CHAPTER VI
DISCUSSION AND CONCLUSIONS

6-1. INTRODUCTION

In this chapter, the results obtained so far in the previous chapters are discussed on the basis of existing ideas about the luminescent properties of substances. Further, an attempt is made to correlate the different results obtained in the investigation of TL in the tartrate crystals regarding the effect of; mode of mechanical crushing, temperature, irradiations and simultaneous charge produced at fracture.

Before concluding the experimental results, some of the facts such as luminescence in organic crystals, waves and vibrations in solids, exo-electron emission, dislocations and defects in crystals and fracture of solids will be discussed briefly because these facts are intimately related to the TL phenomenon.

(A) Luminescence in Organic Crystals

Luminescence is observed in many organic materials in the gaseous, liquid and solid states. Aromatic hydrocarbon such as anthracene containing napthacene shows strong photoluminescence of short duration. This property has provided substance such as p-terphenyl with the addition of diphenyl-stilbene, suitable for use in scintillation counters for the detection of γ-radiation. Some organic dyestuffs, including a number of phthalin dyes, are strongly fluorescent when
dispersed in suitable media. Fluorescence is observed for example, in dilute solutions containing substances such as uramin (fluorescein-sodium), eosin and rhodamine. As the concentration of the dye is increased beyond a certain limit, the fluorescence becomes quenched. This concentration quenching effect can be induced also by the foreign substances such as oxygen and halogen molecules. Luminescence has also been found when the dyes are dispersed in solids including organic resins inorganic bases such as partially dehydrated boric acid. Resin based fluorescent organic dyestuffs are employed in a variety of advertising and display applications. The luminescence in certain organic compounds, in gaseous, liquid or solid forms, can be enhanced by the presence of a suitable sensitizer. The intensity of anthracene vapour, excited by the 2652 A° mercury line at 170°C is increased, for example, by the presence of benzene vapour.

It has been shown that the transfer of the excitation energy takes place in organic phosphors in the same manner as in the case of inorganic phosphors which are, by (a) cascade mechanism, (b) resonance mechanism, (c) exciton migration and (d) electron and hole migration (Ganguly and Chaudhury, 1958; Hochstrasser, 1962; Kallmann, 1962).

(B) Waves and Vibrations in Solids

Let the stresses produced when a body suffers an impact be considered. Fig. 6.1a shows a light elastic wire of length t which receives the impact of a weight W dropped from a height h. The work done by the weight on the wire is

\[(h + \delta t)W,\]
ere, $\delta t$ is the elastic extension when the weight is first brought to rest.

At the same time the weight $W$ produces strain in the wire and the strain energy is

$$\frac{1}{2} \sigma_m^2,$$

ere, $\sigma_m^2$ = maximum value of stress produced in the wire, and $E = $ Young's modulus of elasticity of the wire.

Thus, when the work done ($h + \delta t$) $W$ is converted into strain energy, the value of maximum stress is given by

$$\sigma_m = \sqrt{\frac{2(h + \delta t)E}{At}} \quad \ldots \quad (6.1).$$

When $h \gg \delta t$,

then $\sigma_m = vC_0 L \sqrt{\frac{M}{m}}$ \quad \ldots \quad (6.2).

Where, $M$ and $m$ (= $\rho A$) are the masses of the weight and the wire respectively, $A$ and $\rho$ are the cross-sectional area and density of the wire, $C_0 = \sqrt{\frac{E}{\rho}}$, and $v$ is the striking velocity of the weight ($hW = \frac{1}{2}Mv^2$).

When $h = 0$, i.e. when the load $W$ is suddenly placed at the end of a weightless spring, then

$$\sigma_m = \sqrt{\frac{-2hE}{At}}.$$

$$\sigma_m = \sqrt{\frac{-2W}{A}} \cdot \sigma_m \quad (\therefore \sigma_m = \frac{E}{A} \frac{\delta t}{t}),$$

or $\sigma_m = \frac{2W}{A}$ \quad \ldots \quad (6.3).

Thus, the maximum stress produced in the wire is
twice that from the same load applied statically. The wire then oscillates longitudinally about the static equilibrium point with an amplitude equal to the static equilibrium strain.

The theory discussed above neglects the effects due to the finite speed of stress wave propagation along the wire. Let it be supposed that one end $R$ of a rod is suddenly set in motion with constant velocity $v$, as in Fig. 6.1b. A stress wave runs along it such that all material overrun by the stress wave-front $S$ is in motion and under stress, while all that before it is at rest and unstressed. An observer at rest in the unstressed part of the rod would see the stress front approaching with speed $C_0$. Thus, in a time $\tau$ an initial length $C_0 \tau$, of mass $\rho A C_0 \tau$, is overrun by the wave and given a velocity $v$. The force $f$ required to supply its momentum is

$$f = \frac{2}{2\tau} ( \rho A C_0 \tau v ),$$

$$= \rho A C_0 v \quad \cdots \quad (6.4)$$

The stress in the wave is thus

$$\sigma = \frac{f}{A} = v C_0 \rho = \frac{E v}{C_0} \quad \cdots \quad (6.5)$$

where, $E = \rho C_0^2$, and the strain $\frac{v}{C_0}$ is the change $\nu$ in the length $C_0 \tau$ of the rod.

It is noticed that the wave-front and material move in opposite directions in a tensile wave.

Equation (6.5) shows, in contrast to equation (6.2) that the stress wave starts with an intensity that depends only on $v$, not on $M$. Even a small mass (but large compared with attachment at the struck end) could instantly break the wire
shown in Fig. 6.1b at its struck end, if its velocity were large enough.

