( V(x) = V_0 \)
Hence,
\[
V_0 = \frac{1}{4} A^2 d^2 \hspace{1cm} \text{from eq. (1.26)}
\]
or
\[
d = \frac{2 \sqrt{V_0}}{A}
\]

Substituting the value of \( A \)
\[
d = \frac{2 \sqrt{\frac{V_0 \varepsilon}{\varepsilon_0}}}{\sqrt{8 \pi \kappa \varepsilon_0}}
\]
\[
\therefore d = \sqrt{\frac{V_0 \varepsilon}{2 \pi \kappa \varepsilon_0}} \hspace{1cm} \text{(1.27)}
\]

This gives the width of exhaustion layer.

1.7 FIELD EFFECTS IN EXCITED PHOSPHORS

In addition to pure electroluminescence, the phenomena observed when an electric field and some kind of stimulating radiation are simultaneously or sequentially applied to a luminescent material are also of fundamental
and practical interest. Many effects have also been observed which involve two different types of excitation (for example, ultraviolet and infrared) in addition to an electric field. All these effects are briefly described below.

[a] The Gudden-Pohl and other transient effects

(1) The Gudden-Pohl effect

The earliest study of electrophotoluminescent effect was made by Gudden and Pohl (66) in 1920. If an electric field is applied to certain phosphors previously excited by ultra-violet radiations, x-rays or cathode rays, a burst of light is observed. Gudden and Pohl applied a constant field which was quickly annulled by the internal field, the emission being of short duration. However, a switching off and on of the field could produce a number of successive light pulses.

In an alternating field the emission lasts long(67). If the field is removed and then re-applied, no more emission is observed unless several minutes elapse between cut-off and reapplication. This effect provides an indication of the retrapping in shallower traps during the interval(68).

It is usually assumed that the Gudden-Pohl effect is an emptying of traps by the applied field, while electroluminescence is a field excitation of luminescence centres.

(ii) Effects of fields on infra-red stimulation of luminescence:

One of the examples of infrared-stimulable phosphor
is $\text{SrS:Eu,Sm}$. If the phosphor is irradiated with infrared long after all phosphorescence has ceased, a burst of emission is observed. The infrared stimulation arises from the presence of $\text{Sm}$ but the emission is due to $\text{Eu}$. Low et al. (69) found that application of an alternating electric field to this phosphor during excitation could increase the emission upon subsequent infrared irradiation by as much as 45 percent. Concurrently the effect of an electric field applied during stimulation was much reduced (to as little as 7 percent of its value without a field during excitation). Later on, Steinberger et al. (70) studied the Gudden-Pohl effect in this phosphor during excitation, during phosphorescence and during stimulation. The observed differences include the longer persistence of the Gudden-Pohl peak during stimulation as compared to that during excitation of phosphorescence and some differences in voltage dependence.

[b] Quenching of luminescence by fields:

[i] The phenomena of quenching:

In 1934, Coustal (71) subjected a previously excited $\text{ZnS:Cu}$ or $\text{ZnS:Mn}$ phosphor layer to glow discharge in air. Depending upon circumstances, there is either quenching (Fig.1.8a) or enhancement (Fig.1.8b) of phosphorescence.

In 1935, Dechene (72) performed an electroluminescent experiment under slightly better conditions. A sulphide phosphor powder wet with water was placed between electrodes and a high direct voltage was applied. Under these conditions the ionic conductivity of water was sufficient to maintain
Fig. 1.8- Schematic representation of field quenching and enhancement effects on the brightness of an excited phosphor. The exciting radiation is applied at time zero, while the field is applied at \( t_1 \) and removed at \( t_2 \).

Upon application of the field the brightness \( B \) may be either, depending on the material and on the experimental conditions, depressed to a new value \( B_1 \) or raised to a new value \( B_2 \). At the time the field is applied or removed there are also usually transient effects as shown.
a current of the order of microamperes per square centimeter, sufficient to counteract the polarization of the phosphor particles and maintain a field across them. At the moment of field application a momentary increase in emission (the Gudden-Pohl effect) was observed. This, however, was followed by a sustained quenching of the emission. Upon removal of the applied voltage a second Gudden-Pohl stimulation was observed. Because of these observations the sustained quenching of luminescence by an electric field has sometimes been called the Dechene effect.

In 1943, Destriau (73) reported on field quenching experiments on phosphors using powders imbedded in an insulator and alternating fields. Destriau (31, 74) found that sulphide phosphors with persistent phosphorescence gave large Gudden-Pohl peaks but only a small quenching effect on the other hand, samples with little phosphorescence gave little or no Gudden-Pohl peaks and a large degree of quenching. Therefore, it seems that presence of deep traps is not necessary for quenching.

(ii) Effects of fields on infrared quenching of luminescence:

The quenching of luminescence by infrared radiation is a well-known phenomenon and is usually ascribed to filling of empty luminescence centres from the valence band. The holes left in the valence band are then available for a non-radiating transition. Since electric fields
also exert a quenching action, it seemed of interest to Destriau to combine the two effects. The observations (75) were actually made during phosphorescence rather than for sustained excitation of the phosphor (although the infrared was applied during excitation). Destriau concluded that the field had an intensifying action on the infrared quenching.

