Chapter II

Theory & Mechanisms

![Diagram showing the transition between excited and ground states with fluorescence emission.]
2.1 Introduction

This chapter includes the theoretical details associated with the phenomena of photoconductivity and photoluminescence. Some simple models needed for discussion of these phenomena are dealt first, followed by the mechanism involved in them.

2.2 Some Simple Models
2.2.1 Energy Band Model

The energy states of an isolated atom, derived by Schrödinger wave equation are found to consist of discrete levels separated by region are broadened into bands due to interaction with crystal lattice (Mott and Gurney 1940, Seitz 1939). The highest occupied energy band filled with electrons is known as valence band, and the lowest unoccupied energy band is called conduction band. Non-periodicity due to presence of impurities of lattice irregularities in crystal lattice gives rise to localized levels in the forbidden band. As a result of absorption of energy equal to or greater than the band gap energy, electrons are raised into conduction band leaving behind a positive vacancy known as hole. When the hole migrates into a centre where an electron can recombine with it, this process may give rise to luminescent emission (radiative transition) or may be lost as heat (non-radiative transition). Fig (2.1) shows different kinds of possibility of transitions. Transition ‘A’ is the direct band transition with the wavelength approximately equal to band gap energy. Radiation of energy less then band gap energy may be absorbed by an impurity centre which may result in a transition either to the excited state of the centre ‘C’ or to the conduction band ‘B’ giving rise to band on the longer wavelength side of the
fundamental absorption band. The absorption of energy may also result in a transition in which the hole migrates to the luminescent centre and captures its ground state electron, the loss of which is compensated by an electron from the conduction band; such recombination of electrons with centre gives rise to luminescence.

Schön-Klasens (1942, 1946) and co-workers (1948) proposed a model which is shown in fig (2.2). Free electrons and holes are produced (1) due to absorption of light in the fundamental absorption band. The hole migrates to the impurity centre (2) and captures the electrons from located there (3). This leaves impurity centre vacant so that an electron from conduction band may diffuse to it (4) and when captured (5) gives off the excess energy as emission. The cycle is completed in this way and the process may be repeated. According to this model the decay time of photoconductivity and luminescence.
(Lambe and Kilck 1955) would be expected alike contrary to the observed decay of photoconductivity, which is many times less than that of luminescence. A possible solution to this contradiction may be considered due to presence of non-radiative centres having small cross section for electron and large cross section for holes.

Lambe and Klick (1955, 1956) proposed a model to account for the above-mentioned difference. This model is shown in fig (2.3). The free carrier, which plays the essential role in this model, is hole. Due to absorption of light electron hole pairs are created (1) which gives rise to photoconductivity due to movement in their respective bands (2 and 4). The hole then diffuses to impurity centre where it captures the electron from the centre (3) and gives rise to emission. Finally electron wandering in the
conduction band is captured (5) by the centre with a release of small amount of energy as infrared radiation of vibrational quanta. Since the luminescent transitions and the capture of free electrons occur in different parts of the cycle, a difference in time constant of decay of luminescence and photoconductivity is expected.

Prener and Williams (1956) and co-workers (Apple and Williams 1959, Williams 1960) proposed a model, which is known as donor-acceptor model. This model is shown in fig. (2.4).
Simultaneous incorporation of activator and co-activator in the host lattice results in discrete levels of acceptor (level I) situated just above the valence band and those of donors (level II) situated just below the conduction band. Luminescent transition takes place from the excited state of donor to the ground state of acceptor. According to this model the photon energy of a donor acceptor pair emission (hv) separated by intra-pair distance (r) is given by

\[ hv \leq E_g - E_d + E_a + e^2 / \varepsilon r \]  

where \( E_g \) is the band energy, \( E_d \) and \( E_a \) are the binding energies of the isolated donor and acceptor respectively, \( e \) is the electronic charge and \( \varepsilon \) is the dielectric constant.
Investigations On Electro-Optical Properties Of Some Chemically Deposited Nano And Bulk Rare Earth Doped Semiconducting Films

of the material. Relative cross section \( \sigma (r) \) for a pair of electron and hole was estimated as (Thomas et al. 1965, Dean and Patric 1970)

\[
\sigma (r) = A r^2 \quad \text{.....(2.2)}
\]

where \( A' \) is a constant

The transition probability of a pair emission is given by (Thomas et al. 1965)

\[
W (r) = W_o \exp \left( -\frac{2r}{r_o} \right) \quad \text{.....(2.3)}
\]

where \( W_o \) is a constant and \( r_o \) is the Bohr radius of the shallower hydrogenic level. This model has been successfully applied by a number of workers (Hopfield et al. 1963, Thomas et al. 1964, 1965, Dean et al. 1969, Shionoya 1966 and Bhushan et al. 1979) to different systems. Bhushan and Diwan (1986) found that in photoconductivity of rare earth doped ZnO; release of electrons from rare earth donors is responsible for sensitisation effect in this system.

There are certain models, which explain the system absorbing exciting energy from the host solid or in a centre called sensitizer and emitting or dissipating energy without movement of charge carrier in centre called activator which is different from that responsible for absorption. Such models are named as cascade mechanism, resonance transfer mechanism and exciton migration mechanism. In cascade mechanism; the radiative transfer of energy takes place through the emission of photons by one centre and the absorption of these emitted photons by the second centre. An essential condition for these mechanisms to hold is that the spectral distribution of sensitizer must overlap the absorption spectrum of activator. In resonance transfer mechanism, non radiative transfer
of energy takes place between sensitizer and emitter (Klick and Schulman 1957) due to near field interaction (Teegarden 1966). For this transfer to be efficient a fairly strong overlap in energy exists between the states of relaxed sensitizer and those of an activator. According to exciton migration mechanism, exciton created due to absorption of exciting energy at the sensitizer is virtually migrated to the activator by return of an electron at sensitizer from excited state to ground state. Thus electron is excited at activator. The efficiency of this process depends on the probability that an activator ion will reside within a critical volume surrounding the sensitizer and hence the concentration of the activator (Windischmann 1970).

### 2.3 Mechanism of Photoconductivity

#### 2.3.1 Electronic Transitions

When a crystal absorbs sufficient energy of light, free electrons and holes are created. After excitation as long as the photo-excited carriers remain free in the crystal they contribute to the photoconductivity. This process of photoconductivity involves the following phenomena:

(i) **Absorption and Excitation**

Optical absorption in solids results from any of the five principle processes (a) excitation of crystal vibrations (b) formation of excitons (c) excitations of free electrons and holes within allowed bands (d) excitations of free electrons and holes from the valence band to the conduction band. The last absorption process involving excitation of electrons across the forbidden gap, gives rise to photoconductivity. Considering the
absorption due to the presence of imperfection, the different transitions are shown in fig (2.5).

