Mobile interstitial model and mobile electron model of mechano-induced luminescence in coloured alkali halide crystals

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Abstract. A theoretical study is made on the mobile interstitial and mobile electron models of mechano-induced luminescence in coloured alkali halide crystals. Equations derived indicate that the mechanoluminescence intensity should depend on several factors like strain rate, applied stress, temperature, density of F-centres and volume of crystal. The equations also involve the efficiency and decay time of mechanoluminescence. Results of mobile interstitial and mobile electron models are compared with the experimental observations, which indicated that the latter is more suitable as compared to the former. From the temperature dependence of ML, the energy gaps between the dislocation band and ground state of F-centre is calculated which are 0·08, 0·072 and 0·09 eV for KCl, KBr and NaCl crystals, respectively. The theory predicts that the decay of ML intensity is related to the process of stress relaxation in crystals.

1. Introduction

X or γ-irradiated alkali halide crystals exhibit intense mechanoluminescence (ML), i.e. light is emitted during their mechanical deformation. Involvements of mobile dislocations and F-centres in the ML emission are indicated by several experimental facts like dependence of ML intensity on the density of F-centres, mechanical bleaching of F-centres, dependence of ML intensity on the number of newly created dislocations, disappearance of ML immediately after interruption of deformation, etc [1–13].

Several dislocation models proposed for the ML excitation in coloured alkali halide crystals are dislocation unpinning model, dislocation annihilation model, dislocation defect stripping model and dislocation interaction model [4]. According to dislocation unpinning model, when a dislocation in X or γ-irradiated alkali halide crystal is unpinned by applying an external stress, then the pinning point like V_k centre [14] may be released whose subsequent recombination with F-centre may give rise to the light emission. According to the dislocation annihilation model, a high local temperature may be produced during the annihilation of dislocations of opposite sign, which may cause the diffusion of the trapped interstitial atoms to the colour centres or it may directly ionize the colour centres. According to dislocation defect stripping model, the moving dislocations may strip interstitial halide atoms which may recombine

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radiatively with the F-centres with the creation of normal ions at the normal sites. According to dislocation interaction model, the moving dislocations may interact electrostatically or mechanically with the colour centres and the electrons released from F-centre during the interaction may subsequently recombine with the holes and give rise to luminescence.

The simultaneous measurements of stress-strain and ML-strain curves of X-irradiated alkali halide crystals show that the ML peaks lag considerably with the onset of more rapid plastic flow [1]. These results indicate that the ML does not occur during the unpinning of dislocations, but occurs during the movement of dislocations in the crystal. Moreover, the ML in coloured alkali halide crystals is observed during elastic deformation of the crystals and during release of pressure where unpinning of the dislocations is not possible. These facts indicate that the dislocation unpinning may not be the dominating source for the ML excitation.

The dislocation annihilation model does not seem to be applicable because of the following reason. The extent of heating during the annihilation of dislocations is usually very small. The upper limit for the increase in the temperature during annihilation may be given by $T_a = Q_d/(\pi \lambda_{ph}^2 \rho C)$, where Q_d is the energy which is released during the annihilation of a unit length of a dislocation, λ_{ph} is the free path length of a phonon, ρ is the density of the crystal and C is the specific heat capacity. The elastic strain energy per atom length of an edge dislocation is given by the equation [15–17]. $E = Gb^3/[4\pi(1-v)] \ln(R/r_0)$, where b is the Burger's vector, G is the shear modulus, v is the Poisson's ratio, R and r_0 are the upper and lower limits of the separation of two edge dislocations, respectively. Thus, the annihilation energy per atomic length, for two edge dislocations is $Q_d = Gb^3/[2\pi(1-v)\ln(R/r_0)$. For LiF, $G = 2.89 \times 10^{11}$ dyn cm^{-2}, $b = 2.01 \times 10^{-8}$ cm, $v = 0.32$, $r_0 = 5 \times 10^{-8}$ cm and $R = 10^{-3}$ cm, therefore, Q_d comes out to be 3.39 eV. For LiF, $\rho = 2.64$ g cm^{-3}, $C = 0.39$ cal gm^{-1} deg^{-1} and $\lambda_{ph} \simeq 10^{-6}$ cm at room temperature [18], therefore, T_a comes out to be $2.29°$C, which is very small. Hence, the annihilation of dislocations is not capable of bringing about a thermal flash in the luminescence of coloured alkali halide crystals. However, the dislocation annihilation model may be realized at very low temperature. It has been shown [19, 20] that the liquid helium temperatures are conductive to an enhancement in the effect of an increase in the temperature on the slipping bands of alkali halide crystals. As the temperature is lowered, the work of plastic deformation increases on account of the increase in the yield point, the thermal conductivity of the crystal becomes worse and its heat capacity decreases in proportion to the third power of the absolute temperature in accordance with Debye's law. If the temperature of the crystal prior to deformation was equal to 4.2 K then, according to the calculation [20], the temperature in the stripping bands is increased by 5 to 50 K. The liberation of hole centres from traps [21] and the excitation of luminescence during the recombination of mobile holes with F-centres are possible at the upper limit of these temperatures.

To date there is no satisfactory analysis related to the suitability of dislocation defect stripping model and the dislocation interaction model. The dislocation defect stripping model shows that the mobile interstitial atoms produced during deformation of the crystal, are responsible for the light emission. However, the dislocation interaction model shows that the mobile electrons produced during deformation of crystals are responsible for the light emission. In the present paper, equations are derived for the

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ML intensity considering mobile interstitial model (the dislocation defect stripping model) and the mobile electron model (dislocation interaction model) and their suitability is analysed by comparing the theoretical results with the experimental observations.

