CHAPTER III

THEORETICAL APPROACH TO THE
LONG DECAY ELASTICO AND
PLASTICO MECHENOLUMINESCENCE
OF II-VI SEMICONDUCTORS
3.1 INTRODUCTION

The II-VI semiconductors are very interesting materials for their luminescence studies. In the last century the ML produced from natural and synthetic zinc sulphides was studied in detail. However, it has been known long back that the rubbing of the surface of mineral sulpharite (ZnS), fields the visible trails of light. The ML spectra of sphalerite (largely ZnS: Mn) was grossly measured by Levison (1904). The ML was excited by rotating a disc pasted with powdered material suspended in glue. He observed the ML spectrum with naked eyes was extended from 550 nm to about 650 nm. Zinc sulphite was fused with a variety of other compounds, e.g. oxides of manganese, tin or silicon by Karl (1907 a,b) and he studied visually the relative ML intensities of new solids. Waggoner (1916) measured the ML spectra of different samples of ZnS:Mn and he compared the ML spectra with the phosphorescent spectra produced under X-ray excitation. He fond that the ML spectra of all the samples had their maximum intensity at a mean value of 557±5 nm which compares well with the mean value of 557±3 nm, the maxima of the phosphorescent spectrum. This fact showed that there is similarity between the mechanoluminescence and photoluminescence spectroscopy.

Nelson (1926) photographed the ML spectra of four natural sphalerites and one commercially available sample of ZnS:Mn powder. He found that the maximum phosphorescent intensity (excited by mercury arc) occurred virtually the wavelength at around 590 nm and 575 nm, respectively. Chudacek (1967) has reported the gas discharge component in the ML spectra of ZnS:Mn. Obrikat et.al. (1967), Meyer
and Obrikat (1969) and Theissen (1970) made investigations for checking whether the mechanism of ML resembles with that of electroluminescence (EL) and photoluminescence (PL) or not and found positive. The ML spectra of ZnS phosphors with different activators and co-activators were observed by them and they reported that the ML spectra was most closely the same as EL spectra. Curie and Prost (1964) have also suggested that EL might be responsible for the ML of ZnS. Meyer and Obrikat (1969) have also made the similar conclusions on the basis of closeness found in the ML and EL spectra of ZnS phosphors.

By spectroscopic method Meyer (1970) observed the correlation between ML and EL. He found that as the ML intensity has the same functional dependence on force, similarly EL intensity has on voltage. He also found that the temperature dependence and the time decay characteristics in both ML and EL are of similar nature. It was proposed that the ML of doped ZnS phosphors may be due to the deformation stimulated luminescence.

Alzetta et.al. (1962) reported that when a top-hat compressional pulse is applied to Mn doped ZnS power suspended in the oil of a pressure cell, a burst of light was emitted at both the instances of rise and fall of the compressional pulse. Alzetta et.al. (1967) further recorded the pressure pulse in cell with the help of a piezoelectric transducer and the ML output. They also applied a voltage pulse, similar to the pressure pulse, to a cell containing an identical suspension of ZnS:Mn powder and observed the EL output. It was found by them that the ML pulse due to application of hydrostatic pressure pulse to the ML cell was most closely the same as the EL pulse created after applying the voltage pulse to the
EL cell. They also found that by applying a periodic sinusoidal varying pressure to a thin layer of ZnS:Mn powder, through piston connected to an electromagnetic vibrator, the frequency of ML pulses became twice the frequency of applied varying force. This fact also showed a kind of similarity between the ML and EL phenomena.

Sodomka and his co-workers (Sodomka 1963, 1964, 1968, Chudacek and Sodomka 1963, Chudacek 1965, 1966) made several investigations on the ML of II-VI compounds. The ML in luminescent ZnS powder was observed by Sodomka (1963) at different pressures. It was found experimentally that the ML appears only when there is a time change in the applied pressure. Similar experiments were carried out by Chudacek and Sodomka (1963) with Cu doped ZnS. They came to a conclusion that the instantaneous ML intensity of luminophors depends on the instantaneous change of pressure and the ML does not occur until a threshold pressure $P_{\text{min}}$ is attained. Sodomka (1964) recorded the variation of ML brightness with the pressure during impact of a load on the luminescent ZnS:Mn and ZnS:Cu powders. The powder was placed in the solid binding matter, as a layer of 0.1 mm thickness with the weight ratio of two parts of binding matter to one part of luminescent powder having a mean grain size of 20 microns. The above experimental study made by Sodomka (1964) showed that the maxima of luminescent pulse was produced only when the pressure pulse decreased. It was thus suggested by Sodomaka that the luminescent brightness at impact in luminescent powder was caused by elastic and plastic fracture. However, it could not be confirmed whether the ML was produced only by elastic or plastic fracture or by influence of both together.
Chudacek (1965) has studied the periodic ML of ZnS using a magnetic vibrator having a frequency of 50 cycles per sec. The ZnS:Mn or ZnS:Cu or ZnS:Ag was scattered in the form of a suspension in different solids. This experiment proved that periodic ML can be stimulated by periodically supplying fracture energy to ZnS luminophors. The frequency of the periodic ML impulses was the same as that of stimulating mechanical frequency. It was also found by Chudacek that at lower pressures, the ML exhibits periodicity, limited in times and the periodicity of ML disappears at a stimulating pressure of 700 kp/cm² onward. Chudacek (1966) showed theoretically that a recombination centre of the Cu⁺ -S⁻ in the ideal ZnS lattice has “local” piezoelectric properties. He made an attempt to explain the ML stimulation on the basis of this logic.

Chudacek (1967) reported that the ML stimulation in ZnS phosphors occurs in two stages, first, during the plastic and elastic deformation and second during the fracture. In the first stage, the mechanical stress affects the local electric field which ionises the luminescence centres. In the second stage, the bonds between the luminophor atoms are broken, which give rise to a large number of free electrons in the region between the fractured surfaces. The luminophor is disturbed to a certain depth below the fractured space at the moment of fracture, which may in turn create free electrons and holes in the conduction and valence bands in the region below the fractured surfaces. This fact produces space charges which cause the ML stimulation.

Kulp and Gale (1966) studied the electrico luminescence properties of CdS, as a function of hydrostatic pressure and uniaxial stress. The ML
was observed when the stress was being applied to the crystal in the low resistivity state. The integrated intensity of ML was found to be independent of the rate of applied stress over a range of one to ten and the ML consisted of the characteristic green-edge emission and a red luminescence centering at about 660 nm.

Meyer et al. (1970a) carried out further the detailed investigations of both on the pressure dependence of ML and voltage dependence of EL. Samples with variously doped ZnS powder in the form of 0.1 mm thick layers were prepared by them and then both a pressure pulse and a voltage pulse were applied to each sample separately. A transient stress was applied by dropping a fixed weight on to the sample kept at the top of hard glass plate. The nature of the stress curve was measured by a piezoelectric disc placed beneath the sample.

Meyer et al. (1970b) have reported that the maxima of ML intensity $I$ for ZnS:Cu, Cl:ZnS:Mn and ZnS:Cu, where the intensity $I$ varies with the values of compressional stress $\sigma$ in the following way, $I_m=I_o \exp (-\alpha / \sigma^{1/2})$, where $I_o$ and $\alpha$ are constants which are different for different phosphors. But other contemporary workers could not reproduce the results which could satisfy the above mentioned relationship. Alzetta et al. (1962) found that the total quantity of ML intensity $I$ after subjecting a ZnS:Mn powder to a hydrostatic pressure step of magnitude $p$ varies as $I \propto \exp(\beta p^2)$, where $\beta$ is the constant. Myazdrikov et al. (1966) studied the ML of ZnS:Mn,Cu by varying the impacts. The impact were varied by the height from which steel ball is dropped on the sample electroluminescent panel and they observed that amplitude of the ML pulse was proportional to the impact energy of the ball.
Alzetta et.al. (1970) investigated the ML of ZnS:Mn phosphor as a function of strain. Results of sample indicated that 5% of the emitted light was observed in the elastic region, 80 % observed during plastic deformation and the rest 15% at fracture. When the strains were recycled, no light emission occurred in the elastic or plastic region of the second application of strain until the magnitude of the previous applied strains were passed. The dependence of ML intensity on the strain rate was also observed by them.

Scarmozzino (1971) applied rapid pulses of hydrostatic pressure 100 times greater than that required to piezoelectrically produce a sufficient electric field. He studied the electroluminescence and with finding no emission, he suggested that moving dislocations were responsible for ML in these crystals.

Djordjevic (1978) has measured the ML spectrum and the roentgeno-luminescence (X-ray excitation) spectrum of the sample of (Zn, Cd)S phosphors. Both spectra have peak at about 540 nm. However, he has found about a 15 nm difference in spectral peaks of Dopant D-screen (ZnS:Ag) with a photo-peak higher and attributed the difference to pressure effects. The ML spectra were obtained by impulsively deforming the phosphors. He concluded that the ML caused by mechanical deformation of a solid cannot be simply assigned to a new mechanism. The complex energy band structure of imperfect crystals allows a multitude of excitation and relaxation processes. However, he believed that the ML emission is comparable to those other well documented and better understood luminescence phenomena. The difference lies in the process of excitation of electrons, while relaxation
with photon emission involves the same optical transition centres as in the other types of luminescence. He has investigated five inorganic ML materials, viz, (i) zinc fluoride: manganese activated (ZnF$_2$:Mn) (ii) zinc sulphide : silver activated (ZnS:Ag) (iii) zinc sulphide : manganese activated (ZnS:Mn) (iv) calcium pyrophosphate : Dysprosium activated (CaP$_2$O$_7$::Dy) and (v) zinc cadmium sulphide (ZnCdS). It was found that ZnCdS, produced the highest ML light output. The overall purpose of Djordjevics work was to apply the ML concept to a wireless fuse system for the army war head. The concept was tested in several prototypes and proved to be successful (Glass et. al. 1975, 1977). He further made efforts to determine the light output of the ML phosphors (ZnCdS) as dependent upon the bonding resin, thickness of phosphor, substratae material (steel and aluminium), impact pressure (projective velocity), and temperature.

Bredikhin and co-workers experimentally showed that during the process of deformation, the ML pulses occur simultaneously with the sudden decrease in the value of electric field at the surface of the crystals (Bredikhin and Shmurak 1974, 1975, 1977 and Bredikhin et.al. 1975). This field can be detected directly; however, it produces a birefringence in the crystals which decreases abruptly with the formation of each pulse of light. The ML intensity pulse could be eliminated completely if the crystal is immersed in a transparent conducting fluid whereas it could be reduced drastically if the sample is immersed in an insulating fluid such as silicon oil (Ossipyan et.al. 1986). The effect can be observed in the crystals with a sufficiently high resistivity for the breakdown to be reached at the strain rate used. External influence affecting the plastic deformation rate of the sample, such as, application of an external electric
field (Bredikhin and Shmurak 1975), illumination in the activator absorption band (Bredikhin and Shmurak 1979), photoplastic effect (Abromova et al. 1971) etc. result in a synchronous change in the number of ML flashes. The spectrum of the pulsed ML contains one peak centered at a particular wavelength depending on the activator in the crystal, and spectrum consisting of a set of lines. For example, the spectrum of pulsed ML in ZnS:Mn crystals consists of broad peak centred at 585 nm and additionally a set of lines in between 300 and 400 nm. As ZnS crystal is almost opaque to wavelength below 338 nm (the band gap of ZnS corresponds to 338 nm), some if not all of these lines must be produced close to the surface. The spectrum differs from that of a discharge in air, in this case, because there is emission below 290 nm.

