CHAPTER I

INTRODUCTION

1-1. LUMINESCENCE

Solid State Physics has acquired a very important status in recent years. An ideal crystal, the unit of solid, may consist of atom or atoms, molecule or molecules arranged in three dimensions according to definite geometrical patterns. It was first thought that it may be possible to interpret the physical properties of such crystals in terms of the electronic structures of the units and the pattern of repetitions. However the solid, we come across, has defects and does not consist of regular structure as defined for an ideal crystal. A major part of the present day research in solid state physics is devoted to the study of the defects in structure of the solid.

Just as the spectroscopy of atoms provides basic information about the atomic structure, investigations on LUMINESCENCE of solid provide an important tool to investigate and to understand the band structure, the energy levels of the impurities and imperfections in solids. The properties of luminescence are convenient and sensitive indications of changes in composition, structure, and atomic interactions in solid and have contributed much to our improved understanding of the solid state of matter.
Luminescence is one of the oldest known phenomenon, but a systematic study of this phenomenon started only in the middle of the nineteenth century. It still remains as one of the most fascinating fields in science. In 1888 Wiedemann introduced the term luminescence and gave the first, though not very accurate definition of this phenomenon as "the excess emission over and above the thermal emission background" (Wiedmann 1888). Luminescence means emission of light which is not purely thermal in origin. Luminescence is the general term for the emission of the visible or non-visible (ultraviolet and infrared) radiation from a substance during or following the absorption of energy from many of the varied sources as ultraviolet, X-ray or high energy particles or simply from the application of electric field (Wiedmann 1889, Randall and Wilkins 1945, Garlick 1949). The luminescence emission is not due to incandescence, hence, it is often called the "cold light". It is not the thermal radiation as it does not follow the Kirchoff's law. On the basis of the time delay in emission, it can not be explained by Raman and Compton effects. In the case of luminescence the time delay after excitation is greater than $10^{-9}$ sec. Where as Raman and Compton effects are completed in an interval of about $10^{-14}$ sec (Leverenz 1949, 1950).

Fluorescence and phosphorescence are two special aspects of luminescence. When excitation is removed there
is invariably an exponential afterglow, whose decay-rate is independent of excitation intensity and of temperature. This is fluorescence. There is an additional component of this afterglow which decays more slowly and with more complex kinematics dependent on temperature. This component is phosphorescence. According to Leverenz pure fluorescence is obtained only during the first $10^{-8}$ sec of excitation and pure phosphorescence only after $10^{-8}$ sec after the cessation of the excitation (Leverenz 1950).

Garlick defines fluorescence as the emission during the excitation and phosphorescence as that which persists after the excitation has ceased (Garlick 1949). The demarcation between the two phenomena may be fixed at $10^{-8}$ sec after the cessation of excitation as this is the time of relaxation of an ionised gaseous ion in the excited state. On the basis of the physical processes taking place during fluorescence and phosphorescence, Perrin (1929) gave the following definition. The phenomenon is fluorescence, if the emission takes place by one or more spontaneous transitions. If on the contrary, the emission occurs with the intervention of a metastable state followed by return to the excited state due to the addition of energy, then this is phosphorescence. The distinction between the two processes is also made on the basis of the variation of the luminescence decay with temperature. The decay of fluorescence is little dependent on the temperature, but the decay of phosphorescence is strongly temperature-dependent (Curie 1963).
According to mode of excitation the luminescence has been classified as under:

**Photoluminescence:** It is produced by absorption of photons of energies from a few to several electron volts for example, from ultraviolet radiation.

**Cathodoluminescence:** It is produced by energetic electrons or cathode rays.

**Electroluminescence:** It is produced by voltage applied to the luminescent substances.

**Mechanoluminescence:** It is produced during the mechanical deformation of solids.

**Chemiluminescence:** It is produced by the application of energy released by chemical reaction.

**Thermoluminescence:** It is produced when a substance is warmed to a moderate temperature which releases the previously absorbed radiation.

**Radioluminescence:** It is excited by any or all radioactive disintegration products.

**Xenogenoluminescence:** It is a specific case of radio luminescence produced by X-rays.

**Sonoluminescence:** It is produced by ultrasonic waves.

**Bioluminescence:** It is produced by the energy from biochemical reactions.
Galvanoluminescence or Voltaluminescence:- It is a luminescence phenomenon accompanying the passage of electric currents through aqueous solutions.

Aqoluminescence or Lyoluminescence:- It is produced during dissolution of certain coloured crystals (by high energy radiations) in aqueous solution.

Crystalloluminescence: - It is produced during growth of the crystals from solutions.

There are further sub-classification of the luminescence such as : photo-electroluminescence, electro-photo luminescence, mechano-thermoluminescence, thermomechano-luminescence etc. The first prefix in such luminescence denotes the controlling and the second denotes its source of power that stimulates it. In certain types of luminescence like photoluminescence, cathodo-luminescence electroluminescence, chemiluminescence, thermoluminescence, radioluminescence Roentgeno-luminescence, bioluminescence, and galvanoluminescence, the energy related to the prefix in the luminescence, directly populates the excited states of the molecules or atoms comprising the luminescent materials. In the other types of luminescence, like sono-luminescence, mechanoluminescence, aqoluminescence and crystalloluminescence, the action related to the prefix in the luminescence induces some other process which populates the excited states.
1-2 TERMS USED IN LUMINESCENCE

(A) Phosphor

A substance which can emit cold radiation is generally called the luminophor, the light bearer, or phosphor. The term phosphor is mainly used for inorganic solid luminophors. Generally, the phosphors are crystalline insulators. Phosphors are very sensitive to structural changes and are strongly influenced by the chemical composition of the base compound, physical condition of preparation, and the presence of traces of impurities, known as activators. The main constituent of a phosphor, the crystalline material itself is known as host material or matrix. An efficient phosphor is that which converts a large portion of the absorbed excitation energy into luminescence emission with inappreciable energy losses by increase in lattice vibration or electron emission or chemical or structural changes (Leverenz 1950). There are two basic types of phosphors: (I) The impurity activated phosphor in which luminescence is due to the addition of an activator in the form of traces of impurity, and (II) the so called "self activated" phosphor, which exhibit luminescence in the pure state in which the luminescence is apparently due to the specific atomic groups or atoms (Randall 1939).

