# CHAPTER I

•

1

# INTRODUCTION

### INTRODUCTION

#### 1:1 ' GENERAL INTRODUCTION :

The emission of light which is not purely thermal in origin ( as in 'incandescence' ) is known as 'luminescence'. In this process, the emitting substance is raised from ground state to the excited state by absorption of energy and then it returns to the ground state with emission of light. The various types of luminescence are distinguished accourding to the mode of excitation ( ultra-violet-photoluminescence, chemical reaction-Chemiluminescence, electrons - cathodoluminescence, etc. ). The phenomenon of generation of light by the direct action of an electric field on semiconductors is known as " electroluminescence " ( abbrevated as EL. ). The semiconducting material ( a phosphor ) which is used as a source of light may be taken in powder or crystalline form. The phosphor is sandwitched between two parellel electrodes, one of which is in the form of wire gauze or a conducting glass. The phosphor, dispersed in an insulating material such as castoroil, is excited by application of an a.c. field with consequent emission of light, which can be seen through the transparent electrode. It involves the direct conversion of electric energy into radiation, without recourse to any intermediate energy form, such as heat. Whereas the emission

from incandescent bodies is determined by the temperature alone, 'cold' emission from an electroluminescent phosphor has been shown to depend on its chemical and physical constitution. The phenamenon was first observed by Destriau<sup>1-a,b</sup> in 1936, and hence it is also known by his name. Since then, there has been a rapid progress in the field of electroluminescence, so as to take advantage of this effect in production of more efficient light sources of the future.

After Distriau's discovery of electroluminescence, a multitude of papers has appeared on the subject and progress has been made toward elucidating the mechanism of light production. Several materials and composite systems, which are solely inorganic have been prepared with a view to study their El. properties and improve the brightness to attain higher efficiency. It was found that small variation in preparative conditions lead to a remarkable change in the observed electroluminescence with respect to spectral distribution and intensity of emission. The dependence of intensity and spectral distribution of El. emission on the voltage and frequency of exciting field has also been studied. Influence of the geometry of the electroluminescent cell and the period of operation of the cell also play an important role in the investigation.

Electroluminescence from organic systems has been known for a number of years, but fewer examples are known than for

inorganic systems. The first report of El. in organic crystals is probably attributable to Pope  $\mathbf{e}t \cdot \mathbf{al.}^2$ , who performed measurements on single crystals of anthracene and anthracene doped with tetracene. Later on Bernanose and his collaborators<sup>3-7</sup> developed the technique of organic electroluminescence and studied the El. properties of number of organic compounds such as acridine orange, carbazole and various derivatives of 8hydroxyquinoline and was able to show that the intensity of light emitted was dependent on voltage and frequency in the same way as the emission from inorganic phosphors.

From survey of literature, it seems that no systematic efforts have been made to investigate the electroluminescent properties of pure organic compounds and two-phase organic systems. It is our intention in the present investigation to study the electroluminescent properties of pure organic compounds such as pyrene, anthracene, perylene and two phase organic systems like anthracene doped with pyrene, pyrene doped with perylene etc. and to correlate the influence of some of the parameters mentioned above, on electroluminescent emission. We have selected these compounds

mainly because they can be prepared in a pure from and further more no work on electroluminescence seems to have been done on these compounds and two phase systems.

#### 1:2 HISTRORICAL INTRODUCTION- :

A review of the earlier work shows that the problem of

electroluminescence has been studied mainly along the following lines.

1:2:1 General aspects of electroluminescence.

1:2:2 Mechanism of electroluminescence.

1:2:3 Applications of electroluminescence.

#### 1:2:1 GENERAL ASPECTS OF ELECTROLUMINESCENCE

The work done on the electroluminescence constitutes the following problems :

a) Preparation of electroluminescent materials,

- b) Construction of El. cell,
- c) Measurement of El. intensity,
- d) Dependence of El. emission intensity on various parameters such as voltage and frequency of applied field.

## 1:2:1-a) PREPARATION OF ELECTROLUMINESCENT MATERIAL :

The methods of preparation of the organic and inorganic electroluminophors differ considerably. In inorganic phosphors, El. is improved by presence of impurities. The incorporation of impurities in the base material follows the principle of charge compensation, as described by Kroger and Dikhoff<sup>8-a,b</sup>. Hundreds of phosphors of various types have been synthesised so far.

High and variable impurity content of the commercial organic compounds makes them unsuitable for systematic studies

and therefore, the purification of the organic compounds often must be performed prior to electroluminescence study. Methods of purification varies from compound to compound. The hydrocarbons such as anthracene, pyrene, tetracene etc. are purified by the column chromatography method<sup>2,9,10</sup> and by the sublimation, whereas most of other organic compounds are purified by recrystallization<sup>9,11</sup> method using a suitable solvent. Purified crystals are then zone refined<sup>10</sup> and ground to fine powder.

Doping of one compound into other is carried out by dissolving the calculated amounts of host material and dopant in suitable volatile organic solvent and then crystals are grown by slow evaporation<sup>11</sup>. The doped crystals are also grown from the melt of the mixture of depant and host<sup>12</sup>. In single crystal study method, crystals are grown from the melt using Bridgman technique<sup>10</sup>. The crystals are then cut from the boules in the form of plane parellel platelets typically 0.5 - 0.48 mm thick.

