

## A search for mechanoluminophors capable of pressure-induced thermal population of excited states

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**Abstract.** During the process of deforming a crystal, a high pressure is developed near the tip of mobile cracks, which may in turn produce a new ground state by thermal electron transfer. Upon sudden release of pressure, the electron can either relax to one atmosphere ground state or remain in the excited state potential well long enough to relax to one atmosphere and radiatively transfer back to the ground state. For analysing the pressure induced thermal population of the excited state, the mechanoluminescence (ML) and high pressure photoluminescence (PL) of several organic and inorganic crystals were measured. The study indicated that usual pressure coefficient of energy shift of the order of  $50\text{--}100\text{ cm}^{-1}/\text{kbar}$  and the stress at the crack-tip of the order of  $5\text{--}10\text{ kbar}$ , are not sufficient to cause the thermal population of the excited state. If by any means the product of pressure coefficient and stress at the mobile crack-tip can be increased by 50 to 100 times, then the thermal population of the excited states may take place. Using the pressure coefficient of energy shift and the difference in ML and PL spectra, and using independently the change in relative intensities of the vibronic peaks, the pressure at the emitting mechanoluminescent crystal sites is evaluated and it is found to be of the order of several kbar which varies from crystal to crystal.

**Keywords.** Mechanoluminescence; triboluminescence; photoluminescence; high pressure phenomena.

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### 1. Introduction

Mechanoluminescence (ML) is emission that occurs as a result of mechanical stress excitation of solids. During fracturing of a crystal, an uneven pressure is being applied to the system. Although this pressure is certainly not hydrostatic, luminescence measurements of solids at high hydrostatic pressures may provide useful information on the behaviour of the system under pressure and in turn may help in understanding the excitation process of ML.

A ML mechanism involving population of the excited state due to the formation of a new ground state under pressure may be possible. This mechanism can be viewed in two steps: First, thermal electron transfer may produce a new ground state at high pressure and secondly, the sudden release of stress during failure of the crystal may result in luminescence as the electron returns to the 1 atmosphere ground state configuration. If the mechanism related to the thermal population of a pressure induced ground state is operative, the relative displacement of the ground and excited

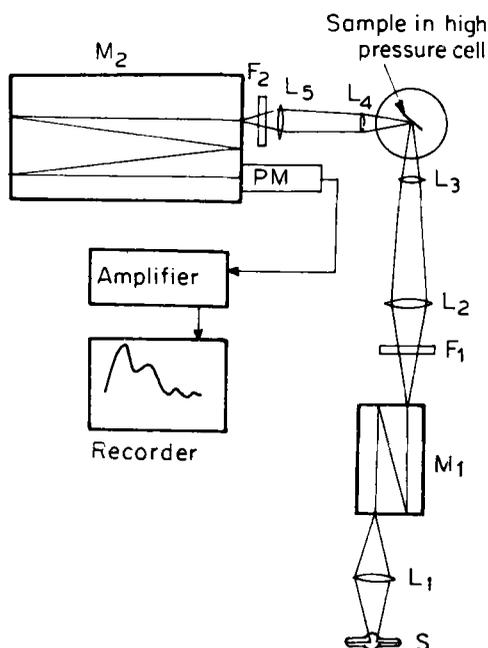
electronic states under pressure should be larger in mechanoluminescent crystals than that in non-mechanoluminescent crystals.

What is the pressure at the emitting mechanoluminescent crystal sites when ML occurs? In general, internal pressure of the order of several kilobars may be attained before fracture of the crystal relieves the stress (Knauss 1965). Local pressure at the tips of moving cracks may be significantly higher. The effects of pressure on PL spectra can be accurately measured under hydrostatic condition (Drickamer and Frank 1973). Two observations from the hydrostatic pressure experiments can, in principle, be used to determine the pressure at mechanoluminescent site – the shift of the wavelength of the emission maximum with pressure and the changes in the intensities of emission peaks. If the variation in relative vibronic intensities is caused by a change in the Frank–Condon factors, when the emitting molecule is under stress, examination of the PL as a function of pressure should reveal a spectrum at same applied load similar to the ML. In this way, the pressure at which the ML and PL are identical will help to identify what magnitude of force is operating during the ML process (Zink *et al* 1980; Zink 1981).

The purpose of this portion of the research programme is to investigate the behaviour of some organic crystals and inorganic phosphors under high pressure. Trends in the shift of the emission energy maximum with pressure are examined in view of the presence or absence of ML in the crystal in order to determine if the thermal population of a pressure induced ground state is a significant contribution to ML. Furthermore, from the comparison of ML and PL spectra and by using the pressure coefficient of energy shift of the crystals, the evaluation of stress near the tip of a mobile crack is made.

