CHAPTER IV

DEPENDENCE OF MECHANOLUMINESCENCE INTENSITY IN COLOURED KCl AND NaCl CRYSTALS ON THE NUMBER OF NEWLY-CREATED DISLOCATIONS

4.1. INTRODUCTION

The concept of a linear lattice imperfection, called a dislocation, arose primarily from the study of plastic deformation processes in crystalline materials. 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, these defects in the crystal are called edge dislocation. However, the screw dislocation is another type of defect, which can be formed as follows. The crystal is cut part way 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 dislocation exist along the edge of the cut. This line defect is called screw dislocation. The most useful definition of a dislocation is given in terms of the Burgers circuit. A Burgers circuit is any atom to atom path taken in a crystal containing dislocations which forms a closed loop. The
vector required to complete the Burgers circuit is called the Burgers vector. The Burgers vector of an edge dislocation is normal to the line of the dislocation. However, the Burgers vector of a screw dislocation is parallel to the line of the dislocation. In most cases the dislocation line lies at an arbitrary angle to its Burgers vector and the dislocation line has a mixed edge or screw character. Theoretically, a screw dislocation may glide in any direction but edge dislocation and all other than pure screws dislocation 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 applied stress 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 (Frank 1948, Johnston and Gilman 1959, 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 distorted fashion that further dislocation motion becomes difficult. This phenomenon is called "work-hardening". Dislocations also interact with a free surface. In fact, 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 towards the region of tension, since in this way the tension becomes less in this region. On the other hand, if the impurity atoms are smaller than the host atoms, then they tend to be deposited in the region of compression.

The appearance of ML during the elastic and plastic deformation of X or $\gamma$ irradiated alkali halide crystals indicates that the creation of the newly-created dislocations should be responsible for the ML emission. The correlation between the ML intensity and the number of newly-created dislocations has not been investigated to date. The present chapter reports the dependence of ML in coloured KCl and NaCl crystals on the number of newly-created dislocations.

4-2. METHODS OF MEASURING DISLOCATIONS

Dislocation density is the total length of the dislocation lines in a unit volume or the number of dislocation lines crossing a unit area in the crystal. The density
ranges from below $10^2$ dislocations/cm$^2$ in the best germanium and silicon crystals to $10^{11}$ or $10^{12}$ dislocations/cm$^2$ in heavily deformed metal crystals. The optical, electron and field ion microscopes and x-ray diffraction techniques have been used for the investigation of the dislocation, arrangement, and density of dislocations and for determining their properties. The techniques can be divided into five main groups: (1) surface methods, in which the point of emergence of a dislocation at the surface of a crystal is revealed; (2) decoration methods in which dislocations in bulk specimens transparent to light are decorated with precipitate particles to show up their position; (3) transmission electron microscopy in which the dislocations are studied at very high magnification in specimens 0.1 to 4.0 μm thick; (4) x-ray diffraction, in which local differences in the scattering of x-rays are used to show up the dislocations; (5) field emission and field ion microscopy, which reveals the position of individual atoms. The following table represents the details about the methods used for the determination of the dislocation densities (Johnston 1961, Kittel 1976).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Specimen thickness</th>
<th>Width of image</th>
<th>Maximum practical density per cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron microscopy</td>
<td>1000 A°</td>
<td>100 A°</td>
<td>$10^{11} - 10^{12}$</td>
</tr>
<tr>
<td>X-ray transmission</td>
<td>0.1 - 1.0 μm</td>
<td>5 μm</td>
<td>$10^4 - 10^5$</td>
</tr>
<tr>
<td>X-ray reflection</td>
<td>2 μm(min) - 50 μm(max)</td>
<td>2 μm</td>
<td>$10^6 - 10^7$</td>
</tr>
<tr>
<td>Decoration</td>
<td>10 μm(depth of focus)</td>
<td>0.5 μm</td>
<td>$2 \times 10^7$</td>
</tr>
<tr>
<td>Etch pits</td>
<td>no limit</td>
<td>0.5 μm</td>
<td>$4 \times 10^8$</td>
</tr>
</tbody>
</table>
The dislocation density in heavily deformed crystals may be estimated from the increased internal energy that results from plastic deformation. The dislocation energy is about $5 \times 10^{-4}$ erg/cm, or about 8 eV per atom plane through which the dislocation passes. The maximum energy stored in lattice distortions as a consequence of severe plastic deformation, as by twisting, filing or compressing, has been measured thermally for several metals. If the deformation is not too great, about 10 percent of the energy expended in plastic flow is stored in the lattice. Upon continued plastic flow, however, the stored energy approaches a saturation value. The observed values of the stored energy are about $10^8$ ergs/cm$^3$. If the energy per unit length of the dislocations is $5 \times 10^{-4}$ erg/cm, then there must be about $10^{11}$ cm of dislocation lines per cubic centimeter of crystal, or about $10^{11}$ dislocations/cm$^2$.