When the far end of the rod is free, reflection at this free surface produces a stress wave of opposite sign, which cancels the incident wave, because the boundary condition now is zero stress, at the reflecting surface. An important effect follows from this when the incident wave is a compressive pulse of finite duration $\tau$, where the reflected tensile pulse overlaps the incident pulse, there is cancellation of stress. Later, as the waves pass each other, a tensile stress appears, where the reflected wave is no longer cancelled. The tensile stress appears first at a distance $\frac{1}{2}C_0\tau$ from the free end and subsequently grows into a fully formed tensile wave. If this tensile stress is large, it may fracture the material. The far end of a free bar can thus be broken off by striking the near end sharply in compression (Cottrell, 1964).

(C) Exo-electron Emission

Exo-electron emission is the emission of electrons from the surfaces of solids as a result of structural changes stimulated by such things as mechanical deformation, heat, X-rays, ultraviolet, particle bombardment, chemical reaction etc. (Donald et al., 1966). This phenomenon is also known as Kramer-effect.

A satisfactory theory of exo-electron emission has not yet been developed. Generally, the surface of the material represents a potential barrier for the emission of electrons. When the material gets sufficient thermal stimulation or photo-
stimulation, electrons get excited over this barrier and is known as thermionic and photoelectric emission respectively. Exo-electron emission involves changes in the normal emission characteristics of the material. For metals, exo-electron emission is noted to depend on electrons which are thermally released from shallow traps at the surface (presumably traps associated with the oxide layer at the surface) (Grunberg, 1958). The exo-electron emission from non-metals has also been explained on the basis of shallow surface traps similar to those for metals. The parallelism between the thermoluminescence and exo-electron emission supports this reasoning.

By heating up the sample, electrons in traps are raised to the conduction band, a part of them can recombine with activation centres resulting in emission of light (thermoluminescence). Some electrons in the high energy tail of the Maxwell's distribution in the conduction band leave the crystal and are responsible for exo-electron emission. The temperature of the glow peaks correspond to the energy difference between the traps and the lower border of the conduction band. Sometimes, the exo-electron curves show peaks at slightly higher temperatures than the corresponding thermoluminescence peaks probably due to the electron affinity of the material (Levshin and Pipinis, 1961). In certain cases, the exo-electron emission peaks differ from the thermoluminescence peaks. This is attributed to isolated atomic luminescent centres such as rare-earth centres, in which there is no conduction band involvement in the luminescence process. The other possible reason is the ejection of electrons in the course of non-radiative transitions i.e. by transitions of such energy that
the associated radiation is not detectable with the sensing device employed, or by populating the traps into which the electrons would drop, thereby eliminating radiative transitions. The first case is very structure-sensitive and is an accurate monitor of minor changes in surface defect structure and population (Lewis and Orr, 1964).

(D) **Defects and Dislocations in Crystals**

(1) **Defects in Crystals**

The perfect periodicity of crystals is disturbed by the presence of several types of defects in them. A common type of imperfections occurring in crystal is that of the ion vacancy. These vacancies occur at random throughout the lattice of the crystal. The diffusions in ions in solids is due to the presence of vacancies in them. However, during the preparation of many types of chemical compounds in the solid state, the proper proportion of each type of element in the compound is not precisely maintained. Such deviations are called stoichiometric. The excess atoms, in such defects, present either substitutionally or interstitially. Instead of like atoms the presence of unlike atoms or ions in the lattice either substitutionally or interstitially also represents a type of imperfection. This type of imperfection can be controlled in order to produce a material with desired properties.

When an interstitial is caused by the creation of a vacancy in the normal site, then it is called Frankel defect. On the other hand, interstitial atoms can be produced by atoms
moving from the surface into the crystal interior and vacancies can be formed by atoms diffusing from the crystal interior to the surface. This type of distribution of interstitials or vacancies is referred to as Schottky defects.

The electric fields of the crystal perturb the electronic states of the defects and thus introduce an extra electronic energy levels in the normally forbidden energy region of the defects. Sometimes, the electric fields of defects perturb the electronic states of the pure substances and thereby introduce an extra electronic energy levels in the normally forbidden energy region of the crystal (Goldberg, 1966).

(ii) Dislocations in Crystals

Dislocation, a special kind of defect in crystals, is the relative displacements of macroscopic two-dimensional arrays of constituent atoms with respect to the rest of the lattice. Dislocations are of two main types such as (1) edge dislocation and (2) screw dislocation. When the periodicity of the crystal is disturbed by the presence of an extra row of atoms or by the absence of a row of atoms, then such defects in the crystal is called edge dislocation. However, the screw dislocation is another type of defect, which can be formed as follows. The crystal cut part away and the material on one side of the cut is pushed down relative to the other by one atomic spacing and the row of atoms then placed back into contact. A line of distortion exist along the edge of the cut. This line defect is called screw dislocation.

Theoretically, a screw dislocation may glide in any
direction but edge dislocation and all other than pure screws glide only on a possible plane. Glide is preferred on the crystallographic planes which are of low Miller indices and of close-packing. The motion of dislocation out of its glide plane is called climb. It involves the emission or absorption of indigenous point defects either lattice vacancies or interstitial atoms, at the dislocation line. Since a whole line of such point defects will not, diffuse away or attach themselves simultaneously, the emission or absorption takes place at points where the dislocation steps from one glide plane to another. The velocity of dislocations increases with rise of the stress applied on the crystal and it attains a saturation value equal to the velocity of elastic waves in crystal for higher values of the applied stress (Franck, 1948; Cotner, 1964).

Dislocations interact strongly with other dislocations. In the beginning of plastic flow a nearly perfect crystal flows easily. However, as the deformation increases, the stress necessary to continue the deformation becomes larger. The reason is that the dislocation content increases greatly during the process of deformation, and the dislocations become tangled together in such a disordered fashion that further dislocation motion becomes difficult. This phenomenon is called "work-hardening". Dislocations also interact with a free surface. Infact, any dislocation will be attracted by a free surface, since a motion towards the surface would reduce the strain energy. When the pressure is applied on the crystal, then due to the stress fields around the dislocations, impurities get
attracted to edge dislocations. The impurities larger than those of host atoms, tend to move toward the region of tension, since in this way the tension becomes less in this region. On the otherhand, if the impurity atoms are smaller than the host atoms, then they tend to be deposited in the region of compression.

