CHAPTER III

IMPULSIVE EXCITATION OF MECHANOLUMINESCENCE IN CENTRO-

SYMMETRIC AND NON-CENTROSYMMETRIC CRYSTALS

3-1. INTRODUCTION

Since mechanoluminescence is produced during deformation of a crystal, a correlation between the ML intensity and crystal deformation is expected. Various techniques have been used to date for deforming the crystals for ML studies. In the device used by Lang-

chamton (1975), an air blast propels crystals at high speed on a quartz plate, normally placed directly in front of the entrance slit of a spectrometer. A similar device for ML studies has also been designed by Zdeska (1969). In the spiral mill technique devised by Meyer and Obrikat (1969), six high speed air-blasts are directed to lie along the edges of a regular hexagon. Crystals directed into the spiralling air collide with others already in the spiral. Since the fracture is produced due to impact between like materials, this technique eliminates the possibility of the effects due to contact potential differences. Meyer and Polly (1965a,b) have used a device in which a steel or sapphire needle impacts with a known energy on the crystal surface. One impact occurs per revolution of the cam in the device and the energy at the impact is controlled by varying the load on the beam. A virgin region of the crystal can be secured.
for each impact by advancing the slide on which the crystal is mounted. The whole equipment can be mounted inside a vacuum chamber and the temperature of the sample can be changed by placing a heated plate beneath the sample.

A crystal milling technique has been used by Moyer et al. (1970), in which the crystals were cut for the ML measurements by a rotating milling cutter. To continue the process of cutting the crystals, an arrangement is provided for pressing the crystal against the milling cutter. Aizetta et al. (1970) have made a device which allows the simultaneous measurements of the stress-strain characteristics and the ML-strain characteristics of a single crystal. The crystal under test is supported freely at its ends and the force is applied through a knife edge in a direction perpendicular to the axis of the crystal. The displacement of the knife edge is measured by comparing the resonance frequency of the cavity terminated with a piston connected to the arm driving the knife, with the resonance frequency of a fixed cavity. The force was measured using a quartz piezoelectric crystal.

The ML versus strain curves of crystal has been determined by Hesse et al. (1957) by using a small tensile machine modified for the compression test. Butler (1966), and Chandra and Silk (1980) have used Instron testing machine for studying the stress-strain and the ML strain curves of the crystals. Karten and Rand (1966) have
suggested that if a periodic stress is required, then a loudspeaker or other electromagnetic device unit is very convenient. Dewar (1901) has fractured the crystals by dropping them into liquid hydrogen. Nick (1937), and Guerrero and Alvarez Rivas (1978) have measured the ML by deforming the crystals with a vise. Belyaev et al (1966) and Hardy et al (1979) have excited ML by deforming the crystals with laser pulses.

The superficial studies have always indicated that the ML intensity should depend on the area of newly created surfaces of the crystals. The effect of deformation on the ML intensity of crystals has not been studied satisfactorily to date. In the present study, the ML is excited impulsively by dropping loads on the crystals from different heights. The present chapter reports the effect of impact velocity on the ML intensity of the crystals. Only few centrosymmetric crystals of Tables 2-1 and 2-2 (in Chapter II), that is, NaCl, NaBr, KF, LiF and LiCl are chosen for the present investigation. The alkali halide crystals have been chosen because of the availability of literatures related to their physical properties, which may be helpful in the discussion. The impulsive excitation of ML in some of non-centrosymmetric molecular crystals like tartaric acid, acetamide and ethyl stearate has also been studied, and it is speculated that the comparative study of the ML of centrosymmetric and non-centrosymmetric crystals may
be helpful in identifying the mechanism of ML excitation in centrosymmetric crystals. It has been reported that tartaric acid, acetamide and ethyl stearate crystals belong to $P2_1\bar{1}$, $R3c$ and $C_4$ space groups respectively, which are non-centrosymmetric (Beaver et al 1952, Demay and Ondik 1972, Nathanson and Walsh 1968). These crystals exhibit intense ML and their ML spectra also resemble the spectra of the emission from the second positive group of molecular nitrogen (Chandra 1981, Chandra et al 1983). The ML efficiency of tartaric acid, acetamide and ethyl stearate crystals are 1.0, 6.4 and 3.3 times less respectively to that of sucrose crystals.