## 1:2:1-b) CONSTRACTION OF AN EL. CELL :

An electroluminescent cell consists of an El. phosphor dispersed in a dielectric medium and sandwitched between two plane parellel electrodes. One of the electrodes must be transparent so as to observe the emission of light. The geometry of cell plays an important role in measurement of El. intensity, because voltage actually given to phosphor particles is a function of thickness of phosphor layer and the medium in which it is dispersed. Hence, construction of El. cell is very important

to get full advantage of the applied field.

Cells used for solid inorganic and organic phosphors are nearly identical. Destriau<sup>1-a,b,</sup> applied a thin paste of the phosphor, dispersed in castor-oil, on a metal plate. This paste was covered with a sheet of mica upon which was spread a layer of "Glycerined sea water", which served as the second electrode. When a.c. field was applied between the electrodes, light was emitted by the phosphor.

In the study of El. of organic compounds Barmanose and others<sup>3-7</sup> used cellophane film having uniform coating of El. meterial. The cellophane film was prepared by dipping it in a hot saturated solution of electroluminescent compound. The film was dried to evaporate solvent and placed with melted paraffin was between a plate of aluminium and transperent mica. The cell was compressed before cooling to exclude air bubbles. In order to provide electrical contects, the sheet of mica was wetted on its exterior surface by saline glycerol solution. Using such an El. assembly, Barnanose and co-workers investigated El. in gonacrine, acridine orange E and carbazole.

Methods of obtaining El. differ in the way in which a thin layer is prepared and mounted between electrodes. In the work of **S**hort and Hercules<sup>13</sup>, one electrode was made from stainless steel and the other from tin oxide coated glass. Their methods of obtaining thin layer of organic material included deposition of material from a hot saturated solution,

solidification of melt, embedding in resin and evaporation of suspension.

The transparent electrode used in the construction of E1. cell is generally a conducting glass plate. Conducting glass having a resistance of 100-400 ohms per sq.cm. and 80 % or more transparancy can be prepared either by spraying a solution of tin salt in acetone or alcohol<sup>14</sup> on to a glass plate heated to just below the melting point or by exposing the glass plate to the vapours of silicon, tin or tinanium chloride followed by cooling in a reducing atmosphere. Vacuum deposition of various oxides such as SnO<sub>2</sub>,  $\text{SnO}_2$ ,  $\text{TiO}_2$  and  $\text{InO}_2^{15}$ also serves as a transparent conducting layer on the glass.

In the single crystal El. study contact electrodes are used. R . Nowak et.al.<sup>16,17</sup> have used cathodes of sodium potassium alloy and anodes of silver paste, in the study of steady state El. in perylene doped anthracene crystals. M. Pope et.al<sup>2</sup>. have used two electrode configuration. In one case silver paste electrodes were epoxided onto the crystal while in other ohmic contacts of 0.1 M sodium chloride solutions on opposite sides of crystals were used.

The cells used by Gurnee<sup>11</sup> consisted of a chromium-plated steel-backed electrode upon which a 1-mil polycrystalline layer of the hydrocarbonconductor mixture was placed. A 1-mil polystyrene film separated the conducting layer from a transparent

tin oxide-coated glass electrole. A thin film of silicone oil was used on each side of the dielectric layer in order to displace air present in the cell. The cells prepared by Gurnee et.al.<sup>11</sup> were similar to these used in the technique of Lehmann<sup>18-4</sup>, who excited a number of non-luminescent inorganic materials by mixing them with a finely divided conductive powder.

A review article on various types of El. cell and El. devices has been presented by Meczynska and Oczkowiski<sup>19</sup>. Since then, there does not seem to be any noteworthy contribution to the El. cell model.

#### 1:2:1-c) MEASUREMENT OF EL. INTENSITY :

The intensity measurement of El. emission requires a dispersing unit ( a monochromator ) and a detecting unit. A monochromator is necessary for isolating light output at different wavelengths for spectral distribution studies. Interference filters and prism monochromator ( constant deviation spectrometer ) can serve the purpose. Thus, Goldman and co-workers<sup>20</sup>, Bonfiglioli, and Co-workers<sup>21</sup>, Hariau and others<sup>22</sup>, Singh and Mohan<sup>23</sup>, etc. used a c.d. spectrometer for dispersion while Levialdi and others<sup>24</sup>, Butter and others<sup>25</sup>, etc. used interference filters. However, A. Miniewicz and others<sup>16,17</sup> used SPM-2 monochromator.

As a radiation detecting device, a photocell can be used in close proximity of the phosphor, if the time averaged intensity

is to be measured. Lehmann<sup>18-b</sup> used a photoconducting PbS cell in this way. However, a photomultiplier tube is necessary for a study of spectral energy distribution. Various types of P.M. tubes have been used by several workers. Use of IP-21, IP-22<sup>20, 25, 26</sup>, PM-10M and FEV-12<sup>20</sup>, R-136<sup>22</sup>, RCA-6217<sup>24</sup>, etc. has been reported. R.Nowak et.al.<sup>16,17</sup> were recorded El. spectrum using an FEU-79 photomultiplier tube, while M.Pope and others<sup>2</sup> detected the light emission from anthracene and doped anthracene crystals with a photomultiplier using a DuMont 6292 tube.