2. Mobile interstitial model for the ML in coloured alkali halide crystals

Suppose a crystal contains N_d dislocations of unit length per unit volume. When a dislocation of unit length moves through a distance dx, then the number of interstitial atoms interacting with the dislocation is $r_i dx N_i$, where r_i is the radius of interaction of the dislocations with interstitials and N_i is the density of the interstitial atoms (hole centres) in the crystals.

If p_i is the probability of the sweeping of activated interstitial atoms with the dislocations, then the number of interstitial atoms swept out by N_d dislocations is given by

$$dN_{is} = p_i N_d r_i N_i dx. \tag{1}$$

As the diffusion of atoms takes place only from the compression region above the dislocation line and not from the expansion region below the dislocation line [22], the factor 2 has not been included in the above equation.

If a dislocation moves the distance dx in time dt, then the rate of generation g of the interstitial atoms being swept out by moving dislocations may be given by

$$g = p_i N_d r_i N_i \frac{dx}{dt}$$

or

$$g = p_i N_d r_i N_i v_d \tag{2}$$

where v_d is the average velocity of the dislocations.

Equation (2) may be written as

$$g = \frac{p_i r_i N_i \dot{\varepsilon}}{b} \tag{3}$$

where, $\dot{\varepsilon} = N_d b v_d$, is the strain rate of the crystal and b is the Burgers vector [23, 15].

After room temperature irradiation, the defects incorporated in alkali halide crystals are F-centres (their aggregates) and the clusters of interstitial halogen atoms. Thus, in an irradiated alkali halide crystal, the interstitial is a hole centre i.e. electron deficient centre like X or X_2, where X is a halogen atom. According to the dislocation defect stripping model, the moving dislocation may release interstitial halogen atoms from clusters of various sizes and their subsequent recombination with F-centres may cause light emission with normal ions created at normal sites.

Now, the rate equation for the change in the number of interstitial halogen atoms being swept out by moving dislocations may be written as

$$\frac{dn_{is}}{dt} = g - \sigma_r n_F v_d n_{is}$$

or

$$\frac{dn_{is}}{dt} = g - \frac{n_{is}}{\tau} \tag{4}$$

where n_{is} is the number of interstitial halide atoms being swept out by moving dislocations at any time t, n_F is the density of recombination centres, i.e. F-centres, σ_r is the capture cross-section of these centres and $\tau = 1/\sigma_r n_F v_d$, is the lifetime of activated interstitial atoms. Here, the velocity of activated interstitial atoms has been taken to be equal to the velocity of dislocation because, in the interacting region they will be swept out with the velocity of dislocation [22, 24]. In this case, the recombination of activated interstitials with deep hole traps and the retrapping of interstitials have been neglected because the density of deep hole traps may be very small and the retrapping involves considerably higher activation energy.

Integrating (4), we have

$$\log\left(g - \frac{n_{is}}{\tau}\right) = -\frac{t}{\tau} + C_1.$$

Taking $n_{is} = 0$ at $t = 0$, C_1 comes out to be $\log(g)$ and we get

$$n_{is} = g\tau[1 - \exp(-t/\tau)]$$

or

$$n_{is} = \frac{p_i r_i N_i \dot{\varepsilon}}{b\sigma_r n_F v_d}[1 - \exp(-\sigma_r n_F v_d t)]. \tag{5}$$

Thus, the ML intensity due to the recombination of interstitial halide atoms with the F-centres may be given by

$$I = \eta \times \text{rate of recombination}$$

or

$$I = \eta \sigma_r n_F v_d n_{is}$$

where η is the probability of radiative recombination of halide atoms with F-centres. Substituting the value of n_{is} from (5), we get

$$I = \eta \frac{p_i r_i N_i \dot{\varepsilon}}{b}[1 - \exp(-\sigma_r n_F v_d t)]. \tag{6}$$

In a crystal of volume V, there will be $N_d V$ dislocations. Thus the ML intensity may be given by

$$I = \eta \frac{p_i r_i N_i \dot{\varepsilon} V}{b}[1 - \exp(-\sigma_r n_F v_d t)]. \tag{7}$$

The above equation shows that the ML intensity I will initially increase with time and then it will attain a saturation value I_s for the longer duration of straining time. The value of I_s may be expressed by the equation

$$I_s = \frac{\eta p_i r_i N_i \dot{\varepsilon} V}{b}. \tag{8}$$

When a crystal is being deformed uniaxially at a given strain rate in a machine, the mobile dislocations in the crystal is of a suitable density and their velocity satisfy the equation, $\dot{\varepsilon} = N_d b v_d$. If the cross-head of the deforming machine is stopped, then the stress in the crystal does not remain constant but decreases up to a certain extent with time. The mobile dislocations do not stop immediately but the cross-head does and continue to move, assisted by the thermal fluctuations. Thus, although the cross-head is stationary, the plastic deformation increases. This is stress relaxation and it is allowed to continue for a significant time [23]. The thermal fluctuations are able to assist the mobile dislocations over all the short range obstacles and the stress in the crystal which is equal to the applied stress, falls to the value of the long-range internal stress and thereafter the barrier cannot be surmounted with the aid of thermal fluctuations. Etching experiment suggests that there is no dislocation multiplication during the process of relaxation [25].

Suppose a crystal is being deformed at a constant strain rate $\dot{\varepsilon}$, and then the cross-head is stopped at a time $t = t_c$, at which the ML intensity had attained a saturation value I_s. The experimental observations of Hagihara *et al* [10] show that the stress in γ-irradiated KCl crystals decreases slowly from its value at $t = t_c$ to some lower value. On the basis of this result, let us assume that the dislocation velocity decreases exponentially from its value v_{do} at $t = t_c$, and follows the relation $v_d = v_{do}\exp[-\alpha(t - t_c)]$, where v_d is the dislocation velocity at any time $(t - t_c)$ and α is the rate constant.