1-2. EXPERIMENTAL

The alkali halide crystals were obtained as reported in Chapter II. The crystals of tartaric acid, acetamide and ethyl stearate were grown by the slow evaporation of their aqueous solution. The crystals were made to the required size by grinding and polishing or by cleaving and polishing. The size of the crystals used in the present investigation was $3 \times 3 \times 3$ mm (other sizes used for some measurement were specified there). The NaCl, NaBr, NaF, LiCl and LiF crystals were crushed along their (100) direction of crystallographic axis. The crystals of tartaric acid, acetamide and ethyl stearate were crushed along their $a$, $b$ and $c$ directions of the crystallographic axis respectively. The crystals of NaCl, NaBr, NaF, LiCl and LiF were annealed at $450^\circ$C for about 4 hours and cooled very slowly.
For the measurements of ML intensity at different impact velocities, a lead of particular mass and shape was dropped from different heights by using the experimental set up shown in Fig.1-1a. For the determination of the time dependence of ML, the crystal was placed on a transparent lucite plate inside a sample holder below the guided cylinder. The luminescence was monitored from below the transparent plate by using an WP 21 photomultiplier tube connected to Sylvania R150 oscilloscope having CRT P7 phosphor bargraph screen. In a dark room, a trace appeared on the oscilloscope screen, is visible for more than a minute. The electrical connections of the photomultiplier tube is shown in Fig.1.1b. A resistance of 34.1 kΩ is connected between the anode and the ground because it decreases the response time of the photomultiplier-detector system. The response time in the microsecond range is necessary because we are interested in measuring the pulses due to ML emission which are of less than a millisecond duration. The response time is tested by the 5 μs pulses from a xenon lamp which indicated that the response time of our photomultiplier-detector system is less than 5 μs. The response time of the photomultiplier tube can also be reduced by connecting condensers of appropriate values between the dynodes.

The crystal was covered with a thin aluminium foil and fixed with a adhesive tape. This arrangement eliminates the error in the ML intensity measurements due to the scattering of crystallite fragments during the impact
Fig. 2. Schematic diagram of the experimental arrangement used for measuring the time dependence of M.E. in crystals (1-stand; 2-hilley; 3-metallic wire; 4-load; 5-guiding cylinder; 6-aluminium foil; 7-crystal; 8-transparent lucite plate; 9-wooden block; 10-photomultiplier tube; 11-Iron base mounted on a table; (10, 11) -Connecting wires).
Fig. 3-1b. Schematic diagram of the electrical circuit used for measuring the rise and decay times of Kα.
of the load on the crystals. The aluminium foil was connected to one terminal of an 1.5 V battery which was connected to a resistance of 100 kΩ. The other end of resistance was connected to the metallic wire used for dropping the load through a frictionless pulley (Fig.1-1a). When the dropped load touched the aluminium foil on the crystal, a pulse appeared across the resistance of 100 kΩ. This pulse was used to trigger the oscilloscope. The PL intensity was monitored by the photomultiplier tube whose output was fed to one channel of the oscilloscope. For determining the rise and decay time of PL at different impact velocities, the trace on the oscilloscope screen was recorded on a tracing paper. The velocity of the load could be changed up to 400 cm/sec by changing the distance between the load to be dropped and the crystal on the lucite plate. For determining the effect of load on the PL intensity, the mass of the load to be dropped could also be changed. Since the pulley and guided cylinder used were of negligible friction, the impact velocity, \( v_0 \) was taken as \( \sqrt{2gh} \), where \( g \) is acceleration due to gravity, and \( h \) is the height through which the piston is dropped. Furthermore, this estimation will not make any difference because we will be interested in taking the relative measurements of PL.

Many workers have used the integrating sphere for the accurate measurement of the efficiency of luminescence (Pereiasen and Santmann 1974, 1975, Zwing et al 1968, Bannan and Paulson 1971). In a good integrating sphere, the following two conditions should be fulfilled:
(1) Constancy of the photomultiplier output for a given light source when placed anywhere inside the sphere except in direct view of the photomultiplier, and (2) constancy of the photomultiplier output over a period of time during constant illumination.

For the ML measurements, no one has used to date the integrating sphere, perhaps because of the complicated device needed for the ML excitation. In all the works done on ML to date, the procedure similar to that described in the present investigation has been adopted. It has been found that when the crystal of small cross-sectional area as compared to the light-sensitive area of the photomultiplier tube, is crushed close to the photomultiplier tube, the ML intensity measured will be proportional to the intensity of ML. Because of the limitations of our laboratory, we were not, able to measure the ML intensity absolutely. However, we have normalized the ML intensity of all the crystals in terms of the ML intensity of sucrose crystals (Chapter II).