The photocurrent signal of the photocell or P.M. tube is either fed to a double beam Oscill\_oscope<sup>1-c,d,f</sup> or to an ultrasensitive microammeter or to a sensitive spot reflecting galvanometer<sup>26</sup>. The peak height of the brightness wave is taken as the measure of the intensity in the former case, while the photocurrent in microamps ( or in arbitory units if a sensitive spot reflecting galvanometer is used ) gives the relative intensity.

## 1:2:1-d) FACTORS AFFECTING EL. EMISSION :

Besides the geometry of the El. cell and dielectric medium used, El. intensity of a given phosphor depends on the following factors.

i) The voltage and excitation frequency of

the applied field,

ii) Time of operation of the cell,

- iii) Temperature dependence of El. emission during
  excitation,
  - iv) Effect of magnetic field,
  - v) Effect of incident radiation.
  - i-a) Voltage Dependence :

It is observed that the intensity of El. emission (L) increases rapidly with increasing applied voltage (V), the relation between L and V being exponential rather than linear. Several attempts have been made to find a mathematical expression for the dependence of intensity (L) on the applied voltage (V), some of them are based on theoretical grounds but many pertain to experimental data only.

The first relation between L and V was given by Destriau<sup>1-a,b</sup> as :

$$L = A \exp\left(\frac{-B}{V}\right) \qquad \dots \qquad (1)$$

which was later modified by  $himself^{1-e}$ , as

$$L = A V^{H} \exp(-B/v)$$
 .. (2)

where A, B and n are constants, 'n' being of the order of two.

Several equations for L as a function of V have been  $proposed^{27-31}$ .

Thus, for a single phosphor particle, the variation was found to be linear by Waymouth and Bitter<sup>29</sup>. They also observed

that a minimum thershold voltage is necessary to commence the effect. Similar observations were also made by others<sup>31,32</sup>.

However, there seems to be a meagre evidence in favour of a minimum voltage thershold for electroluminescence. A careful investigation by Destriau and Doumergue<sup>30</sup> covered a range of very low brightness levels without detecting any discontinuity arising from minimum threshold voltage. The various theories were put forth to explain the phenomenon which rule out the possibility of any threshold voltage.

Alfrey and Taylor<sup>31</sup> gave relation as

$$L = Lo \exp\left[-\frac{Vo}{V}\right]^{0.5} \qquad .. (3)$$

Which was based on the exhaustion barrier theory. Nagy  $^{33-a}$  derived the following relation.

$$\mathbf{L} = \mathbf{A} \exp\left[\frac{-\mathbf{B}}{(1+\mathbf{C}\mathbf{v})^2}\right] \quad \dots \quad (4)$$

Where A,B and C are constants. The equation was based on impact ionization mechanism.

Similar types of relations are proposed by other workers<sup>34,37</sup>. Kale et.al<sup>38</sup>. observed a complicated variation in the threshold voltage. Lehmann<sup>18-b</sup> suggested the equation,

$$L = a.v.\exp\left[\frac{-b}{(V + Vo)}\right] \quad .. \quad (5)$$

Where a, b and Vo are constants which vary nearly linearly with frequency. According to this equation, L should become infinite for infinite voltages.

The first report of El. from organic phosphors was presented by Bernanose and co-workers<sup>3-7</sup> who have published a number of studies in this area. These authors reported following important points on El. emission.

i) The intensity of El. was found to vary with the applied voltage  $^{39,40}$  according to the relationship.

$$I = AV^2 \exp \left(\frac{-B}{V}\right),$$

where A and B are constants.

ii) An expression relating El. power radiated and applied field was given by Barnanose<sup>7-a</sup> as :  $W = 9 N \quad \chi^4 \quad \Lambda^7 \neq 64 \quad \Pi^2 \subset T^2 \quad .. \quad (6)$ 

where N is total number of organic molecules,  $\bigwedge$  applied field (Stat volt/cm ).

iii) In some organic compounds they observed the thereshold voltage of 400-800 V in El. emission and intensity of light amission increases as voltage rises to 2500 volts.

Bernanose results has been confirmed in subsequent studies by Namba and coworkers<sup>41</sup>. Gurnee et. al.<sup>11</sup> have studied El. produced by aromatic hydrocarbons in the presence of a finely divided electric conductor. For example, anthracene in the presence of about 1 % carbon black showed a blue El.characterstic of anthracene fluorescence and brightness of such a cell was found to be a function of applied voltage in the same fashion as the cells described by Bernanose. However, Short and Hercules<sup>13</sup> studied the El. of a variety of fluorescent organic compounds by a technique similar to that of Gurnee's except that they found it was not necessary to add the conductive material to the fluorescent organic layer. They observed that the light output increases with voltage and frequency and there was evidences of saturation at high voltages.

