Bull. Mater. Sci., Vol. 27, No. 6, December 2004, pp. 505–509. © Indian Academy of Sciences.

Temperature dependence of pulse-induced mechanoluminescence excitation in coloured alkali halide crystals

NAMITA RAJPUT*, S TIWARI[†] and B P CHANDRA[†]

Department of Post Graduate Studies and Research in Physics and Electronics, Rani Durgawati University, Jabalpur 482 001, India

[†]Pt. Ravi Shanker Shukla University, Raipur 492 010, India

MS received 4 June 2004; revised 17 August 2004

Abstract. In practice, the relative efficiencies of different crystals are often determined under identical conditions of temperature and excitation. If the temperature of a crystal is increased or decreased with respect to room temperature, luminescence efficiency may get increased or decreased according to the composition of the crystal. When coloured crystals of NaCl, NaBr, KCl and KBr are excited by pulse-induced excitation at different temperatures, the mechanoluminescence (ML) intensity increases with temperature. The ML intensity of first peak, I_{ml}, second peak, I_{m2} and the total ML intensity, I_T, initially increase with temperature and then tend to attain an optimum value for a particular temperature of crystals. The ratio, I_{m2}/I_{ml}, is found to increase with increasing temperature of the crystals. The expression derived on the basis of rate equations, are able to explain the temperature dependence of ML intensity on several parameters.

Keywords. Mechanoluminescence; dislocations; pulse-induced excitation; alkali halides; radiative recombination.

1. Introduction

Mechanoluminescence (ML), the phenomenon of cold light emission induced during mechanical deformation of solids, links the mechanical, spectroscopic, electrical, structural and other properties of solids. A large number of organic and inorganic crystals and amorphous solids exhibit the ML phenomenon (Longchambon 1925; Walton 1977; Zink 1978; Chandra 1985). On the basis of the deformation in solids needed for producing ML, we can classify ML into three types, viz. fracto-induced ML, plastico-induced ML and elastico-induced ML.

It has been found that in the substances showing luminescence at room temperature, the luminescence is quenched at some higher temperature. On the other hand, many substances which are not luminescent at room temperature, show luminescence at low temperature. Therefore, studies on the temperature dependence of luminescence is very interesting, sometimes yielding information to understand the nature of the crystals and to determine the effective trap depth (Leverenz 1950; Curie 1963; Chandra *et al* 1983). However, comparison of temperature dependence of luminescence efficiency and decay rates gives information about the location of dissipative transition and permits the calculation of activation energies and frequency factors for these transition in certain cases. The present paper reports the effect of temperature on the ML produced by pulse-induced excitation of coloured alkali halide crystals of NaCl, NaBr, KCI, KBr and KI.

2. Experimental set-up for ML measurement

The technique similar to Bridgman method was used in the present investigation for the growth of pure alkali halide crystals. In this method, solid–liquid interface was achieved by variation of the temperature gradient by varying heater current. In this process the material was melted in a ceramic crucible and then cooled slowly through the melting point. Chemical of AR (analytical reagent) grade supplied by E. Merck company were used as starting materials. The firing was done using a tabular furnace supplied by M/s INDFUR, which controls the temperature within ± 10°C. The temperature of the furnace was measured by a chromel-alumel thermocouple. For growing single crystal, the material (in powder form) was melted in crucible and cooled very slowly through the melting point down to room temperature. Grown crystals were taken out of the crucible and cleaved to proper size.

Circuit diagram of the arrangement used for measuring ML activity is shown in figure 1. The ML was excited by pressure pulse generated by a pulse generator designed for this purpose. A basic monostable multivibrator circuit using IC555 is designed for the generation of pressure pulses of 50 μs duration. The switching time can be varied by adjusting the value of 50 K resistor connected at pin nos 6 and 7 of IC555. The output of 555 is connected to