Bredikhin and Shmurak (1974, 1975, 1977) investigated the spectral, thermal, temporal and several other characteristics of pulsed ML and showed that this have dislocation origin. In II-IV type crystals, the dislocations of a different mechanical sign show opposite electrical charges. The magnitude of the charge is very large and can attain values close to the magnitude of a single elementary charge per interatomic distance along the axis. During plastic deformation, the charged dislocation of opposite signs moves in opposite directions and brings out the charges to the crystal surface. The potential difference across the crystal increases as the deformation proceeds until it reaches a breakdown value at which the pulse of surface electroluminescence is emitted and this process is repeated continuously while increasing deformation of the crystal. A similar luminescence can be produced without any deformation by the direct application of an external electric field greater than that
about 1.2 MVm\(^{-1}\). The experimentally confirmed criteria, needed for the flash deformation glow to occur are \(\varepsilon > \text{const } q V_{br}/R_s\), where \(V_{br}\) is the breakdown voltage, \(R_s\) is the sample resistance and \(q\) is the linear charge density of dislocations (Ossipyam et al. 1986).

The light output from a deformed crystal dominates in pulsed ML, but if it reduces by immersing the crystals in a conducting fluid or by using a crystal of insufficient high resistivity or by short-circuiting the crystals lateral faces. The continuous ML is observed in ZnS, ZnSe and CdS crystals. The ML intensity increases rapidly with an increasing external stress at \(\sigma \sim \sigma_{el}\), then, as deformation proceeds at a constant strain-rate, it attains a constant value \(I_s\) whose magnitude is a linear function of the strain rate (Bredikhin and Shmurak 1977). The number of light quanta emitted at constant strain rate, i.e. \(N_{ML} = \int_0^t I dt\), is directly proportional to the magnitude of residual deformation of the crystal. A comparison of the curves characterizing a change of the luminescence intensity and that of dislocation current magnitude, on the degree of deformation shows their full identity irrespective of the loading type. This implies that these processes have the same mechanism i.e. both the continuous ML and dislocation current in II-VI compounds are caused by the motion of charged dislocations (Ossipyan et al. 1986, Bredikhin and Shmurak 1975, 1979). A parallel investigation of spectral and temperature characteristics of photoluminescence and continuous ML suggests that in II-VI compounds a continuous ML is an intra-centre glow of activators available, for instance, Cu or Mn ions substituted Zn cations in ZnS crystals lattice nodes (Bredikhin and Shmurak 1979). Valiev (1986) has correlated the plastic-induced ML of II-VI semiconductors,
with moving charged dislocation. Vardanyan et al. (1989) have reported that the ML of II-VI semiconductor involves the radiative electrons transition from the conduction band to deep point centres. When crystals are illuminated with the radiation corresponding to its band gap, electrons are excited and held in deep traps which are stable at room temperature. These electrons can subsequently be released by the suitable illumination or by the heat to produce photoluminescence or thermostimulated luminescence. Bredikhin and Shmurak (1979) have found that prior irradiation of this crystal with ultraviolet radiation increases the continuous ML by a factor of 1.5. It is found that the same treatment increases the dislocation charge by about 30 percent. The thermostimulated luminescence that can be produced by heating and a pre-irradiated crystal is reduced by plastic deformation between the irradiation and heating. This result strongly suggests that the deformation vacates the same traps which give rise to the thermostimulated luminescence.

Chandra (1983) has investigated the mechanoluminescence and has found that the pressure photoluminescence of (Zn, Cd) S phosphors shift towards shorter wavelength side as compared to its photoluminescence spectra. However, the photoluminescence spectra shift towards shorter wavelength side with increasing pressure on the phosphor of less pressure coefficient. He rejected the thermal population mechanism on the basis of this result and suggested the electrical excitation mechanism for the ML excitation. The decay of ML after the deformation of (Zn,Cd) phosphors can be controlled by the recombination rate of holes and electrons, i.e. by the processes requiring finite times for the liberation of
the electrons from the traps and for the electrons transport and consequently the decay of ML. The decay of ML that may be similar to of photoluminescence.

Majumdar (1984) studied the ML of impurity doped II-VI semiconductors and mixed phosphors. According to him intense ML is exhibited by (Zn, Cd) S:Cu phosphors, which is more suitable from the application point of view. The ML spectra of phosphors were found to resemble to either the photoluminescence or electroluminescence spectra. The temperature at which ML ceases was found to be much less as then the melting point of the phosphors, and the decrease in ML intensity with temperature was found to be faster as compared to that in PL intensity.

Vardanyan et.al. (1989) have investigated the ML in plastically deformed semiconductor particularly in II-VI semiconductor. Radiative electron transition from the conduction band to deep centres created during plastic deformation of a crystal in the field of a charged dislocation are reported. It is shown that out of many phonon nature of the process the tunnel effect can explain the profile and width of ML spectra and also the shift of the spectrum relative to the PL spectrum of an unstrained crystal. Polarization effects are predicted from ML. Numerical calculations for the spectral properties of the ML gives a good agreement between the theoretical and experimental results.

Xu and the co-workers have reported that the crystallinity and luminescence properties of ZnS:Mn films get improved by post -annealing at higher temperatures (Xu et.al. 1999a,b,c,d, Xu 1998). Agyman et.al. (2002) have investigated the effect of ZnO film used as buffer layers on the mechanoluminescence (ML) intensity of ZnS: Mn
thin film prepared on quartz substrates which uses the RF magnetron sputtering method and annealing technique. Highly oriented ZnO films was first deposited on quartz glass substrate thereafter ZnS:Mn film was successfully deposited on that ZnO film. By annealing at 5% H$_2$ in Air ambient, the crystallinity of both ZnO and ZnS:Mn film was improved. It was found that the addition of the ZnO butter layer greatly improves the ML intensity of the ZnS:Mn films.

Reddy and Reddy (2002) have reported laser-like mechanoluminescence from the spintronic material ZnMnTe. The luminescence was also observed when the material was exposed to UV and X-rays. Photoluminescence spectra consisted of peaks at 386.5 and 648 nm, which may be correspond to the band gap, and Mn$^{2+}$ levels respectively. Lattice contraction, sharpness of the X-ray diffraction peak, and the blue shift in the energy gap confirm the nanostructure of the material. A possible mechanism for lasting has also been suggested.

Tiwari et.al. (2004) have studied the effect of temperature on the mechanoluminescence of gold - doped ZnS phosphors. Choudhary et.al. (2004) have made theoretical study on the tunneling mechanoluminescence produced during cleavage of II-VI semiconductors.

Hollerman et.al. (2006, 2008) have studied the ML induced by hypervelocity impact by projectile on the backside of a plate of which front side was coated with ZnS:Mn phosphors. Preliminary results indicate that the impacts with the minimum energy of 16 mJ produced measurable ML from ZnS: Mn. Light was generated by the interaction of a dropped mass and the small number of luminescence centers in the ZnS:Mn powder. Hypervelocity impact-induced ML has been observed
for both ZnS:Mn and ZnS:Cu. For ZnS:Mn, the ML produced at impact corresponding to velocities 4.7 and 5.7 km/s were more luminous than that at 3.3 km/s. The ML decay time for ZnS:Mn was found to be approximately 292 ms, which is completely consistent with earlier measurements not using the impact as an excitation source. Further, the emission of ML from ZnS: Mn undergoing hypervelocity impact has been demonstrated to have a significant component at the known peak emission wavelength of ZnS:Mn of 585 nm. Weak ML emission generated as a result of hypervelocity impact was also observed from ZnS:Cu.

Fontenot et.al. (2011) have reported the initial evidence of a mechanoluminescence wavelength shift for ZnS: Mn caused by ballistic impacts. The mechanoluminescence emission spectrum was then recorded as the rounds impacted on target. Results show approximately one-nm shift in the emission spectrum with increases impact energy.

The present chapter reports the theoretical studies on the elastico and plastico ML of the II-VI semiconductors and makes a comparison between the theoretical and experimental results. The salient features of the long decay elastico and plastico ML of II-VI Semiconductors are explored.
3.2 MECHANISMS OF THE ELASTICO AND PLASTICO MECHENOLUMINESCENCE OF II-VI SEMICONDURCORS

3.2.1 Charged Dislocations Induced Detrapping Model of the Elastico ML in II-VI Semiconductors

Among the II-VI semiconductors only ZnS:Mn exhibit elastico ML, plastico ML and fracto ML and the other crystals exhibit plastico ML and fracto ML. The elastic ML of ZnS:Mn crystals produced during the movement of charged dislocations can be understudies with respect the following steps (Chandra 1998, Xu et.al.1996, Nelson 1926).

(i) The elastic deformation causes bending of the segments of charged dislocations between pining points.
(ii) The electric field of the charged dislocations causes bending of the valance band and conduction band as well as dislocation band.
(iii) Subsequently, the electrons from the electron trap tunnel to the conduction band.
(iv) The recombination of electrons with the holes gives rise to the light emission characteristic of the activator ions. In the case of Mn doped II-VI semiconductors, the impact of accelerated electrons in presence of electric field of dislocations with the Mn$^{2+}$ centres may also cause the excitation of Mn$^{2+}$ centres and the subsequent de-excitation may give rise to the light emission characteristic of Mn$^{2+}$ ions. Alternately, the light produced during the electron-hole recombination may excite the Mn$^{2+}$ ions and the subsequent de-excitation may give rise to the luminescence characteristic of Mn$^{2+}$ ions.
As the decay of trapped electron in ZnS: Mn is low of the order of $10^{12}$ cm$^{-3}$ (Chandra 1996), the distance between to trapped electron is large of the order of $10^4$ Å the magnitude of the bending of dislocation segment is much less then $10^4$ Å. Therefore the EML o ZnS:Mn may not be due to the electrostatic interaction between trapped electrons and charged dislocations. Furthermore, the appearance of EML in ZnS:Mn during the application of hydrostatic pressure (Alzeta et.al.1962) also indicate that the EML in ZnS:Mn may not be due to the electrostatic interaction between the trapped electrons and charged dislocations, because dislocation can not move during the application hydrostatic pressure. Thus, it seems that EML of ZnS:Mn is caused by the piezoelectrically-detrapping of electron as discussed in the next section.

3.2.2 Charged Dislocation-Induced Detrapping Model of the Plastico ML in II-VI Semiconductors

The plastico ML of II-VI semiconductors produced during the movement of charged dislocations takes place in the following steps (Chandra 1998, Xu et.al.1996, Nelson 1926).