(E) **Fracture and Strength of Solids**

Fracture denotes the separation of a solid into parts by the application of stress. Fractures are termed ductile or brittle, depending on whether or not plastic deformation occurs before fracture. The classifications depend not only on the material but also on size, shape, mode of loading and scale of observation. The transition from ductile to brittle fracture takes place; at large size of crystal, at low temperature and at higher strain rates.

Orowan (1948) has defined the strength as the resistance of a material to fracture; in the quantitative sense, it is a critical value of stress at which fracture occurs. The ideal tensile strength of solid can be estimated theoretically in the following manner.

Considering the case when a cylinder bar of unit cross-sectional area is pulled by a tensile stress $\sigma'$ as shown in the Fig. 6.1c. The atomic bonds joining two neighbouring atomic planes such as $AA'$ and $BB'$ break, when $\sigma'$ reaches the ideal tensile stress $\sigma'_i$. The atomic stress-strain curve of these bonds can be approximated by a sine curve of wavelength $\lambda$, as shown in the Fig. 6.1d. This is reasonable provided
the initial slope agrees with Young's modulus $E$ of the material. Thus,

$$\sigma' = \sigma_t \sin \left( \frac{2\pi u}{\lambda} \right) \quad \ldots \quad (6.6);$$

where, $u$ is the displacement from equilibrium spacing $b$. For infinitesimal strain this reduces to

$$\sigma = \frac{E}{b} \cdot \frac{2\pi u}{\lambda} \quad \ldots \quad (6.7);$$

From Hooke's law

$$\sigma = \frac{E u}{b},$$

therefore

$$\sigma_t = \frac{\lambda}{2\lambda} \cdot \frac{E}{b} \quad \ldots \quad (6.8).$$

The surface energy $\gamma_s$ is given by

$$\gamma_s = \frac{1}{2} \int_0^\lambda \sigma_t' \sin \left( \frac{2\pi u}{\lambda} \right) du.$$

$$\therefore \quad \sigma_t' \approx \frac{\sqrt{E \gamma_s}}{b} \quad \ldots \quad (6.9).$$

The observed values of $\sigma_t'$ are smaller than the above theoretical value by a factor $\sim 10^3$ to $10^4$. Griffith (1920, 1924) assumed that the discrepancy between the theoretically estimated and the observed values of the tensile strength was due to the presence of small cracks or other flaws around which a strong stress concentration arose when the solid was stressed. If a plate containing a flat elliptical hole of major axis $2L$ is subjected to a tensile stress $\sigma$ perpendicular to the major axis, the maximum tensile stress $\sigma_m'$ which occurs at the ends of the major axis is

$$\sigma_m' = 2 \sqrt{\frac{L}{d}}.$$
Fig. 6.1a - Impact of a weight on a tensile wire.

Fig. 6.1b - Stress wave in a rod.

Fig. 6.1c-d - Tensile fracture of a solid bar.
where, \( d \) is the radius of curvature at the ends of the major axis. When \( \sigma_m \) is equal to the ideal tensile strength then

\[
\sigma' \sim \sqrt{\frac{E d}{4b}} \quad \ldots \quad (6.10).
\]

Very near the crack faces the stress \( \sigma' \) is relaxed to zero and very far from them it is unchanged. Hence, roughly, a region of radius \( L \) round the crack is relieved of its elastic energy

\[
\frac{1}{2} E \sigma'^2 \sim \pi L^2
\]

per unit thickness of the body. The exact value obtained by integrating the actual strain field is precisely twice this. When this crack is on the point of growth under the stress, the decrease of elastic energy just balances the increase of surface energy i.e.

\[
-\frac{\partial}{\partial L} \left( \frac{\pi L^2 \sigma'^2}{E} \right) = \frac{\partial}{\partial L} \left( 4 \gamma \right),
\]

the 4 appearing because two surfaces grow at each end of the crack. Thus

\[
\sigma' = \sqrt{\frac{2Y E}{\pi L}} \sim \sqrt{\frac{Y E}{L}} \quad \ldots \quad (6.11).
\]

This is the Griffith stress for the growth of a sharp crack.

Fracture in Crystalline Materials

When an external pressure is applied on the crystal, then the atoms above and below the glide plane move relative to each other and parallel to this plane. Part of the atoms
at the glide plane, experience repulsive forces and part experience attractive forces from their neighbours across the glide plane. To a first approximation, these forces cancel, so that external force required to move a dislocation is quite small. Thus, a crystal becomes very plastic due to the presence of dislocations and it gets fractured at stresses much lower than the theoretically calculated critical stress. However, the brittle fracture takes place in crystals at low temperature and high rate of strain. In such cases, dislocation motion is not able to accomodate the deformation and the Griffith criterion for crack propagation is met at a certain level. Crystals in brittle fracture, often crack along planes of cleavage or along grain boundaries.