*Author for correspondence

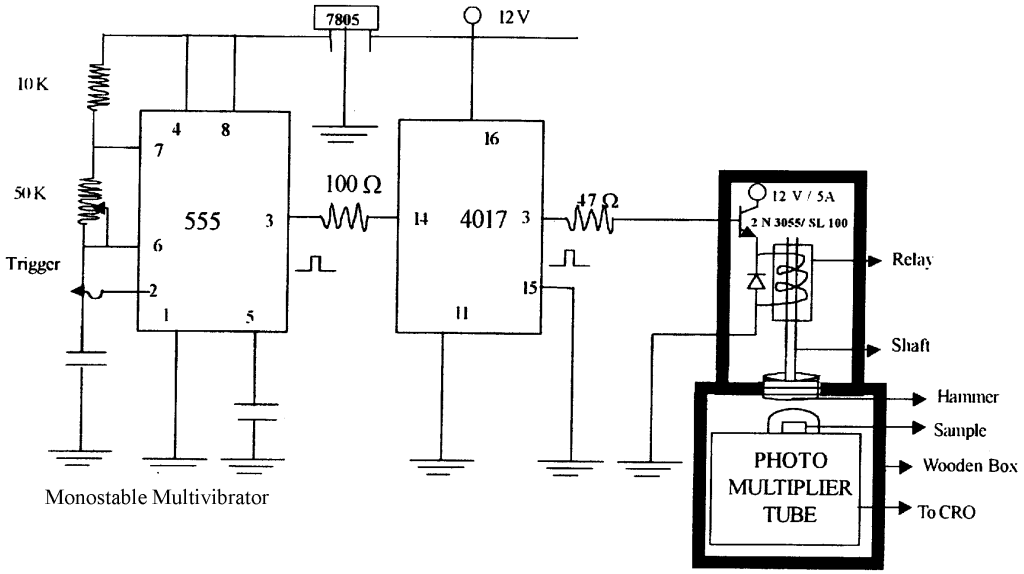

Figure 1. Circuit diagram of pulse-induced mechanoluminescence measuring instrument.

decade counter CD4017 and its output is connected to transistor SL100 which controls the relay and a high power electromagnet specially made for the proposed system is connected to the relay so that it impacts different strength induced ML in crystal. The output of the device is connected to hammer. When a signal trigger is applied to the input of the circuit device it produces electric pulse. This electric energy is converted into mechanical energy by the hammer connected at the output of the device.

For measuring the effect of temperature on ML, the crystals were placed onto a Lucite plate and heated by using two heating filaments (35 watt each) fixed near to it. By changing the voltage applied to the filament, the crystals could be heated at different temperatures. In the present study, the temperature range was from room temperature to 120°C. The ML was excited during the impact of a moving hammer onto the crystal (Chandra *et al* 1980a,b,c) and the luminescence was recorded by a RCA-931A photomultiplier tube (PMT) placed just below the lucite plate. The output of the PMT was fed to the dual beam oscilloscope having P7 phosphorescent screen capable of sustaining a trace in dark for more than a minute. The size of the crystals used for present investigation were $1 \times 1 \times 1$ mm^3, $2 \times 2 \times 2$ mm^3, $3 \times 3 \times 3$ mm^3, $4 \times 4 \times 4$ mm^3. At least four crystals were studied for each set of observations. The temperature of the crystal was measured by a calibrated chromel-alumel thermocouple.

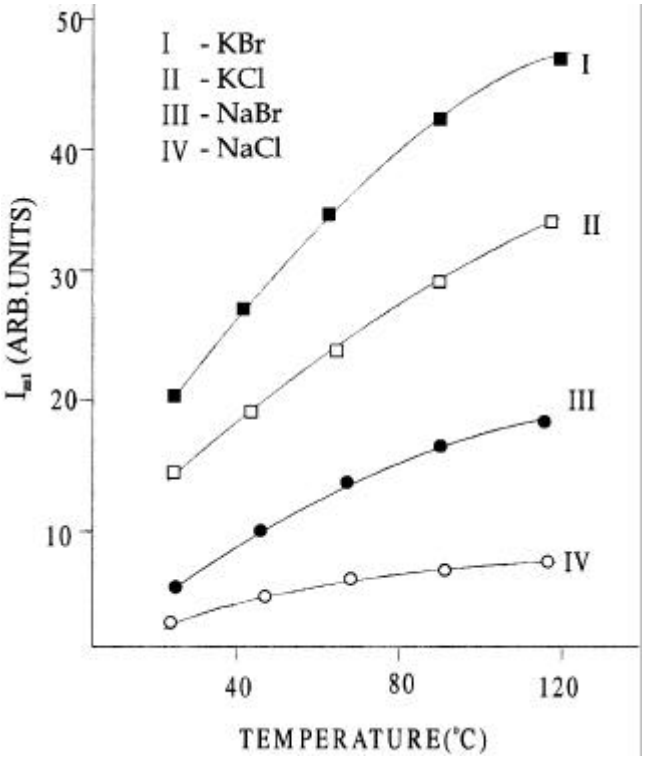

Figure 2. Dependence of the peak ML intensity, I_{m1}, on temperature of *g*-irradiated alkali halide crystals.