Substituting the value of g from (2) and expressing $v_d = v_{do}\exp[-\alpha(t - t_c)]$, eq. (4) may be written as

$$\frac{dn_{is}}{dt} = p_i N_d r_i N_i v_{do}\exp(-\alpha(t - t_c)) - \sigma_r n_F n_{is} v_{do}\exp[-\alpha(t - t_c)]. \qquad (9)$$

Integrating equation (9) and taking $n_{is} = n_{iso}$ at $t = t_c$, we get

$$n_{is} = \left(n_{iso} - \frac{p_i N_d r_i N_i}{\sigma_r n_F}\right)\exp\left[\frac{\sigma_r n_F v_{do}}{\alpha}\{\exp[-\alpha(t - t_c)] - 1\}\right]$$
$$+ \frac{p_i N_d r_i N_i}{\sigma_r n_F}. \qquad (10)$$

As $n_{iso} = p_i N_d r_i N_i/\sigma_r n_F$, equation (10) indicates that $dn_{is}/dt = 0$, i.e. the equilibrium is still maintained where the rate of generation will be equal to the rate of recombination. Thus, the decay of ML intensity in a crystal of volume V may be given by

$$I = \eta p_i N_d r_i N_i v_{do} \, V\exp[-\alpha(t - t_c)]$$

or

$$I = \frac{\eta p_i r_i N_i \, V\dot{\varepsilon}}{b}\exp[-\alpha(t - t_c)]. \qquad (11)$$

After the completion of stress relaxation, if the accumulated interstitials are left, they may diffuse slowly towards the F-centres. Thus, the ML emission having comparatively longer decay time may be observed after the completion of stress relaxation process.

Equation (7) shows that when a crystal is deformed at a fixed strain rate, initially the ML intensity will increase with time and then it will attain a saturation value. When the deformation is stopped, the ML intensity will decrease with the rate constant controlled

by the stress relaxation process (equation (11)). Equation (8) indicates that the ML intensity should increase linearly with strain rate and volume of the crystal. Equation (8) also shows that the ML intensity I_s should increase with the density of interstitial atoms or V-centres in the crystal. However, for higher values of the strain, the density of V-centres (N_i) will decrease due to the deformation bleaching i.e. due to the electron-hole recombinations, and therefore I_s should decrease with the deformation of the crystal. As the strain rate increases with the applied stress [10], an increase in the ML intensity with the applied stress is expected.

When the temperature of a crystal is increased, N_i will decrease because of the thermal bleaching and p_i will increase because of the increased mobility of interstitials [22]. Thus, initially the ML intensity should increase with increasing temperature, attain an optimum value and then it should decrease and disappear at higher temperatures. As η and N_i are different for different crystals, the ML intensity may be different for different crystals.

3. Mobile electron model for the ML in coloured alkali halide crystals

During the plastic deformation, the dislocations only bend between pinning points. When the stress exceeds the yield point, the dislocations are detached from the pinning points, and move throughout the crystal. The dislocation D moving under the action of external stresses, interact with F-centres and capture electrons. In the dislocation energy band, an electron participates in two motions. It may travel along the dislocation (because the dislocation band is one dimensional) and it can travel with the dislocations [26]. If a dislocation containing electrons encounters a defect centre containing holes, the electron may be captured by this centre and luminescence may arise, in which the position of the peaks will be identical with the position of the luminescence emission of the defect centre. From the comparison of ML spectra with the spectra of other types of luminescence in coloured alkali halide crystals, it has been proved that the ML arises due to the recombination of electrons from F-centres with the V_2 centres [27]. Schematically, the ML process can be described by the following equations

$$F + D \rightarrow e_d + [-] \tag{A}$$

$$V_2 (= X^- + X^- + X^0) + e_d \rightarrow 3X^- + D + h\nu \tag{B}$$

where F and D represents F-centre and dislocation, respectively, e_d is the dislocation electron i.e. the electron captured by dislocation, $[-]$ is negative ion vacancy, X^- is halogen ion and X^0 is self-trapped hole.

Suppose a crystal contains N_d dislocations of unit length per unit volume. When N_d dislocations move through a distance dx, then the area swept out by the dislocations is $N_d dx$. According to dislocation interaction model, the ML excitation in coloured alkali halide crystals takes place due to the transfer of electrons from F-centre to dislocation band where the recombination of dislocation electrons with hole containing centres gives rise to luminescence. Near the edge dislocation, some of the F-centres lie in the expansion region and some of them lie in the compression region. In the expansion region, the energy gap between ground state of F-centre and dislocation band (lying just above the F-centre level) decreases due to the decrease in local density of the

crystal, however, the energy band gap between the F-centre level and dislocation band increases in the compression region of the dislocation due to the increase in the local density of the crystal [28]. As a matter of fact, there is a greater probability of the transfer of electrons from the F-centres lying in the expansion region rather than from the compression region of the edge dislocations. Therefore, the interaction volume may be taken only along the expansion region of the crystals and consequently the volume in which N_d dislocations interact while moving through a distance dx may be given by $N_d dx r_F$, where r_F is the distance up to which a dislocation can interact with the F-centres.

If n_F is the number of F-centres in unit volume, then the number of colour centres interacting with the dislocations will be $N_d n_F r_F dx$. If a dislocation moves the distance dx in time dt, then the number of F-centres interacting per second with the dislocations is given by

$$N_d n_F r_F (dx/dt) = N_d n_F r_F v_d$$

where v_d is the average velocity of dislocations.