Transition-1 corresponds to absorption by atoms of the crystal, producing a free electron and a free hole for each photon absorbed. In transition –2, absorption at localized imperfection in the crystal produces a free electron and a hole bound in the neighbourhood of imperfection for each photon absorbed. Transition –3 corresponds to absorption raising an electron from valence band to an unoccupied imperfection level, producing a free hole and an electron bound in the neighbourhood of the imperfection for each absorbed photon. The momentum of an electron in one-dimensional case.
\[ P_e = ħk \] \hspace{1cm} ..... (2.4)

and the momentum associated with the absorbed photon in the crystal is

\[ P_{ph} = 2\pi ħν/c \] \hspace{1cm} ..... (2.5)

where ‘\( k \)’ is the propagation or wave vector, \( ν \) is the frequency of light, \( c \) is the velocity of light and ‘\( r \)’ is the index of refraction. For conservation of momentum

\[ Δk = k' - k = 2πrν/c \] \hspace{1cm} ..... (2.6)

one can compare \( Δk \) with the \( k_{max} = \pi/a \), we assume that energy is conserved approximately for both transitions and the energy difference involved is given by \( ΔE = ħν \).

Then

\[ Δk / k_{max} = 2πrν/c = 2πrΔE/ħc \] \hspace{1cm} ..... (2.7)

Now when \( k = 0 \), we get a transitions indicated by a vertical line on a plot of \( E \) vs. \( k \) as shown in fig (2.6). Such vertical transitions are also called direct transitions and are the only important transitions when both conduction and valence band extrema are located at the same value of \( k \). But in many other materials, the conduction band minimum occurs for different \( k \) values from the valence band maximum. In such situations, there is the possibility of indirect transitions \( (Δk ≠ 0) \) along with the direct transitions \( (Δk = 0) \).

Indirect transitions involve either the absorption of both a photon and a phonon or the absorption of a photon and emission of a phonon.

The momentum and energy conservation relation for indirect transitions are given by

\[ k_{pm} = k_f - k_i \] \hspace{1cm} ..... (2.8)
where $k_{pn}$ is the k vector for the phonon and $k_i$ and $k_f$ are the k vectors for the initial and the final states of the transitions. For the conservation of energy

$$E_{pn} + E_{pm} = E_G$$

...... (2.9)

where $E_{pn}$ is the energy of the photon, $E_{pm}$ is the phonon energy and $E_G$ is the width of the forbidden gap. In terms of direct transitions, absorption coefficients can be expressed in the following way

$$\alpha \propto \epsilon_v - E_i^{\gamma/2}$$

for allowed transitions

and

$$\alpha \propto \epsilon_v - E_i^{\gamma/2}$$

for forbidden transitions

---

**Fig. 2.6 Direct and indirect transitions between Valence and Conduction band**
where $E_v$ is the energy of the top valence band, $E_i$ is the energy of initial state from where the transitions is made. For indirect transitions, we have

$$\alpha \propto (E_{pt} - E_G)^2$$

If allowed direct transitions at $k = 0$

$$\alpha \propto (E_{pt} - E_G)^3$$

If forbidden direct transitions at $k = 0$

Absorption may also give rise to excitons, which are electron hole pairs held tighter by Coulomb attraction but free to migrate through a crystal. The presence of excitons is usually manifested by a series of narrow absorption lines at the low energy side of the intrinsic band gap absorption. These appear for measurements at low temperature only, since for most materials the excitons are thermally dissociated at room temperature.

(ii) Tapping and Capture

Once electrons and holes have been freed by absorption of a photon of sufficient energy, they will remain free until they are captured at an imperfection. The capturing centres are classified as trapping or recombination centres.

Fig (2.7) pictures trapping and thermal release of electrons in traps (transitions 5 and 5') and those of holes in hole traps (electron transitions 4 and 4'), (electron transitions 6 and 7) in recombination centres. However, a centre with an energy level lying near one of the band edges will be more likely to act as a trap than as a recombination centre and vice versa for centres with levels lying near the middle of the forbidden gap, the distinction between traps and recombination centres is drawn on the basis of the relative probability of thermal ejection versus recombination. Centre at one
condition of temperature and light level acting as a trap, at another condition of temperature and light level may act as recombination centre.

(iii) Recombination Mechanism

It can be referred as the process of energy transfer by which an excited carrier gives up its energy in order to recombine with a carrier of opposite type that determines the capture co-efficient $C_n$ and $C_p$. The energy transfer can take place through any of the following three ways.

(a) Emission of photons (radiative recombination)

(b) Emission of phonons (non-radiative recombination)
(c) Increase in energy of another free carriers (Auger recombination)

(a) Radiative Recombination

The simplest recombination is that occurring between free electrons in conduction band and free holes in valence band. In this case, the capture coefficient for radiative recombination can be evaluated by equating the absorption of black body radiation with the emission of radiation by a material in thermal equilibrium with its surroundings. This direct radiative transition has been shown in fig (2.8) by transition 8. The energy emitted as photon is approximately the energy of the band gap and the emission is called the edge emission. As in the more usual case, recombination

![Fig 2.8 Electronic Transitions (Recombination)]
may also occur, through recombination centres, either an electron being captured by an excited centre containing a hole (transition 10). These transitions may also be radiative. In these process the capture coefficient for radiative recombination is given as

\[ C_r = \left( \frac{\hbar^2}{8\pi^2 c^2 d(kT)^2} \left( m_e^* m_h^* \right)^{3/2} \frac{E_g}{\hbar c} \right)^2 \]  

\[ \text{..... (2.10)} \]

where \( r \)-is the refractive index, \( d \)-is the thickness in which the photons are absorbed.

(b) Non-Radiative Recombination

In this case, the energy of recombining carrier is dissipated by the emission of phonons. If the initial capture is in an excited state of the centre, recombination occurs with subsequent cascade down to the ground state with non-simultaneous emission of the required number of photons. The maximum cross-section of a Columbian attractive centre can be obtained by knowing the radius at which a free electron diffuses in the centre. The cross section for non-radiative process is given by

\[ S = \pi r_e^2 = 9\pi e^4 / 16\varepsilon^2 (kT)^2 \]  

\[ \text{..... (2.11)} \]

(c) Auger recombination

Auger recombination is a three-carrier process two of which take part in recombination process. When the energy dissipation corresponding to the recombination between photo excited electron and holes occur by a three collision, the excess energy being given up to a third carrier and the process is called as Auger recombination. This recombination process might make use of an exciton, one member of exciton carry off the excess energy to be dissipated in the capture of the other member. This recombination is shown in fig (2.9). For Auger recombination involving an imperfection level, the corresponding lifetime is given by
in n-type of material. The first term expresses Auger excitation of a minority carrier. In most extrinsic materials the second term dominates and the constant B is the Auger recombination co-efficient.

**Fig 2.9 Auger recombination process**

### 2.4 Photoconductivity Process

**General Concept**

(i) **Conductivity**

If \( n \) and \( p \) represent the densities of free electrons and holes respectively and \( \mu_e \) and \( \mu_h \) are the mobilities of electrons and holes, then the conductivity of an insulator or semiconductor is given by
\[ \sigma = e(n\mu_e + p\mu_h) \] 

For a material having more electrons, the dark conductivity is expressed by the following formula: 

\[ \sigma_0 = n_0e\mu_0 \] 

and the conductivity under illumination is 

\[ \sigma = n_e\mu \] 

where, \[ \sigma = (\sigma_0 - \Delta\sigma), \quad n = (n_0 + \Delta n) \quad \text{and} \quad \mu = (\mu_0 + \Delta\mu) \].