3. Results

During pulse-induced excitation of *g*-irradiated alkali halide crystals, two peaks are observed in the ML intensity versus time curves. The first peak lies in the deformation region and the second peak in the post deformation region. The ML in the deformation region is due to the recombination of dislocation trapped electrons with the holes in defect centres. The ML in the post deformation region is due to the transient thermostimulated luminescence from shallow traps which get populated due to the Auger process occurring during transfer of dislocation trapped electrons to deep traps. I_{m1}, I_{m2} are the intensities

corresponding to first and second peak, respectively in the ML intensity versus time curve and I_T is the total ML intensity, i.e. the integrated area below this curve.

Figures 2–4 show the dependence of I_{m1}, I_{m2} and I_T, respectively, on temperature of coloured NaCl, NaBr, KCl and KBr crystals. It is found that I_{m1}, I_{m2} and I_T initially increase with temperature and then attain an optimum value for a particular temperature of the crystals.

Figure 5 shows the plot of I_{m2}/I_{m1} with temperature for coloured alkali halide crystals. It is found that the ratio, I_{m2}/I_{m1}, increases with increasing temperature of the crystals.

Figures 6 and 7 show the dependence of I_{m1}, I_{m2} and I_T on temperature for coloured KI crystals. It is found that I_{m1}, I_{m2} and I_T decrease with increasing temperature of KI crystals.

4. Discussion

Consider a crystal having length, L, breadth, W and thickness, H. If the crystal is deformed along the plane parallel to its breadth side, then the rate of creation of new surfaces is given by $2\,Wv$, where v is the average velocity of crack propagation.

It is known that a large number of moving dislocations are generated near the tip of moving cracks. If B is the correlation factor between the rate of generation of moving dislocations and rate of generation of new surfaces, then the rate of generation of moving dislocations may be written as

$$G_d = 2\,BWv. \tag{1}$$

If r_F is radius of interaction between the moving dislocations and F-centre, l the mean free path of moving dislocations, n_F the density of F-centres and p_F the probability of capture of F-centre electrons by the moving dislocations, then the rate of generation of dislocation electrons may be expressed as (Chandra 1996)

$$g = 2\,l\,p_F\,r_F\,n_F\,BWv/b'\,[1 - \exp(-b't)], \tag{2}$$

here $b' = 1/t_i$ and t_i the pinning time of moving dislocations.

On the basis of (2) we shall discuss the characteristics of ML in coloured alkali halide crystals.

4.1 *Kinetics of the transient ML*

For $b' t < 1$, (2) may be written as

$$g = 2\,l\,p_F\,r_F\,n_F\,BWvt. \tag{3}$$

The electrons captured by moving dislocations, move with them and they encounter with the defect centres like hole centres, deep traps, stationary dislocations and other

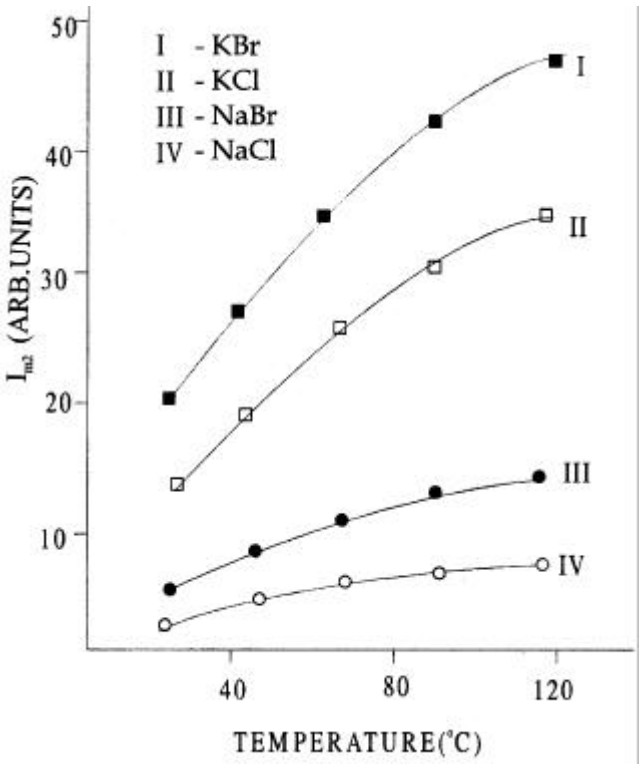

Figure 3. Dependence of the peak ML intensity, I_{m2}, on temperature of g-irradiated alkali halide crystals.