6.2. DEPENDENCE OF TRIBOLUMINESCENCE INTENSITY IN TARTRATE CRYSTALS ON THE MODE OF MECHANICAL CRUSHING

It has been observed in Chapter II that the TL intensity in a given mass of the tartrate crystals increases with crushing mass \((M)\) and the crushing height \((h)\) which follows the relation

\[
I = I_0^n \sqrt{Mh} \exp \left( - \frac{b}{\sqrt{Mh}} \right) \quad \ldots (6.a)
\]

up to a particular value of crushing mass. The TL intensity attains a saturation value after a particular value of crushing mass for a given crushing height. The saturation value of TL intensity increases with crushing height and follows the relation

\[
I_{n2} - I_{n1} = I_0^n (\sqrt{h_2} - \sqrt{h_1}) \exp \left[ C (\sqrt{h_2} - \sqrt{h_1}) \right] \ldots \ldots (6.b).
\]
The relation (6.1) has been derived on the basis of the fact that the area of the surface created due to fracture increases as the applied stress on the crystal increases. However, at much higher values of the applied stress, the further creation of surface by the applied stress gets limited due to work-hardening as discussed in detail in Chapter III. Therefore the TL intensity gets saturated for higher values of the applied stress on the crystal.

The saturation of TL intensity after certain value of crushing mass shows that the complete fracture of crystals takes place at and beyond that crushing mass. But the increase of TL intensity with crushing height in impulsive crushing indicates that the velocity of impact produces some change in the luminescent property of the crystal.

It has been described earlier in this chapter that when a weight is dropped on a wire then two types of impact stresses are generated in the wire: (1) the stress depending on the mass of the weight, but independent of the crushing height and (2) the stress depending on the velocity of the impact but independent of the crushing mass. In these two types of stresses the magnitude of the stress due to first type is approximately thousand times greater than the stress due to second type in the present investigation. However, it has been observed in Chapter II that the TL intensity in impulsive crushing of the tartrate crystals is 4-12 times greater than that in the statical crushing. This indicates a separate action of the stress due to shock-wave on the crystals. The stress due to first type is produced in the crystal due to the compression of
the crystal along its thickness. However, the stress due to second type is produced by the propagation of elastic wave along the length of the crystal. The fracture of crystals is possible due to both the types of stresses. But in the present investigation, the stress due to second type (shock-wave) which is $10^6$ - $10^7$ dynes/cm$^2$; is unable to produce fracture of the crystals as the fracture strengths of the tartrate crystals have been found to be order of $10^7$ - $10^8$ dynes/cm$^2$. Thus, the fracture of the crystals in the present investigation is only due to the stress of first type. Even the fastest crack in the crystal moves with a velocity smaller than the velocity of the elastic wave in the crystal (Cottrell, 1964) and at the same time the shock-wave travels in crystals with velocity higher than the velocity of elastic waves. (Rice et al. 1958). Thus any separate type of action on the crystal by the stress of second type is possible before the fracture of the crystal due to stress of the first type.

It is well known fact that the shock-wave produces compressions in crystals and instantly decreases the equilibrium distance between two lattice points of the crystal (Donald et al. 1966). Reiffel (1960) has shown that the luminescence efficiency of crystals changes with their compression. Thus, for different values of shock-wave intensity the crystal will behave having different luminescence efficiency due to different values of the compression.

Distortion in the Configuration Co-ordinate Curve of a Tribo-luminescent Centre due to the Passage of Shock-wave in the crystal

Assuming that the impact stresses produce in the
Fig. 6.2 - Distortion in the Configuration Co-ordinate curve of triboluminescent centre due to the passage of shock-wave in the crystal.
crystal are of similar type as discussed in the case of wire, the variation of saturation value of TL intensity with crushing height can be discussed as follows.

Considering the configuration co-ordinate curve model as shown in the Fig. 6.2 and assuming its curve to be a parabola; the potential energy $W(r)$ of an excited level for a separation $r$ between the two atoms of a molecule may be written as (Johnson and Williams, 1953)

$$W(r) = \frac{1}{2} C_m (r - r_0)^2 + W_o \quad \ldots \quad (6.12);$$

where, $C_m =$ force constant of the crystal,
$r_0 =$ equilibrium separation of the ground state in statical crushing,
and $W_0 =$ minimum energy of the ground state in statical crushing.

In impulsive crushing an additional stress-wave of intensity

$$C_0 \sqrt{2g} \sqrt{\hbar}$$

flows through the crystal and the potential energy will be given by

$$W(r) = \frac{1}{2} C_m (r - r_0)^2 + W_o + \alpha C_0 P \sqrt{2g} \sqrt{\hbar} r \quad \ldots \quad (6.13);$$

where, $K_1 = \alpha C_0 P \sqrt{2g}$,
and $\alpha =$ effective area of influence surrounding the excited molecule of the crystal.

To obtain the value of equilibrium separation $r_0$ under impulsive crushing, equation (6.13) is differentiated with
respect to \( r \) and equated to zero as

\[
\frac{\partial W(r)}{\partial r} = \frac{1}{2} Cm 2(r - r_0) + K_1 \sqrt{h} = 0
\]

\[
\therefore \quad r = r_0 - \frac{K_1 \sqrt{h}}{Cm}
\]

or

\[
\eta_h = r_0 - \frac{K_1 \sqrt{h}}{Cm} \quad \ldots \quad (6.14)
\]

It may be concluded from equation (6.14) that the equilibrium separation \( \eta_h \) in the configuration co-ordinate curve, is larger in statical crushing and decreases as the height \( h \) through which weight is dropped on the crystal increases (Fig. 6.2).

Change in the Activation Energy \( E_h \) for Thermal Radiation due to Distortion in the Configuration Co-ordinate Curve of a Triboluminescent Centre

The energy at equilibrium under impact will be (from equations 6.13 and 6.14)

\[
W(\eta_h) = \frac{1}{2} \left( - \frac{K_1 \sqrt{h}}{Cm} \right)^2 + W_0 - \frac{K_1^2 h}{Cm} + K_1 \sqrt{h} r_0 \quad \ldots \quad (6.15);
\]

and the energy for thermal collapse is

\[
W(r_0 + r_c) = \frac{1}{2} Cm r_c^2 + W_0 + K_1 \sqrt{h} r_0 + K_1 \sqrt{h} r_c \quad \ldots \quad (6.16).
\]

Where, \( r_c \) = the radial displacement from equilibrium position \( (r_0) \) in statical crushing at which the ground and excited state curve cross each other (Fig. 6.2).