By substituting these values in equation (2.15) we obtain 

\[ \Delta\sigma = (\sigma - \sigma_0) = e\mu_0\Delta n + n_e\Delta\mu \] 

Thus, photo-excitation produces change in both carrier density and mobility.

(ii) Lifetime

If \( f \) represents the electron hole pairs per sec. per unit volume created due to photo-excitation, then:

\[ \Delta n_n = f\tau_n \]

and 

\[ \Delta n_p = f\tau_p \] 

where \( \tau_n \) and \( \tau_p \) represent the free lifetime of an electron and a hole respectively.

According to equation (2.17) change in carrier density can occur either by a change in excitation rate ‘\( f \)’ or in lifetime ‘\( \tau_n \)’ i.e.

\[ \delta(\Delta n) = \tau_n\delta(f) + f\delta(\tau_n) \] 

A change in \( \Delta n \) with a change in ‘\( f \)’ is concerned with “normal photoconductivity”. A change in \( \tau_n \) with a change in ‘\( f \)’ must also be allowed since mechanisms governing the
recombination rate and hence $\tau_n$ may change with change in ‘f’. Three ranges may be distributed as:

\[
\Delta n \propto f^1; \quad \tau_n \text{ Constant, independent of ‘f’} \quad \text{..... (2.19)}
\]

\[
\Delta n \propto f^{<1}; \quad \tau_n \propto f^{-a}, \quad 0 < a < 1 \quad \text{..... (2.20)}
\]

\[
\Delta n \propto f^{>1}; \quad \tau_n \propto f^a, \quad a > 1 \quad \text{..... (2.21)}
\]

In the above-mentioned three equations, the behaviour shown by first equation is called linear variation, while second and third equations show the sub linear and super linear variation respectively.

(iii) Photoexcitation Dependence of Mobility

Mobility can be function of photoexcitation by following three simple processes. Firstly, changes in mobility by a factor of two or less are common under photoexcitation intensities. These change the free carrier density by many orders of magnitude in high resistivity semiconductors or insulators. This process is for photoexcitation to remove the charge on charged impurity centres dominating the scattering of free carrier. A second process might involve the excitation of carriers from a low mobility band to a high mobility band, thus producing photoconductivity even though $\Delta n = 0$. In the third process a change in $\mu$ may be considered to result from a photoexcitation reduction of barrier heights to free carrier flow in an inhomogeneous material. If $\mu_b$ represents the mobility of carriers moving though the material with barrier height $E_b$ then it is represented by

\[
ne\mu_b = (ne^{-E_b/kT}) e\mu \quad \text{..... (2.22)}
\]

Where n and $\mu$ are the values in the non-barrier regions of the material, then the mobility
\[ \mu_b = \mu e^{-E_b/kT} \]  

(2.23)

Since \( E_b \) may be reduced by photoexcitation that produces trapping of charged carriers in or near the barriers, the mobility defined in this way becomes a strong function of excitation intensity and temperature.

(iv) Photosensitivity

Photosensitivity (Gain) is defined as

\[ G = \Delta i / eF \]  

(2.24)

Where \( \Delta i/e \) is the number of electrons passing per second and \( F \) is the total number of photons absorbed per second producing electron – hole pairs. Gain is also expressed as ratio of carrier lifetime to transit time between the electrodes

\[ G = \tau_n / t_n \]  

(2.25)

Using the expression of transit time given by

\[ t_n = L^2 / \mu V \]  

(2.26)

Therefore

\[ G = t_n \mu V / L^2 \]  

(2.27)

Thus, the gain is directly proportional to the applied voltage, mobility and lifetime and inversely proportional to the square of the electrode spacing. So, gain is a function of materials and device property.

(v) Quasi or Steady State Fermi Levels

If \( E_{p_h} = E_0 - E_f \) and \( E_{p_e} = E_f - E_v \) then the densities of carriers in a semiconductor are given by

\[ n = N_e e^{-E_{p_e}/kT} \]  

(2.28)
\[ p = N_e e^{-E_{fn}/kT} \] 

From the product of these two expressions

\[ E_{fn} + E_{fp} = kT \ln \left( \frac{N_e N_v}{np} \right) \] 

So,

\[ E_{fn} + E_{fp} = E_g - kT \ln \left( \frac{np}{n_i^2} \right) \] 

Since

\[ E_g = kT \ln \left( \frac{N_e N_v}{n_i^2} \right) \]

In thermal equilibrium

\[ np = n_i^2 \]

and so,

\[ E_{fn} + E_{fp} = E_g \]

The Fermi levels describe the density of free electrons and holes in steady state. Equation (2.32) and (2.33) show that the two steady state Fermi levels are separated by energy equal to \( kT \ln(np/n_i^2) \) as shown in fig. (2.10). The case of occupation of all imperfection levels, which are still essentially in thermal equilibrium under photo-excitation, can also be described by them. Thus the occupation of levels in thermal

[Diagram]
Fig. 2.10 Steady state electron and hole Fermi levels
-equilibrium with the conduction and valence bands may be given by \( E_{fn}^* \) and \( E_{fp}^* \) respectively. Taking the difference between these, we have

\[
E_{fn}^* - E_{fp}^* = kT \frac{(m_e^* m_h^*)^{3/2}}{p/n}
\]

….. (2.35)

This is valid for thermal equilibrium as well as steady state equilibrium

(vi) Growth and Decay Curves

To discuss the growth and decay of photoconductivity we shall consider the following facts: (1) The very slow growth of photoconductivity found under suitable circumstances (2) The increase in the decay rate attainable when thermal freeing of holes from sensitizing centres competes with thermal freeing of electrons from traps (3) growth and decay transients involving overshoots and undershoots of the equilibrium value and (4) the effect on the decay of the photoconductivity caused by the application of high electric fields for short periods during the decay.

Decay curves can be expressed by the expression,

\[
\Delta i = \Delta i_0 / (1 + at)^b
\]

….. (2.36)

where ‘a’ and ‘b’ are constant which may vary with light intensity and temperature during the decay time. The growth and decay curves of photoconductivity must include the contribution of traps. The probability of an electron (hole) escaping from a trap with depth \( E \) and cross-section for capture of an electron (hole) \( S_e \) at a temperature \( T \), is given by

\[
P = N_{eff} VS_e \exp \left(-E/kT\right)
\]

….. (2.37)
where, $N_{\text{eff}}$ is the effective density of states in conduction (valence) band. If the possibility of re-trapping of freed electrons by empty traps is neglected, the rate of change of trapped electrons during decay is

$$\frac{dn_t}{dt} = -n_t P$$  \hspace{1cm} (2.38)

The solution of the above equation is

$$n_t = n_0 \ e^{-P_t}$$  \hspace{1cm} (2.39)

The decay equation is given by

$$\Delta n_t = n_0 \ \tau \ Pe^{-P_t}$$  \hspace{1cm} (2.40)

where the lifetime

$$\tau = \{vS, N_r\}^{-1}$$

If there are many different kinds of traps, with different $E$ value (depths), the resulting decay curve can be considered as the sum of many exponentials of the form given in eq. (2.40). If retrapping is included the rate of trap emptying must be multiplied by the ratio of the capture probability for recombination centres and empty traps in equation (2.38).