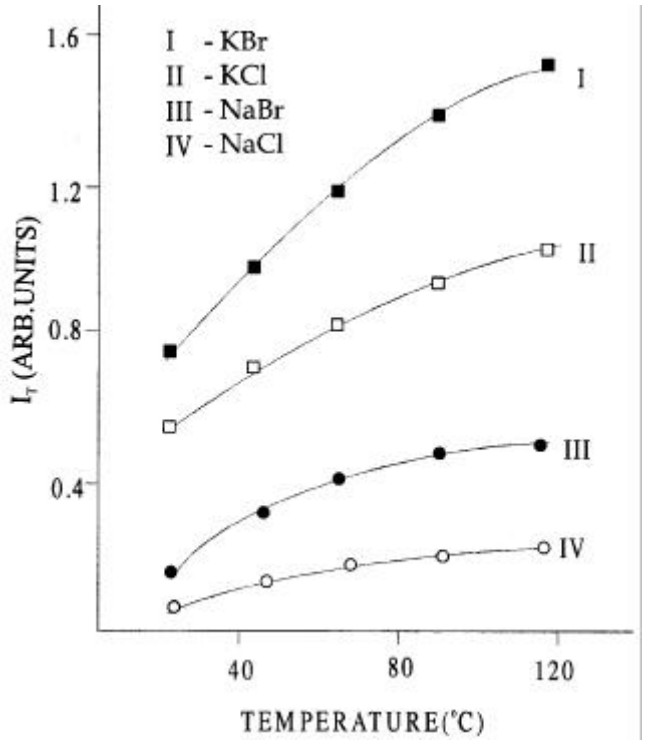

Figure 4. Dependence of the total ML intensity, I_T, on temperature of g-irradiated alkali halide crystals.

compatible traps, they may be captured by these defect centres. If s_1, s_2, s_3 and s_4 are the cross-sections, N_1, N_2, N_3 and N_4 are the densities of the hole centres, deep traps, stationary dislocations states, and other compatible traps, respectively and h is the probability of radiative recombination of moving dislocation electrons with hole centres, then the time dependence of the transient ML intensity may be expressed as

$$I_r = 2h\, s_1 N_1\, l\, p_F\, r_F\, n_F\, BWvt/ (s_1 N_1 + s_2 N_2 + s_3 N_3 + s_4 N_4). \quad (4)$$

The velocity of crack propagation may be given by

$$v = H/t_{ml}. \quad (5)$$

4.2 *Estimation of I_{m1}*

From (4) and (5), the value of first peak ML intensity, I_{ml} at $t = t_m$ may be given by

$$I_{ml} = h\, s_1 N_1\, l\, p_F\, r_F\, n_F\, B\, A/ (s_1 N_1 + s_2 N_2 + s_3 N_3 + s_4 N_4), \quad (6)$$

where $A = 2WH$ is the area of the newly created surfaces of the crystal.

4.3 *Estimation of I_{m2}*

The delayed ML is actually due to the recombination of electrons moving in the stationary dislocation band with the hole centres. If $g_s = 1/t_s$ and t_s is the life time of electrons in the stationary dislocation band, the value of second peak ML intensity, I_{m2}, may be given by

$$I_{m2} = h\, s_3 N_3\, l\, p_F\, r_F\, n_F\, B\, g_s\, A/ b\ell\, (s_1 N_1 + s_2 N_2 + s_3 N_3 + s_4 N_4). \quad (7)$$

It is evident from (6) and (7) that both I_{ml} and I_{m2} depend directly on h, p_F and n_F. At low temperature, h and n_F remain nearly constant and therefore, I_{ml} and I_{m2} should increase with increasing temperature of the crystals. On the other hand, at higher temperature, n_F, decreases significantly due to the thermal bleaching of colour centres. Thus, in the higher temperature range, I_{ml} and I_{m2} should decrease with increasing temperature of the crystals. Thus, both I_{ml} and I_{m2} should be optimum for a particular temperature of the crystals.