(i) The plastic deformation causes movement of charged dislocations.

(ii) The electric field of the charged dislocations causes bending of the valance band and conduction band as well as dislocation band.

(iii) Subsequently, the electrons from the electron traps tunnel to the conduction band.

(iv) The recombination of electrons with the holes gives rise to the light emission characteristic of the activator ions. In the case of Mn doped II-VI semiconductors, the impact of accelerated electrons in presence of electric field of dislocations with the Mn$^{2+}$ centres may causes the excitation of Mn$^{2+}$ centres and the subsequent de-excitation may give
rise to the light emission characteristic of Mn$^{2+}$ ions. Alternately, the light produced during the electron-hole recombination may excite the Mn$^{2+}$ centres and the subsequent de-excitation may give rise to the luminescence characteristic of Mn$^{2+}$ ions.

In the case of plastic deformation dislocation lines move from its original position upto the surface of the crystal. Therefore, the dislocation may move the distance greater than $10^4$ Å and therefore, the electrostatic interaction between the filled electron traps and charged dislocation may cause plastico ML in II-VI semiconductor. Since plastico ML appears during the application of hydrostatic pressure on ZnS:Mn crystals, the PML of ZnS:Mn may arise also due to the piezoelectrically-induced de-trapping of electrons. Thus, in ZnS:Mn both the dislocation model and piezoelectric model cause the PML emission. It has been found that, at low strain rate the PML due to movement of charged dislocation is dominating; however, for high strain rate the EML due to piezoelectrically induced de-trapping is dominating in II-VI semiconductors.

### 3.2.3 Piezoelectrically-Induced Detrapping Model of Elastico ML and Plastico ML in II-VI Semiconductors

Both the elastico ML and plastico ML of II-VI semiconductors can be understood with respect to the following points:

(i) As II-VI semiconductors are non-centrosymmetric, the applied pressure produces the piezoelectric field. The application of pressure produces local piezoelectric field in the crystals, whereby the piezoelectric field near activator ions may be high due to the change in the local structure or due to the presence of photo-generated dipoles (Chandra 2011, Chandra et.al. 2013).
(ii) The local piezoelectric field may reduce the trap-depth of the carriers or it may cause the band bending.

(iii) In the case of decrease in trap-depth of the carriers, thermal de-trapping of the carriers may be produced. In the case of band bending, the trapped charge carriers may tunnel to the respective band.

(iv) In the case of Mn doped II-VI semiconductors, the impact of accelerated electrons in presence of piezoelectric field with the Mn$^{2+}$ centres may cause the excitation of Mn$^{2+}$ centres and the subsequent de-excitation may give rise to the light emission characteristic of Mn$^{2+}$ ions. Alternately, the light produced during the electron-hole recombination may excite the Mn$^{2+}$ centres and the subsequent de-excitation may give rise to the luminescence characteristic of Mn$^{2+}$ ions.

It has been found that the ML in ZnS:Mn phosphors is produced by the application of hydrostatic pressure (Alzetta et.al.1962). As the hydrostatic pressure can not cause the movement of dislocation in the crystals, it seems that the ML in II-VI semiconductors are also produced by the piezoelectric field produced during the application of hydrostatic pressure. Generally the ML induced by the movement of charged dislocations arises in II-VI crystals of insufficient high resistivity at low strain rates (Bredikhin and Shmurak 1979); however, the ML induced by the piezoelectric field is produced in II-VI semiconductors, both at low and high strain rates, whereby at high strain rates the ML induced by the piezoelectric field dominates the ML produced by the movement of charged dislocation (Chandra 2011).
As the density of filled electron traps in ZnS:Mn is of the order of \(10^{13} \text{cm}^{-3}\) (Lampert and Mark 1970), the average distance between the two filled electron traps is of the order of 3300\(\text{Å}\). Because the radius of interaction of dislocations with the filled electrons traps is of the order of 100\(\text{Å}\) (Bredikhin and Shmurak 1979), only a few filled electrons traps close to the bending segments of dislocations may interact with the bending dislocations and thus the EML induced by the electrostatic interaction between the dislocations and filled electron traps will be tens. As the piezoelectric field of the photo-generated dipoles is high (Chandra et.al.2013), it seems that, for the elastico ML of ZnS:Mn the piezoelectric field of the charged dislocations is the major cause as compared to the electrostatic field of the charged dislocations. It is to be noted that repeatable EML produced by successive loading, and the EML produced during release of pressure whose intensity is comparable to that produced during the application of pressure cannot be understood on the basis of charged dislocation model, whereas it can be understood on the basis of piezoelectric model.

In the case of plastico ML, both the ML caused by the charged dislocations and piezoelectricities may cause the high emission because, in this case, the dislocations move the significant distance in the crystals.
Fig. 3.1 (a) Schematic diagram of the EML emission in ZnS:Mn crystals (1-detrapping of electron and its movement in conduction band, 2-electron-hole recombination, 3- transfer of energy to Mn$^{2+}$ ion and excitation of Mn$^{2+}$ ion, and 4-emission of light. (after Chandra, 2011).

Fig. 3.1(b) Schematic diagram for the mechanism of plastic-ML in II-VI crystals (after Chandra, 2011).
### 3.3 THEORETICAL APPROACH TO THE CHARGED DISLOCATIONS-INDUCED DE-TRAPPING MODEL OF THE ELASTICO AND PLASTICO ML OF II-VI SEMICONDUCTORS

#### 3.3.1 Theoretical Approach to the Charged Dislocation-Induced Elastico ML of II-VI Semiconductors

The movement of dislocations takes place during the plastic deformation of crystals, but only the bending of dislocation segments takes place during the elastic deformation of crystals. With increasing of bending, the area swept out by the dislocation segments will increase. Assuming that the bending of dislocation segment between the pinning points is proportional to the strain, the area swept out by the dislocation segments can be taken to be proportional to the strain $\varepsilon$ of the crystals (Chandra 2008), that is, $S = B\varepsilon$, where $B$ is a proportionality constant. Therefore, the rate of sweeping of surface area by the bending segments of dislocations can be written as

$$ \frac{dS}{dt} = B\dot{\varepsilon} \quad ----- (3.1) $$

In the II-VI Semiconductors, if $n_t$ is the concentration of filled electron traps of, $r_t$ is the radius of interaction of filled electron traps with dislocations, and $dS$ is the surface area swept out by the dislocation segments in time $dt$, then the transfer of electrons from filled traps conduction band, in time $dt$ is given by $n_t r_t dS$ (Chandra et. al. 2009). Thus, the rate of transfer of electrons from electron traps to the conduction band can be expressed as $n_t r_t dS/dt$. As the rate of generation $g_i$ of interacting filled electron traps will be equal to the rate of transfer of electrons from filled electron traps to the conduction band, we can write

$$ g_i = n_t r_t \frac{dS}{dt} \quad ----- (3.2) $$
From Equation (3.1) and (3.2), we get

$$g_i = Bn_i r_i \dot{e}$$

----- (3.3)

If $\gamma_1$ is the rate constant for the jumping of the electrons from interacting filled electron traps to the conduction band, and $\gamma_2$ is the rate constant for the dropping back of electrons from the interacting filled electron traps levels to other levels, then we can write the following rate equation:

$$\frac{dn_i}{dt} = g_i - \gamma_1 n_i - \gamma_2 n_i = Bn_i r_i \dot{e} - \gamma n_i$$

----- (3.4)

where $\gamma = (\gamma_1 + \gamma_2)$, and $1/\gamma$ is the lifetime of interacting filled electron traps or the pinning time $\tau_p$ of the dislocation segments, and $n_i$ is the number of interacting filled electron traps at any time $t$.

Integrating Eq. (3.1) and taking $n_i = 0$, at $t = 0$, we get

$$n_i = \frac{Bn_i r_i \dot{e}}{\gamma} [1 - \exp(-\tau)]$$

----- (3.5)

Using Eq. (3.5) the rate of generation of electrons in the conduction band can we written as

$$g_c = \gamma_1 n_i = \frac{\gamma Bn_i r_i \dot{e}}{\gamma} [1 - \exp(-\tau)]$$

or, $g_c = p \gamma_1 Bn_i r_i \dot{e} [1 - \exp(-\tau)]$

----- (3.6)

where, $p = \gamma_1 / \gamma$, is the probability of transfer of the electrons of interacting traps to the conduction band by the bending dislocation segments.

If $\tau_c$ is the lifetime of electrons in the conduction band, then we can write the following rate equation

$$\frac{dn_c}{dt} = g_c - \frac{n_c}{\tau_c}$$

$$\frac{dn_c}{dt} = p \gamma_1 Bn_i \dot{e} [1 - \exp(-\tau)] - n_c$$

----- (3.7)
where $\beta' = 1/\tau_c$, and $n_c$ is the number of electrons in the conduction band at any time $t$.

Integrating Eq. (3.7) and taking $n_c = 0$, at $t = 0$, for $\beta' >> \gamma$, we get

$$n_c = \frac{Bp \cdot r \cdot n \cdot \dot{\varepsilon}}{\beta} [1 - \exp(-\gamma t)]$$

----- (3.8)

3.3.1.1 Rise of EML Intensity

If $\eta$ is the luminescence efficiency, then using Eq. (3.8) the EML intensity can be expressed as

$$I = \eta \cdot \beta' \cdot n_c = \eta \cdot Bp \cdot r \cdot n \cdot \dot{\varepsilon} [1 - \exp(-\gamma t)]$$

----- (3.9)

For $\gamma t << 1$, Eq. (3.9) can be written as

$$I = \eta \cdot Bp \cdot r \cdot n \cdot \dot{\varepsilon} \cdot \gamma t$$

or, $I = \eta \cdot Bp \cdot r \cdot n \cdot \gamma \dot{\varepsilon}$

----- (3.10)

Equation (3.10) indicates that for $\gamma t << 1$, the ML intensity should increase linearly with the deformation time or strain of the crystals. Equation (3.10) also shows that for a given strain the ML intensity should increase linearly with the density of electron in the traps.

3.3.1.2 Saturation value of the EML intensity

For $\gamma t >> 1$, $\exp (-\gamma t) << 1$, and therefore, from Eq.(3.9) the saturation value of the ML intensity can be expressed as

$$I_s = \eta \cdot Bp \cdot r \cdot n \cdot \dot{\varepsilon}$$

----- (3.11)

3.3.1.3 Dependence of the EML intensity on strain rate

Equation (3.9) indicates that for a given deformation time, the ML intensity should increase linearly with the strain rate. It is evident from Eq. (3.11) that the saturation value of the EML intensity should also increase linearly with the strain rate of the crystals.
3.3.1.4 Dependence of the EML intensity on the concentration of filled electron traps

Equation (3.9) shows that for a given a strain the EML intensity should increase linearly with the concentration of filled electron traps. Equation (3.11) shows that the saturation value of the EML intensity should also increase linearly with the concentration of filled electron traps.