Usually uniform distribution of traps is considered. The form of distribution can be obtained from measurements of decay by using the equation

$$\frac{\tau}{\tau_0} = \left(\frac{n_t}{n}\right) kT/n$$  \hspace{1cm} (2.41)

where $\tau_0$ is the measured decay time, $\tau$ is the lifetime of a free carrier as determined from the gain under steady excitation and $(n_0)kT$ is the density of traps on a width $kT$ of the forbidden gap below the location of the Fermi level during steady excitation.
(vii) Spectral Response

One way to calculate the shape of the spectral response curve is to consider the competition between excitation at a certain depth from the surface on which the radiation is incident, with diffusion to the surface recombination and with volume recombination (Devore 1965). The geometry is shown in fig. (2.11).

Fig 2.11 Geometry for the calculation of photoconductivity excitation spectrum when the excitation is incident normal to the electric field direction

If it is assumed that the radiation is incident on the crystal at right angle to the direction of the applied electric field, the rate of change of density of excited carriers at a distance x from the surface is

\[ \frac{dn(x)}{dt} = Ae^{-\alpha x} - \frac{di}{dx} - \frac{n}{\tau} \]  

\[ \cdots (2.42) \]

The first term on the right represents the generation rate and is related to total light absorbed (L) by the relation
\[ L = \int_{0}^{\infty} A e^{-ax} = A/\alpha \]  

….. (2.43)

The second term is the diffusion term with

\[ i = n dx/dt = -D dn/dx \]  

….. (2.44)

where, \(D\) is the diffusion constant for the minority carriers. The steady state from of equation (1.64) is given by

\[ d^2n(x)/dx^2 = n(x)/D\tau - (L_\alpha / D) e^{-ax} \]  

….. (2.45)

The general solution of equation (2.40) is

\[ n(x) = C_1 e^{x/(D\tau)^{1/2}} + C_2 e^{-x/(D\tau)^{1/2}} + \{L_\alpha \tau /(1 - \alpha^2 D\tau)\} e^{-ax} \]  

….. (2.46)

This general solution is subject to the following two boundary conditions

\[ i = n_0 S = D dn/dx \bigg|_{x=0}; i = n_1 S = D dn/dx \bigg|_{x=1} \]  

…… (2.47)

Where ‘S’ is the surface recombination velocity. The complete solution is obtained by applying the boundary conditions of equations (2.47) to the particular solution of equation (2.46) and then integrating

\[ n = \int_{0}^{1} n(x) dx \]  

….. (2.48)

The result of this calculation can be written in the following form, using dimensionless parameters to emphasize the physical process acting

\[ n/L\tau = (1 - e^{-z})/[1 + R \coth (W / 2)] \times [(1 + RW [W \coth (W / 2) - Z \coth (Z / 2)]) / (W^2 - Z^2)] \]  

….. (2.49)

where ‘W’ is the thickness parameter, given by

\[ W = 1/ (D\tau)^{1/2} \]  

….. (2.50)
It represents the ratio of the thickness of the crystal to one diffusion length, i.e. the distance covered by diffusion in a lifetime. The parameter ‘\( R \)’ is the recombination parameter

\[ R = \frac{S \tau}{(D \tau)^{1/2}} \]  

..... (2.51)

this is proportional to the lifetime for volume recombination divided by the lifetime for surface recombination. The parameter \( Z \) is the absorption parameter

\[ Z = \alpha I \]  

..... (2.52)

There are certain limiting cases that illustrate the applicability of this solution and that are observable upon inspection of equation (2.52). If the absorption is very weak, \( Z \) and \( n \) both go towards zero. If the absorption is very strong, \( Z \) becomes very large and \( n \) becomes a constant. If the material is very thin, \( W \) goes to zero and there is no maximum in the \( n \) and \( \lambda \) curve. But if \( R \) is large, corresponding to a high surface recombination probability, then a maximum is found.

(viii) Electrical Contacts (Electrode Effects)

For photoconductivity studies one of the pre-requisites is the use of proper electrodes. The ideal electrode should have no resistance and should not be affected by illumination, temperature variation and appropriate fields. There are a number of factors, which control the behaviour of semiconductor or insulator metal constant. The important factors, which control the behaviour, are (a) improper matching of work functions between the metals and semiconductors (b) presence of the surface states of the semiconductors producing an intrinsic surface barriers (c) presence of a thin layer of third
material which in turn causes barrier for reasons (a) and (b). Considering work function as a dominant factor, following kinds of contact can be considered.

**(a) Non-Ohmic Contact**

Considering a contact between a metal and a n-type of semiconductor having the work function of the metal greater than that of the semiconductor, transfer of electrons from semiconductor to metal occurs as shown in fig.(2.12). In this case, depletion layer result in semiconductor from which all free electrons have been removed. If it is considered that the total change in this region comes from ionised donors, then the potential distribution in the depletion layer, is given by

\[
\frac{\partial^2 V}{\partial x^2} = -4\pi N^+ e / \epsilon 
\]

….. (2.53)

where, \(N^+\) represents the ionised donor density. The solution of this equation is

\[
V = -2\pi N^+ e x^2 / \epsilon 
\]

….. (2.54)

The thickness of the depletion layer is given by

\[
d = (\epsilon V_0 / 2\pi N^+ e)^{1/2} 
\]

….. (2.55)

The current voltage characteristic of such a contact is also shown in fig. (2.12). When the metal contact is positive with respect to the semiconductor, the barrier for electron flow from semiconductor to metal is reduced and large currents flow. When the metal contact is negative (the cathode) however, only very small currents can be drawn until very high voltage is applied and the barrier breaks down from some process such as tunnelling from the metal into the semiconductor. The capacitance associated with such a barrier of depletion layer is given approximately by the relation

\[
C = \epsilon A l / (4\pi l) 
\]

(With no applied bias voltage)
Fig 2.12 Potential barrier of a non-Ohmic contact

\[
1/C^2 = \frac{8\pi V_0}{\varepsilon A^2 N^+ e} \quad \text{..... (2.56)}
\]

Or with a positive bias of \( V \)-volts

\[
1/C^2 = \frac{8\pi (V_0 - V)}{\varepsilon A^2 N^+ e} \quad \text{..... (2.57)}
\]

Form this relation it is clear that form a plot between \( 1/C^2 \) and applied voltage a straight line is obtained with slope related to \( V_0 \).

If these are acceptor levels in the material then \( N^+ = N_D - N_A \). In this case photoexcitation will result in capture of photoexcited holes by this acceptor resulting in increase of positive charge in depletion layer. Photoconductors having non-ohmic electrons can give gain greater than unity.

