CHAPTER – I

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 according to the mode of excitation (Ultra violet- Photoluminescence, Chemical reaction- Chemiluminescence, Electrons- Cathodoluminescence). The phenomenon of generation of light by the direct action of an electric field on semiconductors is known as " electroluminescence " (El.). The semiconducting material (Phosphor or Electroluminophor) which is used as a source of light may be taken in powder or crystalline form. The electroluminescent material (El. material) is sandwitched between two parellel electrodes, one of which is in the form of wire guaze or a conducting glass. The phosphor, dispersed in an insulating material such as castor oil,silicon oil or high vacuum grease, is excited by application of an ac.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 phenomenon being thus ' Structure Sensitive', provides Possibility of control of the constitution which is important in many practical ways. The phenomenon itself provides an opportunity to further our understanding of electric processes in the phosphor materials, and as such, the phenomenon has gained an increasing interest in research workers.

The El. phenomenon was first observed by Destriau[1] in 1936, and hence it is also known by his name. Since then, there has been a rapid progress in the field of electroluminescence and a great deal of attention has paid to prepare more efficient light sources of the future. On the subject multitude of papers has appeared to elucidate 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 imporve the brightness to attain higher efficiency. It was observed that the intensity of El. emission depends on various factors such as preparative conditions, structure of material,voltage and frequency of the exciting field, geometry and the period of the operation of El. cell.

Electroluminescence in organic crystals was first observed by Pope et al.[2], who performed measurement on single crystals of anthracene and anthracene doped with tetracene. El. from organic systems has been known for a number of years, but very few examples are known than for inorganic systems. Organic El. can occur under similar conditions of excitation as for inorganic phosphors. Inorganic El. is generally observed in solid state,while organic El.both in the solid as well as in solution.

Bernanose and his collaborators[3-7] developed the technique of organic El. and studied the El. properties of number of organic compounds such as acridine organge,. carbazole and was able to show that the intensity of emitted light was dependent on voltage and frequency in the same way as from inorganic phosphors.

From survey of literature, it seems that no efforts have been made to investigate the El. properties of metallic salts of 8- hydroxyquinoline. Stevens[8]has extensively studied several metallo- complexes of 8- hydroxyquinoline and reported their fluorescence properties. It is our intention in the present investigation to study the electroluminescence properties of some metallic salts of 8- hydroxyquinoline, and to correlate the influence of some of the parameters mentioned above, on electroluminescent emission. We have selected these metallic complexes mainly because they can be prepared in a pure form and furthermore no work on electroluminescence seems to have been done on these metallo- complexes.

1. 2 HISTORICAL INTRODUCTION

A review of the earlier work shows that the problem of El. has been studied mainly along the following lines.

1:2:1 General aspects of Electroluminescence.

1:2:2 Mechanism of Electroluminescence.

1 . 2 . 1 GENERAL ASPECTS OF ELECTROLUMINESCENCE,

To cover all the aspects of El.,one has to consider the following points

a) Preparation of El. materials,

b) Construction of El. cell,

c) Measurement of El. intensity, and

d) Voltage and frequency dependence of El.emission.

1 . 2 . 1 a) PREPARATION OF ELECTROLUMINESCENT MATERIALS:

The preparation methods of organic and inorganic phosphor differ considerably. In inorganic phosphors, El. is imporved by presence of impurities. The incorporation of impurities in the base material follows the principle of charge compensation,as described by Kroger and Dikhoff.[9,10] Hundreds of phosphors of various types have been synthesised so far.

Small impurity in the organic El. material will lead to large changes in the El. intensity and it makes then unsuitable for systematic study. Therefore, commercial organic compounds must be purified prior to El. study. Methods of purification varies from compound to compound. Hydrocarbons are purified by column chromatography[2,11,12] most of the organic compounds are purified by recrystallisation[11,13] method using suitable solvent. Purified crystals are zone refined and then ground to fine powder. In single crystal study method, crystals are grown from the melt using Bridgman technique.[12] Lossev[14] first reported emission from silicon carbide crystals. The crystals are then cut from the boules in the form of plane parellel platelets typically o.5 - o.48 mm thick. 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.[13] The doped crystals are also grown from the melt of the mixture of dopant and host.[15]

1 . 2 . 1 b) CONSTRUCTION OF AN ELECTROLUMINESCENT CELL :

An El.cell consist 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 El. emission,because voltage actually given to El. material is a function of thickness of El. material layer and the medium in which it is dispersed. The dispersion medium should have a low power factor, high dielectric strength and chemically inert.[16]

Mager[17] used nitrocellulose lacquer plasticized with castor oil,camphor or dioctyl-phthalate. Siddall[18] have described various preparatory techniques using a very thin layer of viscous silicon oil as adhesive.