(B) Luminescent Centres

Luminescence can only occur efficiently in materials where there are specific atomic or molecular sites
at which the absorbed energy can be re-emitted optically by means of electron transitions. In solid, these are called "luminescent centres". The nature of luminescent centres determines the spectral distribution of the emission of the phosphors. Here the probability of radiative transition is much greater than that for the non-radiative transition. If the probability of non-radiative transition is more, the centre is called a "killer centre" and the impurity producing it as poisons (Aigrain 1956).

(C) Traps

Traps are metastable levels in the phosphors capable of capturing electrons or holes within them and rendering them immobile. These trapped electrons can be released later by supplying an optimum amount of thermal or optical energy (Bube 1960, Garlick 1960). An electron thus released from a trap can either combine with a luminescence centre or can be trapped in another trap. The trap provides the mechanism of energy storage in most of the electronically active solid including phosphors and are responsible for the phenomenon of phosphorescence and thermoluminescence (Sproull 1963). The trapping levels owe their origin to impurity atoms, preparative conditions or imperfections in the crystal lattice (Kroger 1948). A normally occupied electron trap is called a "donor level" while a normally occupied hole trap is called an "acceptor level."
(D) **Stimulation and Quenching**

If the emission intensity of a phosphor is increased by irradiating it with a long wavelength visible or infrared radiation, it is known as optical stimulation. Conversely, if the intensity is diminished it is called optical quenching. Stimulation or quenching effects can also be observed by the application of a strong electric field to a phosphor previously excited with ultraviolet radiation. Lenard et al (1928) have studied these effects in the phosphors of alkaline earth sulphide with infrared radiation. In stimulation, the radiation releases trapped electrons, which can not make transition to the dominant activator centres due to insufficient quantum energy. However, in the case of quenching, the excitation releases positive holes from empty emission centres which then migrate to traps and capture electrons in non-radiative transition.

1-3. **Theories of Luminescence**

Phosphors can emit line or band or both types of spectra separately or simultaneously. Band emission is usually caused by interaction between the activator and the host matrix. Line spectra is however, attributed to electronic transitions occurring within shielded electronic orbitals (within the luminescence centre) so that there is little interaction with the matrix (Leverenz 1950). Such discrete levels often occur when well ionised impurity ions
with incomplete inner-shells form luminescence centres. The band emission is attributed to the outer valence electrons making transitions between levels having different principal and angular quantum numbers. The luminescent spectra differ from atomic spectra in two respects: (1) the spectra do not consist of lines but are broadened into bands whose width may be of the order of hundreds of angstroms, and (2) the emission band is displaced to the lower energy side of the absorption band by as much as an electron volt or more. All the interpretations of the luminescence phenomenon have been based implicitly or explicitly on some modification of the "configuration coordinate model" or the energy band model (Williams 1950). The first model neglects atomic re-arrangements while the second neglects the energy transport.

(A) Configuration Co-ordinate Curve Model

One dimensional configuration co-ordinate curve model was first proposed by Van Høipel (1938) and was successfully applied to problems of luminescence by Seitz (1939). Later quantum mechanical modifications were proposed by Schon (1948). This model is best suited to the explanation of quasi-atomic system like KCl:Tl. The interaction can be represented by using a single configuration co-ordinate to give the distance between the luminescent ion and its nearest neighbours in the surrounding lattice. The configuration co-ordinate curve model is illustrated in Fig.1.1. The total energy of the system for
the ground and the excited states of the centre including both ionic and electronic states is represented along the ordinate. The abscissa represents a configuration coordinates specifying the configurations of the ion around the centre. On absorbing an amount of energy $h\nu$, the centre is raised to its excited state at $B$ from the equilibrium state $A$. The transition is a vertical one (line $AB$ in Fig. 1.1) following Frank-Condon principle, according to which electronic transition occurs in a time shorter than that necessary for an ion to move appreciably. After the centre has reached to $B$, the ions of the system adjust until a new equilibrium position is reached at $C$. The energy difference between $B$ and $C$ is given off as lattice vibrations. After the centre has reached at $C$, it may return to the ground state at $D$ by emitting a quantum of luminescent light $h\nu'$. The centre relaxes from $D$ to $A$ by giving off the energy again in the form of lattice vibrations. Because of these losses, the emitted energy $h\nu'$ is lower than the absorbed energy $h\nu$. This shift is known as stoke's shift. In the case of KCl:Ti this shift is of several electron volts at room temperature (Klick and Schulmann 1957).

Mott and Gurney (1940) have shown that given sufficient thermal energy the centre in the excited state $C$ might reach a point such as $E$ where the curves approach each other closely. The system may then return from the excited state to the ground state by a non-radiative transition. This is known as thermal quenching of luminescence.
An alternative mechanism has been suggested by Weitz to explain the absence of luminescence in a number of solids (Fig. 1-2). After the absorption of light the system in the excited state relaxes to such an extent that its minimum is shifted away from the minimum of the ground state curves. In approaching this minimum, the possibilities of radiationless transition exist at point such as $\hat{\alpha}$. The model proposed by Dexter et al. (1955) requires less lattice relaxation around a centre that does the model of Weitz (1939). If the transition is to a point $\delta$, the energy at which is higher than at $\hat{H}$ (the point of closest approach between ground and excited states energy curves), then before reaching its new equilibrium state, a radiationless transition to the ground state can occur at $\hat{H}$ (Fig. 1-3).

Configuration co-ordinate curves has been obtained experimentally by many workers (Williams 1951, Klick and Schulmann 1952, Williams and Johnson 1960) in the case of non-photoconducting phosphors for example, alkali halides, tungstates etc. These curves have also been applied to doubly activated phosphors and to explain the process of sensitization (Fondal 1955, Bottem 1948). On the basis of disagreement in calculated and observed values of activation energy for non-radiative transition Maeda (1959) has proposed a multidimensional model in preference to the simple one dimensional model discussed above.
Fig. 1.1 - Schematic Configuration Coordinate Curves.