3.3.1.5 Decay of the ML intensity

(i) Fast decay of the EML intensity

When the crosshead of the testing will be stopped, then \( \dot{\varepsilon} = 0 \), and from Eq. (3.4), we get

\[
\frac{dn_i}{dt} = -\gamma_i \\
----- (3.12)
\]

Using Eq. (3.11) and following the procedure used previously for the derivation of the EML intensity, the fast decay of the EML intensity can be expressed as

\[
I_{\alpha} = I_0 \exp[\alpha(t - t_c)] \\
----- (3.13)
\]

where \( t_c \) is the time at which the crosshead of the machine deforming the crystal is stopped, and \( I_0 \) is the EML intensity at \( t = t_c \).

(ii) Slow decay of the ML intensity

During the deformation of ZnS:Mn crystals some of the electrons moving in the conduction band may be transferred to the shallow traps of the crystals (Chandra 1998). Thus, the thermal ionization may release the electrons from the shallow traps to the conduction band and subsequently the depopulation of the shallow traps of the crystals may take place. If \( \tau_s \) is the lifetime of electrons in the shallow traps, then the slow decay of the EML intensity can be expressed as
\[ I_{ds} = I'_0 \exp[-\chi(t - t'_c)] \]  \hspace{1cm} (3.14)

where \( \chi = 1/\tau_s \), \( t'_c \) is the time at which the fast decay of the EML intensity becomes negligible, and \( I'_0 \) is the EML intensity at \( t = t'_c \).

### 3.3.1.6 Temperature dependence of the ML intensity

With increasing temperature of the crystals the linear charge density of the dislocations will decrease (Molodaskii 1989), and moreover, the ML efficiency \( \eta' \) will also decrease. The decreasing lower charge density of dislocations will cause the decrease in the tunneling probability of trapped electrons, and decrease in the value of \( \eta' \) will decrease the radiative probability of electron-hole recombination. Thus, overall EML intensity will decrease with increasing temperature of crystals.

### 3.3.1.7 EML Spectra of ZnS:Mn Crystals

The energy release during the electron-hole recombination may be transferred to Mn\(^{2+}\) centres, and consequently, the excitation of Mn\(^{2+}\) ion will take place, and subsequent de-excitation will give rise to the light emission characteristics of the Mn\(^{2+}\) ions (Chandra 1998, 2011).

### 3.3.2 Theoretical Approach to the Charged Dislocations-Induced Plastico ML of II-VI Semiconductors

If \( G_d \) is rate of generation of moving dislocations caused by the deformation of a crystals at a fixed strain rate, and if \( \tau_p = \frac{1}{\phi'} \) is the pinning of dislocations, then we can write the following equation

\[ \frac{dN^m}{dt} = G_d - \frac{N^m}{\tau_p} = G_d - \phi' N^m \]  \hspace{1cm} (3.15)

Integrating Eq. (3.15) and taking \( N_m = 0 \), at \( t = 0 \), we get
\[ N_m = \frac{G_d}{\phi} [1 - \exp(-\phi' t)] \] ----- (3.16)

If \( v_d \) is the velocity of dislocations, then the rate of sweeping out the area by the dislocation can be expressed as
\[
\frac{dS}{dt} = \frac{G_d v_d}{\phi'} [1 - \exp(-\phi' t)]
\] ----- (3.17)

where \( S \) is the surface area swept out by the dislocations at any time \( t \).

As \( \frac{G_d v_d}{\phi'} = G_d v_d \tau_p \), and \( G_d \tau_p \) is the number \( N_d \) of dislocations moving in equilibrium, \( G_d v_d \tau_p \) will be equal to \( N_d v_d \). From the relation \( \dot{\epsilon} = N_d v_d b \), we get \( n_d v_d = \frac{\dot{\epsilon}}{b} \) (where \( b \) is the Burgers vector). Thus Eq. (3.17) can be written as
\[
\frac{dS}{dt} = \frac{\dot{\epsilon}}{b} [1 - \exp(-\phi' t)]
\] ----- (3.18)

Following the procedure, the ML intensity in the present case, can be given by
\[
I = \frac{2\eta \dot{\epsilon}}{b} p, r, n, [1 - \exp(-\phi' t)]
\] ----- (3.19)

Equation (3.19) indicates that initially the ML intensity should increase linearly with time and for \( \phi' t >> 1 \), it should attain a saturation. Thus \( I_r \) and \( I_s \) are given by the following equations
\[
I_r = \frac{2\eta \dot{\epsilon}}{b} p, r, n, \phi' t = \frac{2\eta}{b} P_r r, n, \phi' \epsilon
\] ----- (3.20)

and,
\[
I_s = \frac{2\eta \dot{\epsilon}}{b} p, r, n_i
\] ----- (3.21)

Equation (3.21) indicates that the saturation value of the ML intensity should increase linearly with the strain rate and also with the density of sphalerite Mn\(^{2+}\) centres in the crystals. It is to be noted that for higher values of Mn\(^{2+}\), concentration quenching will take place and thus
the ML intensity should be optimum for the particular concentration of the Mn$^{2+}$ centres in the crystals.

Similar to the case of electro ML the fast and slow decay of the ML intensity in this case, can be given by the following equations, respectively

$$I_{af} = I_0 \exp[-\phi'(t - t_c)]$$  \hspace{1cm} ----- (3.22)

and,

$$I_{as} = I'_0 \exp[-\chi(t - t'_{c})]$$  \hspace{1cm} ----- (3.23)

It is to be noted that the slow component of ML decay will be observed only when $\phi' \gg \chi$, that is, only for very high strain rate of the crystals.

### 3.4 THEORETICAL APPROACH TO THE PIEZOELECTRICALLY-INDUCED ELASTICO AND PLASTICO ML OF II-VI SEMICONDUCTORS

#### 3.4.1 Theoretical Approach to the Piezoelectrically Elastico ML of ZnS:Mn crystals

Among the II-VI semiconductor, only ZnS:Mn exhibit elastico ML (Xu et.al.1999, Alzetta et.al.1970). For the measurement of elastico ML of ZnS:Mn (Xu et.al.1999) fabricated the thin film of ZnS:Mn nanoparticles on various substracts by physical vapour deposition of ion plating or sputtering method. Alzetta et.al.(1970) used a needle shaped ZnS:Mn crystal grown by an improved flow method in which crystals were transparent and in wurtzite-type needle form. Xu et.al.(1999) excited EML by compressing the crystal at uniform strain rate and Alzetta et.al. excited the elastico ML by bending the crystal along c axis at uniform strain rate. For the measurement of EML of the thin films of ZnS:Mn are coated by physical vapour deposition of ion plating or spattering method. Xu et.al. (1999) also excited the EML in the sample is
excited by applying a load or by the impact of a small ball from a low height.

If $\Omega$ is the activation volume near an activator ion at which the piezoelectric constant is high, $N_c$ is the number of crystallites in the sample, $N_l$ is the number of activators in a crystallite and $N_t$ is the concentration of traps, then the total number of traps in the sample is given by, $N_0 = \Omega N_c N_l N_t$. Considering the exponential distribution of traps in the activation volume near the activator ions in the crystallites, the number of traps $N_c(E_i)$ of energy $E_i$ is given by the following Boltzmann statistical formula (Bergeon et al. 2006, 2008 and Reddy & Reddy 2002).

$$N(E_i) = ZN_0 \exp(-ZE_i) \quad \text{----- (3.24)}$$

where $N_0$ is the total number of traps in the activation volume of the crystallites and $Z=1/kT$ is the distribution coefficient, in which $k$ is the Boltzmann constant and $T$ is the absolute temperature of the crystals.

Up to the threshold energy $E_{\text{th}}$ the trap-depths are comparable to $kT$, and therefore, the shallow traps lying between zero and $E_{\text{th}}$ are thermally detrapped. Thus, the detrappable traps will be present only from $E_{\text{th}}$ to $E$ and using Eq. (3.24), the total number $N_t$ of detrappable traps from $E_{\text{th}}$ to $E$ can be expressed as

$$N_t = \int_{E_{\text{th}}}^{E} ZN_0 \exp(-ZE) \, dE = N_0 \left[ \exp(-ZE) - \exp(-ZE_{\text{th}}) \right] \quad \text{----- (3.25)}$$

When an external pressure is applied, then the piezoelectric field $F$ is produced. If $\alpha$ is the decrease in the trap-depth per unit electric field, then the decrease in trap-depth for the field $F$ will be $\alpha F$. Due to the decrease in trap-depth detrapping of electrons will take place and consequently the total number of filled traps will decrease. If $N_d$ is the
total number of detrapped traps after change in the trap-depth \( \alpha F \), then from Eq. (3.25), we get

\[
N_d = N_0 \left[ \exp(-Z\alpha F) - \exp(-Z\alpha F') \right] 
\]

----- (3.26)

where \( F_{th} \) is the threshold piezoelectric field for the EML.

Differentiating Eq. (3.26), we get

\[
\frac{dN_d}{dF} = N_0 Z \alpha \left[ \exp(-Z\alpha F) \right] 
\]

----- (3.27)

Equation (3.27) can be expressed as

\[
\frac{dN_d}{dt} = N_0 Z \alpha \dot{F} \left[ \exp(-Z\alpha \dot{F} t) \right] 
\]

----- (3.28)

where \( \dot{F} = \frac{dF}{dt} \)

As the de-trapped electrons are transferred to the conduction band the rate of generation of electrons in the conduction band is given by

\[
g = \frac{dN_d}{dt} = N_0 Z \alpha \dot{F} \left[ \exp(-Z\alpha \dot{F} t) \right] 
\]

----- (3.29)

It is evident from Eq. (3.29) that, for significant value of \( Z\alpha F \), the value of \( g \) will decrease with increasing deformation time of the crystals.

If \( \tau \) is the lifetime of electrons in the conduction band, then for \( 1/\tau \gg \alpha \), the change in the number of electrons in the conduction band, that is, the change in the carrier density can be expressed as

\[
\Delta n = g \tau = N_0 Z \alpha \dot{F} \left[ \exp(-Z\alpha \dot{F} t) \right] \tau 
\]

----- (3.30)

If \( \sigma \) is the capture cross-section of the electrons, \( v_d \) is the drift velocity of electrons and \( n_r \) is the concentration of the energy states for the excited Eu\(^{2+} \) ions, then the rate of generation of the excited Eu\(^{2+} \) ions can be expressed as

\[
R = \sigma v_d n_r \Delta n = \sigma v_d n_r N_0 Z \alpha \dot{F} \left[ \exp(-Z\alpha \dot{F} t) \right] \tau 
\]

----- (3.31)

If \( \mu \) is the mobility of electrons in the crystals, then \( v_d = \mu F \), and Eq. (3.31) can be expressed as

\[
R = \sigma \mu F n_r N_0 Z \alpha \dot{F} \left[ \exp(-Z\alpha \dot{F} t) \right] \tau 
\]

----- (3.32)
Case I: EML under increasing stress and fixed stress condition

(i) Rise of EML intensity

It is to be noted that up to $F_{th}$ there are no detrapping of charge carriers because the trap-depths up to this energy are comparable with $kT$ and consequently traps are thermally detrapped. Thus, the detrapping takes place from the trap-depth $E_{th}$ to $E$ or for the piezoelectric field $F_{th}$ to $F$. If $\eta$ is the efficiency for the radiative decay of excited Eu$^{2+}$ ions, then using Eq.(3.32) the EML intensity can be expressed as

$$I = \eta R = \eta \sigma m, N_0 Z \alpha \tau \dot{F} (F - F_{th}) \exp(-Z \alpha \dot{F} t)$$

----- (3.33)

If $B$ is the correlating factor between $F$ and the piezoelectric charge $Q$, then $F=BP$. For the piezoelectric constant $d_0$ near the localized piezoelectric region in the crystal, applied pressure $P$ and pressing rate $\dot{P}$, $\dot{F} = B \dot{Q} = B d_0 \dot{P}$ and $F = BQ = B d_0 P$, and therefore, Eq.(3.33) can be expressed as

$$I = \eta \sigma m, N_0 Z \alpha \tau B^2 d_0^2 \dot{P} (P - P_{th}) \exp(-Z \alpha B d_0 P)$$

----- (3.34)

In the elastic region, $P$ is low, and therefore, $Z \alpha B d_0 P << 1$, and Eq.(3.34) can be written as

$$I = \eta \sigma m, N_0 Z \alpha \tau B^2 d_0^2 \dot{P} (P - P_{th}) [1 - (Z \alpha B d_0 P)]$$

----- (3.35)

where $P_{th}$ is the threshold pressure for the EML emission.