Cells used for solid inorganic and organic phosphors are nearly identical. Destriau[1] 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. Butter et al.[19] used the same cell with some improvements.

Methods of obtaining El.differ in the way in which a thin layer is prepared and mounted between electrodes. To achive a high field, the layer should be very thin. On the other hand, to achive uniform light emission,it must always be thick compared with the grain size of the phosphor used. A comparative thickness is usually adopted[20]. It is between o.ool and o.oo4 inch for an operating voltage of 100-600 V.

The transparent electrode used in the construction of El.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 stannous chloride in acetone or alcohol[21,22,23] on to a glass plate heated to just below the melting point or by exposing the glass to the vapours of silicon,tin or titanium chloride[24] followed by cooling in a reduced atmosphere[25] or by vacuum deposition of various oxides such as SnO[26], SnO_2[27-28], TiO_2[29] and InO_2[30-31] which forms a conducting layer on the glass.

In the single crystal study contact electrodes are used. R.Nowak et al.[32-33] have used cathodes of sodium potassium alloy and anodes of silver paste. M.Pope et al.[2] have used two electrode configuration. In one case silver paste electrodes were epoxided on to the crystal while in other ohmic contacts of o.1 M Sodium Chloride solutions on opposite sides of crystals were used.

The cells used by Gurnee[13] consisted of chromium-plated steel-backed electrode upon which a 1- mil polycrystalline layer of the hydrocarbon conductor mixture was placed. A 1- mil polystyrene film separated the conducting layer from a transparent tin oxide-coated glass electrode. A thin film of silicon 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.[13] were similar to those used in the technique of Lehmann[34].

Short and Hercules[35] obtained thin layer of organic phosphor included, deposition of material from a hot saturated solution,solidification of melt,embedding in resin and evaporation of suspension. A metallo-organic chemical vapour deposition method was described by Hirabayashi et al.[36] and Svechikov et al.[37] In the study of organic compounds Bernanose and others[3-7] used cellophane film having uniform coating of El. material. The cellophane film was prepared by dipping it in a hot saturated solution of El. compound. The film was dried to evaporate solvent and placed with melted paraffin wax between a plate of aluminum and transparent mica. The cell was compressed before cooling to exclude air bubbles. In order to provide electrical contacts, the sheet of mica was wetted on its exterior surface by saline glycerol solution.

The review of literature on this aspect serves as a sort of guidance in designing a cell, suitable for measurements on El. emission. A brief review on various types of electroluminescent devices, largely based on American achievements, has recently been presented by Meczynska and Oczkowski[38].

1.2.1 c) MEASUREMENT OF ELECTROLUMINESCENCE INTENSITY,

The intensity measurement of El.emission requires a dispersing unit (a monochromator) and a detecting unit. A monochromator is necessary for isolating light out put at different wavelengths for spectral distribution studies. Interference filters,prism and grating monochromator can serve the purpose. Thus, Goldman and co-workers[39], Bonfiglioli and co-workers[40], Hariu and others[41], Singh and Mohan[42], etc. used constant deviation spectrometer for dispersion while Levialdi and others[43], Butter and others[19], etc. used interference filters.

A photomultiplier tube can be used as a radiation detecting device. Various types of photomultiplier tubes like IP-21,IP-22,[19,39,44] PM-10M, and FEV-12,[39] R-136,[41]RCA-6217,[43] etc. has been reported by serveral workers.

The photocurrent signal of the photomultiplier tube is either fed to a double beam oscilloscope[45,46] or to an ultrasensitive microammeter or to a sensitive spot reflecting galvanometer.[44] The peak hight of the brightness wave is taken as the measure of the intensity in the oscilloscope, while the photocurrent in microamps or in arbitrary units (A.U.) if a sensitive spot galvanometer is used,gives the relative intensity.