Surface methods are generally used for the observation of dislocations in alkali crystals. The principle of the surface methods is described below. If a crystal containing dislocations is subjected to an environment which removes atoms from the surface, then the rate of removal of atoms around the point at which a dislocation emerges at the surface may be different from that for the surrounding matrix. The rate of removal of the atoms is different due to one or more number of properties of dislocation (Hull 1975): (1) lattice distortion and strain field of the dislocation, (2) geometry of planes associated with a screw dislocation so that the
reverse process to crystal growth produces a surface pit, (3) concentration of impurity atoms at the dislocation which changes the chemical composition of the material near the dislocation. When the rate of removal is more repeated around the dislocation, pits are formed at these sites, and when it is less, rapid hillocks are formed. Many methods are available for the slow, controlled removal of atoms from the surface. The most common and most useful are chemical and electrolytic etching. Other methods include thermal etching in which the atoms are removed by evaporation when the crystal is heated in a low pressure atmosphere at high temperatures, and cathodic sputtering in which the surface atoms are removed by gas ion bombardment. The last two methods usually reveal only the screw dislocations.

The dislocation density is measured by the number of etch pits in an area of one square cm. Etch pits are counted by making use of a microscope. A graticuled eyepiece is used which contains a one square cm mesh at the position of the cross wire. If the magnification of the objective is \( m \) then an area of \( 1/m^2 \) of the crystal surface is magnified by the objective to one square cm, to the size of the mesh. If \( N \) is the number of etch pits that fall within the mesh when seen through the eye-piece, then the dislocation density is given by \( \xi = N/m^2 \).

4-3. EXPERIMENTAL

The crystals were made ready for the counting of etch pits by polishing, rinsing and etching. The solution
of the polishing agent is taken in a flat bottomed container. The crystal block is lightly held with a forceps and is placed gently in the solution at the bottom of the container such that the face to be examined is uppermost. The container is shaken for two minutes taking care to see that the crystal block does not slide and strike against the sides of the container. The top layers of the sides of the block which might contain any surface dislocation loops generated by cleaving and handling are thus removed. The block is then rinsed in a suitable rinsing agent for suitable time. The crystal is then transferred to flat bottom of another container filled with the appropriate etching solution. The container is shaken gently for one or two minutes taking the same precautions as those taken during the polishing. The crystal is then rinsed in the solution of the rinsing agent and dried with the help of a soft blotting paper. Then the number of etch pits was counted in one square cm mesh (placed at the position of the crosswire) or a Carl Zeiss microscope. The microscope has an arrangement so that its magnification can be fixed to any of the values 8, 20, 40, and 95. The dislocation density was measured at least at 30 different places of the crystals. In the present investigation, the dislocation density was measured only for the faces which lie along the direction of the compression.

The etchant used for different crystals are as described below.

(1) NaCl - 50 mg of FeCl₃ (anhydrous) in 1000 cc glacial acetic acid (Jesensky 1958, Amelinkx 1954).
(2) KI - Concentrated solution of NH₄Cl in a mixture of methyl alcohol and n-butyl alcohol in the ratio of 3:4 by volume (Naidu 1970).

(3) KBr - Concentrated solution of NH₄Br in a mixture of methyl alcohol and n-butyl alcohol in the ratio of 3:4 by volume (Moran 1958).

(4) LiF - 4.7 x 10⁻⁶ M aqueous solution of FeCl₃ (Gilman et al 1958, Gilman 1957, Conter and Weartman 1964).

(5) KI - Iso-propyl alcohol (Moran 1958).

A saturated solution of NH₄I in a mixture of methyl alcohol and n-butyl alcohol in the ratio of 3:4 by volume was found to be a good polishing agent for NaCl and KCl crystals. Isobutyl alcohol proved to be a good rinsing agent for NaCl and KCl crystals.