For the crystals having low value of $Z, \alpha$ and $d_0$, the product $Z \alpha B d_0 P$ is much less than 1, and therefore, Eq.(3.35) can be written as

$$I = \eta \sigma m, N_0 Z \alpha \tau B^2 d_0^2 \dot{P} (P - P_{th})$$

----- (3.36)

The number $N_t$ of trapped electrons is given by $N_t = (N_0 - N_d) = [N_0 - N_0 \{1 - \exp(-Z \alpha B d_0 P)] = N_0 \exp(-Z \alpha B d_0 P) = N_0 \exp(-\beta P)$, where $\beta = Z \alpha B d_0$. 

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Thus, $\beta=Z\alpha B d_0$ is the rate constant for deformation de-trapping or coefficient of deformation de-trapping.

Equation (3.36) indicates that, in the crystals in which $Z\alpha B d_0 P << 1$, after $P_th$, the EML intensity should increase linearly with the applied pressure $P$. Equation (3.35) indicates that, in the crystals in which $Z\alpha B d_0 P$ is significant, the EML intensity should increase nonlinearly with the applied pressure $P$. As $\beta=Z\alpha B d_0$, is the coefficient of deformation de-trapping, Eq.(3.35) indicates that, in the crystals having high value of the coefficient of deformation de-trapping the nonlinearity in the I versus P plot will occur and they will not be suitable for the EML-based stress sensors. However, in the crystals having low value of the coefficient of deformation de-trapping the nonlinearity in the I versus P plot will not occur and they will be suitable for the EML-based stress sensors. It is also evident from Eq.(3.35) that the EML intensity will be optimum for the crystals having a particular value of the coefficient of deformation de-trapping hence, the crystals having moderate value of the coefficient of deformation de-trapping will be more suitable for the EML-based sensors.

Substituting the value of $N_0$, Eq. (3.36) can be written as

$$I = \eta \sigma \mu, \Omega N \alpha N, N, Z\alpha B^2 d_0^2 \dot{P}(P - P_th)$$

----- (3.37)

Equation (3.37) can be written as

$$I = \eta \sigma \mu, \Omega N \alpha N, N, Z\alpha B^2 d_0^2 \dot{P}^2 (t - t_0)$$

----- (3.38)

Equation (3.38) can also be expressed as

$$I = \eta \sigma \mu, \Omega N \alpha N, N, Z\alpha B^2 d_0^2 Y^2 \dot{\varepsilon}^2 (t - t_0)$$

----- (3.39)

where $t_0 = P_th / \dot{P}$, that is, the time at which the EML emission starts after pressing the sample at a fixed pressing rate, $Y$ is the Young’s modulus of elasticity and $\dot{\varepsilon}$ is the strain rate.
Equation (3.37) indicates that for a given pressing rate or strain rate, after the threshold pressure $P_{th}$, the EML intensity should increase linearly with pressure $P$. Equation (3.39) indicates that for a given strain rate the EML intensity should increase linearly with the deformation time $t$.

(ii) Fast decay of EML intensity

Recent experimental measurements made on the dynamics of EML (Levision 1904 and Nelson 1926) have shown that, when the crosshead of the machine compressing the sample stops instantaneously, then the fast components of the EML decay does not appear and it appears only when the crosshead keeps on moving for some time after turning off the electric power given to it. Thus, the fast decay of EML is related to the decrease of the strain rate of the sample with time. If $\tau_m$ is the time-constant or machine constant for stopping the crosshead, then the decrease in strain rate with time can be expressed as

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp\left[-\frac{(t-t_m)}{\tau_m}\right] = \dot{\epsilon}_0 \exp[-\phi(t-t_m)] \quad ----- (3.40)$$

Where $\phi = 1/\tau_m$, $t_m$ is the time at which the electrical power to the crosshead is turned off, and $\dot{\epsilon}_0$ is the strain rate at $t = t_m$.

From Eq. (3.40), the change in pressure $dP$ in time $dt$ is given by

$$dP = \dot{P}dt = Y\dot{\epsilon}dt = Y\dot{\epsilon}_0 \exp[-\phi(t-t_m)]dt \quad ----- (3.41)$$

Integrating Eq. (3.41) and taking $P = P_m$, at $t = t_m$, we get

$$P = P_m + \frac{Y\dot{\epsilon}_0}{\phi} [1 - \exp\{-\phi(t-t_m)\}] \quad ----- (3.42)$$

Thus, in this case, $F = Bd_0 P$, and $\dot{F} = Bd_0 \dot{P}$, and therefore, $F$ and $\dot{F}$ can be expressed as

$$F = Bd_0 P_m + \frac{Bd_0 Y\dot{\epsilon}_0}{\phi} [1 - \exp\{-\phi(t-t_m)\}] \quad ----- (3.43)$$
and \( F = \frac{dF}{dt} = B d_{0} Y \hat{e}_{0} [\exp(-\phi(t-t_{m}))] \) \hspace{0.5cm} \text{----- (3.44)}

Using Eqs. (3.38), (3.43) and (3.44), the EML intensity for \( Q >> Q_{th} \), can be written as

\[
I = \eta \sigma m_{e} \Omega N_{i} N_{e} N_{v} Z \alpha \beta B^{2} \times \left[ d_{0} P_{m} + \frac{d_{0} Y \hat{e}_{0}}{\phi} [1 - \exp(-\phi(t-t_{m}))] d_{0} Y \hat{e}_{0} [\exp(-\phi(t-t_{m}))] \right] \]

\hspace{0.5cm} \text{----- (3.45)}

As \( \phi \) is very large, \( d_{0} P_{m} >> \frac{d_{0} Y \hat{e}_{0}}{\phi} \), and Eq. (3.45) can be written as

\[
I_{df} = \eta \sigma m_{e} \Omega N_{i} N_{e} N_{v} Z \alpha \beta B^{2} d_{0}^{2} P_{m} Y \hat{e}_{0} \exp[-\phi(t-t_{m})] \]

or, \( I_{df} = I_{m} \exp[-\phi(t-t_{m})] \) \hspace{0.5cm} \text{----- (3.46)}

where \( I_{m} = \eta \sigma m_{e} \Omega N_{i} N_{e} N_{v} Z \alpha \beta B^{2} d_{0}^{2} P_{m} Y \hat{e}_{0} \) (from Eq. 3.40), is the EML intensity at \( t = t_{m} \)

\textbf{(iii) Slow decay of EML intensity}

During the deformation of the crystals some of the de-trapped electrons moving in the conduction band get trapped at the shallow traps lying in the normal piezoelectric region of the crystals where the piezoelectric field is less and later on such trapped electrons are thermally released form the traps and their subsequent capture in excited state of Eu\(^{2+} \) ions gives rise to the light emission. In this case, the slow decay of EML intensity is given by

\[
I_{ds} = I_{0s} \exp \left[ -\frac{(t-t_{c})}{\tau_{s}} \right] \]

or \( I_{ds} = I_{0s} \exp[-\chi(t-t_{c})] \) \hspace{0.5cm} \text{----- (3.47)}

where \( t_{c} \) is the time at which the fast decrease of EML intensity becomes negligible, \( I_{0s} \) is the EML intensity at \( t = t_{c} \), \( \tau_{s} = 1/\chi_{s} \) is the lifetime of electrons in the shallow traps lying in the normal piezoelectric region of the crystals.
(iv) Estimation of \( I_m \) and \( I_T \)

If the crystal is compressed at a fixed strain rate for a time \( t_m \), where the pressure is \( P_m \), then from Eqs. (3.38) and (3.39), the maximum intensity \( I_m \) of the EML is given by

\[
I_m = \eta \sigma \mu n_x \Omega N_i N_i N_c Z \alpha \tau B^2 d_0^2 (P_m - P_{th}) \frac{dP}{dt}
\]

or,
\[
I_m = \eta \sigma \mu n_x \Omega N_i N_i N_c Z \alpha \tau B^2 d_0^2 Y (P_m - P_{th}) \dot{\varepsilon}
\]

----- (3.48)

It is evident from Eq.(3.48) that the EML intensity will be maximum for the pressure \( P_m \) corresponding to time \( t_m \) at which the crosshead of the machine is stopped.

Integration of Eq. (3.38) gives that the total ML intensity \( I_{TD} \) during the deformation of the sample can be expressed as

\[
I_{TD} = \int_0^{t_m} I dt = \int_{P_{th}}^{P_m} \eta \sigma \mu n_x \Omega N_i N_i N_c n_z \alpha \tau B^2 d_0^2 (P - P_{th}) dP
\]

or,
\[
I_{TD} = \eta \sigma \mu n_x \Omega N_i N_i N_c n_z \alpha \tau B^2 d_0^2 \left( \frac{(P_m^2 - 2P_m P_{th})}{2} \right) \mu
\]

or,
\[
I_{TD} \approx \eta \sigma \mu n_x \Omega N_i N_i N_c n_z \alpha \tau B^2 d_0^2 \left( \frac{P_m^2}{2} \right) \mu
\]

----- (3.49)

(as \( P_m \gg P_{th} \))

Equation (3.49) indicates that the total EML intensity in the deformation region should increase quadratically with the applied pressure. This fact indicates that the total EML emission is directly related to the total mechanical energy given to the sample.