## 2. Experimental

The high pressure PL spectra were measured using a cell similar to the one suggested by Drickamer type I high pressure optical cell (Chandra 1982). The cell has three sodium chloride windows. Each window, which has an outer diameter of 6.3 mm, is gradually reduced to around 1 mm for the inner diameter. The phosphor or crystalline powder was packed into the cylindrical chamber within the cell as follows. A thin tungsten piston was placed adjacent to the large piston followed by a 3 mm diameter disc of sodium chloride. These two layers elevated the sample so that its placement was in front of the windows. A small amount of phosphor or crystalline powder was ground in an agate mortar and pestle along with an equal amount of sodium chloride. Due to the mixing of the phosphor or crystalline powder in this manner, the applied pressure becomes more hydrostatic. The phosphor (or crystalline powder) – NaCl mixture was placed lightly into a half moon shaped piece of salt about 1.5 mm thick. The other half of the sample chamber was filled with a solid half disc of NaCl of the same thickness. It was necessary for the packing to be done in this manner due to the tendency of solids to absorb and emit at their surface. The displacement of the cell by trial and error helps in proper alignment of the luminescence emission with the exit window. Another 3 mm diameter salt disc was placed on top of the packed sample followed by a thicker tungsten piston. The sample was then closed off by the large piston. Filtered ultraviolet excitation light from 100 W Hg lamp was focussed by a lens through one of the windows. Emission from the sample was focussed by a



**Figure 1.** Schematic of the device used for exciting and recording high pressure PL (S-light source,  $M_1$  and  $M_2$  monochromators,  $L_1, L_2, L_3, L_4$  and  $L_5$  – lenses,  $F_1$  and  $F_2$  – filters, and PM-photomultiplier tube).

lens and monitored at right angles to the excitation. Pressure was applied to the sample by means of hydraulic press which pushed the outer piston. These pistons in turn transferred the force to the small tungsten pistons and finally to the sample. The pressure was measured by a strain gauge connected to a load cell in the hydraulic press. The gauge was calibrated by ruby emission to read 50 strain units for each 3 kbar of pressure. After each increase in pressure it was necessary for the pressure to equilibrate throughout the system. Emission signals passed through a chopper which was coupled to a lock-in amplifier. The emission then entered a Jarrah-Ash monochromator which was scanned over the peak maximum. The signal was detected by an IP 28 photomultiplier tube and was recorded on a strip chart recorder. The experimental arrangement used for recording high pressure PL is shown in figure 1. The spectra were recorded using the procedure reported previously (Chandra 1982).

The  $ZnS:Cu, Cl$ ,  $ZnS:Ag, Cl$ ,  $(Zn, Cd)S:Ag, Cl$ ,  $ZnS:Au, Cl$  and  $ZnS:Mn$  phosphors were prepared in nitrogen atmosphere by firing at  $1100^\circ C$  for one hour. The crystals of tetrahedral Mn(II) complexes, N-acetylanthranilic acid, phenanthrene, uranyl nitrate hexahydrate and  $Cs_2[Pt(CN)_4] \cdot H_2O$  were obtained following the technique reported in our earlier investigations (Chandra 1981, 1982, 1983; Chandra *et al* 1982, 1987; Goodgame and Cotton 1961; Cotton *et al* 1962). The crystals of anthracene were grown by Bridgman technique and the crystals of naphthalene were obtained by vacuum sublimation technique. Donated crystals of 9-anthrylethanol were used.

### 3. Results

Figure 2 shows that the ML spectra of ZnS:Cu, Cl, ZnS:Ag, Cl, ZnS:Au, Cl and (Zn, Cd)S:Ag, Cl phosphors shift towards shorter wavelength side as compared to the PL spectra. However, the ML spectra of ZnS:Mn phosphor shift towards longer wavelength side as compared to its PL spectra. It is seen from figure 3 that the ML spectra of  $(\text{Ph}_3\text{PO})_2\text{MnBr}_2$  and  $(\text{Et}_4\text{N})_2\text{MnBr}_4$  crystals are shifted towards higher wavelength side as compared to their PL spectra. The ML spectra of non-photoluminescent  $(\text{Ph}_3\text{PO})_2\text{MnCl}_2$  crystals have peak at 515 nm. The ML of tetrahedral Mn(II) complexes has been found also to contain nitrogen emission which is not shown in the figure. Figure 4 shows the ML and PL spectra of N-acetylanthranilic acid, 9-anthrylethanol and phenanthrene crystals. It is seen from figure 4 that the ML spectra of N-acetylanthranilic acid crystals closely resemble their PL spectra with slight shift towards higher wavelength side. The PL emission of 9-anthrylethanol crystals have peak at 430, 450 and 475 nm, the relative intensities of their peaks are 2.6:2.2:1.0 (figure 4). The ML spectra of these crystals have peaks at 433, 453 and 478 nm, the relative intensities of these peaks are 2.4:2.0:1.0. The PL emission of phenanthrene crystals has three bands at 410, 430 and 460 nm; let us refer them 1, 2 and 3 bands (figure 4) respectively. In the case of ML, these bands are slightly shifted towards higher wavelength side. Relative intensities of these bands are 6.7:4.4:1.0 in

