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Mechanoluminescence of coloured KCl crystals

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Abstract. The gamma-irradiated KCl crystals exhibit mechanoluminescence during elastic, plastic and fracture deformation. The mechanoluminiscence (ML) intensity varies linearly with the number of newly-created dislocations and decreases with successive application and release of uniaxial pressure. The total ML intensity increases with applied pressure as well as with the temperature of the crystals. On the basis of the movement of the dislocations, the pressure and temperature dependence of ML is discussed.

Keywords. Mechanoluminescence; alkali halides; mechanical deformation.

1. Introduction

Mechanoluminescence (ML) is a type of luminescence produced during mechanical deformation of solids. The mechanoluminescent substances may be divided into those whose ML spectra resemble (i) other type of luminescence spectra, (ii) molecular spectra of the surrounding gases and (iii) both these spectra. The possible uses of mechanoluminescent substances as mechano-optico transducers and in fuse system are attracting increasing interest. The crystal structure correlation of ML and the memory-effects related to plastic deformation may also be interesting (Chandra 1981; Chandra and Elyas 1979; Hardy *et al* 1981; Grabec 1974). The ML studies provide a suitable probe for studying the fracture dynamics of the crystals (Chandra and Zink 1980a). On the basis of mode of excitation, ML may be classified as piezo-induced, dislocation-induced, cleavage-induced, tribo-induced, chemi-induced and adsorption-induced. The coloured alkali halide crystals exhibit ML (Walton 1977); which is not satisfactorily understood. The present paper reports the ML of coloured KCl crystals and shows that the ML in alkali halide crystals may primarily be attributed to annihilation of the dislocations of opposite sign during the mechanical deformation.

2. Experimental

The KCl single crystals ($4 \times 3{\cdot}8 \times 2{\cdot}5$ mm) used in the present investigation were supplied by the National Physical Laboratory, New Delhi. The small size crystals were annealed at 450°C for 2hr and cooled very slowly. The γ-irradiated specimen wrapped in aluminium foil was kept in dark for an hour to allow the after-glow to decay to a value, well below that expected in the ML measurements. Exposure of the irradiated crystals to stray light was avoided. A uniaxial pressure was applied to the crystal by placing

heavy loads statically (Chandra and Elyas 1977). The crystal was kept pressed for 30 sec. The ML intensities both during pressing and release were measured in terms of the deflection of a ballistic galvanometer connected to the amplifier coupled to an IP 28 photomultiplier tube. The process of pressing and release was repeated periodically till the ML intensity became small. All measurements were made by applying pressure along (100) direction of the crystals. A heater coil was wound round a cylinder for heating the crystal. The cylinder was mounted on a crystal platform and by changing the voltage, the crystals could be heated to any desired temperature. The ML was measured when the device attained a steady temperature. The crystal temperature was measured by a copper-constanton thermocouple. Temperature effect on the ML of the crystals was studied for a fixed load of 12·5 kg. To avoid heating of photomultiplier tube, a thick rubber sheet with a hole at its centre was placed between the glass plate and the photomultiplier housing. Four crystals were studied at each temperature and the standard error was $\pm$ 6%.

The ML spectra, the stress-strain and the ML-strain curves were determined following the method described earlier (Hardy and Zink 1976; Chandra and Zink 1980). The ML intensity was monitored by a *X–Y* recorder. The dislocation density was measured by the etch pit technique in which a concentrated solution of NH_4Cl in a mixture of methyl alcohol and *n*-butyl alcohol in the ratio of 3:4 by volume was used as etchant (Naidu 1970).