Fig. 1.2 - The model illustrated by Seltz for radiationless transitions.

Fig. 1.3 - The model illustrated by Dexter at al for radiationless transitions.
(B) **Continuous Dielectric Model**

In the configuration co-ordinate curve model the interaction of the centre with the lattice is restricted to the first and second nearest neighbours. Huang and Rhys (1950) has proposed a theory in which they ignored these short range forces and computed interaction of a centre with the phonon field of the lattice. This interaction is an electrical one and the development treats the lattice as a continuous dielectric in which the centre is embedded. In absorption, for instance, the centre experiences a difference in charge distribution, when the system jumps from the ground to the excited state. This re-arrangement in charge, induces in turn, a change in lattice polarization which is accompanied by the creation of lattice phonons.

(C) **Energy Band Model**

This theoretical model adopted to explain the characteristics of photoconducting sulphide and silicate phosphors was first put forward by Riehl and Schon (1939) and independently by Johnson (1939) on the basis of the collective electron model originally developed by Bloch (1928) to explain the energy states of a perfect lattice (Fig. 1.4). This model is based on the general quantum mechanical treatment of the interaction of valence electrons with the three dimensional periodic potential of the crystal lattice. In an isolated atom the energy states for electrons consist of discrete levels separated by regions of forbidden energies. The allowed states are
defined by Schrödinger's wave equation. But in a perfect crystal lattice when the atoms or ions are arranged in an orderly manner and in close proximity, the discrete levels are disturbed by mutual interaction and so broadened into bands of allowed energy separated by bands of forbidden energy. In an insulator, the uppermost filled continuous energy band is called the valence band and the lowest empty continuous energy band is called the conduction band.

Impurities introduced to produce emission centres for luminescence will usually give rise to discrete localized states (L) in the forbidden zone above the filled band (F), with the ground state of the each centre occupied (Fig.1.4). Presence of other impurities, vacant lattice sites and other lattice defects will provide unoccupied levels in the forbidden zone (T) just below the conduction band, where the electrons can be trapped.

If the phosphor is excited by X-rays, ultraviolet rays, γ-rays, or in some cases by visible radiation, then the energy may be absorbed by an atom in the crystal lattice. In this process an electron will be raised to the conduction band from the valence band represented by the transition shown in (Fig.1.4) leaving behind a positive vacancy known as a hole capable of moving through the lattice in an applied field. The absorption bands, due to such transitions are called fundamental absorption bands, of
the phosphor matrix and is generally situated in the ultraviolet or near the visible regions of the spectrum.

The radiation of lower energy which is not absorbed by the matrix may be absorbed by the impurity centres. In such cases the electron transition can take place either to an excited state of the centre or to the conduction band giving rise to additional absorption bands lying on the longer wavelength side of the fundamental absorption bands.

In alkaline halide crystals, although the absorption takes place in the matrix, the excited electrons are not raised to the conduction band, but remain bound to their respective positive holes. These bound electron-hole pairs are known as "excitons" (Sakata 1930). The absorption of energy may also result in the transition from the filled band directly to the trapping states $T$ (Urbach et al 1948, Such 1940). An important limitation of this model is that the energy bands and levels are characteristic of a particular atomic configuration, hence, the atomic re-arrangements that occur during luminescence are ignored.

(9) Models for Luminescence Centres in Photoconductive Phosphors Involving Transfer of Charge

This type of luminescence emission is mostly due to recombination of electron and hole at an imperfection. The following models have been assumed to explain the phenomenon of luminescence in photoconducting phosphors.
(1) Schon-Klasen's Model

This model was proposed by Schon (1942) and developed by Klasen and coworkers for sulphide phosphors (Kise and Klasen 1948, Lambe and Klick 1955). This model makes use of the energy band scheme of a solid in which the activators (or quenchers) are supposed to cause localized levels, not far above the valence band. Fig.1-5 illustrates the model for the case of a single luminescence centre. The sequence of events is as follows:

(1) Absorption of light in the matrix leads to an electron in the conduction band and a hole in the valence band.

(2) The hole may migrate towards the impurity centre B.

(3) The luminescence centre has a net negative charge and attracts the hole with a Coulombian attraction. 
    The hole is captured by the impurity centre giving out infrared radiation.

(4) The electron wanders through the lattice D and is finally captured by the centre E, where it recombines with the captured hole giving off luminescence emission.

(ii) Lambe and Klick Model

This model shown in Fig.1-5 assumes that the luminescent levels are near the conduction band. The mode of operation of the system is as follows (Lambe and Klick 1955, Lambe and Klick 1956).
(1) Light is absorbed exciting an electron to the conduction band, leaving a hole in the valence band A.

(2) The hole and the electron move about in their respective bands and eventually the hole migrates near an impurity centre B because of its effective negative charge.

(3) The hole is captured by the impurity centre C giving off luminescence emission and the centre becomes neutral in charge.

(4) The electron wanders through the lattice until finally it comes near the centre C.

(5) The electron is finally captured by the centre C giving off a small amount of energy as infrared radiation or as a lattice phonons B.

(iii) **William-Prener Model**

This model also known as associated donor-acceptor model has been proposed by William and Prener to explain the luminescence phenomenon in ZnS:Cu phosphors (Fig. 1.7). Williams (1960), Williams and Prener (1956), Prener and Williams (1956).

In this model shown in Fig. 1.7, centres involve a ground state I near the valence band which have a high probability for hole capture (acceptor-level) and an excited state II near the conduction band which has a high probability for electron capture (donor-level). After the capture in each type (A and B) emission can take place by transition of the electron from level II to level I. The only condition to be fulfilled is that the
Fig. 1.4 - Energy Band Model
C - Conduction band,
F - Filled band
L - Luminescence centre
T - Trap

Fig. 1.5 - Schon-Klasen's model

Fig. 1.6 - Lambe-klick model

Fig. 1.7 - Williams Prener Model
temperature should not be very high, because in that case
the electrons in state II are raised to the conduction
band and hence the emission is quenched (Prener and Wiel
1959, Klick and Schulmann 1956, Williams 1957). Klasens
(1959) has used this model to explain the photoconducting
and temperature dependence of fluorescence in ZnS phosphor.