4.4 *Estimation of total ML intensity, I_T*

The total ML intensity, I_T, i.e. the integrated area below the ML intensity versus time curve, may be given by

$$I_T = \int_0^\infty I\, dt,$$

$$I_T = h\, l\, p_F\, r_F\, n_F\, B\, (s_1 N_1 + s_3 N_3)\, A/ b\ell\, (s_1 N_1 + s_2 N_2 + s_3 N_3 + s_4 N_4). \quad (8)$$

The total ML intensity, I_T, depends directly on h, p_F and n_F and it depends inversely on the rate constant for the pinning of dislocation i.e. $b\ell$. Since p_F increases with increasing temperature of the crystals and h, n_F and $1/b\ell$

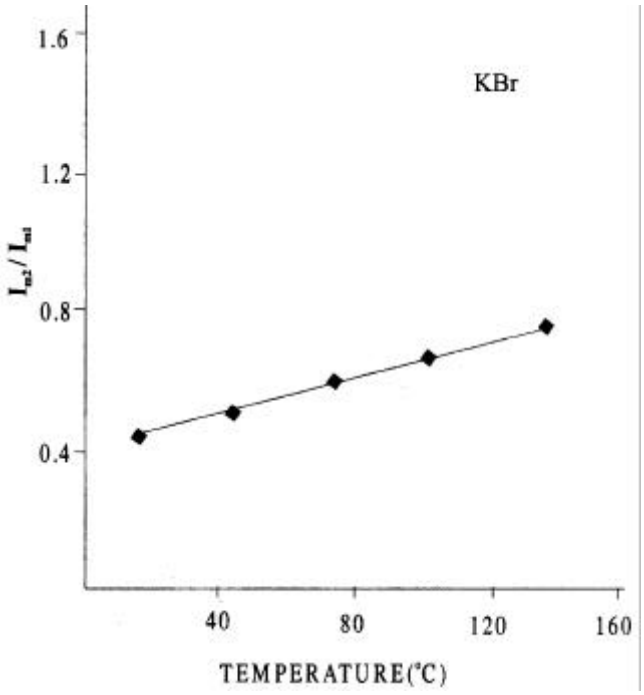

Figure 5. Dependence of I_{m2}/I_{m1} on temperature for *g*-irradiated alkali halide crystals.

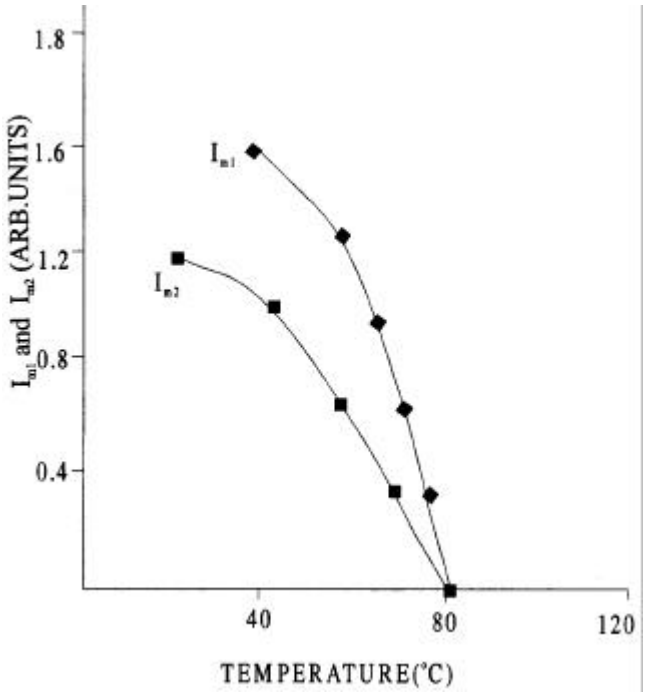

Figure 6. Dependence of the peak ML intensity, I_{m1} and I_{m2}, on temperature of irradiated KI crystals.