Thirty samples of nearly the same dimension each exposed to 40 minutes to X-irradiations were chosen and were divided in six batches. The dislocation density was measured in five crystals of the first batch without any application of the pressure. The crystals of the second batch were compressed by applying the pressure of 4.5 kg and the intensity of KI during the compression was measured by the device described in Chapter II. Then, the dislocation density was measured in once compressed crystals of the second batch. Similarly the KI intensity and the dislocation density was measured in the crystals of batches third, fourth, fifth and sixth for the second, third, fourth and
fifth number of pressings of the crystals. It becomes difficult to measure the dislocation density in the crystals after fifth or sixth applications of the pressure.

The dependence of the Xl intensity on the number of newly created dislocations could be successfully investigated only for NaCl and KCl crystals. Since, the Xl crystals are sensitive to moisture, the newly created surface becomes contaminated and so dislocations could not be observed clearly in our laboratory. The dislocation density in unpressed crystals of X-irradiated LiF and KBr crystal was of the order of $10^7$ dislocations/cm². It increases so much with the application of pressure, that it was not possible to measure the change in the dislocation density with the successive number of applications of the pressure in LiF and KBr crystals.

4.4. RESULTS AND DISCUSSION

Figure 4.1 shows that the total number of dislocations in X-irradiated KCl and NaCl crystals increases with the number of pressings. Figure 4.2 shows that the plot between the logarithm of the number of newly created dislocations and $(n_p-1)$, (where $n_p$ is the number of pressing) is a straight line with a negative slope. This indicates that the dependence of the number of newly created dislocations on the number of application of the stress follows the relation

$$N_n^p = N_1^p \exp \left[ \alpha (n_p - 1) \right] \quad ...(3.1)$$

where $N_n^p$ and $N_1^p$ are the number of newly created
Fig. 4.1: Dependence of the total number of dislocations in X-irradiated KCl and NaCl crystals on the number of applications of the pressure (4.5 kg).
dislocations in the nth and 1st pressing and $\alpha$ is a constant. The value of $\alpha$ estimated from Fig. 4-2 is nearly equal to the value of $\beta$ which is the slope of $\log I_n^p$ versus $(n_p - 1)$ curve. The values of $\alpha$ and $\beta$ are determined for the same value of the applied pressure and for the crystals of nearly the same dimensions.

Table 4-1 shows dependence of the total number of dislocations, number of newly created dislocations at different numbers of pressings, and the ML intensity, on the number of applications of the pressure. Figure 4-3 shows the plot of logarithm of the ML intensity versus logarithm of the number of the newly created dislocations is a straight line with a positive slope of value nearly equal to one. This finding suggests a linear relation between the ML intensity and the number of newly created dislocations.

The linear correlation between the ML intensity and the number of newly created dislocations suggests the direct responsibility of the dislocations for the ML excitation. This fact is further supported by nearly the same values of $\beta$ (slope of $\log I_n^p$ versus $n_p$ curve) and $\alpha$ (slope of $\log A_n^p$ versus $n_p$ curve). The correlation between the ML intensity and the number of newly created dislocations is found to be of great importance in analysing a suitable dislocation-model for the ML excitation (Chapter VII).
FIG. 4.2—PLOT OF THE LCG OF NEWLY-CREATED DISLOCATIONS VERSUS (np-
4.3 Plot of the log of ML intensity versus the log of newly created dislocations.
| Number of applications of the pressure (4.5 Kg load) | X-irradiated KCl crystals |  |  |  |  |  |  |  |
|--------------------------------------------------|----------------------------|---|---|---|---|---|---|
| Total number of dislocations per cm² \( \times 10^5 \) | Average number of newly created dislocations per cm² \( \times 10^5 \) | ML intensity during the application of pressure (arb. units) | Total number of dislocations per cm² \( \times 10^5 \) | Average number of newly created dislocations per cm² \( \times 10^5 \) | ML intensity during the application of pressure (arb. units) |
| 0 | 9.1 ± 4.3 | 0.00 | -- | 1.7 ± | 0.00 | -- |
| 1 | 53.2 ± 10.0 | 44.1 | 300 ± 20.5 | 16.8 ± 8.2 | 15.1 | 3.5 ± 0.2 |
| 2 | 78.4 ± 22.5 | 25.2 | 25 ± 1.7 | 21.2 ± 6.0 | 5.4 | 0.8 ± 0.1 |
| 3 | 100.5 ± 22.0 | 22.1 | 20 ± 1.3 | 25.6 ± 11.0 | 4.4 | 0.5 ± 0.1 |
| 4 | 118.8 ± 15.0 | 18.3 | 16 ± 1.1 | 28.4 ± 9.1 | 2.8 | 0.3 ± 0.1 |
| 5 | -- | -- | -- | 30.1 ± 10.3 | 1.7 | 0.2 ± 0.1 |