(3) Luminescence Processes Involving Energy Transfer
without Movement of Charge

The phenomenon in which the centre responsible
for emission is not the same in which absorption has taken
place, is known as sensitization. The mechanism does not
involve the movement of charge carriers in the transport
and transfer of excitation energy from the absorber to the
emitting centre. The following mechanisms of energy
transfer have been proposed.

(1) Cascade Mechanism

According to this mechanism, one centre after
absorbing excitation energy emits radiation, which on being
absorbed, excites a second centre. This mechanism involv-
ing radiative transfer of energy between the two centres
is known as cascade mechanism. This process is better
applicable to organic phosphors than to inorganic ones,
because in the latter case one frequently deals with acti-
vation having forbidden transitions (Klick and Schulmann
(ii) Resonance Transfer

In this process the energy absorbed by the sensitiser is transferred to the activator without any emission by the sensitiser. This is due to the resonance mechanisms by dipole-dipole or dipole-quadrupole or exchange interaction (Proster 1948, Dexter 1953, Schulmann et al. 1950).

When the concentration of the activator is increased singly activated phosphor is/beyond a certain value, it is observed quite generally that the luminescence efficiency decreases. This is known as concentration quenching. The concentration quenching can be explained by the resonance mechanism of energy transfer. Dexter and Schulmann (1954) have shown that from activator to another activator resonance transfer of energy takes place until it arrives at one of the quenching sites. These quenching sites may be other impurity atoms or lattice defects.

(iii) Exciton Migration

This model proposes the transfer of energy through lattice by metastable excitons (Haken 1958, Konobeev 1963, Broser 1958) and Balkanski (1958) have demonstrated experimentally the possibility of exciton action at large distances from their point of creation. They have shown that such exciton action is possible only in pure and defect free crystals.
When certain solids are subjected to stress beyond particular levels, light emission follows their deformation. This physical process of light emission is known as "mechanoluminescence" or "triboluminescence". Since the light emission during the mechanical deformation of the solids is not attributed to friction, the nomenclature "mechanoluminescence" is preferred in some of the recent literatures (Chandra and Shrivastava 1978, Sodomka 1978, Chandra et al 1980). The nomenclature "mechanoluminescence" has also been preferred in this thesis and it has been approved by the Research Degree Committee of the Ravishankar University, Raipur (M.P.). Since the mechanical energy can not directly populate the excited states of the molecules comprising the crystals, some alternate process should be responsible for the ML excitation. In fact the mechanoluminescence (ML) is a representation of mechano-induced luminescence. The ML is considered to be a complex process for a number of reasons. The mechanical deformation of a solid can result in elastic and plastic deformation as well as fracture. The fracture process involves crack initiation, propagation, stress amplification and in some instances, the production of high electric fields. The scientific literature from 1600's to date often gives varied and seemingly conflicting or inconsistent results on the process. In order to evaluate the current status of ML research, a summery of the previous studies is given somewhat chronologically with emphasis on the important results and discussions.
The first recorded observation of ML was by Sir Francis Bacon (1605). Bacon observed that light was emitted when lumps of sugar were fractured. Later, Waller (1684) reported a study of ML from sugar, rock salt, agate and jasper and concluded that these materials were able to "hold the light which they receive", which could be released by fracture.

By the end of 1700's, the emission has been observed in a number of minerals and pottery materials (Harvey 1937). Wedgwood (1792) reported the ML of many substances, including quartz, diamond and ruby. It was found that fracture was necessary in order to observe the emission and since the sparks from the stones were sufficiently hot to ignite gunpowder, he attributed the light to be due to the surface particles becoming red hot or white hot as a result of the friction. The phenomenon was named "trennungslicht" (light of shearing) by Heinrich (1820). Heinrich believed the emission was from electrification caused by friction or from chemical decomposition as a result of the electricity. The nomenclature triboluminescence (light of rubbing) was proposed by Wiedemann (1888).

Burke (1898) observed the ML spectrum of sugar through a spectroscopy and determined that the emission was at wavelengths shorter than 480 nm. This finding was considered to be evidence against Wedgwood's proposed
"red hot" particle mechanism. Dewar (1901) observed the ML in uranyl nitrate during placing or removing the crystals from liquid helium. This fact was against Heinrich's frictional electrification mechanism.

A series of papers appeared in the early part of this century which were essentially competitions of previously reported and newly discovered mechanoluminescent crystals. Tschugaeff (1900) gave a list in which out of 400 organic crystals, 121 are mechanoluminescent and only 6 out of 110 inorganic crystals are mechanoluminescent. A list of 260 mechanoluminescent materials was given by Trautz (1905, 1910). Gernez (1905) listed 82 inorganic salts, Lindener (1910) reported 110 minerals, and Imhof (1917) reported 40 inorganic crystals, which exhibit the phenomenon of ML.

Later on the attention turned to the spectroscopic investigation of ML. Weiser (1918) reported the spectral characteristics of ML of NaCl and As₂O₃ crystals using a series of filters. Longchambon (1922) published the ML spectra of sugar using a spectrometer equipped with a photographic plate. He identified the spectrum as the electrical discharge of molecular nitrogen and recorded similar spectra for a variety of other mechanoluminescent materials including copper sulphate, barium chloride and aniline hydro chloride (Longchambon 1925). He tried to explain the ML excitation on the basis of the piezoelectricity of the crystals. He showed that majority of
the mechanoluminescent crystals were non-centrosymmetric and proposed that piezoelectric charging of the crystal caused the dielectric breakdown of the air around it. In samples, where Longchambon observed other emission in addition to the nitrogen discharge, such as uranyl nitrate, he suggested that they were the result of photoluminescence excited by the ultraviolet gas discharge. To justify his piezoelectric mechanism he reported that the single crystals of sugar and tartaric acid did not show ML when cleaved parallel to their piezoelectric axis, though they were intensely mechanoluminescent when cleaved in all other directions.