During the interaction of moving dislocations with the F-centres, electrons are excited from F-centre to the dislocation band. If p_F is the probability of transfer of electrons from F-centres to the dislocation band during the interaction, then the rate of generation g^l of the electrons in the dislocation band is given by

$$g^l = p_F N_d n_F r_F v_d. \tag{12}$$

As $\dot{\varepsilon} = N_d b v_d$, g^l may be expressed as

$$g^l = \frac{p_F n_F r_F \dot{\varepsilon}}{b}. \tag{13}$$

When the dislocations containing electrons are moving in a crystal, then the electrons may recombine with the defect centres containing holes, and also with the deep traps present in the crystals. The retrapping of dislocation electrons in the negative ion vacancies may also take place. Thus, the rate equation may be written as

$$\frac{dn_d}{dt} = g^l - \sigma_r N_i v_d n_d - \sigma_1 N_1 v_d n_d - \sigma_2 N_2 v_d n_d \tag{14}$$

where n_d is the number of electrons in the dislocation band at any time t. N_i, N_1 and N_2 are the densities of recombination centres, deep traps and negative ion vacancies (without trapped electrons), respectively, and σ_r, σ_1 and σ_2 are the capture cross-sections of the recombination centres, deep traps and negative ion vacancies, respectively. Here, the velocity of electrons has been taken as the velocity of dislocations because the electrons are moving with dislocations.

Integrating equation (14), we get

$$\log(g^l - n_d/\tau_d) = -t/\tau_d + C_2$$

where,

$$\tau_d = \frac{1}{(\sigma_r N_i + \sigma_1 N_1 + \sigma_2 N_2) v_d} \tag{15}$$

is the lifetime of the electrons in the dislocation band and C_2 is a constant.

In an undeformed crystal, the stationary dislocations may capture the electrons from nearby F-centres. Subsequently the dislocation captured electrons may disappear during their recombination with the holes being diffused towards the dislocation lines. The dislocation captured electrons may also disappear due to the electron-hole recombination during the movement of dislocation electrons along the dislocation lines [26]. Once the electrons from the F-centres lying within the interacting distance are captured by a dislocation and subsequently annihilated, the stationary dislocations cannot capture electrons from other F-centres without change in temperature or without their movement. Thus, for the crystal which is not under deformation, the rate of thermal generation of dislocation electrons may be negligible and we may assume $n_d \sim 0$ at $t = 0$. This gives $C_2 = \log(g^l)$, and therefore, we get

$$n_d = g^l \tau_d [1 - \exp(-t/\tau_d)].$$ (16)

If η^l is the probability of radiative recombination of electrons with hole containing centres, then the ML intensity may be written as

$$I = \eta^l \sigma_r N_i v_d n_d$$

or

$$I = \eta^l \sigma_r N_i v_d g^l \tau_d [1 - \exp(-t/\tau_d)]$$

or

$$I = \frac{\eta^l \sigma_r N_i p_F n_F r_F \dot{\varepsilon}}{(\sigma_r N_i + \sigma_1 N_1 + \sigma_2 N_2) b} [1 - \exp(-t/\tau_d)].$$ (17)

As the recombination entities are different in both the cases, n may not be equal to η^l. Since a crystal of volume V will contain $N_d V$ dislocations of unit length, the ML intensity may be given by

$$I = \frac{\eta^l \sigma_r N_i p_F n_F r_F \dot{\varepsilon} V}{(\sigma_r N_i + \sigma_1 N_1 + \sigma_2 N_2) b} [1 - \exp(-t/\tau_d)].$$ (18)

Equation (18) shows that for a given strain rate, the ML intensity will initially increase with time and then it will attain a saturation value I_s for longer duration of the deformation time. The value of I_s may be written as

$$I_s = \frac{\eta^l \sigma_r N_i p_F n_F r_F \dot{\varepsilon} V}{(\sigma_r N_i + \sigma_1 N_1 + \sigma_2 N_2) b}.$$ (19)

As the dislocations move in a limited region of the crystal, the interacting volume at low strain rate is much less as compared to the total volume of the crystal [12]. Thus, for the limited deformation, n_F may be considered effectively to be a constant. However, for higher values of the strain, the mechanical bleaching may be significant and n_F may decrease considerably. According to (19), I_s may decrease with the strain of the crystal. Butler [29] and Chandra [30] have reported the decrease of I_s for higher deformation of the crystals.

The dependence of ML intensity I_s on the density of F-centres may be understood from (19) in the following way. Since in irradiated alkali halide crystals the density of deep traps N_1 is much less as compared to density of holes N_i [11], the factor $\sigma_1 N_1$ in the denominator of (19) may be neglected as compared to $\sigma_r N_i$. Furthermore, near the

core of dislocations (within distance r_F) the probability of capture of electrons from F-centres is greater than the probability of capture of dislocation electrons by the nearby negative ion vacancy. Hence, the probability of retrapping of dislocation-captured electrons may be negligible and consequently the effective value of σ_2 may be negligible. As a matter of fact, the factor $\sigma_2 N_2$ in the denominator of (19) may also be neglected. Thus, the value of I_s from (19) may be expressed as

$$I_s = \frac{\eta^l p_F n_F r_F \dot{\varepsilon} V}{b}.$$ (20)

The above equation shows that I_s should increase linearly with the density of F-centres.

As p_F, η^l, n_F and r_F are different for different alkali halide crystals, equation (20) shows that some alkali halide crystals may show higher ML, however, some alkali halide crystals may show weak ML.

With increasing temperature, the probability p_F of the transfer of electrons from F-centres to the dislocation band will increase, following the relation

$$p_F = p_{FO} \exp(-E_a/kT)$$ (21)

where E_a is the energy gap between the dislocation band and the ground state of F-centres [26, 18, 11].