3. Results

Figure 1 shows the ML *vs* compression and the force *vs* compression curves of 5 × 4 × 6·3 mm γ-irradiated KCl crystals. It is seen that the ML appears in the elastic, plastic as well as fracture regions of the crystals. The stress and the ML intensity of the crystals are seen to vary with strain. The plot of log of ML intensity *vs* log of the number of newly created dislocations (figure 2) suggests a linear rela-

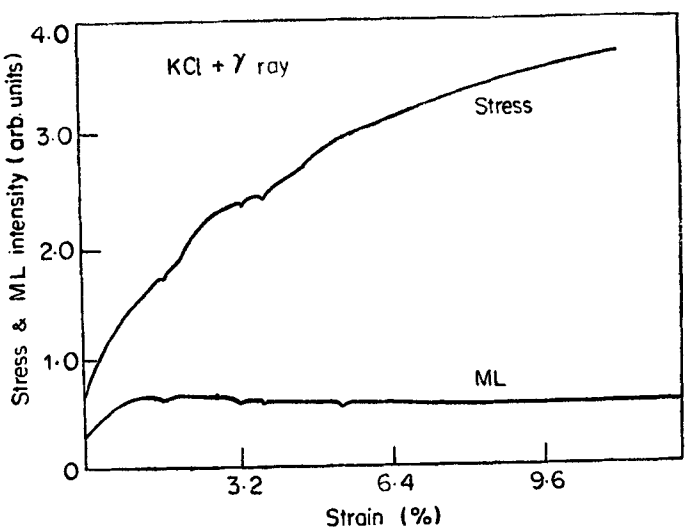

Figure 1. Mechanoluminescence *vs* compression and the force *vs* compression curves for γ-irradiated KCl crystal.

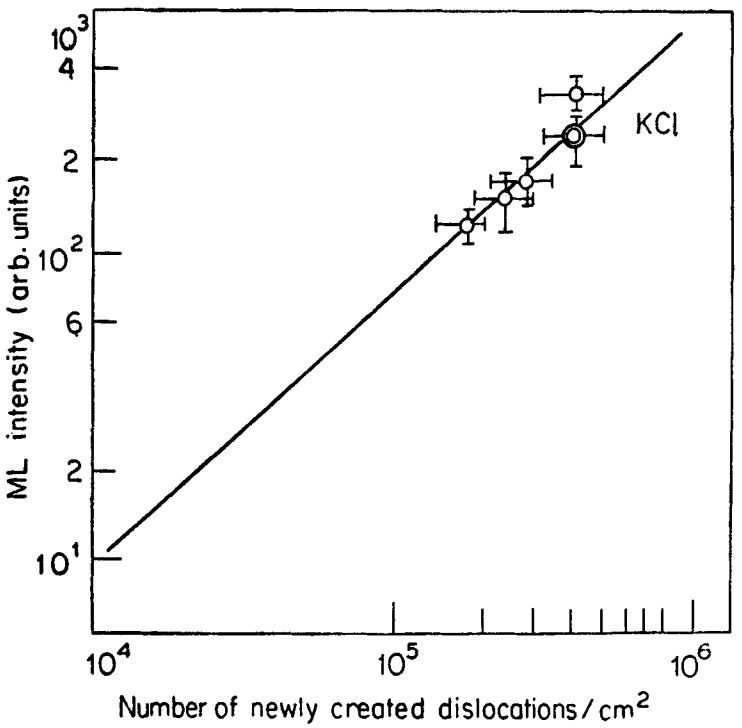

Figure 2. Plot of log ML intensity *vs* log number of newly created dislocations.

tion between the two. After certain number of applications of the uniaxial pressure, the dislocation density increases so much that it is difficult to determine the dislocation each pit counts for the highly deformed crystals.

The intensities of ML produced during application and release of the pressure, i.e. I_n^p and I_n^r of γ-irradiated KCl crystals decreases with the successive number n_p and n_r of application and release of pressure and follow the relations (figures 3a, b)

$$I_n^p = I_1^p \exp\,[-\beta(n_p - 1)], \tag{1}$$

$$I_n^r = I_1^r \exp\,[-\beta_1(n_r - 1)], \tag{2}$$

where β and β_1 are constants, and I_1^p and I_1^r are the ML intensity during the initial application and release of pressure respectively. The I_1^p and I_1^r values increase with pressure, however, the β and β_1 values decrease with pressure. For a given value of pressure β is always greater than β_1.

Figure 4 shows that the dependence of the ML intensity on successive application and release of pressure at different temperatures also follow (1) and (2). The β and β_1 values increase slightly with temperature. However, for a given temperature, the β_1 value is always $< \beta$.