Using Eq. (3.46) the value of total ML intensity in the post-deformation region, from the time \( t_m \) to \( \infty \) is given by

\[
I_{TPD} = \int_{t_m}^\infty I_m \exp[-\phi(t - t_m)] dt
\]

or,
\[
I_{TPD} = \frac{I_m}{\phi} \exp[-\phi(t - t_m)]
\]

\[
= \frac{\eta \sigma \mu n_x \Omega N_i N_i N_c n_z \alpha \tau B^2 d_0^2 Y (P_m - P_{th}) \dot{\varepsilon}}{\phi}
\]
or, \( I_{\text{ppD}} = \frac{\eta \sigma m \Omega N_i N_e n_e Z \alpha \tau B_0^2 d_0^2 \delta P_m \delta}{\phi} \) \hspace{1cm} (3.50)

(as \( P_m \gg P_{\text{th}} \))

From Eqs. (3.49) and (3.50), the total ML intensity is given by

\[ I_r = I_m + I_{\text{ppD}} \]

or,

\[ I_r = \frac{\eta \sigma m \Omega N_i N_e n_e Z \alpha \tau B_0^2 d_0^2 P_m^2}{2} \left( 1 + \frac{2 \ddot{Y} \dot{\varepsilon}}{\phi P_m} \right) \] \hspace{1cm} (3.51)

As \( P_m = \dot{P} t_m = \ddot{Y} \dot{t}_m \), and \( \phi = 1/\tau_m \), Eq. (3.51) can be written as

\[ I_r = \frac{\eta \sigma m \Omega N_i N_e n_e Z \alpha \tau B_0^2 d_0^2 P_m^2}{2} \left( 1 + \frac{2 \tau_m}{t_m} \right) \] \hspace{1cm} (3.52)

3.4.2 Theoretical Approach to the Piezoelectrically-Induced Plastico ML of II-VI Semiconductors

Alzetta et al. (1962) have measured the ML induced by the application of hydrostatic pressure on ZnS:Mn phosphors. In that experiment, the phosphor was introduced into a pressure cell either as an oil suspension or with other liquids, and subjected to rapid compression through a piston acted on with electromagnets. The mode of light emission was followed on the screen of an oscilloscope through the glass window of the cell using an RCA 6810 A photomultiplier tube with a conventional low-noise circuit. Pressure picks-ups of the type 401 (Pz-14) and 422 of the Kistler SLM indicators were used to measure the pressure. The rise time of the pressure steps was 4 ms.

If \( \tau_r \) is the time constant for the rise of the hydrostatic pressure, then the rise of pressure with time can be expressed as

\[ P = P_o \left[ 1 - \exp \left( - \frac{t}{\tau_r} \right) \right] \]

or,

\[ P = P_o \left[ 1 - \exp \left( - \dot{\xi} \tau r \right) \right] \] \hspace{1cm} (3.53)
where $\xi = 1/\tau_r$ is the rate constant for the rise of pressure and $P_o$ is the final value of the pressure.

If $\Omega$ is the activation volume near an activator ion at which the piezoelectric constant is high, $N_c$ is the total number of crystallites in the sample, $N_l$ is the number of activators in a crystallite, and $N_t$ is the concentration of traps in the sample, then the total number of traps in the sample is given by, $N_0 = \Omega N_c N_l N_t$. Considering the exponential distribution of traps in the activation volume near the activator ions in the crystallites, the number of traps $N(E_i)$ of energy $E_i$ is given by the following Boltzmann statistical formula (Yazici et.al. 2002, Gomez-Ros et.al. 2006, Correcher et.al. 2008).

$$N(E_i) = ZN_0 \exp(-ZE_i)$$

(3.54)

where $N_0$ is the total number of traps in the activation volume of the sample and $Z = 1/kT$ is the distribution coefficient, in which $k$ is the Boltzmann constant and $T$ is the absolute temperature of the phosphor material.

Up to the threshold energy $E_{th}$, the trap-depths are comparable to $kT$, and therefore, the shallow traps lying between zero and $E_{th}$ are thermally detrapped. Thus, the detrappable traps will be present only from $E_{th}$ to $E$ and using Eq. (3.54), the total number $N_t$ of detrappable traps from $E_{th}$ to $E$ can be expressed as

$$N_t = \int_{E_{th}}^{E} ZN_0 \exp(-ZE) dE$$

or

$$N_t = N_0 \left[ \exp(-ZE_{th}) - \exp(-ZE) \right]$$

(3.55)

When an external pressure is applied, then the piezoelectric field $F$ is produced. If $\alpha$ is the decrease in the trap-depth per unit electric field, then the decrease in trap-depth for the field $F$ will be $\alpha F$. Due to the decrease in trap-depth de-trapping of electrons will take place and consequently the total number of filled traps will decrease. If $N_d$ is the
total number of de-trapped traps after change in the trap-depth $\alpha F$, then from Eq. (3.55), we get

$$N_d = N_o[\exp(-Z\alpha F_{th}) - \exp(-Z\alpha F)] \quad ----- (3.56)$$

where $F_{th}$ is the threshold piezoelectric field for the ML. Differentiating Eq. (3.56), we get

$$\frac{dN_d}{dF} = N_o Z\alpha \exp(-Z\alpha F) \quad ----- (3.57)$$

Equation (3.57) can be expressed as

$$\frac{dN_d}{dt} = N_o Z\alpha \dot{F} \exp(-Z\alpha \dot{F}t) \quad ----- (3.58)$$

where $\dot{F} = dF / dt$

As the de-trapped electrons are transferred to the conduction band, using Eq. (3.58) the rate of generation of electrons in the conduction band is given by

$$g = \frac{dN_d}{dt} = N_o Z\alpha \dot{F} \exp(-Z\alpha \dot{F}t) \quad ----- (3.59)$$

It is evident from Eq. (3.59) that, for significant value of $Z\alpha \dot{F}$, the value of $g$ will decrease with increasing deformation time of the crystals.

If $B$ is the correlating factor between $F$ and the piezoelectric charge $Q$, then $F = BQ$. For the piezoelectric constant $d_0$ near the localized piezoelectric region in the crystal, then for the applied pressure $P$ and pressing rate $\dot{P}$, we get, $\dot{F} = BQ = B\dot{P}$ and $F = BQ = B\dot{P}$, and therefore, Eq. (3.59) can be expressed as

$$g = N_o Z\alpha B d_0 \dot{P} \exp(-Z\alpha \dot{F}t) \quad ----- (3.60)$$

From Eq. (3.53), $\frac{dP}{dt}$ can be expressed as

$$\frac{dP}{dt} = \dot{P} = P_o \xi \exp(-\xi t) \quad ----- (3.61)$$

Thus, from Eq. (3.60) and (3.61), we get

$$g = N_o Z\alpha B d_0 P_o \xi \exp(-\xi t)[\exp(-Z\alpha \dot{F}t)] \quad ----- (3.62)$$
As \( z \alpha \xi t \) is much less than 1 and \( \xi \) is a large, Eq. (3.62) can be written as

\[
g = N_o Z \alpha B d_o P \xi \exp(-\xi t) \quad \text{----- (3.63)}
\]

Furthermore, as ZnS:Mn is a semiconductor, the recovery of vacated traps by the pressure may also take place by the breaking of bonds and subsequent generation of free electrons and holes.

If \( \tau \) is the lifetime of electrons in the conduction band and \( v_d \) is the drift velocity of electrons, then the mean free path of the electrons is given by \( \lambda = v_d \tau \). If \( \mu \) is the mobility of electrons, then \( v_d = \mu F \), and thus, \( \lambda = \mu F \tau = \mu d_o P \tau \). Since exponential increase of the ML intensity does not take place with increasing \( F \) or \( P_0 \) or \( v_o \), it seems that the excitation of Mn\(^{2+} \) centres does not take place by the impact excitation. The linear increase of \( \lambda \) with \( v_0 \) indicates that the ML excitation is caused by the light produced during the electron-hole recombination. Now, considering that the number of Mn\(^{2+} \) ions excited by the process of electron-hole recombination is proportional to the mean free path of the electrons, for \( P_0 >> P_{th} \), the rate of excitation of Mn\(^{2+} \) ions can be expressed as

\[
R = N_o \sigma n_h \lambda \alpha B^2 d_o P_o \xi \exp(-\xi t) Z \quad \text{----- (3.64)}
\]

where \( \sigma \) capture cross-section of electrons and \( n_h \) is the concentration of hole centres in the crystallites.

Now, substituting the value of \( \lambda \), Eq. (3.64) can be written as

\[
R = N_o \sigma n_h \alpha B^2 d_o P_o \xi \exp(-\xi t) Z \mu d_0 P \tau
\]

or,

\[
R = N_o \sigma n_h \alpha B^2 d_o P_o^2 \xi \exp(-\xi t) Z \mu d_0 \tau [1 - \exp(-\xi t)]
\]

or,

\[
R = N_o \sigma n_h \alpha B^2 d_0 P_o^2 \xi Z \mu t [\exp(-\xi t) - \exp(-2\xi t)]
\]

\text{----- (3.65)}

If \( \tau_e \) is the lifetime of the excited state of Mn\(^{2+} \) ions, then we can write the following rate equation

\[
\frac{dN_{ex}}{dt} = N_o \sigma n_h \alpha B^2 d_0 P_o^2 \xi Z \mu t [\exp(-\xi t) - \exp(-2\xi t)] - \alpha N_{ex}
\]

\text{----- (3.66)}
where $\alpha = 1/\tau_c$, and $N_{\text{ex}}$ is the number of excited at any time $t$.

Integrating Eq. (3.66) and taking $N_{\text{ex}} = 0$, at $t = 0$, we get,

$$N_{\text{ex}} = N_0 \sigma_n h B^2 d_0^2 P_0^2 \xi Z \mu t \left[ \frac{\exp(-\xi t)}{(\alpha - \xi)} - \frac{\exp(-2\xi t)}{(\alpha - 2\xi)} + \frac{\xi \exp(-\alpha t)}{(\alpha - \xi)(\alpha - 2\xi)} \right]$$

----- (3.67)

For $\alpha >> \xi$, Eq. (3.67) can be written as

$$N_{\text{ex}} = N_0 \sigma_n h B^2 d_0^2 P_0^2 \xi Z \mu t [\exp(-\xi t) - \exp(-2\xi t)]$$

----- (3.68)

If $\eta$ is the efficiency for the radiative decay of excited Mn$^{2+}$ ions, then using Eq. (3.68) the ML intensity can be expressed as

$$I = \eta \alpha N_{\text{ex}} = \eta \alpha N_0 \sigma_n h B^2 d_0^2 P_0^2 \xi Z \mu t [\exp(-\xi t) - \exp(-2\xi t)]$$

----- (3.69)

Substituting the value of $N_0 = \Omega N_c N_i N_l$, Eq. (3.69) can be written as

$$I = \eta \alpha N_{\text{ex}} = \eta \alpha \Omega N_c N_i N_l \sigma_n h B^2 d_0^2 P_0^2 \xi^2 \sigma_n h \mu \tau t [\exp(-\xi t) - \exp(-2\xi t)]$$

----- (3.70)

(i) **Rise of ML intensity**

For $\xi << 1$, Eq. (18) can be written as

$$I_r = \eta \alpha \Omega N_i N_c Z B^2 d_0^2 P_0^2 \xi^2 \sigma_n h \mu \tau t$$

----- (3.71)

The above equation shows that for low value of time the ML intensity should increases linearly with time.