Chapter II
(b) Ohmic Contacts

If a junction is made between a metal and n-type semiconductor for which the work function for metal is smaller than that of the semiconductor, transfer of electrons from metal to semiconductor will occur as shown in fig. (2.13), the result is an accumulation layer of excess charge in the semiconductor. The I-V characteristic of such a contact is also shown in the same figure. The I-V characteristics of such type of contact are Ohmic over a range of voltages. At a sufficiently high voltage the injected charge becomes comparable to the charge already present in the semiconductor itself after that a space charge limited current flows. The potential variation with distance is described by the following equation

$$\frac{\partial^2 V}{\partial x^2} = -4\pi e^2 n(x)/\varepsilon$$

\[\text{Fig 2.13 Ohmic contact between a metal and semiconductor}\]

\[\text{\ldots (2.58)}\]
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\[ V(x) = 2kT \ln \left[ \frac{x}{x_0} + 1 \right] \quad \ldots (2.59) \]

Where

\[ x_0 = \left( \frac{e kT}{2\pi e^2 n_0} \right)^{1/2} \quad \ldots (2.60) \]

So that,

\[ n(x) = n_0 \frac{x_0}{(x + x_0)^2} \quad \ldots (2.61) \]

Under the application of an electric field, the potential distribution is found as shown in fig. (2.13). The accumulation layer behaves like virtual cathode to supply charge to the semiconductor to maintain charge neutrality.

(c) Injection

When charges move into a crystal from an ohmic contact under the effect of an applied electric field to produce a condition of non-charge-neutrality resulting in the space charge limited current, the phenomenon is known as single injection if only one type of carries are injected. The significance of injected current is that the dielectric relaxation time of the material be equal to the transit time of the injected carrier, i.e.

\[ V = \frac{4\pi \sigma L^2}{\varepsilon \mu} \quad \ldots (2.62) \]

If Ohmic contacts for both types of carriers are present on a crystal, application of voltage leads to injection of both electrons from cathode and holes from the anode. Such phenomenon is called double injection. The current density is given in terms of the total injected charge.
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\[ j = \mu_e \mu_h \tau V^3 / 4\pi L^5 \]  

….. (2.63)

Mayer et al. (1965) have found \( V^3 \) variation in a p-I-n silicon junction device.

2.5 Models for Photoconductivity

The following models have been considered for the phenomenon of photoconductivity.

(i) Junction Models

When a p-n junction is reverse biased (fig.2.14) there is a high dark resistance for the junction, since the p-region cannot supply free holes to the n-region. Due to photo-excitation an electron hole pair can be formed within a diffusion length of the junction and such pairs can traverse the junction. The photoconductivity process would come to an end when the excited electron-hole pairs cross the junction. The maximum gain in this case is greater than unity. In a p-I-n junction a high resistive intrinsic region is introduced between p – type and n-type regions and the collections of photo-excited carriers can be controlled by an applied electric field.

Fig 2.14 A barrier of height \( E_b \) to the majority carrier (electron) flow
In a n-p-n junction the forward bias p-n junction plays the role of an electrode that replenishes electrons and hence it is possible to have gains greater than unity. The gain $G$ is expressed as:

$$G = \frac{L_{pn} n_e \mu_e}{w_p \mu_n} \quad \ldots \quad (2.64)$$

Here $L_{pn}$ represents the diffusion length of the holes in the first n-region. The gain in such junctions may be as high as several hundreds. Apart from the above mentioned regions in thin films or layers of photo-conducting materials inter-grain barriers in a poly crystalline layer also occur whose heights are reduced due to photo-excitation. The conductivity in presence of thin barrier is given by:

$$\sigma = n e^2 \nu_a l_b e^{-E_b / kT} / kT \quad \ldots \quad (2.65)$$

Where, $\nu_a$ is an appropriate average velocity and $l_b$ is the average distance between barriers. If one considered $\sigma = n e \mu_b$, we have

$$\Delta \mu_b = -e \nu_a l_b \Delta E_b e^{-E_b / kT} / kT \quad \ldots \quad (2.66)$$

The barrier height changes presumably due to the trapping of minority carriers in the immediate vicinity of the barrier. Since $\Delta n$ due to photoexcitation is determined by lifetime of free majority carriers, so under these conditions the trapping time of minority carriers, captured near the barrier before recombination with a majority carrier takes place which determines the $\Delta \mu_b$ due to photoexcitation. Therefore if the $\Delta n$ modulation is important, one is concerned about majority carrier lifetime and if $\Delta \mu_b$ modulation is important, then the concern is made about the trapped time of minority carriers near the barriers. However, quite different behaviour is found for PbS films (large $\Delta \rho$ and small $\Delta \mu$) and Cd(S-Se) (large $\Delta \mu$ and small $\Delta n$)
(ii) Models for Homogeneous Materials

Five simple models are illustrated in fig. (2.15) these depend on (i) nature of the contact suitable for such materials and (ii) the freedom of a carrier to move through the crystal. In system 1, (fig 2.15a) electrodes are Ohmic for both electrons and holes and thus both electrons and holes are free to move through the crystal. Only direct recombination between a free electron and a free hole terminates the additional conductivity resulting from photo-excitation.

![Fig 2.15 Models for Photoconductivity in a homogenous material](image)

The gain is the sum of the electron and hole gains and is given by the following equation:

\[
G = \frac{(\tau_n \mu_e + \tau_p \mu_h)}{l^2} V
\]

..... (2.67)
In system- 2 fig.(2.15b) the cathode is Ohmic for electron flow but the anode is blocking for hole flow. Both electrons and holes are free to move through the crystal. Here the hole lifetime is terminated when the hole passes out of the crystal at the cathode, thus the hole lifetime is equal to the hole transit time. When the replenishment of electrons stops, then the lifetime of electron is also equal to the hole transit time. The gain is given by the following equation-

\[ G = \frac{\tau_p}{\tau_n} + 1 = \frac{(\mu_e + \mu_h)}{\mu_h} \quad \text{(2.68)} \]

The gain exceeds unity but not by as large as in system-1. In system-3, fig.(2.15c) describes the situation; neither the system is ohmic neither for electrons nor for holes. This is the case for homogeneous material with two blocking contacts. It is analogous to the case of p-n junction. In such system, the maximum gain is unity. In system-4, fig. (2.15d) the cathode is ohmic to electron flows but the anode is non-ohmic for hole flow. In addition, only electrons are free to move through the crystal because of photoexcited holes being captured at imperfections. The gain is contributed slowly by electrons and is given by equation 2.27. The electron lifetime depends on the capture cross-section of the imperfections, if this cross section is sufficiently small, large values of \( \tau_n \) and \( G \) results. This system is the homogeneous analogous of the n-p-n junction case. In system-5 fig.(2.15e), the contacts are blocking and only electrons are free to move through the crystal. In this case, no steady state photoconductivity is possible, since a positive space charge builds up in the crystal to counter balance the applied electric field.
2.6 Photoluminescence

Photoluminescence is the optical radiation emitted by a material (in addition to thermal equilibrium of black body radiation) resulting from its non-equilibrium state caused by an external light excitation (Bhattacharya, 1997). A material will emit radiation only when the excitation energy is absorbed. That is photoluminescence basically involve absorption and emission of radiation.

2.6.1 Theories of Luminescence

Luminescence systems (including PL) can be divided into three categories (Byrant 1972): (a) System in which the transport of energy by charge carrier is the dominant features (b) System in which absorption occurs in one centre and luminescence is emitted by another centre, the energy transfer taking place without accompanying movement of charge carriers and (c) System in which the absorption and emission of energy both take place in the same centre.