Figure 5 reveals that the total ML intensity, i.e., the sum of the areas below I_n^p *vs* n_p and I_n^r *vs* n_r curves of γ-irradiated KCl crystals increases with temperature. The annealing time at this temperature, does not significantly alter the ML intensity of γ-irradiated KCl crystals.

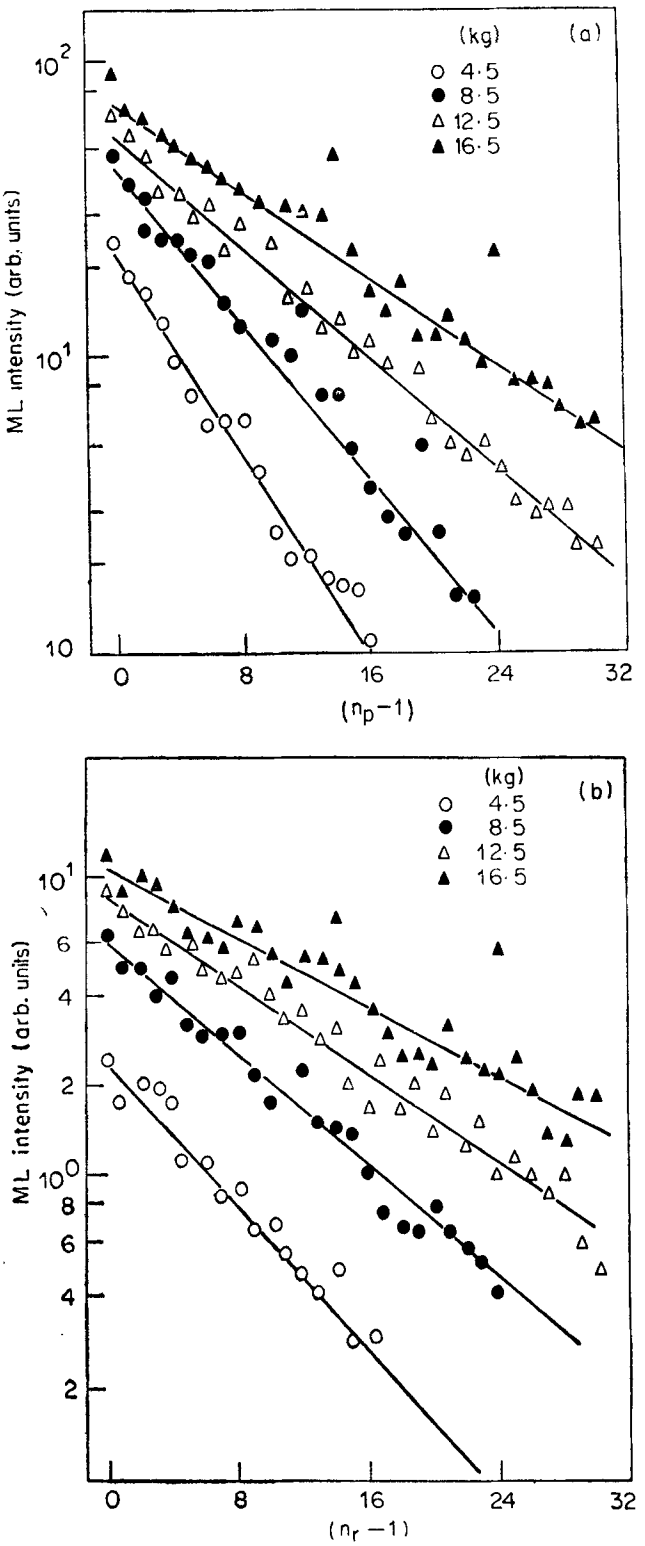

Figure 3. Plot of log ML intensity *vs* **a.** $(n_p - 1)$ **b.** $(n_r - 1)$ in γ irradiated KCl crystals for different values of uniaxial pressure.