The thermal activation energy \( E_{ah} \) under impulsive crushing is (as shown in Fig. 6.2)

\[
E_{ah} = W(r_0 + r_c) - W(\eta_h)
\]
\[ \rho = \frac{1}{2} Cm(r_c)^2 + K_1 \sqrt{r_c} + \frac{1}{2} \frac{K_1^2 r_c}{C_m} \]

\[ = E_{a_0} \left[ 1 + \frac{K_1 r_c \sqrt{b}}{E_{a_0}} \right] + \ldots \]

\[ = E_{a_0} \left[ 1 + K_2 \sqrt{b} \right] \] \hspace{1cm} (6.17);

where, \( K_2 = \frac{K_1 r_c}{E_{a_0}} \),

and \( E_{a_0} = \frac{1}{2} Cm r_c^2 \), is the energy of cross-over between ground and excited state under statical crushing.

Equation (6.17) shows that the shock-wave increases the thermal activation energy of the centre. This fact is in accordance with the discussion of Flynn (1972) which also reports the increase of the activation energy with shock-wave intensity.

Enhanced Triboluminescence Intensity in Impulsive Crushing of the Tartrate Crystals.

Now, let the effect of shock-wave on the saturation value of TL intensity in the tartrate crystals be considered. It has been shown in Chapter III that the saturation value of the surface created due to fracture of the crystal may be written as

\[ S_s = \frac{B \rho_0 \sigma'}{2F} \] \hspace{1cm} (6.18);

where \( \sigma' = \) value of stress applied on the crystal,

\[ B, \rho_0 \text{ and } F \text{ are constants.} \]

It has been observed in Chapter V, that the TL intensity in the tartrate crystals is higher when the piezo-
induced charge produced at fracture is less. This reasoning suggested that the TL intensity in the tartrate crystals depends on the mechanical component of the stress in the crystal. Many workers have discussed that the modulus of elasticity of the piezo-electric crystals decreases with increase of their polarization, thereby the mechanical stress in the crystals decreases as (Cady, 1946; Mason, 1950 and Huntington, 1950)

\[ \sigma' = E \varepsilon - dp \cdot P \quad \ldots \quad (6.19); \]

where, \( E \) = Young's modulus of elasticity of the crystal,
\( \varepsilon \) = strain in the crystal,
\( dp \) = piezo-electric constant of the crystal,
and \( P \) = polarization in the crystal.

As the strain attains a saturation value for much higher values of the applied stress on the crystals, the equation (6.19) may be written as

\[ \sigma' = C_1 - dp \cdot P \quad \ldots \quad (6.20); \]

where \( C_1 = E \varepsilon \) = constant at much higher value of the applied stress.

The polarization \( P \), depends on the displacement of atoms in the crystals (Dekker, 1952). It is seen from the equation (6.14) that the displacement of atoms takes place in the impulsive crushing of crystals. Hence the variation of the mechanical component of stress \( \sigma' \) in the crystal with the velocity of impact may be written as

\[ \sigma' = C_1 - C_2 \left( r_0 - \frac{K_4 \sqrt{R}}{Cm} \right); \]

where \( C_2 \) = constant depending on the polarization and piezo-
electric constant of the crystal;

\[ \sigma' = c_3 + \alpha_2 \sqrt{h} \]  

(6.21);

where, \( c_3 = c_1 - c_2 r_0 \),

\[ \alpha_2 = \frac{k_1}{c_0} \]

Thus the saturation value of the surface \( S_s \) created due to fracture at a crushing height \( h \) may be written as from equations (6.18) & (6.21)

\[ S_s = \frac{B_n_0}{2F} (c_3 + \alpha_2 \sqrt{h}) \]  

(6.22).

The number \( n_0 \) of the TL centres getting excited due to the application of stress on the crystal, will be proportional to the corresponding area of surface \( S_s \) created due to fracture of the crystal. Hence

\[ n_0 = \frac{c_4 B_n_0}{2F} (c_3 + \alpha_2 \sqrt{h}) \]  

(6.23);

where \( c_4 = \) constant.

Read (1953), Seitz (1952) and Mott (1951) have discussed that the motion of dislocations produces vacancies and interstitials in crystals, which may diffuse if their existing thermal vibrations are sufficient. Since at the fracture of crystals large number of dislocations are created, it is essential to consider the diffusion of excited TL centres.

Due to fracture of the crystal, the \( n_0 \) centres get excited and reach the position B in the excited state of configuration co-ordinate curve (Fig. 6.2). Some of the excited
TL centres are able to cross the barrier of height $E_a$ due to their thermal vibrations and thus diffusion of TL centres takes place. The number of TL centres diffusing in such a manner may be determined with the help of the relation (Mott and Gurney, 1957).

$$D_i = D_0 \exp \left( -\frac{E_a}{kT} \right)$$

(6.24)

where, $D_i =$ coefficient of diffusion,

$D_0 =$ a constant depending on the crystal,

and $E_a =$ activation energy for thermal radiation.

Thus, it may be inferred from the above relation (6.24) that out of the excited centres $n'_0$, a fraction

$$n'_0 \exp \left( -\frac{E_a}{kT} \right)$$

get diffused. Hence the remaining number of centres $n'$ left for TL activity are

$$n' = n'_0 - n'_0 \exp \left( -\frac{E_a}{kT} \right)$$

$$n = n'_0 \left[ 1 - \exp \left( -\frac{E_a}{kT} \right) \right]$$

(6.25)

With the help of equations (6.17), (6.23) and (6.25) the total number of TL centres $n_h$ responsible for TL activity at the crushing height $h$ may be written as

$$n'_h = \frac{C_1 B n'_0}{2F} \left( C_3 + C_2 \sqrt{h} \right) \left[ 1 - \exp \left( -\frac{E_a(1 + K_2 \sqrt{h})}{kT} \right) \right]$$

(6.2)

The saturation value of TL intensity $I_{sh}$ for a crushing height $h$ will be proportional to the number of centres $n'_h$ responsible for TL activity at the crushing height $h$. Hence
where \( I_s' \) = constant.