From equations (20) and (21), I_s may be written as

$$I_s = \frac{\eta^l n_F r_F p_{FO} V \dot{\varepsilon}}{b} \exp(-E_a/kT).$$ (22)

Since the movement of dislocations does not stop just after stopping the cross-head used to deform the crystal, for some time the generation and recombination of dislocation electrons may take place and the ML may appear even after stopping the cross-head. Following the derivation of (11), in the present case the decay of ML intensity may be given by

$$I = \frac{\eta^l p_F r_F n_F V \dot{\varepsilon}}{b} \exp[-\alpha(t - t_c)].$$ (23)

After the completion of stress relaxation process, the dislocation velocity $v_d = v_0 \exp[-\alpha(t - t_c)]$ becomes negligible. If the dislocations still possess captured electrons, then the captured electrons may recombine with the holes, firstly, due to the movement of electrons along the dislocations and, secondly, due to the diffusion of nearby interstitial atoms from the compressed region of dislocations towards the dislocation lines. Thus, the ML emission having comparatively longer decay time may be observed after the completion of stress relaxation process.

4. Experimental support to the proposed models

To analyse the suitability of the proposed models, the ML measurements were performed on KCl, KBr and NaCl crystals grown by Czochralski technique. The crystals were coloured by exposing them to ^{60}Co source. The absorption spectra were recorded using Shemadzu UV spectrophotometer and the density of F-centres were
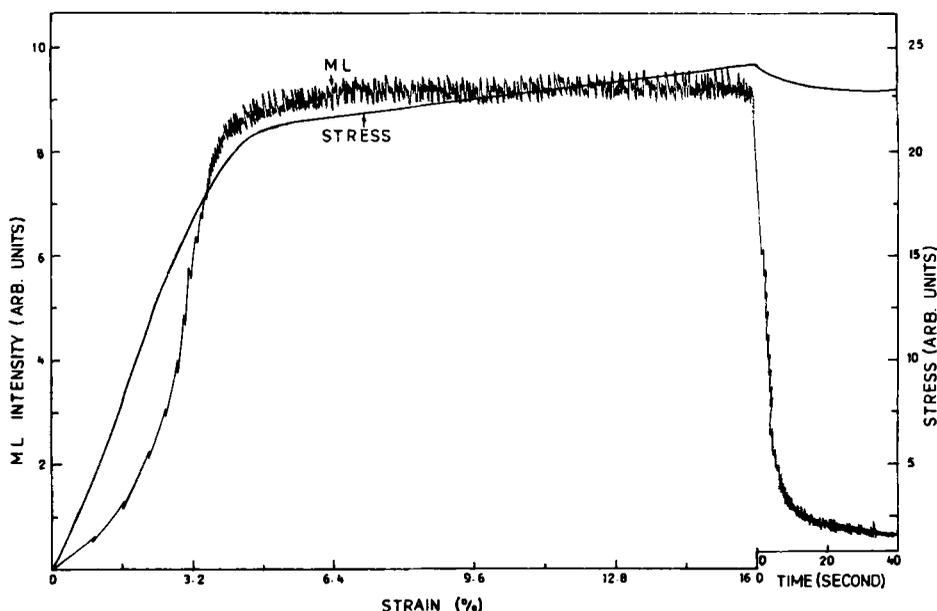
Figure 1. ML versus strain and stress versus strain curves of a γ-irradiated KCl crystals (dimension = $5 \times 5 \times 5 \, \mathrm{mm}^3$, $n_F \approx 10^{17} \mathrm{cm}^{-3}$, $\dot{\varepsilon} = 10^{-14} \mathrm{sec}^{-1}$).

calculated using Smakula formula. The ML versus strain and stress versus strain curves were determined at different strain rates using a table model Instron testing machine where the ML intensity was measured with the help of an RCA IP28 photomultiplier tube. The stress was measured by 907·2 kg capacity Lebow Load Cell (Model No. 3354–2 K), and the strain was measured using a linear variable differential transducer (LVDT) (Model No. 025 MMR, Schaevitz Engineering Company). The ML, thermoluminescence (TL) and after-glow spectra were recorded by using a Baush and Lomb 1/2 m grating monochromator and EMI 9558, photomultiplier tubes, following the technique described previously [31]. For the measurement of ML below room-temperature, one end of a spiral copper tubing immersed into liquid nitrogen was connected to a cylinder of dry nitrogen and the cooled gas coming out of the other end of the copper tubing cooled the crystal. By changing the rate of flow of nitrogen gas, the crystal could be cooled to different temperatures. The temperatures of the crystal was measured by a copper constanton thermocouple. The TL appears during heating of γ-irradiated crystals and AG appears when the crystals are removed from ^{60}Co source.