M.Pope et.al.<sup>2</sup> showed that El. of single crystal of anthracene depend only on the instantaneous voltage and not on any previous voltage history. The El. brightness data could be very well represented by linear plot of lnB against  $\sqrt{-\frac{1}{2}}$ . In the case of anthracene doped with 0.1 % mole of tetracene the voltage required to produce El. was always much higher, however, the voltage dependence of the brightness are the same as that of pure anthracene. R.Nowak and others<sup>16</sup> observed that El. emission in anthracene and doped anthracene crystal commences at a distinct therehold voltage.

It is appearent from foregoing discussion that there does of not seem to be any noteworthy contribution to the study voltage intensity relationship of organic compounds. Hence, it needs a fresh examination of the problem.

## i-b) Frequency dependence of El.emission :

El. brightness of the compounds depend not only on the voltage applied to material but also on the frequency of applied voltage. An increase in El. brightness with increase in frequency has been observed not only for microcrystlline powder phosphors <sup>42-a,b</sup>, but also for single crystals <sup>43-a,b</sup> and for thin films. However, the variation of brightness with frequency is more complicated.

For singly-activated phosphor, it appears to be linear at low frequencies although at higher frequencies the brightness saturates or in some cases actually decreases. Accourding to  $\operatorname{Zalm}^{42-a,b}$ , the voltage drop (V) across the El. cell is not equal to the amplitude of the applied voltage (Vo) but it is function of extra-capacitance (C), and resistance (R) of the cell. The relation between 'V' and 'Vo' is given by,

$$V = \left[ \frac{WRC}{\sqrt{1 + W^2 R^2 C^2}} \right] Vo \qquad .. (7)$$

When RC  $\langle \frac{1}{W} \rangle$ , the voltage drop (V) across cell, and hence the lumin**erus** brightness increases linearly with frequency but when RC  $\gg \frac{1}{W}$ . V is independent of frequency and also the brightness is independent of frequency. It is thus, possible to describe any observed dependence with a suitable distribution in RC value of the system. Piper and William $^{43}$  have proposed a physical model to account for the linear frequency dependence in quite different way. Lehaman $^{18-C}$  found that for ZnS:Cu phosphaor poisoned by Fe, Co and Ni, brightness increases much faster than proportional to frequency although proportionality was observed in some cases.

Dzhuzeev and Chernyavskii studied the dependence of El. brightness (B) on electrical conductivity of 2nS:Cu,Cl and 2nS: Mn single crystals, They observed that  $\ln B - \ln V$  and  $\ln B - \ln \sigma$  relations were linear at low frequencies and reached a saturation at high frequencies (10 KHz) regardless of field strength.

It is general observation that for a phosphor having more than one band, a change in frequency results in a change in spectral distribution towards shorter wavelengths. It is observed that for ZnS phosphors, at higher frequencies the saturation sets more quickly in green band than for blue band. Thus, Waymouth and Bitter<sup>29</sup>, observed that for ZnS:Cu, Pb phosphors green band saturates above 1000 HzS, although blue band hehaves linearly upto atleast 2000 HzS.

Ballentine and Ray<sup>45</sup> for a single band ZnS:Cu phosphor,

expressed brightness B as

$$B = aoF^{X} exp \left(-\frac{bo}{0.5}\right) \dots (8)$$

where ao and bo are constants which are independent of Voltage and frequency and X = 1 for blue band at high voltages and  $X = \frac{1}{2}$  for green and red band.

A change in spectral composition of emission towards shorter wavelength with increase in frequency has also been observed by Kulkarni, V.S. and Ambardekar, D.S.<sup>46</sup> in case of (Zn,Cd) S:Cu,Mn phosphors.

Bernanose<sup>7</sup> and short and Hercules<sup>13</sup> observed that intensity of organic compounds increases with increase of frequency. Similarly, Tripathi and others<sup>26</sup> have shown that El. brightness increases with increase: of frequency. They could not obtained the peak value in the applied range of frequencies.

ii) Effect of time of operation of El. cell :

If an El. cell is operated continuously under indentical conditions of excitation, then it is found that El. intensity first increases for a few hours and then decreases continuously.

It was observed by Roberts  $^{47-c}$  that the rate of aging of cell was nearly independent of the voltage. He expressed the El. intensity 'L' as a function of time 't',

$$L = Lo \quad \frac{1}{1 + t} \qquad \dots \qquad (9)$$

Where Lo was the initial brightness and to was the half life period of the cell. ( The half life period may be defined as the time required to reduce the brightness of a cell to half of its initial value ). The values of to were much lower at higher frequencies. He showed that this aging effect was due to changes in the phosphor grains and not due to changes in the dielectric medium used. Similar observations were made by Hahn and Mimkes<sup>48</sup> and by Thornton<sup>49-a,b,c</sup>. Many attempts have been made to improve half life periods<sup>18-e,50</sup>.

iii) Temperature Dependence :

The temperature dependence of El. brightness is very complex. However, Destriau had given following empirical equation showing the variation of El. brightness with temperature,

$$B = Bo \exp \left[ \frac{-b}{(To-T)} \right]$$

where Bo, b and To are constants.

Alfrey and Tailor<sup>31</sup> observed that for ZnS single crystal, the El is virtually independent of temperature, then it increases linearly and finally saturates at still higher temperatures. They have attributed this behaviour to the effect of temperature on conductivity of the phosphor.