(ii) **Evaluation of $t_m$ and $I_m$**

From Eq. (3.41), the time $t_m$ at which the ML intensity will be maximum may be expressed as

$$t_m = \frac{l}{\epsilon} \ln 2$$

----- (3.72)

For $P_0$ comparable to $P_{th}$, there will be a time delay $t_d$ between the applied pressure pulse and the corresponding ML pulse because the ML
will appear when $P$ will be greater than $P_{th}$. In this case, $t_m$ will be given by

$$(t_m + t_d) = \frac{1}{\xi} \ln 2$$

or, $$t_m = (\frac{1}{\xi} \ln 2) - t_d$$

----- (3.73)

As the strain rate will increase with the increasing pressure $t_d$, the time for attaining the pressure $P_{th}$ will decrease with the increasing value of the applied pressure and for $P_0>>P_{th}$, $t_d$ will become negligible and $t_m$ will be given by Eq. (3.73).

Substituting the value of $t_m$ from Eq. (3.73) in Eq. (3.70), the ML intensity $I_m$ corresponding to the peak of ML intensity versus time curve is given by

$$I_m = \eta \alpha \Omega N_i N_i Z B^2 d_0^2 P_0^2 \xi \sigma n_h \mu \tau$$

----- (3.74)

For $P_0$ comparable to $P_{th}$, the increase of $I_m$ with $P_0$ will be given by

$$I_m = \frac{\eta \alpha \Omega N_i N_i Z B^2 d_0^2 P_0^2 \xi \sigma n_h \mu \tau (1 - P_{th}/P_0)}{4}$$

----- (3.75)

As the number $N_l$ of the activators in the sample increases linearly with the volume of the sample and $\xi$ remains nearly constant. It is evident from Eq. (3.75) that $I_m$ should increase approximately linearly with the volume of the sample.

(iii) **Estimation of Total ML Intensity $I_T$**

Using Eq. (3.70), the total ML intensity $I_T$, i.e., area below the ML intensity versus time curve can be expressed as

$$I_T = \int_0^\infty \int_0^\infty \eta \alpha \Omega N_i N_i \sigma n_h B^2 d_0^2 P_0^2 \xi Z \mu \tau [\exp(-\xi t) - \exp(-2\xi t)]$$

or,
\[ I_T = \frac{\eta \alpha \Omega N_1 N_i \gamma_n h B^2 d_0^2 P_0^2 \xi Z \mu \tau}{2} \]  \quad ----- (3.76)

For \( P_0 \) comparable to \( P_{th} \), the increase of \( I_T \) will be given by

\[ I_T = \frac{\eta \alpha \Omega N_1 N_i \gamma_n h B^2 d_0^2 P_0^2 \xi \mu \tau (1 - \frac{P_{th}}{P_0})}{2} \]  \quad ----- (3.77)

Since \( N_i \) increases linearly with the increasing volume of the sample, it is seen from Eq. (3.77) that the total ML intensity \( I_T \) should increase linearly with volume of the sample.

**iv) Fast Decay of ML Intensity**

From Eq. (3.70), we get

\[ I = \eta \alpha \Omega N_1 N_i \gamma_n h B^2 d_0^2 P_0^2 \xi Z \mu \tau \exp(-\xi t_m) \{ \exp(-\xi t) - \exp(-2\xi t) \} \]

or,

\[ I = \eta \alpha \Omega N_1 N_i \gamma_n h B^2 d_0^2 P_0^2 \xi \gamma_n h \mu \tau \exp(-\xi t_m) \exp(-\xi t-t_m) \left[ 1 - \exp(-\xi t) \right] \]

or

\[ \frac{I}{1 - \exp(-\xi t)} = \eta \alpha \Omega N_1 N_i \gamma_n h B^2 d_0^2 P_0^2 \xi \gamma_n h \mu \tau \exp(-\xi t_m) \exp(-\xi(t-t_m)) \]  \quad ----- (3.78)

For \( \xi \gg 1 \), then Eq.(3.78) can be written as

\[ I_{dr} = \eta \alpha \Omega N_1 N_i Z B^2 d_0^2 P_0^2 \xi \gamma_n h \mu \tau \exp(-\xi t_m) \exp(-\xi(t-t_m)) \]  \quad ----- (3.79)

Eq.(3.78) shows that the semi log plot of \( I/[1-\exp(-\xi t)] \) versus (t-\( t_m \)) should be a straight line, in which the slope will be equal to \( \xi = 1/\tau_r \).

Eq. (3.79) shows that for \( \xi \gg t \), the semi log plot of \( I \) versus (t-\( t_m \)) should be a straight line, in which the slope will be equal to \( \xi = 1/\tau_r \).

**v) Slow Decay of ML Intensity**

During the deformation of the crystals some of the detrapped electrons moving in the conduction band may get trapped at the shallow
traps lying in the normal piezoelectric region of the crystals where the piezoelectric field is less and later on such trapped electrons are thermally released from the traps and their subsequent capture in excited state of Eu$^{2+}$ ions may give rise to the light emission. In this case, the slow decay of ML intensity is given by

$$I_{ds} = I_{0s} \exp \left[ - \frac{(t - t_c)}{\tau_s} \right] = I_{0s} \exp [-\chi (t - t_c)]$$

where $t_c$ is the time at which the fast decrease of ML intensity becomes negligible, $I_{0s}$ is the ML intensity at $t = t_c$, $\tau_s = 1/\chi$, is the lifetime of electrons in the shallow traps lying in the normal piezoelectric region of the crystals.

(vi) **Effect of temperature on ML**

Equations (3.75) and (3.77) indicate that both $I_m$ and $I_T$ depend on the ML efficiency $\eta$ and the piezoelectric constant $d_o$. Since $\eta$ and $d_o$ decrease with increasing temperature of the crystals, both $I_m$ and $I_T$ should decrease with increasing temperature of the crystals. Beyond a particular temperature $d_o$ may decrease to such an extent that the de-trapping and consequently, the ML emission may not be possible.

(vii) **Concentration Quenching**

At low concentration of Mn$^{2+}$ the ML intensity increases with increasing concentration of Eu$^{2+}$ because the number of luminescence centres increases with increasing concentration of the dopant. However, at higher concentration the ML intensity decreases with increasing concentration of Eu$^{2+}$ because of the concentration quenching. Thus, the ML intensity is optimum for a particular concentration of Mn$^{2+}$ in ZnS:Mn phosphors.
(viii) **Spectroscopy of ML**

In ZnS:Mn phosphors the ML spectra are similar to their photoluminescence and electroluminescence spectra. It has been reported that the luminescence induced by stress in ZnS:Mn phosphors arises from the emitting center of Mn, due to the $^4T_1 \rightarrow ^6A_1$ transition of Mn$^{2+}$ ions (Xu et.al. 1999 and Chandra et.al. 2010).
3.5 EXPERIMENTAL SUPPORT TO THE PROPOSED THEORY

Xu et.al. (1999) fabricated the thin film of ZnS:Mn nanoparticles on various substrates by physical vapour deposition of ion plating or a sputtering method. The source material of ZnS:Mn was pretreated at 1050°C for 3h in a vacuum sealed quartz tube before deposition. A highly oriented film was achieved by selecting a deposition rate of 2nm/s and a substrate temperature of 160°C. The chemical composition determined by X-ray diffraction pattern showed that the Mn amount in the film was the same as in the source material, i.e., 1.5 percent. Moreover, the X-ray diffraction pattern showed only one strong diffraction peak at 28.49° in the 20 range of 10°-90°, which was attributed to the (111) plane of ZnS, indicating that the film was highly oriented. The field emission scanning electron microscope (FE-SEM) and XRD techniques indicate that the ZnS:Mn film was composed of nano-sized crystallites with a mean size of 20 nm. The elastico ML was induced by compression stress of 500 N, which was applied by a material testing machine with a cross-head speed of 0.1 mm/minute. The EML intensity was measured by a photon counting system, and the EML spectra were recorded using a spectrometer attached to a photonic multichannel analyzer.

Fig. 3.2 shows that when a load is applied on to the film of ZnS:Mn nanoparticles coated on a quartz substrate, then initially the EML intensity increases with time, attains a peak value and later on it decreases with time (Xu et.al. 1999). It is seen that when pressure is released, then the EML emission also takes place. It is evident from Fig. 3.2 that when the load is applied for the second time, then also the EML emission takes place during the application and release of the applied pressure. This fact shows the reproducibility of EML corresponding to
the application and release of pressure, whereby two EML pulses I’ and II’, respectively are generated during one cycle of the applied pressure, and all of which were reproducible as shown in I’ and II’ in Fig. 1. The threshold pressure for the appearance of EML in ZnS:Mn nanoparticles is nearly equal to 1 MPa.

Fig. 3.2 ML response of ZnS:Mn nanoparticles coated on a quartz plate for the compression stress of 500 N, which was applied by a material test machine with a cross-head speed of 0.10 mm/min. (after Xu et al., 1999).

Fig. 3.3 shows the plot between the log of EML intensity I and (t-t_m). The plot between log I and (t-t_m) for the EML induced by release of pressure, is also similar to Fig. 3.3 In this case, the value of slope is higher because the rate of release pressure is high; however, the total EML intensity is equal to that obtained during the application of pressure. The value of \( \gamma \) is determined from a slope of the Fig. 3.3 using Eq. (3.46), and it is found to be 0.11 sec\(^{-1}\) and this gives that the decay time of EML intensity should be equal to 9.1 sec.
It is seen from Fig. 3.4 that for a given strain rate the EML intensity increases linearly with the applied stress. This is in accord with Eq. (3.47).

Fig. 3.5 shows that the EML intensity increases linearly with the strain rate. This finding follows Eq. (3.47) The EML spectra of ZnS:Mn phosphors are similar to their electroluminescence (EL) and photoluminescence (PL) spectra. The ML, EL and PL, emissions are related to $^4T_1 \rightarrow {}^6A_1$ transition of Mn$^{2+}$ ions.
Fig. 3.5 Strain rate dependence of the EML intensity (Theoretical).

Fig. 3.6 (a,b) shows stress-strain and the ML-strain curves of ZnS:Mn crystals at a fixed strain rate. It is seen that the ML appears in the elastic region as well as in the plastic region. Initially, the ML intensity increases with time and then it tends to attain a saturation value for larger value of the deformation. It is evident from Fig. 3.6(c) that the ML pulses appear concurrently with the steps occurring in the stress-strain curve of the crystal. As the step in the stress-strain curve is related with the movement of dislocations, it seems that the moving dislocations are responsible for the ML emission in ZnS:Mn crystals. It is to be noted that there is no time delay between the movement of dislocations and the appearance of ML pulses. This fact shows that the ML emission takes place as soon as the movement of dislocation starts.
Fig. 3.6 (a) stress-strain and, (b) ML-strain curves of ZnS:Mn crystal when deformed by bending at a fixed strain rate. (c) is the magnified portion of two curves shown in (a) and (b) (after Alzelta et al., 1970).