For, two crushing heights \( h_1 \) and \( h_2 \), the equation (6.27) may be written as

\[
I_{sh1} = \frac{I_s' C_4 B n_o (C_3 + \alpha_2 \sqrt{h_2})}{2 F} \left\{ 1 - \exp \left[ - \frac{E_{ao} (1 + K_2 \sqrt{h_2})}{k T} \right] \right\} \ldots (6.28),
\]

and

\[
I_{sh2} = - \frac{I_s' C_4 B n_o (C_3 + \alpha_2 \sqrt{h_2})}{2 F} \left\{ 1 - \exp \left[ - \frac{E_{ao} (1 + K_2 \sqrt{h_2})}{k T} \right] \right\} \ldots (6.29).
\]

From the equations (6.28) and (6.29)

\[
I_{sh2} - I_{sh1} = \frac{I_s' C_4 B n_o (\sqrt{h_2} - \sqrt{h_1})}{2 F} \left\{ 1 - \exp \left[ - \frac{E_{ao} (1 + K_2 \sqrt{h_2})}{k T} \right] \right\} + \exp \left[ - \frac{E_{ao} (1 + K_2 \sqrt{h_1})}{k T} \right] \ldots (6.30)
\]

\[
= \frac{I_s' C_4 B n_o (\sqrt{h_2} - \sqrt{h_1})}{2 F} \left\{ \frac{E_{ao} (1 + K_2 \sqrt{h_2})^2}{k T} - 1 \right\}
\]

\[
= \frac{1}{2} \frac{E_{ao}^2 (1 + K_2 \sqrt{h_2})^2}{k T} + 1 - \frac{E_{ao} (1 + K_2 \sqrt{h_1})}{k T}
\]

\[
\ll \frac{E_{ao} (1 + K_2 \sqrt{h_2})}{k T} \ll k T
\]

\[
\sim \frac{I_s' C_4 B n_o (\sqrt{h_2} - \sqrt{h_1})}{2 F} \left\{ 1 + \frac{E_{ao} (1 + K_2 \sqrt{h_2})}{k T} \right\}
\]

\[
= \frac{E_{ao}}{k T} \frac{E_{ao} (1 + K_2 \sqrt{h_1})}{k T}
\]

\[
\approx \frac{I_s' C_4 B n_o (\sqrt{h_2} - \sqrt{h_1})}{2 F} \left\{ 1 + \frac{E_{ao} K_2 \sqrt{h_2}}{k T} + \frac{E_{ao} K_2 \sqrt{h_2}}{k T} \right\}
\]
I_n = \frac{I_0' C B n_0 \alpha C}{2 F} \left( \sqrt{E_2} - \sqrt{E_1} \right) \left[ 1 + \frac{E_0 K_2}{kT} \right]

or \ I_{n2} - I_{n1} = I_{n} = \frac{I_0' C B n_0 \alpha C}{2 F} \exp \left[ C \left( \sqrt{E_2} - \sqrt{E_1} \right) \right] \quad \ldots \ (6.30);

where, \ I_{n0} = \frac{E_0 K_2}{kT}

and \ C = \frac{E_0 K_2}{kT}.

Thus, the shock-wave produced in the crystal due to the impact of the crushing mass distorts the configuration co-ordinate curve of TL centres in such a way that the probability for radiative transition increases.

The empirical relation (6.6) obtained experimentally in Chapter II, is same as the equation (6.30), which supports the above discussion.

The above discussion also explains the fact that certain crystals do not show TL by grinding them, but they show TL when struck with a hammer (Trinks, 1933; Alzetta et al., 1962). The shock-wave will not produce in crystals when they are ground simply and thus there will be no considerable distortion in the configuration co-ordinate curve of the corresponding TL centres and all the excited TL centres may give radiationless transition. On the other hand, when the crystals are struck with a hammer, a shock-wave of high intensity will produce in the crystals. The shock-wave will distort the configuration co-ordinate curve of the TL centres and thereby the probability of radiative transition increases and the crystals show TL.

It has been shown in Chapter II that the relation
\[ I = I_0^n \sqrt{Mn} \exp \left( -\frac{1}{\sqrt{Mn}} \right) \]

holds up to a particular value of applied stress on the crystal. However, the relation

\[ I_{n2} - I_{n1} = I_0^n (\sqrt{h_2} - \sqrt{h_1}) \exp \left[ \alpha (\sqrt{h_2} - \sqrt{h_1}) \right] \]

holds for much higher values of the stress on the crystal.

The above two equations reveal that at lower values of the applied stress, the creation of new surfaces by fracture of the crystal predominates the effect of shock-wave; however, at much higher values of the applied stress, the creation of new surfaces by fracture of the crystal gets limited and thus the effect of shock-wave becomes pronounced.

6.3. TL DUE TO DISCHARGE OF THE GASES BETWEEN THE FRACTURED SURFACES

Inoue et al. (1939) have made a spectroscopic study of the TL in tartaric acid crystals and have shown that its tl spectrum resembles with the discharge spectra of the nitrogen gases. As a matter of fact, the TL intensity in the tartrate crystals has been measured in the present investigation, by crushing the crystals inside the liquid anhydrous diethylether. It is found that the TL intensity gets much decrease when the tartrate crystals are crushed inside the liquid (Chapter II). Thus it seems that the TL intensity in the tartrate crystals is composed of two parts:

1. TL due to the luminescence property of the crystal
2. TL due to the discharge of the gases between the fractured surfaces of the crystal.
It has been shown in Chapter II, that the TL due to luminescence part is 7-8% and the TL due to discharge part is 92-93% approximately.