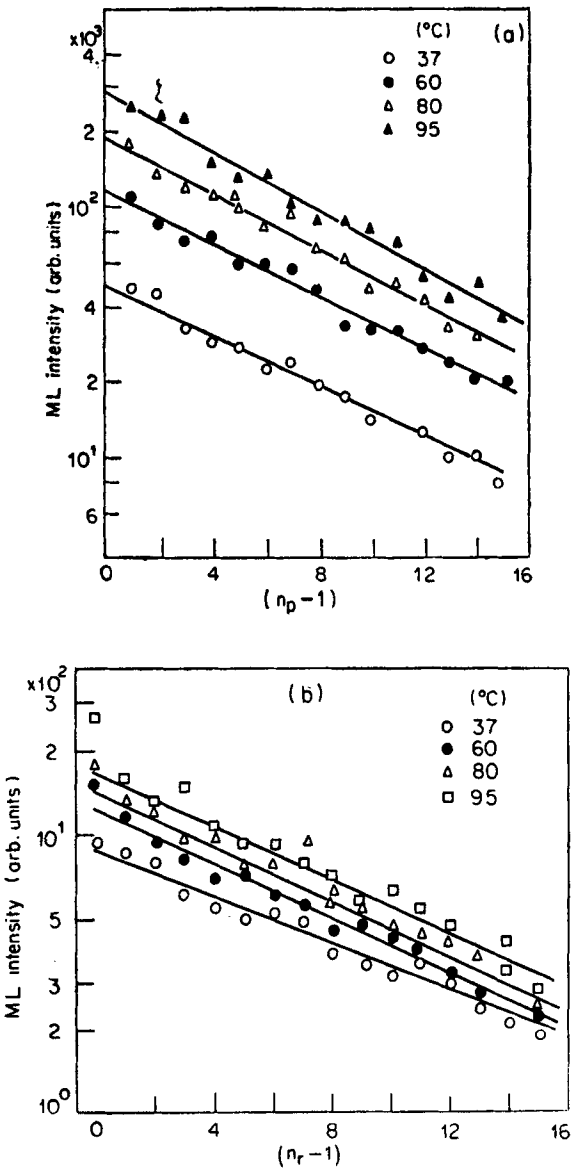

Figure 4. Plot of log ML intensity *vs* **a.** (n_p-1) **b.** (n_r-1) in γ irradiated KCl crystals for different values of temperature.

The ML intensity is directly related to the density of the colour centres (Butler 1966; Metz *et al* 1957), which is directly related to the area below the thermoluminescence (TL) glow curves of the crystals (Ausin and Alvarez 1972; Jain and Mahendru 1965). Hence, the ML intensity was normalized for the decrease in the density of the colour centres with temperature of the crystals using TL glow curves. The TL glow curves of these crystals have been reported earlier (Elyas *et al* 1982). The plot of $\log I_T \times A_T/(A_T - \int_{T_0}^{T} I_{TL}\,dT)$ *vs* $1/T$ (where I_{TL} is TL intensity, A_T is the

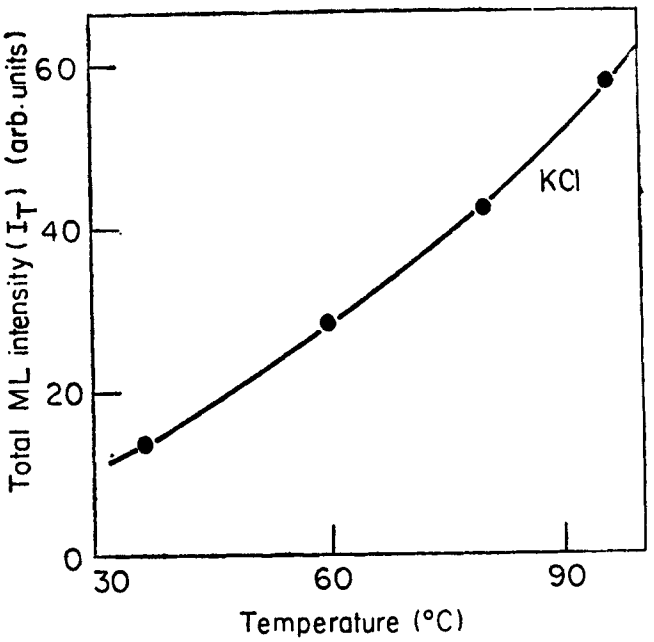

Figure 5. Effect of temperature on the total ML intensity I_T of γ irradiated KCl crystals.