Fig. 3.7 shows the dependence of the ML intensity on the deformation or deformation time for ZnS:Cu, Cl crystal, where deformation is performed at a fixed strain rate. It is seen that initially the ML intensity increases linearly with time, and then it attains a saturation value. These results are in accordance with Eqs. (3.49) and (3.50).

Fig. 3.7 ML intensity versus deformation time and stress versus deformation time curves of ZnS:Cu, Al crystals deformed at a strain rate of 10 µm/min (after Bredikhin and Shmuralk, 1979).
Fig. 3.8 shows the plot of log I versus (t-t_c). It is seen that the plot is a straight line with negative slope. This result follows Eq. (3.26). From the inverse of the slope of this plot the value of the pinning time of dislocations is determined and it is found to be 90.91 sec. As the pinning time of dislocations is less, the fast decay of the ML intensity could not be observed.

![Graph](image)

**Fig. 3.8** In I versus (t-t_c) plot for the decaying portion of the ML intensity of ZnS:Cu,Al crystal for $\dot{\varepsilon} =10\mu m/min$.

Fig. 3.9 shows that the ML intensity of ZnS: Mn crystals increases with the strain rate. This result is in accordance with Eq. (3.50). It has been found that the ML intensity of ZnS:Mn crystals is optimum for a particular concentration of the crystals. Initially the ML intensity increases with increasing concentration of Mn as the number of luminescence centres increases; however, for higher concentration of Mn the ML intensity decreases because of the concentration quenching. Thus, the ML intensity is optimum for a particular concentration of Mn in ZnS.
Fig. 3.9 Stress-strain curve and ML-strain curve of ZnS:Mn for different strain rates (after Alzelta et al., 1970).

Fig. 3.10 shows the effect of temperature on the ML intensity of ZnS:Cu, Cl crystals. It is seen that the decrease in the ML intensity with temperature is faster as compared to that of the photoluminescence (PL) intensity. As the ML intensity depends on η and charge density of the dislocations or the radius of the interaction between charged dislocation and filled electron traps, however, the PL intensity depends only on η, and both η and the charge density of the dislocations decrease with temperature, a faster decrease of ML intensity as compared to that of the PL intensity occurs with increasing temperature of the crystals.
Fig. 3.10 Temperature dependence of the photoluminescence intensities of the blue (curve1), green (curve2), orange-red (curve3) photoluminescence bands, and the temperature dependence of the green band (curve4) of the ML in ZnS:Cu,Al crystals (after Brediktin and Shmurak, 1979).

Fig. 3.11 shows the ML, PL and EL spectra of II-VI semiconductors. It is evident that the ML spectra are similar to the PL and EL spectra. This fact shows that although the excitation mechanism is different in ML, PL, and EL, the emission of photons occurs from the similar transitions.

Thus, it seems that there is a good agreement between the theoretical and experimental results.

Fig.3.11 ML photoluminescence (PL) and electroluminescence spectra of ZnS:Mn film (after Xu et. al.,1999).
3.6 CONCLUSIONS

The important conclusions drawn from the present investigation are as given below:

(i) The ML emission from ZnS:Mn crystals takes place during its elastic and plastic deformation and the ML emission from other II-VI semiconductor takes place during their plastic deformations. The ML emission during the elastic deformation takes place due to the electrostatic interaction between dislocations segments and the filled electron traps and the ML emission during the plastic deformation takes place due to the electrostatic interaction between the moving charged dislocations and the filled electron traps.

(ii) In the elastic region, the ML intensity increases linearly with the strain or deformation time and in this case, the saturation region could not be observed because of the beginning of the plastic deformation before the start of the saturation in the EML intensity.

(iii) In the plastic region, initially the ML intensity increases linearly with the strain or deformation time, and later on it attains a saturation value for large deformation.

(iv) When the deformation is stopped, initially the ML intensity decreases at a fast rate and later on it decreases at a slow rate. The decay time for the fast decaees in the ML intensity gives the relaxation time of bending dislocation segments or pinning time of dislocations, and the decay time of the slow decrease of the ML intensity gives the lifetime of electrons in the shallow traps in the crystals. The slow component of the ML decay should appear only if the pinning time of dislocations will be less than the lifetime of electrons in the shallow traps in the crystals.
(v) The saturation value of the ML intensity increases linearly with the strain rate and also with the density of the filled electron traps in the crystals.

(vi) The ML intensity decreases with increasing temperature of the crystals because of the decrease in the luminescence efficiency and linear charge density of the dislocations.

(vii) From the ML measurements the relaxation time of dislocation segments, pinning time of dislocations and lifetime of the electrons in the shallow traps can be determined.

(viii) The expressions derived for the ML induced by elastic and plastic deformation of II-VI semiconductors at fixed strain rate, indicates that the ML intensity depends on the strain, strain rate, stress, density of filled electron traps, size of crystals, luminescence efficiency, and temperature. A good agreement is found between the theoretical and experimental results.

(ix) When a ZnS:Mn crystal is elastically deformed by applying a load at a fixed rate, then initially the ML intensity increases with time, attains a peak value $I_m$ at a particular time $t_m$, and later on it decreases with time.

(x) After $t_m$, initially the EML intensity decreases exponentially at a fast rate and then it decreases exponentially at a slow rate, in which the decay time of fast decrease in EML intensity is equal to half of the decay time of piezoelectric charges.

(xi) For a given strain rate, whereas the peak intensity $I_m$ increases linearly with the magnitude of applied pressure, the total EML intensity $I_T$ increases quadratically with the magnitude of the applied pressure.

(xii) The ML spectra of ZnS:Mn crystals are similar to their photoluminescence and electroluminescence spectra.
(xiii) The elastico ML in ZnS:Mn crystals can be understood on the basis of the piezoelectrically-stimulated electron detrapping model, in which the local piezoelectric field near the Mn$^{2+}$ centres reduces the trap-depth, and therefore, the detrapping of filled electron traps takes place, and subsequently the energy released non-radiatively during the electron-hole recombination excites the Mn$^{2+}$ centres and de-excitation gives rise to the ML.

(xiv) On the basis of the piezoelectrically-stimulated electron detrapping model, expressions are derived for different characteristics of the EML of ZnS:Mn crystals and a good agreement is found between the theoretical and experimental results.

(xv) The expressions explored for the dependence of EML intensity on several parameters may be useful in tailoring the suitable materials capable of exhibiting ML during their elastic deformation.

(xvi) The values of the decay time of piezoelectric charges, time-constant for the rise of pressure, pressing rate, strain rate and the threshold pressure for EML emission can be determined from the measurement of the ML glow curve.

(xvii) In elastico ML of ZnS:Mn, the piezoelectrically induced light emission may dominate the charged dislocations-induced light emission. However, the plastico ML of insufficient high resistivity ZnS:Mn at low strain rate the dislocation-induced light emission may be comparable to the piezoelectrically induced light emission. But at high strain rate and high pressure, the piezoelectrically induced light emission may dominate the charged dislocation-induced light emission.

(xviii) The expressions derived are as given below:
Dislocation-induced elastico ML

\[ I = \eta B \dot{\varepsilon} p_r r n \left[ 1 - \exp(-\phi t) \right] \]

\[ I_r = \eta \dot{\varepsilon} p_r r n \phi t = \eta \epsilon_p r n \phi \epsilon \]

\[ I_s = \eta B \dot{\varepsilon} p_r r n \]

\[ I_{ds} = I_o \exp[-\phi(t-t_c)] \]

and, \[ I_{ds} = I_o' \exp[-\chi(t-t_c)] \]

Dislocation-induced plastico ML

\[ I = \frac{\eta \dot{\varepsilon}}{b} p_r r n \left[ 1 - \exp(-\phi' t) \right] \]

\[ I_r = \frac{\eta \dot{\varepsilon}}{b} p_r r n \phi' t \]

\[ I_s = \frac{\eta \epsilon}{b} p_r r n \]

\[ I_{df} = I_o \exp[-\phi'(t-t_c)] \]

and, \[ I_{ds} = I_o' \exp[-y(t-t_c)] \]

Piezoelectrically-Induced Elastico ML of II-VI Semiconductors

\[ I_r = \eta \sigma \mu_n \Omega N_i N_p N_e Z \alpha \tau B^2 d_0^2 Y^2 \ddot{\varepsilon}^2 (t-t_0) \]

\[ I_{df} = \eta \sigma \mu_{ne} \Omega N_i N_p N_e Z \alpha \tau B^2 d_0^2 P_m Y \ddot{\varepsilon}_0 \exp[-\phi(t-t_m)] \]

or, \[ I_{df} = I_m \exp[-\phi(t-t_m)] \]

\[ I_{ds} = I_{0s} \exp\left[-\frac{(t-t_c)}{\tau_s}\right] \]

\[ I_{dt} = I_{0t} \exp[-\chi(t-t_c)] \]

\[ I_m = \eta \sigma \mu_n \Omega N_i N_p N_e Z \alpha \tau B^2 d_0^2 (P_m - P_{th}) \frac{dP_m}{dt} \]

\[ I_m = \eta \sigma \mu_{ne} \Omega N_i N_p N_e Z \alpha \tau B^2 d_0^2 Y (P_m - P_{th}) \ddot{\epsilon} \]

\[ I_T = \frac{\eta \sigma \mu_{ne} \Omega N_i N_p N_e Z \alpha \tau B^2 d_0^2 P_m^2}{2} \left( 1 + \frac{2 \tau_m}{t_m} \right) \]
Piezoelectrically-Induced Plastico ML of II-VI Semiconductors

\[ I = \eta \alpha N_{ex} = \eta \alpha \Omega N_{e} N_{i} N_{t} \sigma n_{h} B^{2} d_{0}^{2} P_{0}^{2} \xi \sigma n_{h} \mu t [\exp(-\xi t) - \exp(-2\xi t)] \]

\[ I_{r} = \eta \alpha \Omega N_{i} N_{t} ZB^{2} d_{0}^{2} P_{0}^{2} \xi^{2} \sigma n_{h} \mu t \]

\[ t_{m} = \left( \frac{1}{\xi} \ln 2 \right) - t_{d} \]

\[ I_{m} = \frac{\eta \alpha \Omega N_{i} N_{t} ZB^{2} d_{0}^{2} P_{0}^{2} \xi^{2} \sigma n_{h} \mu t (1 - P_{th} / P_{0})}{4} \]

\[ I_{r} = \frac{\eta \alpha \Omega N_{i} N_{t} \sigma n_{h} B^{2} d_{0}^{2} P_{0}^{2} \xi Z \mu t (1 - \frac{P_{th}}{P_{0}})}{2} \]

\[ I_{df} = \eta \alpha \Omega N_{i} N_{t} ZB^{2} d_{0}^{2} P_{0}^{2} \xi \sigma n_{h} \mu t \exp(-\xi t_{m}) \exp\left\{ -\xi(t - t_{m}) \right\} \]

\[ I_{ds} = I_{0s} \exp\left[ -\frac{(t - t_{c})}{\tau_{s}} \right] = I_{0s} \exp[-\chi(t - t_{c})] \]