A direct hint about the mechanism of discharge of the gases between the fractured surfaces is given by the following two facts:

(1) The TL intensity obtained by crushing the crystal inside the liquid is higher for those tartrate crystals which possesses higher TL by crushing them in air, and
(2) the TL intensity obtained by crushing the crystal inside the liquid varies with the mode of mechanical crushing in the similar manner as the TL intensity obtained by crushing the crystal in air varies.

The above facts suggest that the mechanism of occurrence of luminescence part of TL and the discharge part of TL must be the same i.e. the discharge part of the TL also depends on the excitation of the luminescence centres. At the same time the discharge of gases between the fractured surfaces indicates, the emission of electrons from the fractured surfaces of the crystal. Hence it seems that the fracture of the crystal ionizes the TL centres and these free electrons go to the conduction band. Shallow traps exist near the surface of the crystals (Donald et al., 1966) in which the electrons in the conduction band get trapped and then they are emitted from the shallow traps by the thermal vibrations. Thus, it may be concluded that the discharge part of TL in the tartrate crystals is
due to the exo-emission of the ionized electrons from the TL centres. This conclusion illustrates, the higher exo-emission of electrons in higher TL materials, which has been found by Gross et al. (1955) by observing TL in several crystals.

6-4. TEMPERATURE QUENCHING OF TRIBOLUMINESCENCE IN TARTRATE CRYSTALS

The decrease of TL intensity with rise of temperature of the tartrate crystals has been discussed in Chapter III, as to be due to (1) the decrease of Young's modulus of elasticity of the crystals and (2) the decrease of activation energy for thermal radiation. Mott and Gurney (1957) has shown that the probability of emission of visible radiations from luminescence centres decreases with rise of temperature due to increase in probability of emission of thermal radiation. Such a temperature quenching may also exist in the luminescence part of TL in the tartrate crystals. However, the discharge part of TL depends on the number of electrons in the conduction band. The increase of temperature may help, the emission of these electrons from the fractured surface of crystals. But, it has been shown that in exo-emission, the room temperature is sufficient for the emission of electrons from the shallow traps near the conduction band (Donald et al., 1966). Hence no increase may be expected in the discharge part of TL due to increase of temperature.

It has been said that 7-8% of the TL intensity in the tartrate crystals is due to the luminescence and 92-93% of the TL intensity is due to the discharge of the gases between the fractured surfaces. Thus the temperature quenching discussed by
Mott and Gurney (loc. cit.) may take place in 7-8% of the TL intensity, but 92-93% remains unaffected. However, the existence of such type of temperature quenching is suppressed by the predominating nature of decrease in TL intensity due to decrease in, Young's modulus of elasticity and activation energy for thermal radiation, with rise of temperature of the crystal.

6-5. MECHANISM OF TL IN TARTRATE CRYSTALS

The following results drawn from the preceding chapters are important as they throw a direct light on the mechanism of TL in the tartrate crystals:

(1) The TL intensity is much higher in impulsive crushings than statical one and the increase has been discussed to be due to increase of Young's modulus of elasticity in impulsive crushing (Chapter II).

(2) The TL intensity decreases as the temperature of the crystals increases. It has been suggested that the decrease is due to decrease of Young's modulus of elasticity of the crystal with rise of temperature (Chapter III).

(3) The TL intensity is higher when the simultaneous charge produced at fracture is less because the Young's modulus of elasticity of the crystals decreases with increase of polarization. This result also indicates that the increase of TL intensity is due to the increase of Young's modulus of elasticity of the crystals.

All the results mentioned above illustrate a similar relation between the TL intensity and Young's modulus of
elasticity of the crystals. Hence it seems that the passage of elastic waves in crystals is responsible for the excitation of TL centres in the tartrate crystals.

Further, the excitation of TL in tartrate crystals, resembles with the production of dislocations in the following respects:

1. The TL intensity and the number of moving dislocations increase with the value of applied stress on the crystals;

2. the TL intensity as well as the number of moving dislocations get saturated after a particular value of the applied stress due to the work-hardening in the crystals.

The above analogies suggest that the moving dislocations are responsible for the excitation of TL in the tartrate crystals. The previous mentioned fact, according to which the passage of elastic waves in the crystal is responsible for the excitation of TL centres in the tartrate crystals, also supports the excitation of TL centres in the tartrate crystals due to the movement of the dislocations in the crystal, because the velocity of the dislocations depends on the velocity of elastic wave in the crystal (Frank 1948; Cotner, 1964).

Alzetta et al. (1970) have shown that the TL centres may be excited due to the movement of dislocation in crystals by two different mechanisms: (1) by the unpinning of dislocations from luminescent centres and (2) by the interaction of moving dislocations with luminescent centres. Hence, it is of interest
to know the mechanism, due to which the TL centres in the
tartrate crystals get excited.

It is well known that the crystals possess different
types of defects, such as luminescent centres, intrinsic
defects, foreign atoms, precipitated impurities etc. Hence, it is possible that the grown-in dislocation lines in the
crystal may have got pinned by a certain number of the earlier mentioned defects between the nodes of dislocation-network.
When the external pressure is applied on the crystal, then the
dislocation loops between defects begin to bow out, up to the point where an unpinning of dislocations from defects take place.

Kruglov et al. (1966) have shown that the unpinning of
dislocations from TL centres, releases energy which excites the later. Such emission is seen in elastic regions of the applied stress on the crystal and attains saturation value near the fracture of the crystal, which does not increase with the further fracture of the crystal.