1.2.1 d) FACTORS AFFECTING ELECTROLUMINESCENCE EMISSION:

In general, El.intensity depends on the following factors.

i) The excitation voltage of the applied field,
ii) The excitation frequency of the applied field,
iii) Time of operation of the cell,
iv) Temperature dependance during excitation,
v) Effect of Magnetic field and
vi) Effect of Incident radiation.

i) 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.[47,48] 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[49-55] but many pertain to experimental data only.[56-59]

The first relation between L and V was given by Destriau[1] as:

$$L = A \exp. \left[\frac{-B}{V} \right] \qquad \ldots . \quad 1$$

which was later modified by himself,[60] as :

$$L = A V^n \exp. \left[\frac{-B}{V} \right] \qquad ---- \quad 2.$$

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

Following the work of Destriau, a number of equations for variation of El. brightness (L) as a function of applied voltage (V),have been proposed. For a single phosphor particle,the variation was found to be linear by Waymouth and Bitter.[61] They also observed that a minimum thereshold voltage is necessary to commence the effect. Destriau and Doumergue[62] covered a range of very low brightness levels without detecting any discontinuity arising from minimum threshold voltage. However, there seems to be a meagre evidance in favour of a minimum threshold voltage for electroluminescence.

Kale et al.[63] observed a complicated variation in the threshold voltage. On the basis of exhausion barrier theory, Alfrey and Taylor[64] deduced the following relation.

$$L = L_o \ \exp. \left[\frac{-V_o}{V}\right]^{0.5} \qquad \ldots\ldots \quad 3$$

whereas on the basis of impact ionization mechanism Nagy[57] derived the following relation:

$$L = A. \ \exp. \left[\frac{-B}{(1 + CV)^2}\right] \qquad \ldots\ldots \quad 4$$

where A,B and C are constants. Similar types of relations are proposed by other workers.[65-68] Lehmann[69] suggested the equation,

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

where a,b and Vo are constants which vary 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[3-7] who have published a number of studies in this area. They reported following important points on El.emission.

a) The intensity of El.emission was found to vary according to the relationship.

$$I = AV^2 \ \exp. \left[\frac{-B}{V}\right] \qquad \ldots\ldots\ldots \ 6$$

where A and B are constants.

b) An expression relating El.power radiated and applied field,was given as:

$$W = 9 N \lambda^{4} \Lambda^{n} \quad / 64^{2} CT^{2} \quad ..... \quad 7$$

where N is the total number of organic molecules, Λ applied field (Stat volt /Cm).

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

Bernanose results were confirmed in subsequent studies by Namba and coworkers.[70] Gurnee et al.[13] have studied El. produced by aromatic hydrocarbons in the Presence of a finely divided electric conductor. For example, anthracence in the presence of about 1% carbon black shoed 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[35] 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.[2] 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 ln B against $V^{-0.5}$. Hartman and Amstrong[71] studied El. in organic

Polymers and found that the linear plots of Ln B against V^{-1} fits better than $V^{-o.5}$.

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

ii) FREQUENCY DEPENDENCE OF ELECTROLUMINESCENCE EMISSION:

It has been observed not only for microcrystalline powder phosphors, but also for single crystals[47] and for thin films,[72] that El. brightness of the compounds depend not only on the voltage applied but also on the frequency of applied voltage. However, the variation of brightness with frequency is more complicated. Deviations are observed at high frequencies where the intensity may saturate or even fall with increasing frequency. According to Zalm,[47] the voltage drop (V) across the El. cell is not equal to the amplitude of the applied voltage (Vo) but it is a function of extra- capacitance (C), and resistance (R) of the cell. The relation between 'V' and 'Vo' is given by,

$$V = \left[\frac{WRC}{\sqrt{1+W^2R^2C^2}} \right] Vo. \quad \ldots. 8$$

Thus, it is evident that if $RC \ll \frac{1}{W}$, the voltage drop (V) across the cell, and hence the luminous 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 Williams[48] have proposed a physical model to account for the linear frequency dependence in quite different way. Lehamann[73] found that for ZnS:Cu phosphor poisoned by Fe,Co and Ni, brightness increases much faster than proportional to frequency although proportionality was observed in some cases.

It is a 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[61], observed that for ZnS:Cu,Pb phosphors green band saturates above 1000 Hz,although blue band behaves linearly upto at least 2000 Hz.

Ballentine and Ray[74] for a single band ZnS:Cu phosphor,expressed brightness B as

$$B = a_o \; F^x \; \exp \left[\left(\frac{-b_o}{V^{0.5}} \right) \right] \quad \ldots . \; 9$$

Where a_o and b_o 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.[75] in case of (Zn,Cd) S: Cu,Mn phosphors.