In the case of dispersed powder phosphors, the investigation of temperature dependence should be cautiously dealt

with , because the properties of the insulating matrix may be changing with temperature, involving additional difficulties. Results on various insulating matrix have been reported by several workers.

Hahn and Kerenchen<sup>89</sup> studied the temperature dependence of El. of ZnS:Cu,Al and Zns:Cu, Mn phosphors at 100-450<sup>°</sup>k at different frequencies. Haake<sup>90</sup> had suggested that there should be important connection between temperature dependence of electroluminescence and thermal quenching of photoluminescence. Robotkin and others<sup>91</sup> have studied the temperature dependence of El. brightness between 196-471<sup>°</sup>K, and they showed that the kinetics of the temperature quenching of electroluminescence and photoluminescence is the same. Similar investigations have been carried out by Nuva**y**•'va and others<sup>92</sup>

Measurements of steady state El. spectra of anthracenetrinitrobenzene system were carried out over the temperature range of  $190-300^{\circ}$ K by A.Miniewicz and others<sup>17</sup>. They observed that the relative magnitudes of the bands in the El. spectra, depends strongly on the temperature. Variation in the spectrum at the lower wavelengths are due to the temperature changes of the reabsorption in anthracene, whereas increase of the maximum at 580 nm is mainly due to the temperature variation of emission from the complex. In addition they observed that the integral emission intensity of system increases by almost one order of magnitude between room temperature and 190°K .Similar observations are reported by R.Nowak et. al.<sup>16</sup> for steady state El. in perylene doped anthracene crystals.

# iv) Effect of magnetic field :

Sufficiently high magnetic fields applied perpendicular to the electric field should quench El. emission. However, no such quenching is observed. Thus, Destriau<sup>1-e</sup> observed no quenching of El. due to magnetic fields as high as 6 x  $10^4$  oersteds. Same effect was observed by Ince<sup>57</sup> with magnetic field as high as  $13 \times 10^4$  oersteds.

These results show that the localized electric fields must be many times higher than the average potential gradients applied to the phosphor. These local field strengths have been established to be of the order of 2 x  $10^4$  V/cm to 2 x  $10^5$  V/cm, on the basis of 'contact barrier' theory of Henisch<sup>58</sup> and by Asti and co-workers<sup>59</sup> also.

V) Effect of incident radiation on El.emission :

It has long been known that application of electric fields, whether constant or a.c., can have important effects on the

behaviour of photoluminescent substances subjected to u.v. stimulus. We also distinguish between an enhancement effect on light intensity by applied field, called the "Guden-Pohl" effect and a partial quenching, called the "Dechene effect<sup>60,61</sup>".

Destriau and his colleagues<sup>61</sup> observed an enhancement of x-ray exc ited luminescence by the action of electric fields. These effects may be termed in general way, as "electro-photoluminescence".

These phenomena are concerned with the enhancement of photoluminescence by the electric fields applied to substances which were non-electroluminescent. However,  $Cusano^{62-a,b}_{and}$  Cusano and Williams observed that D.C. electroluminescent emission of a thin film of ZnS:Mn,Cl, ZnS:P,Cl and ZnS:As,Cl phosphor is greatly enhanced by irradiation with either u.v. or x-rays or cathode rays. The enhancement ratio (R) is defined as -

$$R = \frac{L_{\theta}}{L_{E} + L_{p}} \qquad .. (10)$$

where  $L_E$  = intensity due to field only,  $L_D$  = intensity due to radiation only,

 $L_p$  = intensity when both fields are applied.

The above ratio is quite high, 100 times to 500 times as compared to 10 - 15 times in 'Gudden-Pohl' or " Destriau effect". After a certain threshold voltage the enhancement ratio increased rapidly right upto the dielectric breakdown. The enhancement occurs only when metal electrode acts as cathode. Since the effect is nothing but radiation controlled electroluminescence, it is named as "Photo-electroluminsence."

The radiation controlled electroluminescene has opened a new field of research 10 develop solid state amplifiers and scanned picture display screens. Thus, the study of electroluminescence in this aspect has a very bright future.

Alfrey and Taylor investigated the effect of  $\checkmark$ -particles on electroluminescence<sup>63</sup>. Their results indicate that the brightness was reduced when the  $\checkmark$ -particles hit the negative electrode.

#### 1:2:2 MECHANISM OF ELECTROLUMINESCENCE:

Although the El. of crystalline inorganic materials has been extensively studied, there are still many questions concerning the mechanism of El.in any perticular case.

The mechanism of excitation of organic crystals is similar to that of inorganic crystals, except that band gap in organic crystal is greater than inorganic crystals. Theoretically it can be considered that there are five possible excitation mechanisms, that can occur, although not all five of these mechanisms have been authenticated. The mechanisms are,

1) Glow discharge excitation,

II) Field ionization through acceleration mechanism,

III) Impact ionization,

IV) Injection of charge carriers, and

V) Radiative recombination.

A detailed discussion of each of these processes have been given by Piper and Williams<sup>43</sup> and by  $Ivey^{51}$ .

### I) Glow Discharge Mechanism :

In many respects, this mechanism should not be considered true El. When high a.c. voltage of order of 10 V/cm or greater is applied between the two electrodes in a cell, breakdown of gas surrounding the cell can occur, resulting in light emission from the gas. If a fluorescent material is present, the light the emitted by the gas can cause photoexictation of material in the cell. This is particularly common mechanism of El. for organic films.