However, the tartrate crystals do not show TL before their fracture and their TL intensity increases with fracture of the crystals. This suggests that the unpinning of dislocations is not from the luminescent centres. Hence the unpinning of dislocations is from the defects other than the luminescent centres. Thus it may be concluded that the TL centres in the tartrate crystals are excited by the interaction of moving dislocations which get unpinned from defects other than the luminescent centres.

Thus, at fracture of the crystals, large number of
dislocations are created which interact with luminescent centres, thereby changing the electric field in the vicinity of the later. This change of the electric field produces the following processes in the crystal:

(1) The excitation of TL centres takes place and the transition of their electrons from excited state to ground state gives luminescence,

(2) the excitation of TL centres take place and the transition of their electrons from excited to ground state gives thermal radiation,

(3) excitation of TL centres and then its subsequent diffusion take place with radiationless transition,

and

(4) ionization of electrons from the luminescent centres take place which go to the conduction band and subsequent emission from the shallow traps at the surface of the crystal, produce discharge in the gases between the fractured surfaces.

The mechanism discussed above suggests that the discharge part of TL may exist without the occurrence of the luminescence part of TL and also the luminescence part of the TL may exist without the occurrence of the discharge part of TL. Thus the mechanism differs from those suggested by Schmidt (1918) and Curie and Prost (1948), according to which the luminescence part of TL in crystals is due to the discharge of gases between the fractured surfaces. These mechanisms require the existence of the discharge part of TL for the occurrence of the luminescence
part of TL, which contradicts from the experimental observations made for the tartrate crystals, as the TL in the tartrate crystals has also been observed by crushing them inside liquid.

6-6. CONCLUSIONS

The conclusions drawn from the studies on the TL in tartrate crystals may be summarized as under:

(1) The TL intensity in tartrate crystals varies directly as the area of new surface created due to their fracture.

(2) The TL intensity in tartrate crystals depends on the applied stress $\sigma$ and follows the relation

$$I = I_0 \sigma' \exp \left( - \frac{\sigma_k}{\sigma'} \right).$$

(3) The TL intensity in tartrate crystals attains a saturation value after a particular value of crushing mass for a given crushing height.

(4) The saturation value of TL intensity in the tartrate crystals is much higher in impulsive crushing than statical one.

(5) The saturation value of TL intensity increases with the height through which weight is dropped on the crystal and follows the relation

$$I_{sh_2} - I_{sh_1} = I_{po} \left( \sqrt{h_2} - \sqrt{h_1} \right) \exp \left[ \frac{C \left( \sqrt{h_2} - \sqrt{h_1} \right)}{\sqrt{h_1}} \right].$$

(6) The TL intensity in tartrate crystals gets diminished when they are crushed inside liquid but it does not cease.

(7) The TL intensity obtained by crushing the crystals inside liquid is higher in those tartrate crystals which show higher TL when crushed in air.
The TL in tartrate crystals is composed of two parts: (1) TL due to luminescence in the crystal and (2) TL due to discharge of gases between the fractured surfaces.

The TL intensity in tartrate crystals decreases with rise of temperature and follows the relation

\[ I_{T_1} - I_{T_2} = I_0 \exp \left[ \frac{\frac{E}{k}}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)} \right]. \]

The TL intensity is higher at a temperature, when the temperature is attained by heating the crystals than by cooling them from a higher temperature.

The decrease of TL intensity in the tartrate crystals with rise of temperature is due to (1) decrease of Young's modulus of elasticity of the crystal and (ii) the decrease of activation energy for thermal radiation.

The TL intensity in the tartrate crystals decreases with X-rays and radio-active irradiations.

The decrease of TL intensity in the tartrate crystals with X-rays and radio-active irradiations is due to displacement of electrons from TL centres.

The TL in the tartrate crystals is higher when the simultaneous piezo-induced charge produced at fracture is less.

The product of the saturation value of TL intensity and the simultaneous piezo-induced charge produced at fracture is a constant for a given tartrate crystal.

The TL intensity is higher in those tartrate crystals which develop less piezo-induced charge at fracture.
(17) The TL intensity in tartrate crystals depends strongly on the Young's modulus of elasticity of the crystal and it increases as the Young's modulus of elasticity increases and vice versa.

(18) The Young's modulus of elasticity of crystals and the activation energy for thermal radiation may be calculated with the help of TL measurements.

(19) Shock-waves distorts the configuration co-ordinate curve of TL centres and thereby increases the probability of radiative transition.

(20) The discharge part of TL in the tartrate crystals is due to the exo-emission of ionized electrons from TL centres.

(21) Diffusion of TL centres in the tartrate crystals takes place with radiationless transition at the instant of their fracture.

(22) The excitation of TL centres in the tartrate crystals is due to the interaction of moving dislocations with TL centres.

6.7. SUGGESTIONS FOR FURTHER RESEARCH ON TRIBOLUMINESCENCE

Further investigations in the TL of crystals concerning the following aspects may be interesting.

(1) Studies of TL at high shock-pressure on the crystals.
(2) Studies of TL at low temperatures.
(3) Studies on the decay time of TL in crystals.
(4) Studies on the TL spectra.
(5) Studies on the effect of high energy irradiations on TL of crystals.
Studies on the diffusion of defects at high pressure on the crystal with the help of TL.

Investigation of new TL material, which will show intense TL in its elastic region.

As the TL depends on the area of new surface created due to fracture of the crystal, hence its investigation may be advantageous in Surface Physics and Surface Chemistry.

As the phenomenon of TL is due to the fracture of crystals, hence it is expected that its successful investigations may throw a light on the strength of materials, work-hardening in crystals, interaction of dislocations etc.

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SIEITZ, F. (1952): 'Advance in Physics'; 1, 43.


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