An independent experiment was made for the investigation of the dependence of ML on the area of newly created surfaces of crystals. For this experiment, the crystals were made to the required size by grinding and polishing or by cleaving. The size of the crystals used was 5 x 5 x 5 mm. However, the crystals used in cutting experiments were one mm thickness. For the ML measurements, the crystal was fractured instantaneously by compressing it between the two jaws of a screw
gauge. In an independent experiment the crystals were cut instantaneously by a sharp blade. In this measurement, the total NL intensity was monitored by the technique described previously in Chapter II, that is, in terms of the deflection of a ballistic galvanometer.

In the cutting experiment, the newly created area of surfaces was calculated from the known dimension of the crystals. However, in the compressing experiment, the newly created area of surfaces \( s \), is determined from the relation

\[
s = 6 \left[ M_1 \left( \frac{N_1}{d} \right)^{2/3} + M_2 \left( \frac{N_2}{d} \right)^{2/3} + M_3 \left( \frac{N_3}{d} \right)^{2/3} + M_4 \left( \frac{N_4}{d} \right)^{2/3} \right] - S_0,
\]

where \( d \) is density of the crystal and \( S_0 \) is surface area of the crystal before the fracture. The crystallites formed after the fracture were divided into four groups. \( M_1, M_2, M_3 \) and \( M_4 \) denote the average mass of the crystallites of first, second, third and fourth groups respectively. \( N_1, N_2, N_3 \) and \( N_4 \) denote the total number of crystallites of the first, second, third and fourth groups respectively. The newly created area due to the formation of some fine powders is neglected.

3.3. RESULTS

The time dependence of NL of single crystals of NaF is shown in Fig. 3.2 for different impact velocities. The NL appears after the impact of piston on the crystal.
At first, it increases with time, reaches its maximum intensity a few tenths of a millisecond after the impact, and then it decays. The peak in the I versus time curve increases with increasing impact velocity. These may be small time lags between the impact of the piston on the crystal and the appearance of Ir, but we were not able to monitor it in the time scale used in the present investigation.

Fig. 2-3 shows that for rising portion \( m \) with time, the plot of \( \log \tau \) versus \( t \) is linear with a positive slope which suggests the relation

\[ 1 = L \exp \left( -\alpha \tau \right), \tag{3.3} \]

where \( L \) and \( \alpha \) are constants.

It is also seen from Fig. 2-3 that for the decaying portion of \( m \) with time, the plot of \( \log \tau \) versus \( t \) is a straight line with a negative slope which supports the relation

\[ 1 = L \exp \left( -\alpha \tau \right), \tag{3.3} \]

where \( L \) and \( \alpha \) are constants. The values of \( \alpha \) and \( \alpha \) increase with increasing values of the impact parameters \( L \), \( \alpha \), \( \alpha \), and \( \alpha \).

The total intensity \( I \) of \( m \), defined as the area below the \( I \) versus time curve, of all
halide crystals, initially increases with the impact velocity \( v_e \) as shown in Fig. 2-4. The total ML intensity attains a saturation value for higher values of the impact velocity. Fig. 3-5 shows that for lower values of the impact velocity, the plot of \( \log(I_p) \) versus \( 1/v_e \) is a straight line with a negative slope, which suggests the relation

\[
I_p = I_p^0 \exp(-v_e/v_c),
\]

where \( I_p^0 \) and \( v_c \) are constants. The physical significance of these constants will be discussed later on. The value of \( v_c \) is different for different crystals and it is shown in Table 3-1.

Fig. 3-6a shows that the time \( t_p \) corresponding to the peak in the ML intensity versus time curve of NaP crystals decreases with increasing values of the impact velocity \( v_e \). Fig. 3-6b shows that for higher values of the impact velocity, the plot of \( t_p \) versus \( 1/v_e \) is a straight line with a positive slope.

Fig. 3-7 shows the dependence of peak intensity \( I_p \) of ML intensity versus time curve of alkali halide crystals on the impact velocity \( v_e \). It is seen that for higher values of the impact velocity, the peak intensity \( I_p \) increases linearly with the impact velocity.

The time dependence of ML in the non-centrosymmetric crystals, that is, in tartaric acid is shown in Fig. 3-8 for different values of the impact velocity. In every respect (except intensity), it is similar to that of the
centrosymmetric crystals (Fig. 1-2). The impact velocity dependence of the total ML intensity $I_\tau$ of the non-centrosymmetric crystals tartaric acid, acetamide and ethyl stearate is shown in Fig. 1-9. It is seen that $I_\tau$ attains a saturation value for higher values of the impact velocity. For lower values of the impact velocity, the plot of $\log I_\tau$ versus $1/\nu$ is a straight line (Fig. 1-10), which suggests the suitability of equation (1.4) also for these crystals. Fig. 1-11 shows that the peak intensity $I_\nu$ of ML intensity versus time curve of tartaric acid, acetamide, and ethyl stearate crystals, increases with the impact velocity and the increase is linear in the higher values region of the impact velocity.