Short and Hercules<sup>13</sup> studied the El. of a variety of fluorescent organic compounds. Spectral observations showed the emitted radiation to be identical with normal fluoresence spectrum. In addition nitrogen emission bands were invariably present in spectra taken in air. No radiation was emitted from cells operated in a helium atmosphere. It is shown that all the experimental data are consistent with the hypothesis that UV emission

22

from excited nitrogen molecules œuses fluorescence excitation of organic material. They also explained the origin of radiation emitted by an El. cell to be the normal fluoresence of the organic compound excited by the ultraviolet radiation from nitrogen. With even a small amount of nitrogen present in the cell, sufficient gaseous discharge could be produced to give fluoresence of organic material. It was found that when the cell was prepared in an atmosphere of helium no light emission could be observed from an organic layer, although a standard commercial electroluminescent zinc sulphide phosphor

#### produced light.

Another strong point suggesting the validity of the gaseous discharge interpretation is that no emission bands could be observed for any material except for those normally fluorescent, in solid state. This also correlates with some of the spurious emission bands observed by Barnanose, who apparently failed to observe most of the nitrogen bands because of the high optical absorption of the mica layers in the region of nitrogen discharge.

An interesting and confusing effect is that the glow discharge mechanism has electrical properties similar to those observed for genuine El. It is doubtless this fact that has been a source of confusion to a number of investigators. It seems, however, that the bulk of El. reported to data in thin cells

under high potential a.c. excitation probably results from a discharge excitation mechanism.

# II) Field Ionization through acceleration mechanism

For the case in which an impurity is present in the lattice, direct ionization of the impurity by an applied field is possible. If such ionization can occur, then electroluminescence can also occur by a recombination reaction between the electron and the hole at the activator site. The major difficulty associated with excitation of El. by field ionization is competition from dielectric breakdown of the matrix either by an avalanche mechanism or by Zener breakdown. Generally, if field ionization is to occur, it would be more likely in the high field region where quantum mechanical tunneling can occur.

Generally, the breakdown of crystalline inorganic materials occur in the vicinity of  $10^6$  V/cm by either the avalanche or Zener mechanism. Calculations on the field necessary to excite El. by field ionization<sup>43-a</sup> have shown that fields in the order of  $10^7$  v/cm are required, an order of magnitude greater than those required for breakdown. Therefore, the occurrence of direct field excitation seems unlikely, and the unambiguous identification of such mechanism in El. has not yet been established. However, the possibility does exist of direct field excitation for an activator system that can be perturbed by the applied potential to an energy low enough to permit a reasonable probability of excitation from the ground state.

Mechanism of breakdown of crystalline insulator involve acceleration of conduction electrons to sufficient kinetic energy, to ionize further valence electrons and thus multiphy into a breakdown current. This mechanism dominate over **Ze**ner breakdown except for the crystals with forbidden energy gap appreciably less than 1 ev. The field requirements for Zener breakdown increases as the square of band gap and at larger band gaps exceed the field requirements for breakdown avalanche.

Franz<sup>64</sup> has made calculations not only for field ionization of valence electrons but also for electrons trapped in a square well potential. His calculations for the field necessary to ionize this localized centre reduces to good approximation, to expression.

1

$$Ei = \frac{10^{7} e^{\frac{1}{2}}g}{8 + \log_{10} EiT} e^{3/2} ... (11)$$

if  $E_i$  is measured in volts/cm, T, the decay constant of the centre in second and  $C_i$ , the depth of the well in ev.

In semiconductor phosphors, there exists additional energy levels, called 'surface states' on the surface of a semiconductor and these levels can act as traps for electric charge. These surface states give rise to a potential hill called as 'Mott-Schottky' barrier. The applied electric field is locally enhanced

at such barrier. This enhanced field Fo at the edge of the barrier is given by.

Fo = -2 
$$\left[ 2 \prod N_{d} e (V_{D} + V_{B}) K \right]^{\frac{1}{2}}$$
 ...(12)

where N<sub>d</sub> is total doner concentration , V<sub>D</sub> and V<sub>B</sub> are diffusion potential and barrier potential. If  $V_B >> V_D$ , the field Fo is proportional to  $V_B^{\frac{1}{2}}$ .

## III) Impact ionization

El. excitation can occur if an electron is injected into the conduction band of a crystl. The electrons may be injected into conduction band directly from the surface of the crystal or may arise from deep traps within the crystal lattice. Similar excitation processes can occur for positive holes accelerated through the lattice.

Under very high electric fields, the carriers gain a substantial amount of energy from the field and this will lead to an increase of average linear speed over and above the values, characterised by the lattice temperature. Thus, the effective 'electron temperature' will be very high. The concept of such 'hot' electrons ( or holes ) was originally introduced by Froelich<sup>65,66</sup> in connection with energy exchanges involved in dielectric breakdown.