Wick (1937) examined the ML of 12 different fluorite samples through the spectroscope. In all the samples he studied, the ML matched the photoluminescence spectra. These findings were similar to the Longchambon's results with other mechanoluminescent materials. Wick (1937) further demonstrated that ML spectra of certain minerals were similar to the thermoluminescence spectra (Wick 1937, 1940). In order to test whether ML was the result of thermoluminescence due to local heating, she treated the sample at red heat for over thirty minutes to exhaust any thermoluminescence and then checked for the ML. The ML emission was observed both in the hot material and in the samples after cooling to room temperature. Juries (1946) proposed an electroluminescent origin of the ML emission in this crystal.
Wolff et al (1952) gave a most up to date list of mechanoluminescent substances. They examined over 1700 compounds and found 154 inorganic substances, 188 organic substances and 16 minerals to be mechanoluminescent. Wolff et al (1954) have also investigated the ML and exoemission of ZnS crystals. Remarkable studies were made on the ML of As$_2$O$_3$ crystals by Stranski and his coworkers. The spectral study of the ML of arsenic trioxide revealed that it contains both nitrogen discharge lines and a broad band centred at 425 nm which corresponds to the photoluminescence (Stranski 1955). Stranski (1951) confirmed Weiser's (1918) earlier observation that the ML intensity of newly formed As$_2$O$_3$ crystals diminished if the crystals were stored for any length of time. After studying this decrease in intensity as a function of time, storage temperature, and conditions of crystallization, they determined that only the arsenolite form was mechanoluminescent. (As$_2$O$_3$ exists in two polymorphs, claudetite and arsenolite. The arsenolite phase generally contains claudetite type defects).

The loss of ML intensity could also be hastened by subjecting the crystals to ultraviolet or $\gamma$ -irradiation (Wolff et al 1952), which was assumed to cause local changes in the crystal structure. The ML could be reactivated by placing the crystal in an electric field (approximately 2 kV/mm) under ultraviolet irradiation for 5 hours (Gross et al 1955). It was concluded that the ML was lost when the claudetite type defects in arsenolite structure were annealed and could be re-activated by
realignement in the intense electric field.

Belyaev et al (1963) examined the ML intensity as a function of uniaxial strain on LiF, NaCl, KCl, CaI, and Tl doped KI crystals. They showed that no emission was observed during elastic or plastic deformation of the unirradiated crystals. The ML produced upon fracture was identified as a nitrogen gas discharge spectra (Belyaev and Martyshev 1969). The study also revealed an acoustic signal accompanying each ML pulse. This signal was detected with a ceramic microphone placed next to the crystal under stress. By placing an antenna around the sample, it was possible to detect a 1.5 MHz radio frequency signal simultaneously with the ML in LiF and NaCl. The amplitude of the rf pulse was proportional to the ML intensity.

Belyaev et al (1963) observed that the ML occurred during the growth of cracks in the alkali halide crystals. This is supported by the fact that the light intensity increased as the rate of uniaxial strain was increased. The ML during fracture did not occur continuously. It appeared in short pulses ranging 20 - 29 nsec in duration and often double pulses separated by 15 - 200 nsec (Belyaev and Nabatov 1963). Belyaev et al (1963) concluded that the crack propagates in a stepwise manner and that ML is produced at a few special parts of the crack.

Belyaev et al (1966) observed ML during fracture of LiF crystals caused by a ruby laser pulse at
694 nm. They reported that the emission produced in this manner was 100 times more intense than the normal thermoluminescence. It is unfortunate, however, that the light intensity was monitored at 347 nm where other effects such as frequency doubling of laser pulse could be important.

By observing a sharp change in the potential difference across the crystal surfaces during the fracture and subsequent light emission, Belyaev and Martyshov (1964, 1969) concluded that electrical discharge was the major component of ML in LiF. The potential difference was assumed to be produced by the movement of charged dislocations. The ML spectra of LiF fractured under a 10⁻⁴ Torr vacuum showed the presence of nitrogen discharge (presumed to be absorbed by the crystal) with increased relative intensity in the high energy region of the spectrum. This high energy emission was proposed to be due to a second minor component of the ML emission produced by radiative transition of electrons from the conduction band to new surface levels created by the cracks.

Meyer and Polly (1965) and Polly et al (1967) investigated the ML in unirradiated LiF, KCl, NaCl and KI crystals. In these studies, the ML was excited by impulse or scratching from a sapphire or steel needle. From the effects of the gas pressure, mechanical treatment and temperature on the ML, it was proposed that the potential differences due to the motion of charged jogs and kinks during plastic deformation, are responsible for the ML
excitation. It was proposed that on impact with the needle, dislocation of opposite charge are created, which then move in opposite directions under strain and produce a potential difference across the crystal. To support this mechanism Polly et al (1967) pointed to the observation of light emission upon needle impact with no visible evidence of crystal fracture. A later report measuring the potential difference during the needle impact showed that the potential dropped on impact and then increased as the needle rebounded. Subsequent discharge was accompanied by a sudden drop in potential (Meyer et al 1970). These results indicated that the fractureless emission observed in the previous study was actually an electrical discharge between the crystal and the needle caused by contact potential differences and not true ML.

Experiments exciting the ML in alkali halides by scratching with a needle or by milling the crystal surfaces led to a new mechanism (Obrikat et al 1967). They determined that the light intensity was proportional to the amount of new surface area created and that just rubbing the crystal surface with a smooth miller did not produce ML. Thus mere contact potential difference were not sufficient. Fracture was necessary. A thermal mechanism is proposed where the emission is correlated to black body radiation of the order of $10^4$ K. According to Meyer et al (1970), this temperature is produced at the tip of the propagating crack.
Frohlich and Seifert (1971) measured the ML in NaCl crystals at 1.5 torr hydrogen atmosphere (gas discharge region of ML) down to temperatures of about 20°K. The ML intensity strongly increases with decreasing temperature. The creation of electric field for the gas discharge is explained, first, by crack and fracture processes leading to parts of charged fracture areas and second, by the separation of microscopic regions of different net charge (due to atomic disorder during the crack formation. It is shown that the charged dislocations cannot be responsible for the creation of the electric field because the temperature dependence of the potential differences due to the charged dislocations is opposite to that of ML.