Fig. 1-12 shows the variation of total intensity $I_\tau$ of ML with the mass of the crystals for the impact velocity 313.2 cm/sec. Fig. 1-13 shows the crystal mass dependence of the peak intensity $I_\nu$ of the ML versus time curve for a constant impact velocity of 313.2 cm/sec. It is found that after a minimum size of the crystals, the total ML intensity increases linearly with the volume or mass of the crystals, and the peak of the ML intensity versus time curve increases linearly with the area of cross-section of the crystals.

Fig. 3-14 shows the dependence of total ML intensity of NaF crystals on the impact velocity, for different masses of the load dropped on the crystals. It is seen that the for higher mass of the load, the
total ML intensity attains a saturation value at lower values of the impact velocity as compared to that for lesser mass of the lead.

Fig.3-13 shows the dependence of total ML intensity on the area of newly created surfaces of NaF, NaCl and tartaric acid crystals. It is seen that the total ML intensity is directly proportional to the area of the newly created surfaces, although the ML efficiency is different for different crystals.

The relative integrated intensities per gm mole of the crystals were determined at an impact velocity of 313.2 cm/sec. No significant changes in ML activity were found with respect to the crushing direction of the crystals. The NaCl, NaBr, NaF, LiCl, LiF, tartaric acid, acetamide and ethyl stearate crystals do not show ML when they are crushed in CO₂ atmosphere.

The rise and decay time of the ML from a single fracture are two orders of magnitude smaller than those observed in the experiments described above. When the oscilloscope time scale knob was kept in microsecond scale and the crystal placed on the lucite plate was fractured statically, then many pulses of microsecond duration appeared (no triggering used). This result shows that the ML pulse due to the action of a single crack is in the microsecond range for the crystals having dimensions of few mm per edge.
FIG. 3-2. Time dependence of ML in 3x3x1 mm NaF crystals at
impact velocity of (i) 313, 1 cm/sec, (ii) 342, 6 cm/sec,
(iii) 377, 6 cm/sec and (iv) 62, 6 cm/sec.
Fig. 3-3. Plot of log I versus t, for rising and decaying portion of Ml, at impact velocity of (i) 313.2 cm/sec, (ii) 177.6 cm/sec, (iii) 62.4 cm/sec.
Fig. 3-4. Dependence of total KI intensity of alkali halide crystals on the impact velocity $v_0$ of the load, on the crystals.
Fig. 3-5. Plot of log I vs. 1/\nu for different alkali halide crystals.
Fig. 3-6a. Dependence of the time $t_m$ corresponding to ML intensity versus time curve on the impact velocity $v_0$ for NaF crystals.
Figure 3: Plot of $t_m$ versus $1/V_0$ for NaF crystals.
Fig. 2-7. Dependence of peak intensity $I_m$ of ML intensity versus time curve of alkali halide crystals on the impact velocity $v_0$.
Fig. 3-6. Time dependence of ML in 2x3x3 cm terephthalic acid crystals at impact velocity of (i) 313.2 cm/sec, (ii) 242.6 cm/sec, (iii) 177.6 and (iv) 67.6 cm/sec.
FIG. 3-9. Dependence of total M1 intensity of piezoelectric crystals on the impact velocity $v_0$. 

- Tartaric Acid
- Acetamide x 0.35
- Ethyl Stearate x 1.4

Impact Velocity (cm/sec) vs. Total M1 Intensity (arb. units)
Fig. 2. Plot of log I vs. $1/V_0$ for piezoelectric crystals.
Figure 3-11. Dependence of peak intensity $I_p$ of AE intensity versus time curve of piezoelectric crystals on the impact velocity $v_0$. 