In order to produce El. by electron collison, three conditions are essential. First, high field regions capable of accelerating charge carriers must be produced. Second, electrons or holes must be injected into this high field region; and third, activator sites in the lattice must be situated such that they can absorb a major fraction of the energy produced by collision. Calculations show that the field necessary for excitation by electron impact is lower than that for breakdown,  $Ca.10^5 \text{ v/cm}^{51}$ . It has generally been considered that El. excitation of the ZnS: Cu system occurs by this mechanism<sup>51</sup>.

An examination of possible excitation mechanisms was made by Bernanose<sup>7-a</sup>. It was pointed out that El. of fluorescent dyes dispersed in cellophane would not be explained by mechanisms involving structure defects, activation centres or crystal abnormalities. These and other considerations led Bernanose to postalate direct field excitation of the molecule as the operative mechanism.

#### IV Injection of charge carriers .

Injection of charge carriers into a perticular region of a crystal is an El. mechanism that occurs in semiconductors. It can occur by injection into either p- or n-type material or at a p-n junction. For n-type material the activator centre has its ground state occupied. Therefore a hole injected into the valence band can be trapped by the activator and cause ionization of the centre. The ionized centre can attract a conduction band electro with subsequent emission of radiation. For p-type material, free holes are available for the activator system in the ground state. Therefore injection of electrons into conduction band causes these electrons to be captured by the activator center and likewise results in El.

For a p-n junction with no applied potential, thermal excitation can lead to some injection and therefore to light emission. With small potentials applied across the p-n junctions, the injection process is temperature dependent, the luminescence efficiency depending on the carrier life time. The El.of SiC has been attributed to charge carrier injection<sup>51</sup>.

Gurnee<sup>52</sup> concluded that excitation of the organic meterial originates in the vicinity of the carbon particles, probably by electron injection into the organic material from the conducting particle. He dlso concluded that the injected electrons were sufficiently energetic to excite the hydrocarbon directly, although hole combination processes were also considered.

## V. Radiative recombination :

For crystalline materials not containing activator centres, it is possible for holes and electrons to combine directly to give rise to photon emission. This process involves introduction of an electron into conduction band of the material and introduction of a hole into valence band and diffusion of the holes and

electrons until they combine. The efficiency of such process depends upon the rate of radiative combination versus the rate of radiation less combination. Radiative combination of holes and electrons is favoured by material of high purity and the presence of high carrier concentration. Such a mechanism has been proposed for infra-red emission is germanium<sup>43</sup> and appears to be operative in a number of crystalline organic electroluminescent materials<sup>17,53-56.</sup>

EL. in organic crystals results from recombination of holes and electrons injected into the crystals by electrodes. To understand detailed mechanism of El emission, one must have knowledge regarding space charge limited currents (SCL) in organic crystals<sup>67</sup>. The present treatment consists of a brief discussion of hole injection into organic crystals, a

When excess carriers than thermally generated **when** are injected into an insultator, the current flowing through it is limited by space charge. In order to obtain SCI current through an insulator, the electrode used must confirm to certain specific requirements. Electrodes must be able to supply an infinite number of carriers i.e. n (o) =  $\infty$ , where n (o) is carrier concentration in insulator facing electrode. Also to observe electron SCL current, it is necessary that  $E_p - \phi > 0$ ,

where  $\mathbf{E}_{\mathbf{F}}$  is the Fermi energy and the electronic work function of electrode meterial. The electrode will show saturation effects if either  $\mathbf{\Phi} - \mathbf{x}$ , is larger than 10 KT, where  $\mathbf{x}$ , is the electron density. Gerard T. Pott and co-workers<sup>68</sup> observed that for sufficient electron injection into anthracene these criteria indicate an alkali metal contact should be satisfactory. However, it is well known that in contact with enthracene the alkali metals react immediately forming negative anthracene ions.

W. Helfrisch and W.G. Schneider<sup>54-a</sup>, indicated that high concentration of carriers in anthracene crystal were obtained by using injecting electrodes. It is known that steady state SGL hole current can be injected into anthracene crystal. From the experimental results on anthracene crystal, Kallamann and Pope<sup>69</sup> showed that the iodine extracts an electron from anthracene crystal, injecting a positive hole inside anthracene which will travel under the action of the applied field through crystal to negative electrode. Their experimental technique consists of anthracene crystal in contact with iodine-iodide electrode.

Mark and Helfrich<sup>70</sup> have studied SCL currents for biphenyl, p-terphenyl, p-quarterphenyl, napthalene and anthracene. They Contact concluded that the acceptor electrode forms an ohmic for hole injection into the crystals and that steady state current

through such crystals is trap-limited as long as the injecting contact is ohmic. The best interpretation below saturation is that they are space charge limited and the current carriers are positive holes.

It has been suggested that Schottky emission is the principle mechanism involved in high field hole injection from silver paste electrodes into anthracene<sup>71</sup>, as well as in other electrode-insulator systems<sup>72</sup>. Indeed, one other mechanism may be appropriate, viz., enhanced hole injection following the formation of an exhaustion Schottky barrier at the anode. According to this mechanism, on application of a sufficiently high electric field, holes will first begin to enter the crystal from the anode by tunnelling through Schottky barrier. These holes will recombine with electron in the vicinity and produce electroluminescence which then increases the free electron density due to optical detrapping. These additional free electrons, which are able to reach the vicinity of the anode, further affect the geometry of the Schottky barrier and increase the " transparency " of the barrier to holes, and the complete process will be self-sustaining. Finally an equilibrium between electroluminescence detrapping and electron injection will be reached, with the electron injected current magnitute being the determining factor.