The ML in the crystals and phosphors of ZnS was investigated by Sodomka and Chudacek (Sodomka 1963, Chudacek and Sodomka 1963, Chudacek 1965, Sodomka 1968). Sodomka (1964) has shown that the ML appears only when there is a time change in the pressure. Chudacek (1966) has shown theoretically that a recombination centre of the type Cu⁺-(5) in the ideal ZnS lattice has "local" piezoelectric properties. On the basis of this logic, an attempt to explain the ML excitation has been made. Chudacek (1967) has reported that the ML excitation in ZnS phosphors takes place in two stages: First, the plastic-elastic deformation, in which the mechanical stress affects the local electric field which ionizes the
luminescence centres. The second stage is fracture, in which the bonds between the luminophor atoms are torn, thus giving rise to a large number of free electrons in the region between the fractured surfaces. At the instant when the fracture occurs, the luminophor is disturbed to a certain depth below the fracture surface. It is therefore necessary to assume the creation of a certain density of electrons and holes in the conduction and valence bands in the region below the fractured surface, at the moment of fracture. The surface states created area filled with charges present and space charge is produced at the fractured surfaces, which causes ML.

Meyer and Obrikat (1969) and Meyer et al (1970) have suggested that the ML of zinc sulphide has an electro-luminescent origin. Study of Mn doped ZnS over a wide range of dopant concentrations showed that ML, electroluminescence and photoluminescence spectra were all identical. The ML spectrum of Cu doped ZnS is significantly different from the photoluminescence spectrum and can be superimposed on the electroluminescence spectrum produced at electric field of frequency 15 KHz (Theissen and Meyer 1970). The ML spectra of Cu doped (Zn, Cd)S samples closely resemble the corresponding electroluminescence spectra but were slightly blue shifted in every case (Meyer et al 1970). This blue shift was explained as a result of contraction of the crystal lattice under high stress. Other non-spectroscopic evidence also linked ML to electroluminescence. The ML intensity was shown to have the same functional
dependence on force as the electroluminescence intensity has on voltage and both the phenomena shared the same temperature dependence and the same temporal decay characteristics (Theissen and Meyer 1970). The observation of double ML pulses was attributed to the reflection of the initial force from the crystal boundaries. Alzetta et al (1962) found that on applications of a square wave from compression pulse to crystals of Mn doped ZnS, ML was observed at both the instances of rise and fall of the compression pulse. This is analogous to the observation of electroluminescence during both the rise and fall of the applied electric field. They also reported that under a sinusoidal compression, the ML pulses occurred at twice the frequency of the applied force (Alzetta et al 1967). When pressure or voltage of the same applied pulse shape was applied to ZnS : Mn the respective ML and electroluminescence appeared identical in shape (Alzetta et al 1967). The emission was examined as a function of strain (Alzetta et al 1970). Results on activated alkali halide crystals indicated that 10% of the light intensity was observed during elastic deformation, 75% during plastic deformation, and the remaining 15% was emitted at fracture. In the case of ZnS : Mn the emission was distributed 5% in the elastic region, 80% during plastic flow, and 15% at fracture. Experiments where the strain was recycled showed that no light was emitted in the elastic or plastic regions of the second application of strain until the magnitude of
the previous applied strain was passed. This ML "memory" was observed in both the activated alkali halide and doped ZnS samples. It is also observed that the ML intensity depends on the rate of strain which suggests that ML mechanism is based on the unpinning of dislocations under stress. Scarmozzino (1971) tested this mechanism on Cu doped ZnS. If ML were the result of piezoelectrically induced electroluminescence, then it should be observed under hydrostatic pressure as well as the previously examined uniaxial compression. Under pure hydrostatic pressure, however, the dislocations are not mobile and ML excited by this mechanism would not be observed. Scarmozzino (1971) applied rapid pulses of hydrostatic pressure 100 times greater than necessary to produce piezoelectrically a sufficient electric field and subsequent electroluminescence in ZnS : Cu crystals. No emission was detected. This established the idea that moving dislocations were responsible for ML in these systems.

1.6. RECENT STUDIES OF MECHANOLUMINESCENCE

In this century, the work on ML have been reviewed by Trautz (1905, 1910), Gernes (1908), Weiser (1918), Longchambon (1925), Lenard et al (1928), Meyer et al (1970), Walton (1977) and by Zink (1978). The details of the history, experimental devices, and the mechanism of ML can be found in the review articles. Recently Chandra (1981) has reported the correlation of ML with the piezoelectric behaviour of more than hundred molecular crystals. The
intensity and the spectra of ML of the crystals are reported. The piezoelectric model of ML is analysed and it is found that most of the piezoelectric crystals exhibit ML. The absence of ML in some of the piezoelectric crystals may be due to insufficient electrification for the ML excitation. Some of the non-piezoelectric crystals like saccharin, salicylamide, phthalic acid, salicylic acid etc. exhibit ML because of the random presence of a piezoelectric phase in the vicinity of the defects. The absence or presence of ML in several polymorphic crystals are reported which is in accord with the piezoelectric model. It has been concluded that the piezoelectric field near the tip of the mobile cracks excites, both the molecules of the crystals and the adsorbed nitrogen. The excited molecules of nitrogen, energetically located above the emitting state of the molecules of the crystals, may rapidly transfer their energy to the crystal before the emission can take place. Depending on the total or partial transfer of energy from the excited nitrogen molecules to the molecules of the crystal, the ML spectra may consist of either only the molecular emission or the combination of the molecular emission and nitrogen emission. For the crystals which do not exhibit other types of luminescence, the ML spectra may consist of only the nitrogen emission.