(iii) The mechanism of quenching:

It is obvious that the quenching effect must involve the introduction of new non-radiating transitions or a change in the balance between radiating and existing non-radiating transitions favouring the latter. Several possible mechanisms suggest themselves:

(a) filling of empty centres, under the action of the field, by electrons from the valence band as is assumed for thermal or infrared quenching;

(b) a direct effect by the field on the energy levels of the luminescence centres so that non-radiating transitions are introduced or increased;

(c) since non-radiating transitions are often assumed to occur at traps, the field may increase this tendency;

(d) the increased velocity of carriers in the presence of the field may change the relative cross-sections of luminescence centres and non-radiative centres;

(e) carriers may be transported through the phosphor by the field to other regions of the crystal such
as surfaces, where they become deeply trapped or non-radiating transitions occur.

(c) Enhancement of luminescence:
(i) The experimental observations:

Woods and Wright (76) observed increased emission from cathode ray excited MgO when it was subjected to static electric fields.

Cusano (77, 78) in 1955 observed another enhancement effect in thin ZnS:Mn,C1 films which he and Williams (77, 79) have described as 'radiation-controlled electroluminescence'. This emission may be greatly enhanced if the film is irradiated with ultraviolet, x-rays (77, 78) or cathode rays (80).

Cusano's enhancement is essentially a d.c. effect. It can also be observed with alternating voltages, the emission is always in phase with the voltage and decreases with increasing frequency. Thornton (81) observed enhancement of the electro-luminescence of a large number of normal phosphor powders when irradiated. For alternating fields normal electroluminescent cells with the phosphor embedded in a plastic dielectric were used. As the applied alternating voltage was increased, quenching was generally first observed by Thornton, followed by enhancement for higher voltages.

(ii) The mechanism of enhancement:

Williams (77, 79) proposed that enhancement observed by Cusano (77, 78) resulted from 'radiation-controlled electroluminescence'. The normal acceleration-collision
mechanism was assumed. The initial electrons for the acceleration, however, were presumed to result from the radiation rather than from the sole effects of fields and/or temperature as for pure electroluminescence. The specific mechanism (77, 79,80) assumed that the radiation not only releases free electrons which are accelerated but also positive holes which are trapped in and cause enhancement of the potential barrier at the cathode. The distribution of potential within the phosphor is thus controlled by an action of the radiation on the barrier. If the barrier field becomes high enough, additional electrons may enter from the electrode by tunnelling as in experiments of von Hippel and his colleagues (82, 83) with alkali halide crystals.

1.8 ELECTRIC FIELD INSIDE THE PHOSPHOR PARTICLES

In order to perform electroluminescence studies, phosphor powders are generally used by embedding them in a dielectric medium. In connection with electroluminescence, Roberts (84) pointed out that the dielectric medium influences the relative field strength in the phosphor particles. The electric field inside the phosphor particles can be calculated if they are assumed to be spheres and dielectric constants of matrix material and that of phosphor particles are known.

If 'd' is the thickness of the cell and V is the applied voltage, then the average field inside the cell is
given by

\[ E_a = \frac{V}{d} \]

.. (1.28)

Consider a phosphor powder of dielectric constant \( k_1 \) embedded in a medium of dielectric constant \( k_2 \). It can be shown (84,85,86) that the electric field strength \( E \) in the interior of the particles is given by

\[ E = E_a \frac{3k_2}{2k_2 + k_1 - C(k_1-k_2)} \]

.. (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 equation (1.29) gives a good working approximation for the electric field inside the phosphor particles.

1.9 STATEMENT OF THE PROBLEM

With the beginning of twentieth century a systematic study of alkaline earth sulphide phosphors (15) began. Wells(87) reported the importance of flux in their preparation. The instability under excitation on atmospheric conditions, in these phosphors, was responsible for a temporary decline of practical and commercial interest, which
has been revived by the discovery of infrared stimulation and sensitization.

The phosphors in the form of microcrystalline powders have been investigated elaborately in our laboratory. The investigations, however, included — determination of optimum conditions for the preparation of efficient phosphors (88), the effect of temperature and duration of firing (89), the role of various fluxes (90), the effect of single activator and double activators on the luminescence efficiency by studying their luminescence spectra (91, 92), thermoluminescence and decay characteristics (93), x-rays structure (94), magnetic properties (95) and absorption and emission spectra (96).

Recently electroluminescence studies were included in the research programme of our laboratory, with a view to start a new line of studies which may be useful from theoretical point of view and its application to light sources. Most of the work in this field has been done on ZnS phosphors. Only a few papers (97, 98) are available on alkaline earth sulphide phosphors.

In the present investigations, two series of phosphors [CaS:Ag and CaS:Mn] were prepared for their comparative studies. A special type of EL Cell, suitable for phosphors with poor EL emission was designed and fabricated in the University Workshop.

Following studies have been performed with phosphors
of both the series:

(i) The variation in electroluminescent brightness by varying the voltage from 120V to 600 volts at constant frequencies (no brightness was recorded at voltages below 120 volts).

(ii) The variation in electroluminescent brightness by varying the frequency from 50 cps to 5000 cps at constant voltages.

(iii) The brightness waves were obtained on the screen of a 'Double Beam Tektronix C.R.O.' and the effect of voltage and frequency was recorded.

Finally, from the informations obtained from these studies an attempt is made to draw conclusions about the variation of EL brightness with activator concentration, the relation representing the variation of brightness with voltage and the process taking place in CaS:Ag and CaS:Mn phosphors prepared for the present investigation.
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