- Tartaric Acid
- Acetamide
- Ethyl Stearate
Fig. 12. Dependence of total intensity of ML on the mass of crystals \( v_0 = 313.2 \text{ cm/sec} \).
Fig. 3-13. Dependence of the peak intensity of H1 versus time curve on the mass of the crystals
\( (\nu_0 = 313.2 \text{ cm/s}) \).
Fig. 2-14. Dependence of total X-ray intensity of NaF crystals on the impact velocity for different masses of the load (curves I, II, and III correspond to 800, 600 and 200 gm of the load respectively).
Fig. 3-19. Dependence of local K intensity on the area of newly created surface.
### TABLE 2-1

Values of certain constants related to the impulsive excitation of ML in crystals.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Crushing direction</th>
<th>( \lambda_\text{a}(x 10^3) ) (for ( v_\text{e}=113.2 ) cm/sec)</th>
<th>( \lambda_\text{b}(x 10^3) ) (for ( v_\text{e}=113.2 ) cm/sec)</th>
<th>( v_\text{e} ) (cm/sec)</th>
<th>Normalized ML activity per mole with respect to that of sucrose crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NaCl</td>
<td>a = b = c</td>
<td>12.6</td>
<td>13.5</td>
<td>52.1</td>
<td>0.67 x 10^{-4}</td>
</tr>
<tr>
<td>2. KBr</td>
<td>a = b = c</td>
<td>12.6</td>
<td>13.1</td>
<td>50.3</td>
<td>0.60 x 10^{-4}</td>
</tr>
<tr>
<td>3. NaF</td>
<td>a = b = c</td>
<td>12.6</td>
<td>13.3</td>
<td>55.2</td>
<td>1.0 x 10^{-3}</td>
</tr>
<tr>
<td>4. LiF</td>
<td>a = b = c</td>
<td>12.6</td>
<td>13.6</td>
<td>61.3</td>
<td>1.1 x 10^{-3}</td>
</tr>
<tr>
<td>5. LiCl</td>
<td>a = b = c</td>
<td>12.6</td>
<td>13.3</td>
<td>51.7</td>
<td>0.67 x 10^{-3}</td>
</tr>
<tr>
<td>6. TARTARIC</td>
<td>acid</td>
<td>b</td>
<td>13.10</td>
<td>17.4</td>
<td>46.5</td>
</tr>
<tr>
<td>7. ACETAMIDE</td>
<td></td>
<td>b</td>
<td>12.00</td>
<td>16.7</td>
<td>43.4</td>
</tr>
<tr>
<td>8. ETHYL</td>
<td>STEARATE</td>
<td>c</td>
<td>11.80</td>
<td>16.3</td>
<td>41.3</td>
</tr>
</tbody>
</table>
24. DISCUSSION

The Pd does not appear in the elastic and plastic regions of HCl, HBr, HI, and other alkali halide crystals. It appears only during the fracture of the crystals. The time duration of the Pd pulse due to the motion of a single crack in the micrometer range, which is of the order of the time needed for a crack to move through the crystal. However, the time duration of a continuous Pd pulse produced during the impact of a load on the crystal is of the order of milliseconds and depends on the impact velocity. Thus, the continuous Pd signal produced during the impact of a load on the crystal should be related to the number of mobile cracks produced in the crystal.

The linear dependence of Pd intensity on the area of newly created surfaces suggests that the area of molecules present on the newly created surfaces are only responsible for the Pd excitation because they are subjected to strong deformation during the movement of cracks in the crystal. This finding may be of considerable importance in the further theoretical and experimental investigation of Pd. Luminescenceprobe of a crystal deformation have been a subject of considerable interest.
the preservation in non-concentrically cored samples. It is known that
the impact velocity dependence of the NL of concentric-
perforator investigation is not a single factor. The impact may also be due to the creation of more surfaces area. The
increase in the impact area due to the creation of more surfaces area
the increase in the NL intensity with the impact

Rasoppe deaced.

correlation may occur because the NL and the density of metal
or microscopic defects (Huang et al., 1994; Pettit et al., 1994)
are found to be randomly distributed across the particulate concentration
area. This is the formation of new surfaces in the cored area. Once
surfaces during etching, they no longer give a response
the closure from K particles between the metal cored
chosen in the present investigation to extrude, the particles cored. In addition, the NL in the cored area
not only during their deformation in the elastic and
tensile yield, etc., occurring and other same corede cylinders. The
consistent. However, the NL in the matrix, not NL. 177.
that deformation gives rise to intrinsic fluorescence,
1977), In these cored oils the defects produced during
on the density of defects produced during the deformation
and the intrinsic fluorescence intensity of NLO can, and also cored
due to the piezoelectricity of the newly created surfaces (Chandra 1981). The similar impact velocity dependence of the ML of centrosymmetric and non-centrosymmetric crystals suggests that the ML excitation in centrosymmetric crystals should also be due to the electrification of the newly created surfaces. The details of the ML excitation in centrosymmetric crystals will be discussed in Chapter VI. The time dependence, impact velocity dependence, and crystal size dependence of ML will be discussed theoretically in Chapter VI, after collecting some more informations in the subsequent chapters.
2.5. REFERENCES


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