Figure 1 shows that during the deformation of a γ-irradiated KCl crystal at a strain rate of $10^{-4} \mathrm{s}^{-1}$, initially the ML intensity increases and then it attains a saturation value after a particular strain. When the deformation is stopped, it is seen that the ML intensity decays, and disappears beyond a particular time. The initial rise and attainment of saturation in the ML intensity are predicted by the mobile interstitial model as well as by the mobile electron model. Both the models show that initially the ML intensity should decay exponentially and later on it should decay slowly with a comparatively
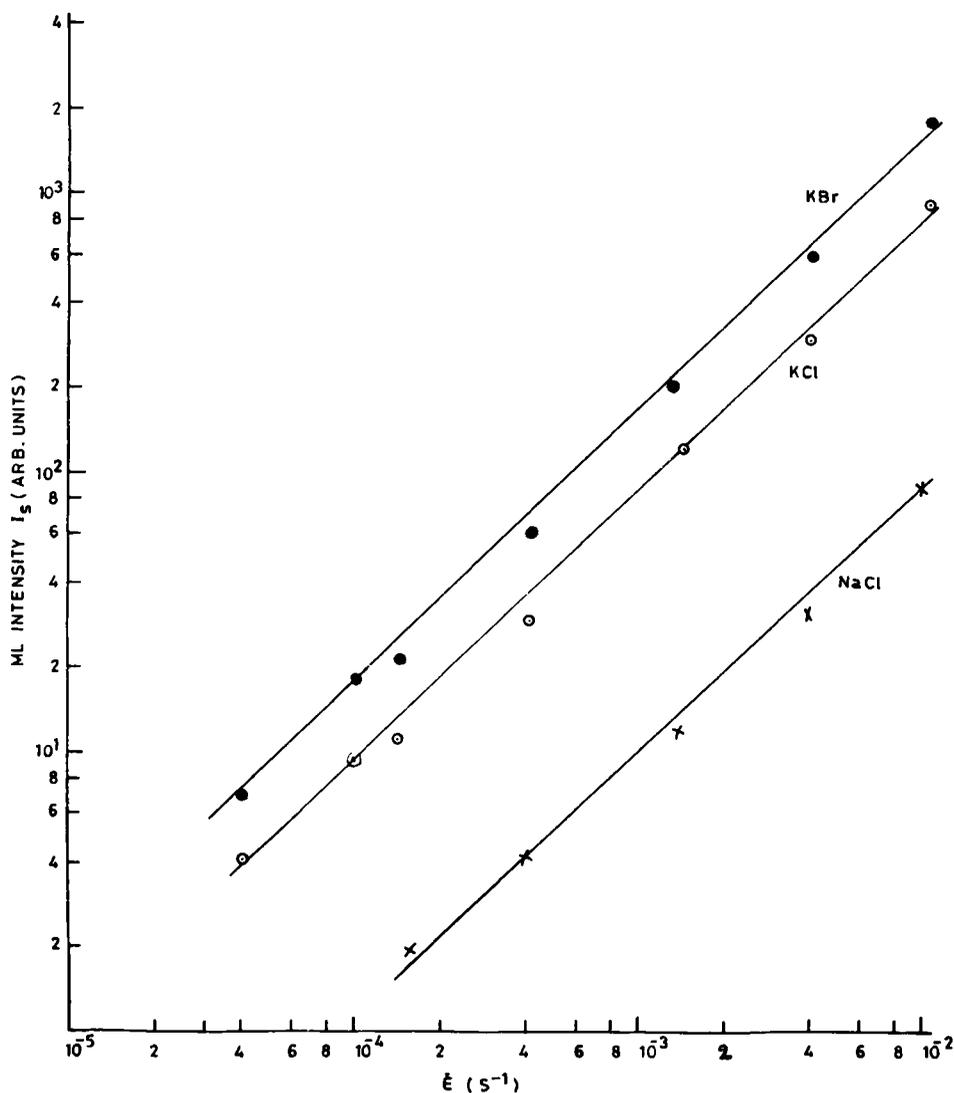
Figure 2. Plot of $\log(I_s)$ versus $\log(\dot{\varepsilon})$ (dimension $= 5 \times 5 \times 5\,\text{mm}^3$, $n_F \approx 10^{17}\,\text{cm}^{-3}$).

longer value of the decay time. Figure 1 shows that after stopping of the cross-head, initially the ML intensity decays with a fast rate and later on it decays with a slow rate.

Figure 2 shows the plot of $\log(I_s)$ versus $\log(\dot{\varepsilon})$ is a straight line where the slope is nearly equal to one. This result shows that the ML intensity is linear with the strain rate of the crystals. Such predictions are made by both the models.

Figure 3 shows the dependence of ML intensity on the density of F-centres. It is seen that I_s increases linearly with n_F. Such prediction is made by both the models. It should
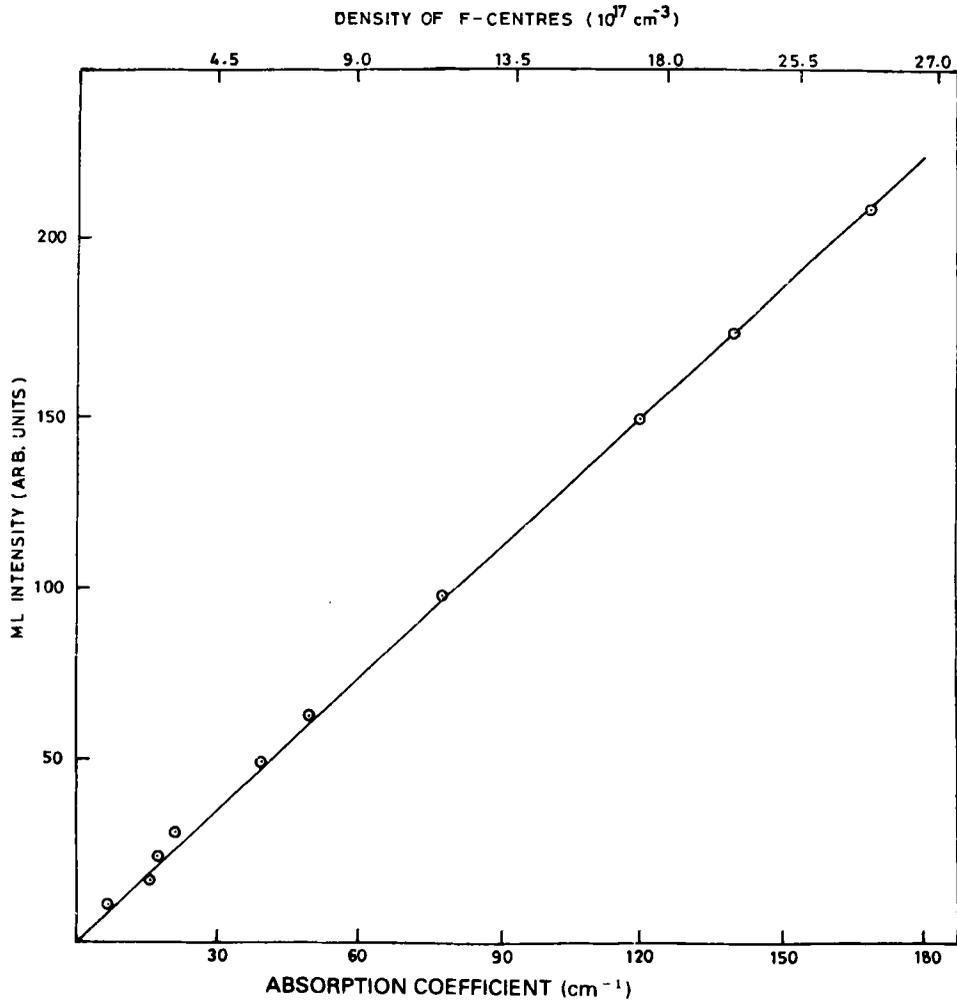
Figure 3. Dependence of ML intensity, I_s, on the absorption coefficients and density of F-centres in KCl crystals ($\dot{\varepsilon} = 10^{-4} \sec^{-1}$).