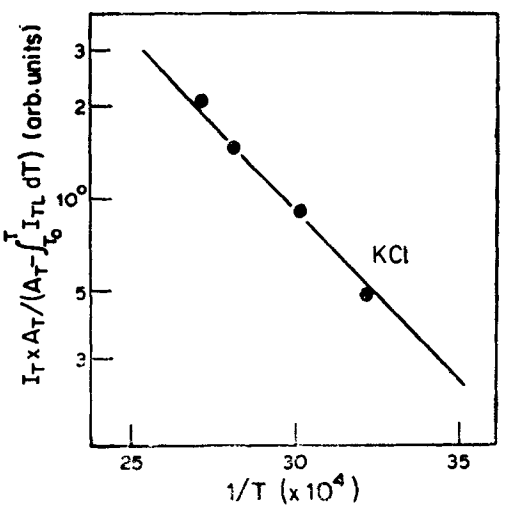

Figure 6. Plot of $I_T \times A_T/\left(A_T - \int_{T_0}^{T} I_{TL}\,dT\right)$ *vs* $1/T$.

total area below the glow curves and T_0 is the room temperature) is a straight line with a negative slope (figure 6), for γ-irradiated KCl crystals. This result suggests the relation

$$I_T \times A_T/A_T - \int_{T_0}^{T} I_{TL}\,dT = A_0 \exp(-E_0/kT), \tag{3}$$

where A_0 is a constant, k is the Boltzmann constant and E_0 is the activation energy. The E_0 value estimated from figure 6 is 0·25 eV for γ-irradiated KCl crystals.

Figures 3 and 4 show that the difference between the extrapolated and the experimental I_1^p values decreases with increasing temperature of the crystals. This suggests that the higher experimental I_1^p values may be due to the presence of shallow traps, which disappear during the initial application of the pressure.

The ML spectra of γ-irradiated KCl crystals (figure 7) are similar to their TL spectra (Ausin and Alvarez 1972). Similar results were also found for the ML of x-irradiated KCl crystals.

4. Discussion

4.1 *Mechansim of the* ML *excitation*

Many possibilities have been discussed earlier (Chandra *et al* 1982) and it has been found that dislocation annihilation is the dominating process for ML excitation. A large amount of stored energy is released whenever two dislocations moving in the same or closely neighbouring parallel slip planes unite by annihilation (Seitz 1952). Thus, the line at which the dislocations combine becomes the seat of a very large source of thermal energy which in turn increases the local temperature. The increase in temperature causes the ML excitation in the crystals. TL studies indicate that the thermal bleaching of colour centres takes place from room temperature to 300 or 400°C in x and γ-irradiated alkali halide crystals. The rise in the local temperature during the annihilation of dislocations of opposite sign may be sufficient to

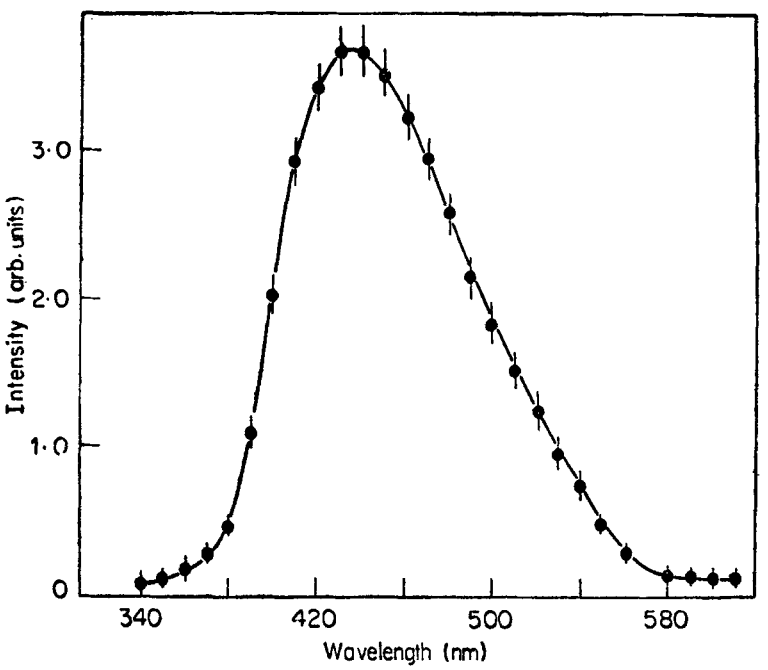

Figure 7. ML spectra of irradiated KCl crystals.