Beruanose[7], short and Hercules[35] observed that E . intensity of organic compounds increases with increase in frequency. Similarly, Tripathi and others[44] have shown that El. brightness increases with increase in frequency. They could not observed the peak value in the applied range of frequencies.

iii) TIME OF OPERATION OF ELECROLUMINESCENT CELL

If an EL. cell is operated continuously under identical 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[76] 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'

$$L = L_o \left[\frac{1}{\left(1 + \frac{t}{tc}\right)} \right] \ldots\ldots \quad 10$$

Where L_o was the initial brightness and tc 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 tc 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[77] and by Thornton[78]. Many attempts have been made to improve half life periods.[79-80]

iv) TEMPERATURE DEPENDENCE

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

$$B = B_0 \exp \left[\frac{-b}{(T_0 - T)} \right] \quad .....11$$

where B_0 , b and T_0 are constants.

Alfrey and Taylor[64] 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.[81-82]

Hahn and Kerenchen[83] studied the temperature dependence of El. emission of ZnS:Cu,Al and ZnS:Cu,Mn phosphors at 100-450 °K at different frequencies. Haake[84] had suggested that there should be important connection between temperature dependence of El. and thermal quenching of photoluminescence. Robotkin and others[85] have studied the temperature dependence of El. brightness between 196-471°K, and they showed that the Kinetics of the temperature quenching of El. and photoluminescence is the same. Similar investigations have been carried out by Nuvareva and others[86]. Gubkina[87] observed the temperature quenching of El. of ZnS:Cu phosphors for various frequencies and different exciting voltages.

El. and its variation with temperature is recently reported by Somaiah and Paracchini[88]. The El. of $CdF_2 : EuF_3$ films at 77-320°K was reported by Vlasenko et al.[89] and the results are discussed in terms of carrier interactions. Bhushan and his coworkers[90] studied photo and electroluminescence of ZnO doped with rare earth at liquid nitrogen temperature and observed that El. phenomenon is more susceptible to traps.

Miniewicz and others[33] have carried out measurements of steady state El. spectra of anthracene-trinitrobenzene system over the temperature range of 190-300°K. 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.[32] for steady state El. in perylene doped anthracene crystals.

V) 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[60] observed no quenching of El. due to magnetic fields as high as 6×10^4 oersteds. Same effect was observed by Ince[91] with magnetic field as high as 13×10^4 oersteds.

These reults 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 2×10^4 V/Cm to 2×10^5 V/Cm, on the basis of ' contact barrier ' theory of Henisch[92] and by Asti and Co-workers[93] also.

vi) EFFECT OF INCIDENT RADIATION.

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 " Gudden- Pohl "[94] effect and a partial quenching called the " Dechene effect[95-96] ". Similar observations on enhancement of El. brightness were later, made by others.[97-98] Destriau and his colleagues[96] observed an enhancement of x-ray excited luminescence by the action of electric fields. These effects may be termed in a general way, as " electro-photoluminescence."

These phenomenon are concerned with the enhancement of photoluminescence by the electric fields applied to substances which were non-electroluminescent. However, Cusano,[99] 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 -

$$R = \frac{L_B}{L_E + L_p} \quad ....12$$

Where L_E = intensity due to field only,
L_p = intensity due to radiation only,
L_B = 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 El., it is named as " Photo-electroluminescence."

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

Alfray and Taylor[100] investigated the effect of α - particles on El. Their results indicate that the brightness was reduced when the α - particles hit the negative electrode.

The quenching and enhancement of photoluminescence of ZnS: Mn by a.c. Voltage has been observed by Gobrecht and Gumlich[101]. Quenching was observed at low voltages and enhancement at high voltages.

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 particular 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

I) Glow discharge excitation,
II) Field ionization through acceleration,
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[48] and by Ivey.[102]

I) GLOW DISCHARGE EXCITATION:

In many respects, this mechanism should not be considered true El. When high a.c. voltage of order of 10^5 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 fl$\overset{u}{\wedge}$orescent material is present, the light emitted by the gas can cause photoexcitation of the material in the cell. This is a particularly common mechanism of El.for organic films.

II) FIELD IONIZATION THROUGH ACCELERATION.

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 El. 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 take place,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[48-a] 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 resonable 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 multiply into a breakdown current. This mechanism dominate over Zener 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 requirement for breakdown avalanche. Franz and others[103-104] have made calculations not only for field ionization of valence electrons but also for the ionization of an electron into the conduction band from a localized state in forbidden band.

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 F_o at the edge of the barrier is given by

$$F_o = -2 \left[2 \pi N_d \; e \; (V_D + V_B) K \right]^{\frac{1}{2}} \quad ..14$$

where Nd is total donar concentration, V_D and V_B are diffusion potential and barrier potential. If $V_B \gg V_D$, the field F_0 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 crystal. 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 charactarised 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[105] and Goffaux[106] in connection with energy exchanges involved in dielectric breakdown.