be noted that both N_i and n_F increase in a similar manner with the radiation doses given to the crystals.

Both the models predict that for a given density of F-centres, the ML intensity should increase linearly with volume of the crystals. As the applied stress increases the strain rate, both the models suggest that the ML intensity should increase with the applied stress.

Figure 4 shows the ML, after-glow (AG) and thermoluminescence (TL) spectra of KCl and KBr crystals. For KBr crystals, the peaks of both the AG and TL spectra lie nearly at 470 nm, however, the peak of their ML spectra is slightly shifted towards the shorter wavelength side and lie at 463 nm. For KCl crystals, the peaks of both the AG

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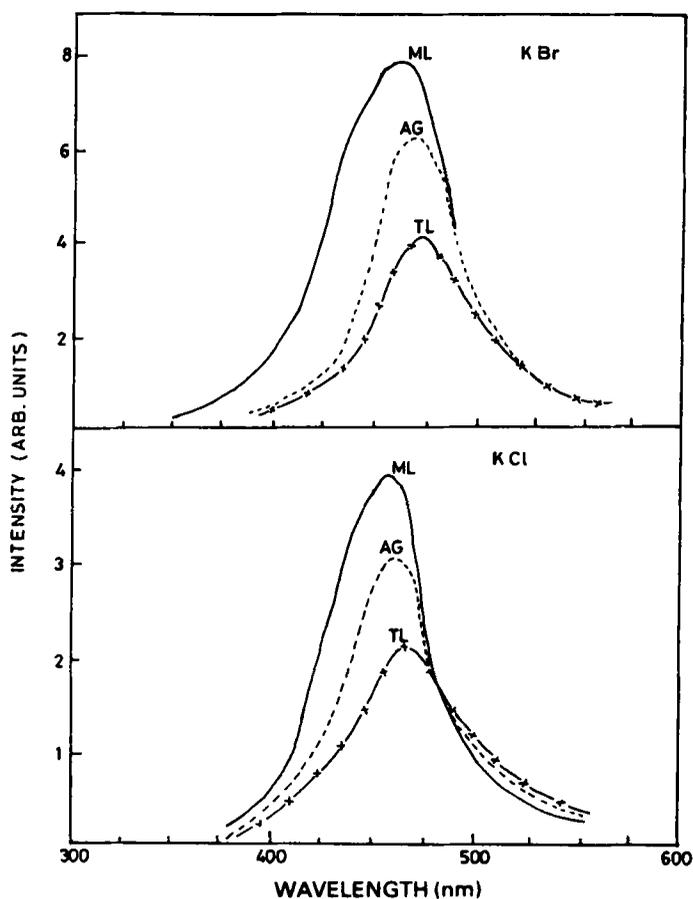
Figure 4. Mechanoluminescence, after-glow, and thermoluminescence spectra of γ-irradiated KBr and KCl crystals.

and TL spectra lie nearly at 460 nm, however, the peak of their ML spectra is slightly shifted towards the shorter wavelength and lie at 455 nm. As the spectra of KBr and KCl crystals shift with pressure at the rate of 0·07 and 0·025 nm/bar, respectively [3], it seems that the spectral shift in the ML spectra as compared to after-glow and thermoluminescence spectra may be due to the local pressure during deformation. It is well established that the light emission in after-glow and thermoluminescence phenomena of alkali halide crystals is mainly due to recombination processes involving liberated electrons from F-centres and holes in V_2-centres. Thus, the similarity of ML spectra with the after-glow and TL spectra suggests that the ML is essentially a recombination process between electrons and holes.

The nature of the ML, TL and AG emission spectra in γ-irradiated KCl and KBr crystals can be understood as follows. It has been proposed that the emission is due to the recombination of F-centre electrons with the V_2 hole centres. Thus, the energy corresponding to the peak of the ML spectra should correspond to the energy

Table 1. Theoretical and experimental values of λ_m for irradiated KCl and KBr alkali halide crystals.

Crystal	E_c(eV) [27, 32]	E_{v_2}(eV) [33]	Calculated value of λ_m (nm)	Experimental value of λ_m (nm) (figure 4)
KCl	8·1	5·40	458	455
KBr	7·3	4·69	476	463

difference between the bottom of the conduction band (E_c) and the energy level of V_2-centre (E_{V2}). The wavelength λ_m corresponding to the peak of ML spectra is calculated from the relation $\lambda_m = [ch/(E_c - E_{V2})]$, where c is the velocity of light and h is the Planck constant. Table 1 shows that the calculated value of the emission peak is approximately the same as that found from the experimental observations.

Some optical measurements may directly decide the reliability of the two models, for example, if the electron from F-centre recombines with the hole centre (mobile interstitial model) or the dislocation-captured electrons recombine with the hole centres (mobile electron model). So far as known to us, such optical measurements have not been made in the past. We were not able to perform such measurements because of certain limitations.