give rise to TL excitation. Although the crystal temperature may not rise considerably, the local temperature may be much higher during annihilation of the dislocations of opposite sign. In such cases the ML appears not only along the line of annihilation, but also in the surrounding regions. The similarity between ML and TL spectra of γ-irradiated KCl crystals supports the thermal origin of ML (Ausin and Alvarez 1972).

4.2 *Effects of pressure and temperature on* ML *excitation*

Let N_1, N_2, N_3, N_n be the number of dislocations created during the first, second, third and nth application of the pressure. The total number, N_{T_n} of newly created dislocations up to the nth pressing may be given by

$$N_{T_n} = N_1 + N_2 + N_3 + \ldots N_n \tag{4}$$

Assuming that the number of new created dislocations decreases exponentially with increasing number of application of pressure, the above equation may be written as

$$\begin{aligned} N_{T_n} &= N_1 + N_1 e^{-\alpha} + N_1 e^{-2\alpha} + \ldots N_1 \exp\,[-(n-1)\,\alpha], \\ &= N_1\,(1 - e^{-n\alpha}) \,/\, (1 - e^{-\alpha}) \\ &= N_0\,(1 - e^{-n\alpha}) \end{aligned} \tag{5}$$

where $N_0 = N_1 \,/\, (1 - e^{-\alpha})$ and α is a constant.

The number N_n^p of the newly created dislocations during the nth pressing may be given by

$$N_n^p = N_1^p \exp\,[-\,(n_p - 1)\,\alpha] \tag{6}$$

where N_1^p is the number of new created dislocations during the first pressing. This result agrees with our dislocation density measurements (Chandra *et al* 1982). When pressure is applied on a crystal, mobile dislocations are produced. Some of these dislocations disappear due to annihilation. The other mobile dislocations relax and become stationary. Thus the density of dislocations increases in the crystal when pressure is applied. The ML intensity measured in terms of the deflection of the ballistic galvanometer is linearly related to the number N of the newly created dislocations. This may be expressed as

$$\int I\,\mathrm{d}t = C\,N,$$

or

$$\int (\mathrm{d}n/\mathrm{d}t)\,\mathrm{d}t = n = C\,N, \tag{7}$$

where n is the number of excited luminescence centres and C is a constant. The linear relation between ML intensity (measured by a $X-Y$ recorder) and the strain rate (Alzetta *et al* 1970) suggests that the excitation rate of the luminescence centres is directly related to dislocation. This is in accord with (7).

If the dislocation annihilation model is the dominant process for the ML excitation in x and γ-irradiated alkali halide crystals, then (7) indicates that the annihilation rate (which is responsible for dn/dt) should be directly proportional to the mobile dislocations. This is because the number of dislocations responsible for the annihilations may be a fraction of the number of mobile dislocations. Thus, the intensity I_n^p of ML (monitored by the deflection of ballistic galvanometer) produced during the nth pressing may be expressed as

$$I_n^p = \eta N_1 \exp\,[-(n_p - 1)]\rho \tag{8}$$

where η is a factor related to the ML efficiency of the crystal, and ρ is the density of the colour centres which decreases with mechanical deformation of crystals (Butler 1966; Senchukov and Shmurak 1970). To simplify the problem, let us assume that the density of the colour centres decreases exponentially with the number of pressings, *i.e.*, it holds a relation

$$\rho_n^p = \rho_0 \exp\,(-\alpha_1 n_p), \tag{9}$$

where ρ_0 and ρ_n^p are the density of the colour centres without pressings and after nth pressings of the crystal respectively, and α_1 is a constant.