#### 1:2:3 APPLICATIONS OF ELECTROLUMINESCENCE :

"Electroluminescence" the newest potential light source has characteristics which have appeal for several applications, where space is an important consideration. When brightness and efficiency figures improved, a great deal of attention was paid to take advantage of electroluminescence as the light source of the future. Hence, EL has become a subject of great technological interest. Lowry<sup>7 3</sup> (1953) has given various applications of EL which can be summarized as follows :

1) Although the El, lamps are not efficient source of light, as compared with conventional lamps, it can, no doubt, replace the need of illumination where much brightness is not essential and sometimes even not desirable. For example, El. lamps are best suited for self luminous object such as instrument dial illumination, radio and clock dials, house numbers, direction signs and similar devices, also in bed rooms and for decorative purposes.

2) Moreover, EL, gives an arce source of light in contrast to the more conventional point source ( the incandescent lamp ) and to the linear source ( electric discharge lamps). Thus, from a 8" x 8" panel is adquate to give a good

3) The panels can be made to luminesce in many different colours depending on the phosphor used. Colour control by adjustment of the frequency is possible but normally impracticable, because the frequency is rarely variable in power systems, and because frequency and intensity are not independent.

4) Electroluminescent panels can be made in highly reliable forms which are mechanically more robust than existing light sources. The self-luminous area can easily be arranged in the form of non-overlapping letters or symbols which, by a suitable switching process can be energized in turn. Multiple-electrods indicator panels can be designed in this way. The audio frequency power supply systems are used in aircraft, after favourable conditions for the application of such light sources.

5) The fact that the EL panels are mostly two dimentional, can in some circumstances lead to an increase in practical efficiency over conventional devices. This arises from the fact that nearly all the light emitted from an EL panel can be directly utilised, whereas light from conventional sources is often absorbed ro scattered over an appreciable portion of the solid ( emission ) angle.

An interesting and important application of EL is for light amplification. Cusano<sup>62</sup> observed that when a cell containing

ZnS:Mn, Cl phosphor which does not emit noticable light under a.c. or d.c. excitation, does so when it is irrediated simultaneously with uv or x-rays and electric field. By the simultaneous effect, the brightness was enhanced. The effect has been used for fluoroscopic image intensification in medical science.

A new type of solid state image amplifier, in which photoconducting CdS sheet is made adjacent to the ZnS phosphor sheet, has been described by Zalm, Diemer and Klasen<sup>27-b</sup>(1957-58). The amplification observed is of the order of 50 light quanta emitted per one incident quantum. Low<sup>74</sup> (1955) suggested the use of EL for nuclear detectors. With the use of a field, of the order of  $10^5$  V/cm, EL phosphors would yield improved detectors.

A detailed survey on EL enamels and their uses has been described by Eichbaum $^{75}$  and by Ranby $^{76}$  (1963).

Following the use of electroluminescence for the production of self-luminous half-tone pictures<sup>77</sup>, Harman<sup>78</sup> (1960) designed electroluminescent microwave receivers. The fact that the lamps are cool in operation and two dimensional, suggests a number of applications in photography and dark room processes<sup>84</sup>, e.g. as dark room safe lights, transparaency illumination, and light

sources in contact printers, Safe lights must, of course, be free from blue emission.

The art of EL display techniques applicable to stimulation of on board displays of future vehicles and displaying computer and (or) video information for use in training devices are described by Lakshmanan and Munt<sup>79</sup> (1966). The display system was improvied by Martel<sup>80</sup> and used for reproducing dynamic radiation images.

The selectivity of the EL. technique<sup>81</sup> as applied in analysis of aromatic hydrocarbons is found to be superior to that of convensional spectro-fluorimetry for organic trace analysis. The method can be extended to the detection of aromatic amines and phenols, which normally do not show significant EL by methylation of the deactivating group. Chernyshev and co-workers<sup>82</sup> (1968) used electroluminescence as a method for estimating biological activity of toxic products. Luminescence was estimated during electrolytic decomposition of lipids extracted from tissues of cyprinus carpio.

Fischer<sup>83-a,b</sup> (1971) describes the present situation of industrial electroluminescence in a very novel way. It is of interest to see that large-area panels were formerly used for general illumination purposes whereas the improved light sources

were tiny single crystalline - p-n didoes, emitting infra-red and red light. The latter were used for various purposes. However, introduction of multielement image display panes, has charged the out-look and brings back the former II-VI EL in its various forms by large scale integrated thin film transister ( TFT ) circuitry.

The idea of a flat, all solid-state electroluminescent TV sets, that can be hung on the wall or carried in the pocket, is an extremely attractive objective. Such a device would be an excellent exploitation of solid state electronics and would result in certain obvious advantageous over the cathode ray tube. On the way towards this ultimate goal, there are simpler and still very useful intermediate payoffs, such as the picture telephone,  $\checkmark$ -numeric - graphic displays, radar screens, and simple miniature lamps, which would find extensive applications.