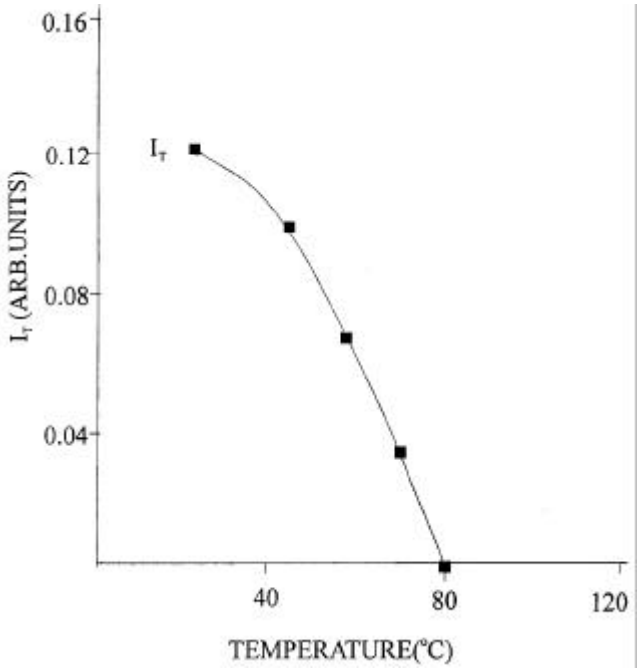

Figure 7. Dependence of the total ML intensity, I_T, on temperature of irradiated KI crystals.

decrease with increasing temperature of the crystals, the total ML intensity, I_T, should also be optimum for a particular temperature of the crystals. It is to be noted that whereas I_{m1} and I_{m2} depend only on h, p_F and n_F, I_T depends on h, p_F, n_F and $1/b'$. Thus in higher temperature range, I_T should decrease with a faster rate as compared to the decrease of I_{m1} and I_{m2} with increasing temperature of the crystals.

4.5 *Ratio of* I_{m1} and I_{m2}

From (6) and (7), we get

$$I_{m2}/I_{m1} = s_3 N_3 g_s / s_1 N_1 b'. \quad (9)$$

It is evident from (9) that the ratio of I_{m2}/I_{m1} depends on the ratio of N_3 and N_1. Since there is no significant change in N_3, N_1 decreases with increasing temperature of the crystals, it seems that the ratio, I_{m2}/I_{m1}, should increase with increasing temperature of the crystals.

5. Conclusions

The main conclusions of the present investigation are as follows:

(I) The peak ML intensities, I_{m1}, I_{m2} and the total ML intensity, I_T, of coloured alkali halide crystals during pulse-induced deformation increase with increasing temperature, and attain an optimum value for a particular temperature of the crystal.

(II) The ratio, I_{m2}/I_{m1}, increases with increasing temperature of the coloured crystals of NaCl, NaBr, KCl and KBr during their pulse-induced deformation. This is due to the fact that N_1 i.e. the density of hole centres, decreases with increasing temperature of the crystals.

(III) It seems that for irradiated KI crystals, the temperature at which I_{m1}, I_{m2} and I_T should attain an optimum value lies below the room temperature. Therefore, a decrease in I_{m1}, I_{m2} and I_T is observed with increasing temperature of KI crystals. When the ML of irradiated KI crystals is measured at low temperature, the increase of I_{m1}, I_{m2} and I_T is observed with increasing temperature of the crystals.

(IV) The effect of temperature on pulse-induced ML of coloured alkali halide crystals may be due to the fact that at lower temperature, the dislocation capture probability of F-centre electrons i.e. p_F, increases with increasing temperature whereas at higher temperature the F-centre density, n_F, decreases due to thermal bleaching.

References

Chandra B P 1985 *Nuclear Tracks* **10** 825
Chandra B P 1996 *Radiat. Eff. & Def. Solids* **138** 119
Chandra B P and Zink J I 1980a *Phys. Rev.* **B21** 816
Chandra B P and Zink J I 1980b *J. Chem. Phys.* **73** 5933
Chandra B P and Zink J I 1980c *Inorg. Chem.* **19** 3098
Chandra B P, Elyas M and Majumdar B 1983 *Solid State Commun.* **42** 753
Curie D 1963 *Luminescence in crystals* (NY: John Wiley & Sons)
Leverenz H W 1950 *An introduction to luminescence of solids* (NY: John Wiley & Sons Inc.)
Longchambon H 1925 *Bull. Soc. Fr. Min.* **40** 130
Walton A J 1977 *Adv. Phys.* **26** 887
Zink J I 1978 *Acc. Chem. Res.* **11** 289