From (8) and (9), I_n^p may be written as

$$I_n^p = \eta\, N_1 \exp\,[-\alpha(n_p - 1)]\; \rho_0 \exp\,[-\alpha_1 (n_p - 1)],$$

or $$I_n^p = \eta\, \rho_0\, N_1 \exp\,[-(\alpha + \alpha_1)\,(n_p - 1)],$$

or $$I_n^p = I_1^p \exp\,[-\beta(n_p - 1)], \tag{10}$$

where $I_1^p = \eta\, N_1\, \rho_0$ is the ML intensity in the first pressing.

It is observed that the plot of $\log I_n^p$ *vs* $(n_p - 1)$ is a straight line with a negative slope, which supports (10). The value of β estimated from the plot of $\log I_n^p$ *vs* $(n_p - 1)$ is nearly equal to the value of the slope α estimated from the plot of $\log N_n^p$ *vs* $(n_p - 1)$ (for the same stress) (Chandra *et al* 1982). It seems that the decrease in the ML intensity with the number of pressings, is primarily due to the decreased creation of limited new dislocations with successive number of pressings. The decrease in the density of colour centres with the number of pressings, is only slightly responsible for the decrease in the ML intensity with the number of pressings.

The ML intensity increases with increasing values of pressure and irradiation time can be understood from (10). I_1^p is also related directly to N_1^p, the number of newly created dislocations in the first pressing. Thus, the intensity will be greater for increased values of pressure (Akulov 1964, Schoeck 1956). I_1^p is also related directly to the density of the colour centres in the crystals, and therefore, the ML intensity may increase with increase in the irradiation time of the crystals. It will get saturated for a longer time of irradiation.

If it is assumed that the ML produced during the pressure release is related to the ML produced during the corresponding number of applications of the pressure, then, from (10), the ML intensity during the nth release of the pressure may be given by

$$I_n^r = I_1^r \exp\,[-\beta_1 (n_r - 1)], \tag{11}$$

where β_1 is a constant. For a given pressure, β is always greater than β_1. The ML emission during the pressure release is related to the number of new traps produced during the deformation of crystal. The number of shallow traps may increase with crystal deformation, which in turn may increase the probability of the ML emission during pressure release. Thus β may be higher as compared to β_1.

It was found that β value decreases with increasing pressure value. This may be due to the plastic deformation in different stress-strain regions of the crystals, where the plastic behaviour may be different.

Since the probability of exciting an electron from the colour centres to the conduction band depends on the thermal spike rather than on the average temperature of the crystals, the smaller variation of the ML intensity with the temperature is expected. It has been described earlier that the ML intensity of γ-irradiated KCl crystals increases with their temperature, and follows the relation

$$I_T \times A_{TL} / A_{TL} - \int_{T_0}^{T} I_{TL}\, dT = A_0 \exp(-E_0 / kT) \tag{12}$$

The E_0 value estimated from ML measurements is 0·25 eV for γ-irradiated KCl crystals. It is known that the number of newly created dislocations for a given value of the applied stress increases with the temperature of the crystals (Akulov 1964; Schoeck 1956). It appears that the increase of ML intensity with temperature (after normalization for the decrease in density of the colour centres with temperature) is due to increase in the number of newly created dislocations. Thus, the factor E_0, should be related to the activation energy for the increase in the number of dislocations with the temperature of the crystals.

The ratio of I_n^r/I_n^p decreases with increasing temperature of the crystals. The number of retrapped electrons may decrease with increasing temperature of the crystals. Since I_n^r is mainly related to the number of re-trapped electrons, its decrease with temperature is expected.

The factor β is related to the rate constant of the decrease in the number of newly created dislocations with the number of application of the pressure. The increase in β and β_1 values with increasing temperature may be due to the change in the stress-strain behaviour with the temperature of the crystals.

Because the ML in coloured alkali halide crystals occur during their plastic deformation, the ML may have great potential for dynamic studies of dislocation interaction. The ML may provide a self-excited luminescence probe for the propagation of dislocation and may complement the techniques of defect luminescence where ultraviolet or cathode ray excitation can cause luminescence from defects formed at the onset of plastic deformation (Chandra *et al* 1975; Velendnilakaya *et al* 1975; Melton *et al* 1980).

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