Since the probability, p_F increases with the temperature and the density n_F of the F-centres decreases with the temperature, the mobile electron model shows that initially the ML intensity should increase with temperature, attain an optimum value, then it should decrease and disappear beyond a particular temperature. Since the probability p_i (probability of sweeping of interstitials with dislocations) increases with temperature and the density of interstitials decreases with increasing temperature, the mobile interstitial model also indicates the occurrence of an optimum ML intensity at a particular temperature. When the value of activation energy is determined by plotting a curve between $\log(I_s)$ and $1000/T$, it is found to be 0·08, 0·072 and 0·09 eV for KCl, KBr and NaCl crystals, respectively (figure 5). This result shows that the activation process is involved in the occurrence of ML.

Although both the mobile interstitial and the mobile electron model are able to explain the dependence of ML intensity of coloured alkali halide crystals on several parameters, the mobile interstitial model fails to explain the following facts:

(i) Photons as well as electrons are emitted during the deformation of coloured alkali halide crystals, where they depend similarly on the deformation, strain rate and F-centre density of the crystals [11, 18]. On the basis of the fact involving dislocation electrons, the dislocation exo-electron emission can be understood in the following way. The recombination of the electrons carried out by dislocation with the deep traps in the crystal, may cause Auger ionization of other dislocation electrons to the conduction band bottom. The subsequent thermal ionization of electrons from the conduction band bottom into vacuum may give rise to the dislocation exo-electron emission. Thus, the mobile electron model is able to explain the simultaneous emission of photons and electrons during the plastic
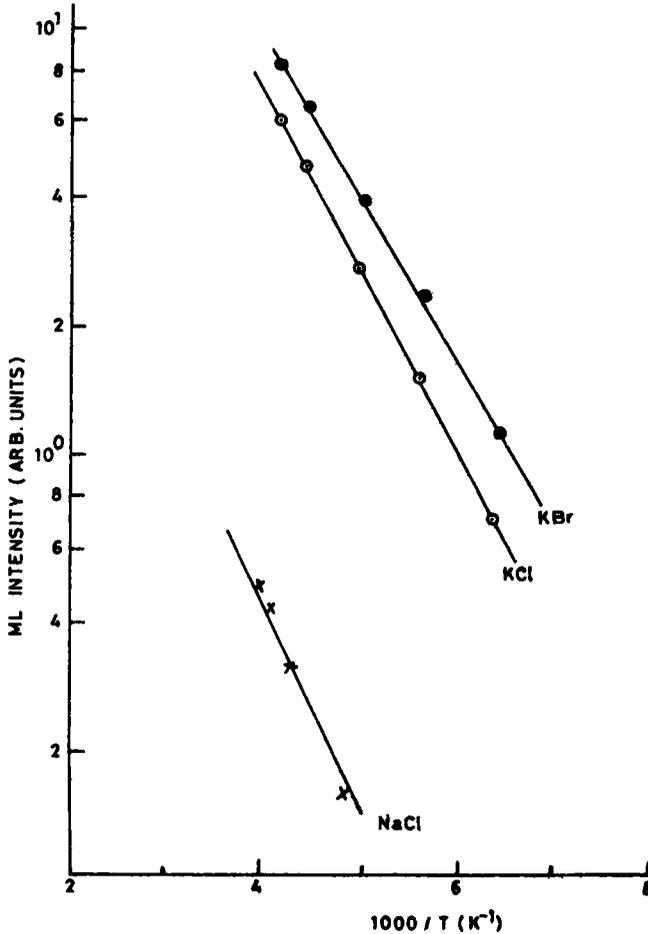
Figure 5. Plot of $\log(I_s)$ versus $1000/T$ for γ-irradiated KCl, KBr and NaCl crystals. $(n_F \approx 10^{17}\,cm^{-3}, \dot{\varepsilon} = 10^{-4}\,sec^{-1})$.

deformation of coloured alkali halide crystals. However, the mobile interstitial model is not able to explain the simultaneous emission of photons and electrons during the plastic deformation of coloured alkali halide crystals.

(ii) Molotskii and Shmurak [11] have reported that additively coloured KCl crystals exhibit weak ML, where the peak of the spectra lies around 2 eV. The ML emission can be schematically represented by the following equations

$$F + D \rightarrow e_d \tag{C}$$

$$L + e_d \rightarrow L^- + hv + D \tag{D}$$
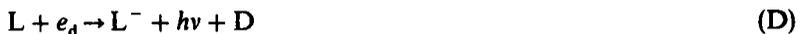
where L is the deep trap and L^- is the deep trap possessing captured electrons.

Since the additively coloured crystals do not possess holes, the mobile hole model is not able to explain the appearance of ML during the plastic deformation of

additively coloured alkali halide crystals. Thus, the ML emission during plastic deformation of additively coloured crystals supports the movement of electrons with dislocations and their subsequent recombination.

(iii) In X or γ-irradiated monovalent impurity doped alkali halide crystals, the holes are captured by the monovalent impurities which change from M^+ to M^{2+} [26]. If the mobile hole model of ML is applicable, then for a given density of F-centres, the ML intensity should decrease with increasing dopant concentration. In contrast, for a given density of F-centres, the intensity of ML in X or γ-irradiated alkali halide crystals increases with the increasing monovalent impurity concentration [26]. This can be understood with the help of mobile electron model in the following way.

$$Me^{2+} + e_d \rightarrow (Me^+)^* \rightarrow Me^+ + h + D$$
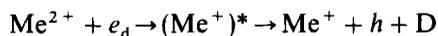
Conclusively, it may be said that the mobile electron model provides a dominating process for the ML excitation in coloured alkali halide crystals.

Acknowledgements

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