In order to produce El. by electron collision, three conditions are essential.

i) High field regions capable of accelerating charge carriers must be produced.

ii) Electrons or holes must be injected into this high field region.

iii) Activator sites in the lattice must be situated such that they can absorb a major fraction of the energy produced by collision. Calculation show that the field necessary for excitation by electron impact is lower than that for breakdown, ca. 10^5 V/cm. It has generally been considered that El. excitation of the Zinc Sulfide-Copper system occurs by this mechanism.[102]

An examination of possible excitation mechanisms for organic electroluminescent material was made by Bernanose[7-a]. 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 postulate direct field excitation of the molecule as the operative mechanism.

IV) INJECTION OF CHARGE CARRIERS.

Injection of charge carriers into a particular 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 electron 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 centre 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 processes are temperature dependent, the luminescence efficiency depending on the carrier life time . The El.of SiC has been attributed to charge carrier injection.[102]

Gurnee[107] concluded that excitation of the organic material originates in the vicinity of the carbon particles, probably by electron injection into the organic material from the conducting particle. He also concluded that the injecting 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 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 a process depends upon the rate of radiative combination versus the rate of radiationless 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 infrared emission in germanium[48] and appears to be operative in a number of crystalline organic El. materials.[33,108]

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.[109] The present treatment consists of a brief discussion of hole injection into organic crystals.

When excess carriers than thermally generated are injected into an insulator, the current flowing through it is limited by space charge. In order to obtain SCL 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 $E_F - \phi > 0$, where E_F is the fermi energy and ϕ the electronic work function of electrode material. The electrode will show saturation effects if either $\phi \rightarrow x$, is larger than 10 KT, where X, is the electron density. Gerard and Co-workers[110] 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 anthracene the alkali metals react immediately forming negative anthracene ions.

Helfrisch and Schneider[111] indicated that high concentration of carriers in anthracene crystals were obtained by using injecting electrodes. It is known that steady state SCL hole current can be injected into anthracene crystal.

Mark and Helfrich[112] have studied SCL currents for biphenyl, P- terphenyl, P- quarterphenyl, napthalene and anthracene. They concluded that the acceptor electrode forms an ohmic contact 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,[113] as well as in other electrode-insulator systems.[114]

Indeed, one other mechanism may be appropriate, Viz; enhanced hole injection following the formation of an exhausion 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 El. 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 El. detrapping and electron injection will be reached, with the electron injected current magnitude being the determining factor.

1. 3 APPLICATIONS OF ELECTROLUMINESCENCE.

" Electroluminescence " the newest potential light source has charactaristics which have appeal for several applications, where space is an important consideration. When brightness and efficiency figures imporved, a great deal of attention was paid to take advantage of El. as the light source of the future. Hence, El. has become a subject of great technological interest.Lowry[115] (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 area source of light in contrast to the more conventional point source (the incandescent lamp) and to the linear source (electric discharge lamps). Thus a 8" x 8" panel is adequate to give a good light illumination for a 12' x 18' room.

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) El. 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-electrode indicator panels can be designed in this way. The audio frequency power supply systems are used in air-craft,after favourable conditions for the application of such light sources.

5) The facts 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 or scattered over an appreciable portion of the solid (emission) angle.

An intersting and important application of El. is for light amplification. Cusano[99] observed that when a cell containing ZnS: Mn,Cl phosphor which does not emit noticeable light under a.c. or d.c. excitation, does so when it is irradiated simultaneously with UV. or X-rays and electric field. The enhancement 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 adjuscent to the ZnS phosphor sheet, has been described by Zalm, Diemer and Klasen[49]. The amplification observed is of the order of 50 light quanta emitted per one incident quantum. Low[116] 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[117] and by Ranby[118].

Following the use of El. for the production of self -luminous half-tone pictures,[119] Harman[120] designed El. microwave receivers. The fact that the lamps are cool in operation and two dimentional, suggests a number of applications in photography and dark room processes[121]. e.g. as dark room safe lights, transparency 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 computor and (or) video information for use in training devices, are described by Lakshmanan and Munt.[122] The display system was improved by Martel[123] and used for reproducing dynamic radiation images.

The selectivity of El. technique[124] as applied in analysis of aromatic hydrocarbons is found to be superior to that of conventional 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[125] used El. 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[126] describes the present situation of industrial El. 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 diodes, emitting infra-red and red light. The latter were used for various purposes. However,introduction of multi-element image display paneles, has charged the out look and brings back the former II - VI El. in its various forms by large scale integrated thin film transistor (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, α - numeric- graphic displays, radar screens, and simple miniature lamps, which would find extensive applications.

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