Godomka (1971) has investigated ML in SiC and other uncommon materials. The possibility of strength
determination of microcrystal from the ML measurements, has been reported (Sodoska 1974). Sodoska (1979) has shown that the ML may be a useful phenomenon for the scientific interpretation of the mechanism of erosion. Recently, Sodoska (1980) has measured simultaneously the ML and acoustic emission during the mechanical deformation of organic glasses, steel and copper plates. It is concluded that the ML and acoustic emission are stimulated by the same sources of deformation.

Reynolds and Wawner (1976) has reported the ML during the fracture of SiC filaments. Sodoska (1978) has shown that the ML spectra of SiC is similar to the cathodoluminescence spectra. Borisova et al (1975) have reported the ML emission during the deformation and fracture of metallic alloys and Molotskii (1978) has reported the ML emission during plastic deformation and fracture of copper. Wawner and Krukonin (1976) have reported the ML emission during the fracture of boron filaments. The crystal of Bis (pentahapto-benzylcyclopenta dienyl) zirconium, dindene, and N-acetylantananillic acid are reported to exhibit intense ML (Dusausoy and Protos-1978, Noland et al 1979, Mascarenhas et al 1980). Takada (1977) has shown that the ML spectra at liquid nitrogen temperature of silver iodine and silver bromide crystals resemble their photoluminescence spectra. Bredikhin and Shmurak (1979) has studied the ML of ZnS : Cu, Al crystals and have found that the interaction of charged dislocations with luminescent centres is responsible for the ML excitation.
Grabec (1974, 1975) has reported the ML emission during the plastic deformation of certain variety of rubbers. He has shown that the ML measurements can provide useful information about the mechanical states of the samples.

Ohman (1978) has reported some laboratory experiments on the thermal emission of glowing iron flakes. Clear effects of polarisation have been found. Sometimes in flakes of small size, indicating polarisation of a kind similar to that appearing in the thermal emission from narrow filaments. Sudden flashes of light appear in the thermal emission from flakes produced in a grinding wheel. At the same time the flakes splits up into two parts. It is suggested that the flash is due to tribo-thermoluminescence. It is shown that the infrared radiation of the solar corona may contain a faintly polarized component due to thermal emission from dust particles.

Recently a quantum mechanical explanation of the ML has been proposed by Sodomska. Two facts discussed in details are: first, the ML excitation in Mn doped ZnS, and second, the possibility of X-ray emission from highly mechanically over-stressed solids. It is shown that the time-dependence pressure applied to the condensed matter may induce broad electromagnetic spectra, spreading from low electromagnetic to X-ray frequency. Lin et al (1980) has developed a theoretical model for the mechano-excitation mechanisms due to the electric field effect and the pressure effect. They have shown how to analyse the
ML spectra to determine the external factors that affect or induce the ML.

Zink and his coworkers have made spectroscopic investigation of the ML and photoluminescence of many organic and inorganic crystals. (Zink 1978, Hardy et al 1977, Chandra and Zink 1981). On the basis of the spectroscopic investigations, eight origins of the ML has been proposed, such as: crystal fluorescence, crystal phosphorescence, luminescence from nitrogen or other gases, metal-centred luminescence, luminescence from charge transfer complexes, luminescence from free radicals, black body radiation, and conduction band to surface-band transitions. Only one or the combinations of several of the above origins contribute to the ML of crystals. A satisfactory correlation of the ML to the crystal structure of the molecular crystal is confirmed,(Hardy et al 1978, 1981; Chandra and Zink 1981). The mechanical characteristic of ML exhibiting gas discharge ML, and the molecular-emission ML has been reported (Chandra and Zink 1980 a,b).

Hardy et al (1979) have studied the luminescence emission, produced during subjecting saccharin (impure), coumarin, NaCl and KCl crystals to a 20 ns, 1060 nm pulse Nd laser (pulse energies ranging from 0.5 to 4 J cm$^{-2}$ 200 MW peak power). The spectra of laser-induced emission in saccharin crystal are similar to the ML spectra. However, the spectra of the laser-induced emission in coumarin do not resemble the ML spectra. The
laser-induced emission in NaCl and KCl crystal is found to be the same as the emission excited in their crystals by X or γ rays.

Hardy and Zink (1976) has studied ML and high-pressure photoluminescence of certain tetrahedral manganese (II) complexes and have concluded that the ML excitation does not take place due to direct excitation of the molecules by the high pressure perturbation. From the comparison of the intensities in the ML and high-pressure photoluminescence emission in linear chain manganese (II) compounds, Zink et al (1980) have concluded that the ML is equivalent to the high-pressure photoluminescence with pressure \( p = (2 \pm 1) \text{kbar} \).

Zink and Chandra (1981) have reported the ultraviolet-visible spectra of the light emitted during crystallization of Ba(ClO\(_3\))\(_2\).H\(_2\)O, As\(_2\)O\(_3\), and methyl salicylate. They have compared the crystalloluminescence spectra to the ML and photoluminescence spectra. The differences between the crystalloluminescence and ML spectra of Ba(ClO\(_3\))\(_2\).H\(_2\)O show that the former does not arise from fracture of the newly-formed crystals. However, in As\(_2\)O\(_3\) and methyl salicylate, the spectral similarities suggest similar origin of the ML and crystalloluminescence.

For the last 12 years, the research group at the Government Science College, Raipur is actively engaged in the studies of ML in a large variety of organic and
inorganic crystals. A satisfactory correlation between the ML and the strength and fracture of the crystals, has been reported (Das et al 1972, Chandra et al 1977). The kinetics of ML has been measured and it has been found that the time-dependence of ML of fluorescent and of non-photoluminescent crystal follows the time dependence of the newly created surfaces (Chandra 1977, 1981b). The kinetics of ML of phosphorescent crystals possesses two rate of decay, one related to the kinetics of the creation of new surfaces and the other related to the kinetics of the phosphorescence (1981b). Various parameters of ML like, stress-dependence, temperature dependence, crystal size dependence, impact velocity dependence etc. have been studied (Das et al 1972, Das and Chandra 1974, Chandra and Elyas 1977, Chandra and Tutakane 1978). The correlation of ML to the crystal-structure and the piezoelectric charge produced during the deformation of the crystals has also been reported (Chandra and Shrivastava 1978, Chandra and Elyas 1979, Chandra and Shrivastava 1979, Chandra et al 1980). A survey of ML in a large number of inorganic crystals suggests that all the piezoelectric and some of the non-piezoelectric crystals exhibit the phenomenon of ML (Chandra and Verma 1980, Chandra and Tutakane 1981). The ML has been investigated in many phosphors of ZnS, CdS, CaS and alkali halides (Chandra and Majumdar 1981).
IV. OUTLINE OF THE PRESENT STUDY