(i) Systems involving energy transfer with movement of charge carriers

Certain systems involve the luminescent phenomenon that accompanies the movement of charge carries within the crystals. Such phenomenon is generally explained in terms of energy band model (Bloch 1992, Mott and Gurney 1940 and Seitz 1937). The concept of the formation of valence band, conduction band and forbidden band gap has been discussed earlier. Any incorporation in the crystal lattice e.g. impurities, vacancies and lattice defects etc. give rise to localized discrete levels in the forbidden gap. When the matrix lattice absorbs energy equal to or greater than the band energy \( E_g \) electrons are raised to the conduction band along with the creation of a positive vacancy.
corresponding to raising of each electron known as ‘hole’ in the valence band. The impurity center may absorb radiations of energy less than $E_g$, which results in a transition either to the excited state of the center or the conduction band giving rise to an emission band on the longer wavelength of the absorption band. Some electrons of conduction band may be captured by the electron traps, which are released only after sufficient activation energy is supplied.

On the basis of this energy band scheme different workers proposed a number of models e.g. Schön (1942) and Klasens et al. (1948), Lambe and Klick (1955, 1966), Prener and Williams (1956) to explain the various observations on different materials. All these models are already described in section 2.2.1.

(ii) System Involving energy transfer with no movement of charge carriers

The mechanisms discussed in this section explain the luminescence in systems, which absorb energy from the host-solid or from a centre and emit or dissipate the energy without movement of charge carriers in a centre different from the one responsible for absorption. When host lattice is responsible for absorption phenomenon it is called host sensitized luminescence and if it appears in presence of some impurities then it is called impurity sensitized luminescence. Energy may be transferred by the three mechanisms (a) Cascade mechanism, (b) Resonance mechanism and (c) Exciton migration mechanism. These mechanisms have already been described in section 2.2.1.

Bettinelli et al. (1990) reported non-resonant energy transfer between $\text{Tb}^{3+}$ and $\text{Eu}^{3+}$ in the cubic $\text{CS}_2\text{NaTb}_{1-x}\text{EuCl}_6$ crystals with $x=0.01-0.15$. He studied luminescent decay for $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ emission at 80K and 293K using pulsed dye laser excitation with
the $^5D_4$ state of Tb$^{3+}$ and $^5D_1$ state of Eu$^{3+}$. For excitations of Tb$^{3+}$, efficient energy transfer occurs to the $^5D_6$ state (but not the $^5D_4$ state) of Eu$^{3+}$ and these is fast energy migration with the $^5D_4$ state. Earlier Rochat et al. (1988) investigated inter subband electroluminescence in a quantum cascade structure based on vertical transition designed for far- infrared ($\lambda = 88\mu$m) emission.

Transfer of energy by resonance process to a ‘killer’ or poison center, which is degraded without luminescent emission give rise to concentration quenching phenomenon (Dextor and Schulman 1954). Rapid resonance non-radiative energy transfer in alexandrite crystal has been reported by Basun et al. (1990).

Exciton energy transfer was reported by Wiesner et al. (1975) in GaP: N Lee et al. (1988) found radiative recombination in PL of GaP : Te crystal to be due to exciton.

(iii) Systems involving absorption and emission in simple centers

Following models explain the luminescence in system in which both the absorption and emission take place at the same center.

(a) Configuration Co-ordinate Model

The interaction between the luminescent emitting center and crystal lattice, particularly for the case of a quasi-atomic emission system can be represented by using a single coordinate to give the distance between luminescent ion and its nearest neighbors in the surrounding lattice (Curie 1963).
The ordinate represents the total energy of the system corresponding to the ground and excited states of the centre (including both ionic and electronic terms) and the abscissa represent the distance between the ions. The model is illustrated in fig. (2.16), the equilibrium position of the ground state is at A. If the center absorbs the energy, it is raised to the excited state B. According to Frank-Condon principle the transition is vertical one since it occurs in a shorter time as compared to the time necessary for an ion to move appreciably. As shown in the figure, it moves to a new equilibrium at C by giving off the energy difference between B and C as lattice vibrations. The center may
now return to the ground state D by the emission of the luminescent light. The center relaxes from D to A by again giving energy to the lattice vibrations. The energy of the emitted photon is thus smaller than that of the absorbed photon because of the energy transfer to the lattice vibrations, this shift to the lattice vibrations. This shift is called as “Stoke’s Shift”.

This model also accounts for a sudden decrease in luminescence efficiency of a center at elevated-temperatures. Having given sufficient thermal energy, a center in the excited state at C might reach a point E and make the transitions to the ground state there. In such a process the usual photon may not be emitted and thermal quenching of luminescence would be observed (Mott and Gurney 1939).

Two other models were suggested to explain the radiation less transition between an excited and the ground state. These models are shown in fig. (2.17). In the first case fig (2.17a), after absorption of light the system relaxes to such an extent that its minimum lies outside the ground state (B) (Seitz 1939) and in the second case, fig (2.17b), the center in the excited state reaches to such a point from where before coming to equilibrium state it returns directly to the ground state of the system (Dexter and Klick 1955). In both the cases usual photon would not be emitted and thermal quenching of luminescence would be observed.
At elevated temperature, the efficiency of luminescence is given by

$$\eta = \frac{P_L}{P_L + P_T}$$  \hspace{1cm} \ldots (2.69)$$

where ‘$P_L$’ represents the probability of luminescent transition and is equal to reciprocal of the decay time $\tau$; $P_T$ represents the probability of radiation less transition and is given by

$$P_T = S \exp \left( \frac{-E_Q}{kT} \right)$$  \hspace{1cm} \ldots (2.70)$$

Where ‘$E_Q$’ is the energy of the intersection point above the minimum of the excited state, ‘$k$’ is the Boltzmann’s constant and ‘$S$’ is the frequency factor.
This classical model predicts a variation in band width proportional to the square root of the temperature (Mott and Gurney 1940). This prediction is not followed by a variety of materials in low temperature region. The quantum mechanical picture of this model, in which the centre is assumed to have the features of a harmonic oscillator, accounts for the low temperature behavior. For an oscillator of frequency $\nu$, this consists of a series of equidistant levels separated by $h\nu$; the lowest level is $h\nu/2$ above the classical minimum. The transition from the vibrational level ‘$n$’ of the excited state $E^e$ to the level ‘$m$’ of the ground state ($E^g$) leads to an emission of a line with frequency $\nu_{nm}$ given by:

$$h\nu_{nm} = E^e_n - E^g_m$$ .... (2.71)

The assembly of these lines of all possible values of $n$ and $m$ form emission band. The same idea applies to absorption. By this assumption the model would lead to a low temperature spectra consisting of large number of closely spaced lines. However, in most of the cases this fine structure is not observed due to sufficient broadening of levels. According to this model the bandwidth ($\omega$) of the absorption and emission band of simple system should satisfy the relation (Curie, 1963).

$$W = W_0 (\cot h\nu / 2kT)^{1/2}$$ .... (2.72)

where ‘$W_0$’ is the bandwidth at absolute zero temperature. This expression fits the experimental data within the experimental error (Russell and Klick 1956). Bhushan and Chukichev (1988) found this relation true for ZnO by studying CL emission from liquid Helium temperature to above.
2.7 Classification of Photoluminescence in Solids

Photoluminescence in solids, i.e., in inorganic and organic insulators and semiconductors, is classified in terms of the nature of the electronic transitions producing it.