Whether intense or weak, nearly half of all inorganic compounds and between a quarter and third of all organic compounds exhibit the phenomenon of ML. The ML appears in insulators, semiconductors as well as in metals. The ML also appears in amorphous solids as well as in glasses. Most of the organic and inorganic crystals exhibit ML only during their fracture. However, the crystals of impurity doped zinc sulphides and coloured alkali halides exhibit ML in their elastic, plastic, and fracture regions (Alzetta et al 1970). The crystals of certain rare earth oxides show ML in their plastic and fracture regions (Williams 1979). Certain variety of rubbers show ML during their plastic deformation (1974, 1975). So far as the work is concerned, the ML may be regarded as an inter-disciplinary subject of research. It has been studied by physicists, chemists, geologists and material scientists. Although, there is divergency in the field of ML research, the aim of all the workers to date are the same and mainly directed towards understanding the excitation mechanism of ML.

The mechanism and the mechanical characteristics of the ML excitation in the coloured alkali halide crystals is least understood. Intense ML is observed in the alkali halide crystals after irradiation with X or Y rays. The irradiation creates colour centres in the crystals. An electron trapped in an colour centre is promoted to the conduction band, when the lattice defects are and destroyed by elastic or plastic flow. Luminescence is observed as the electron recombines with the holes. Thus, even though the mechanical force is necessary, it can not be considered the "cause" of emission any more than the mechanical force on a light switch which can be considered the "cause" for the glow of a tungsten filament.

Only limited studies have been made on the ML of coloured alkali halide crystals. Urbach (1930) and Wick (1939) have reported the ML emission during the mechanical deformation of irradiated alkali halide crystals. Trinks (1938) has shown that the ML of NaCl and KCl crystal increases with irradiation dosage, thickness of the crystal, and the pressure. Metz et al (1957) and Alzetta et al (1970) have found that the light emission in X-irradiated KBr, NaCl and LiF crystals is directly proportional to their strain-rate. Pirog and Sujak (1968) have found the decrease in ML with increasing rate of compression. Many workers have proposed that the ML arises from the recombination of free electrons with the luminescence centres (Metz et al 1957, Leider 1958, Senchukov and Shmurak 1970). Kruglov et al (1966)
have shown that the impact of the moving dislocations with luminescence centres excites the later in irradiated KCl crystals. However, Shmurak and Aliasberg (1967) have reported that the unpinning of dislocations from luminescence centres is the source of the ML excitation in $\gamma$ irradiated KCl crystals. Alzetta et al (1970), and Sanchukov and Shmurak (1970) have shown that the ML in $\alpha$-irradiated alkali halide crystals is the result of interaction of dislocation with the colour centres. Shmurak (1969) has shown that the total number of photons emitted from irradiated KCl is directly related to the area swept-out by the dislocation lines. Ueta et al (1982) have compared the decay of the electric current produced in the absence of an electric field by plastically deforming an unirradiated KCl crystal with the decay of the ML produced by an irradiated KCl crystal. Both the decay curves were found to be of the same form. Guerrero and Alvares Rivas (1978) have studied the dependence of ML and thermoluminescence on the strain of $\gamma$ irradiated KCl crystals. Butler (1966) has shown that the spectra of the ML produced during elastic and plastic deformation of $\gamma$ irradiated alkali halide crystals (which he calls "deformation luminescence" DL) is similar to the luminescence spectra excited by high energy radiation. We have found the ML emission during the application as well as release of a uniaxial pressure in $\alpha$-ray irradiated alkali halide crystals (Chandra and Ellyas 1978).
Since the mechanical energy in the elastic, plastic and fracture regions of the crystals can not directly populate the excited states, there should be some alternate mechanism of the ML excitation. The necessity of both the colour centres and the movement of dislocations for the appearance of ML in coloured alkali halide crystals, suggests that mechanism of the ML excitation should involve the process related to both the colour centre and the movement of dislocations. In this connection four possible mechanisms may be speculated for the ML excitation of coloured alkali halide crystals. They are:

1. Unpinning of dislocation from luminescence centres,
2. Annihilation of dislocations of opposite sign and the ionization of colour centre,
3. Diffusion of interstitial halide ions to the colour centres during the movement of dislocations and consequent ionization of the colour centre, and
4. ML excitation due to the interaction of the mobile charged dislocations with the colour centres.

None of the processes is well understood to date. The interest of the present investigation is to understand the mechanism of the ML excitation, and the ML produced during release of the pressure. To fulfill the object of the present investigation, the following studies have been made:

1. Dependence of ML intensity on the number of applications and releases of pressure in X-irradiated alkali halide crystals.
2. Spectra of the ML produced during applications and releases of uniaxial pressure in X-irradiated
alkali halide crystals.

(3) Dependence of ML intensity on the number of newly created dislocations in \( \alpha \)-irradiated alkali halide crystals.

(4) Effect of periodic stress on the thermoluminescence of coloured alkali halide crystals.

(5) The effect of temperature on the ML of \( \alpha \)-irradiated alkali halide crystals.

The \( \alpha \)-irradiated KBr, KCl, KI, LiF and NaCl crystals are chosen for the present study. Sometimes, the \( \gamma \) irradiated alkali halide crystals were also used for the comparative studies. It should be noted that the unirradiated KBr, KCl, and KI crystals do not exhibit ML. However, the unirradiated LiF and NaCl crystals exhibit ML only during their fracture. The ML does not appear during the elastic or plastic deformation of additively coloured alkali halide crystals (Butler 1966).
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