2.7.1 Intrinsic Luminescence

There are three kinds of intrinsic luminescence: (i) band to band luminescence, (ii) exciton luminescence and (iii) cross luminescence.

(i) Band to band luminescence.

Luminescence owing to band-to-band transition, i.e., to the recombination of an electron in the conduction band with a hole in the valence band can be observed in very pure crystals at relatively high temperatures. This has been observed in Si, Ge and some III-Vb compounds such as GaAs. At low temperatures, this luminescence is transformed into exciton luminescence. Light emission from very bright type light-emitting diodes and semiconductor lasers is due to the band-to-band transition (Shionoya 1998).

(ii) Exciton Luminescence

An exciton is a composite particle of an excited electron and a hole interacting with one another. It moves in a crystal conveying energy and produces luminescence owing to the recombination of the electron and hole. There are two kinds of excitons: the Wannier (or Wannier Mott) exciton and the Frenkel exciton.

The Wannier exciton model expresses an exciton as composed of an electron in the conduction band and a hole in valence band bound together by the Coulomb interaction. Thus, a Wannier exciton is analogous to a hydrogen atom. This model works
well for inorganic semiconductors such as III b- Vb and IIb-VIb compounds. The exciton emits luminescence by the recombination of the electron and the hole composing it.

Wannier excitons are stable only at relatively low temperatures, where the binding energies of excitons are higher than the thermal energy, luminescence of Wannier excitons is observed only at such temperatures. At higher temperatures where the thermal energy is higher, the excitons are no longer stable and band-to-band luminescence appears instead.

The Frenkel exciton model is used in cases where the expanse of the electron and hole wave functions is smaller than the lattice constant. Typical examples are organic molecular crystals such as anthracene and tetracence and inorganic complex salts including transition-metal ions such as Vandates (e.g. VNO₄), Tungstates (CaWO₄) Cyanoplatinates [Ba Pt (CN)ₙ . 4H₂O], and Uranyl salts (CS₂UO₂Cl₄). In these materials the excited state of an isolated molecule or a complex ion transfers from molecule to molecule or from complex ion to ion usually owing to the dipole-dipole interaction. It is, therefore regarded as the exciton state. Luminescence characteristics are similar to those of isolated molecules or complex ions.

(iii) Cross Luminescence

Cross luminescence is produced by the recombination of an electron in the valence band a hole created in the outmost core band (Van Eijk 1994). This luminescence was first observed in BaF₂ under X-ray pulse excitation in 1982. It has now been observed in a number of alkali and alkaline earth halides and double halides.
Cross luminescence can take place only when the energy difference between the top of the valence band and that of the outmost core band is smaller than the band gap energy, i.e. $E_{c-v} < E_g$. If, on the other hand $E_{c-v} > E_g$, an Auger process occurs so that the hole in the outmost core band is filled nonradiatively with an election in the valence band. Therefore, the cross luminescence is observable only in materials satisfying the condition $E_{c-v} < E_g$. A notable characteristic of cross-luminescence is that the decay time is very fast, of the order of a nanosecond or less. It is this characteristics that enable crystals showing efficient cross-luminescence to be used as scintillators.

### 2.7.2 Extrinsic Luminescence

Luminescence caused by intentionally incorporated impurities in most cases metallic impurities or defects is classified as extrinsic luminescence as opposed to intrinsic luminescence. Most of the observed types of luminescence that have practical applications belong to this category. Intentionally incorporated impurities are called activators and materials made luminescent in this way are usually called phosphors.

Extrinsic luminescence in ionic crystals and semiconductors is classified into unlocalized and localized type. In the unlocalized type, the electrons and holes of the host lattice, i.e. free electrons in the conduction band, free holes in the valence band, participate in the luminescence process, while in the case of the localized type the luminescence excitation and emission are confined in a localized luminescent centre.
2.7.3 Hot Luminescence

The term hot luminescence designates luminescence whose band lie in that part of spectrum where usual luminescence is observed at high temperatures (Saari and Rebane 1969, Rebane et al. 1973).

The mechanism of hot luminescence excitation in semiconductor at band to band transition consists of the following transition fig. (2.18). If the sample is excited by an exciting light whose quantum energy is much greater than the band gap $\hbar \nu_{ex} > E_g$, the electron will be taken to higher energy levels in the conduction band, and holes will be
formed in the depth of the valence band. Hot electrons and holes form some additions to those carriers that have already lost their excess energy and are distributed over the bands in accordance with the Fermi-Dirac relation. Recombining, these additional carriers emit hot luminescence photons. Hot luminescence also occurs when electrons are in a quasi-equilibrium state but their effective temperature is higher than that of the lattice (Zimin et al. 1990).

The hot luminescence intensity depends on the ratio of relaxation time to the excited state lifetime. The intensities of hot and usual luminescence are often comparable. The study of hot luminescence yields valuable information about the thermalization rate of excited states in solids, atoms and molecules.

### 2.8 Luminescence of Rare Earth Ions

The rare earth ions are characterized by an incompletely filled 4f shell. The 4f orbital lies inside the ions and is shielded from the surroundings by the filled $^5S_2$ and $^5P_6$ orbital (Blasse and Grabmaer 1994). The allowed optical transitions of the rare earth ions consists of two different types, namely charge transfer transitions, $(4f^n \rightarrow 4f^{n-1}5dL^{-1})$ where L is ligand and $(4f^n \rightarrow 4f^{n-1}5d)$ transitions, charge transfer transitions are found in rare earth ions which can be reduced while $4f \rightarrow 5d$ transitions occur for ions which can be oxidized. The trivalent ions that have a tendency to become divalent (Sm$^{3+}$, Eu$^{3+}$, Yb$^{3+}$), show charge transfer absorption bands in the ultraviolet. In the less electronegative Sulphide also, ions like Nd$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$ and
Tm$^{3+}$) show charge transfer transitions. The trivalent ions (Ce$^{3+}$, Pr$^{3+}$, Tb$^{3+}$) show 4f $\rightarrow$ 5d absorption bands in ultraviolet (Blasse and Grabmaier 1994).

All luminescence is the result of the competition between radiative and non-radiative path ways in the relaxation of an electronically excited species. Lanthanide luminescence forms no exception. The multitude of electronic energy levels due to the f-electrons allows for a rich cascade of radiative and non-radiative relaxation processes in excited lanthanide ions.

**Radiative**

In a hypothetical free lanthanide ion, only magnetic dipole (MD) transitions are allowed. These are selected by the $\Delta J=0, +1$ (but $J = 0 \rightarrow J = 0$ is forbidden) rule. Their probability is relatively easily calculated and practically independent of the surrounding matrix. For example in $^5D_0 \rightarrow ^7F_1$ emission line of Eu$^{3+}$. In a coordinating environment, electric dipole transitions are induced as the ligand field mixes odd-parity configurations slightly into the Xe 4f$^n \rightarrow ^5D_0$ configuration. Most of the absorption and emission lines are such induced electric dipole (ED) transitions.

Since ED transitions in Lanthanide ions are induced by the ligand field, their strengths are quite sensitive to it. Strongly asymmetric or strongly interacting ligand fields lead to relatively intense ED transitions. The intensities of some ED transitions are extremely sensitive to coordinating environment, which means that they can be either completely absent or very intense, depending on the ligand field. An example of such a
hypersensitive transition is the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission line of Eu$^{3+}$ (Blasse & Grabmaeir 1994).

**Non Radiative Relaxation**

The excited states of lanthanide ions, however, do not decay solely by radiative processes. In glasses and crystals the electronic excitation energy can be dissipated by vibrations of the surrounding matrix, a process known as multiphonon relaxations.

As a result of vibration (or phonon) mediated non-radiative decay, luminescence of a given lanthanide ion occurs mainly from one state, which is the state that has a large gap with the next lower lying level. More highly excited states are quickly deactivated to this state, since the higher states form a “ladder” consisting of relatively small gaps that efficiently undergo multiphonon relaxation.

### 2.9 Luminescence Quenching in Rare – Earth Ions

The luminescence of a centre is strongly changed or completely quenched by photo ionization as shown in fig. (2.19). (Blasse & Grabmaeir 1994). The luminescence centre A has its ground state in the forbidden gap between the value and conduction bands. Its excited states lies in the conduction band which implies that in the excited state an electron can easily be ionized from the centre to the conduction band. It may recombine non-radiatively with a hole somewhere else so that the luminescence is quenched. The absence of luminescence in La$_2$O$_3$:Ce$^{3+}$ has been ascribed to quenching by photo ionization (Blasse et al. 1990). Closely related to photo ionization and its consequences is quenching of luminescence by electron transfer as shown in fig. (2.20).
Fig 2.19 Photoexcitation followed by photoionisation

The first excited state is one in which only A is excited \((A^* + B)\). A higher energies we fixed a charge transfer state \(A^+ + B^-\) with a large offset. Although \((A^* + B)\) lies at higher energy than \(A^+ + B^-\), the luminescence \(A^* \rightarrow A\) is quenched via the charge transfer state, while many rare earth ions show efficient luminescence in \(\text{YVO}_4\) the ions \(\text{Ce}^{3+}, \text{Pr}^{3+}\) and \(\text{Tb}^{3+}\) do not. This is due to quenching via charge transfer state \((\text{Re}^{4+} + \text{V}^{4+})\) which is at low energy for these three ions and at much higher energy for the others (Blasse and Grabmaier 1994). Not always all the excitation energy is transferred. If only a part of it is transferred, this is called cross relaxation (Blasse and Grabmaier 1994). The \(^5\text{D}_3\) emission on an ion is quenched by transferring the energy difference \(^5\text{D}_3 \rightarrow ^5\text{D}_4\) to another ion, which is promoted to \(^7\text{F}_0\) level as
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Fig. 2.20 Luminescence quenching by electron transfer

\[
\text{Tb}^{3+}(^5D_3) + \text{Tb}^{3+}(^7F_6) \rightarrow \text{Tb}^{3+}(^5D_4) + \text{Tb}^{3+}(^7F_0) \quad \text{...... (2.78)}
\]

Here, the higher energy level emission is quenched in favour of the lower energy level emission. The closely matched energy difference between \(^5D_4\) and \(^5D_3\) levels and the \(^7F_6\) and \(^7F_0\) levels enables this process. The cross relaxation energy transfer depends strongly on inter ion distance (Silversmith et al. 2006).

2.10 Luminescence of Low-Dimensional Systems

Properties of semiconductor materials vary considerably when their characteristic dimensions become smaller than the mean free path of the carriers. A key aspect of semiconductors in low dimension is the modification of the energy levels and the density

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of states owing to the confinement of charge carriers. The charge carriers are localized in the low dimensional crystal and this leads to a broadening in the band gap. The energy band diagram of nanocrystalline material is shown in the fig (2.21).

![Energy band diagram of nanocrystalline materials](image)

**Fig 2.21 Energy band diagram of nanocrystalline materials**

Luminescence of low dimensional systems (Yoffe 1993), i.e., two dimensional one dimensional and zero-dimensional systems in which electron and holes are spatially confined causing quantum confinement effects, is one of the recent important and interesting topics in luminescence research. Two dimensional systems include quantum wells and layered materials. Quantum wire and linear chain like materials constitute one dimensional system. Due to quantum confinement effect, energy level structures (shown in fig. 2.22), and hence optical properties, become essentially different from those in three dimensional bulk systems.

Let us consider a very thin semiconductor layer that has a thickness less than the extent of the wave function of electron and is regarded as a two dimensional system. The situation is treated in quantum mechanics as an electron in a well with an infinite barrier.
height. The motion of electron in the direction perpendicular to the layer is quantized.

The energy levels are given by

\[
E_n = \frac{\hbar^2}{8\pi^2m_e} \left(\frac{nn}{L_z}\right)^2 \quad n = 1, 2, 3\ldots 
\]  \quad (2.73)

where, \( L_z \) is the thickness of the layer. In semiconductor quantum wells both electron and holes are quantum confined. Therefore, the absorption corresponding to the band to band transition shifts to higher energies with decreasing \( L_z \). Also in one and zero dimensional systems, the absorption shows blueshift as the characteristic size of the system representing the low dimensionality like \( L_z \) decreases.

Fig 2.22 Schematic illustrating discrete electronic configurations in nanocrystals, nanowires and thin films and enlarged band gap between valence band and conduction band.
Characteristics of excitons in low dimensional system are also substantially different from those in three-dimensional system. The binding energy and oscillator strength are noticeably enhanced in low dimensional systems because of the increase in the overlap of electron and hole wavefunctions. The enhancement becomes generally more significant with decreasing dimensionality. Theoretical calculations for the binding energy in two-dimensional system show that in the two dimensional limit corresponding to $L_z=0$ the binding energy reaches a value as high as four times that of three-dimensional systems. Further, calculations for one-and zero-dimensional systems give a much more marked enhancement of binding energy than for two-dimensional systems.

As described above, two quantum effects work, towards the transition energy of excitons in low dimensional systems. The first is the effect of the quantization of the motion of electrons and holes causing blue shift with decreasing characteristic size of the system (Cao 2004). The second is the enhancement of the exciton binding energy causing red shifts. In most cases the blue shifts exceed the redshift, so that the net result is that the exciton absorption shows a blueshift with decreasing characteristic size.

Blue shift of peak position in luminescence spectra has been observed in variety of materials, when the radius decreases e.g. CuCl microcrystallites as reported by Itoh et al. (1988); ZnS: Mn$^{2+}$ nanocrystals (Bhargava et al. 1994), CdS super clusters in Zeolites (Herron et al. 1989) and recently CdS:Pr thin films (Bhushan & Coworkers 2010).