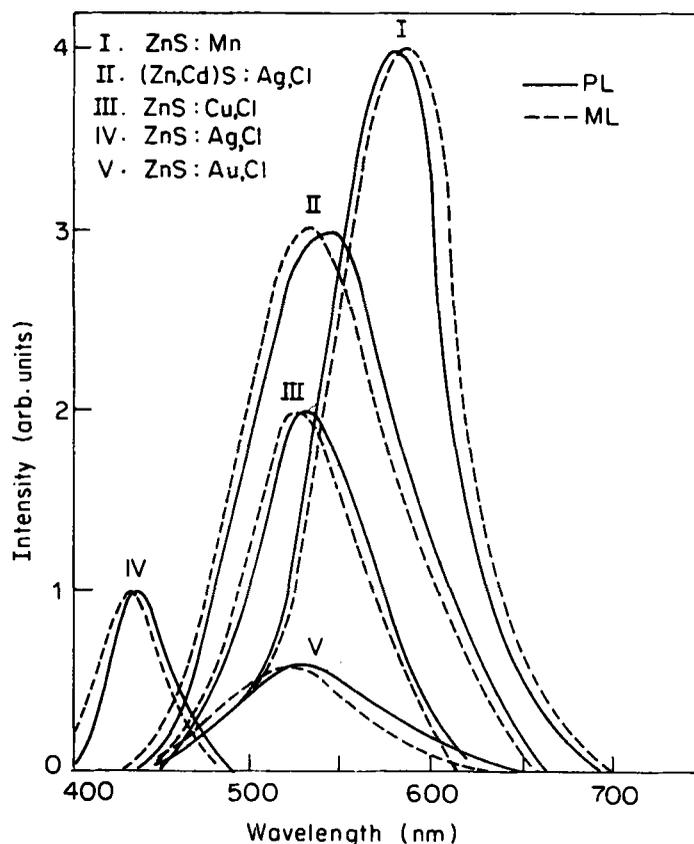


Figure 2. ML and PL spectra of ZnS phosphors.

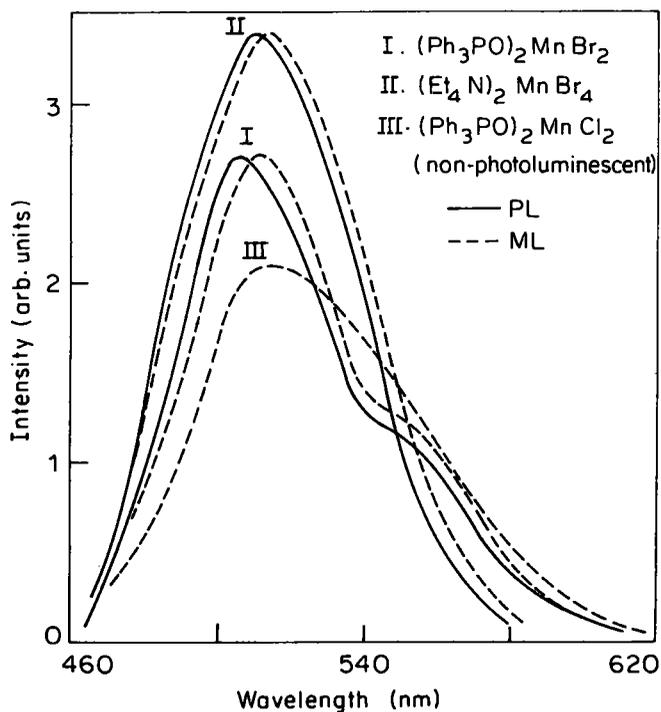


Figure 3. ML and PL spectra of tetrahedral Mn complexes.

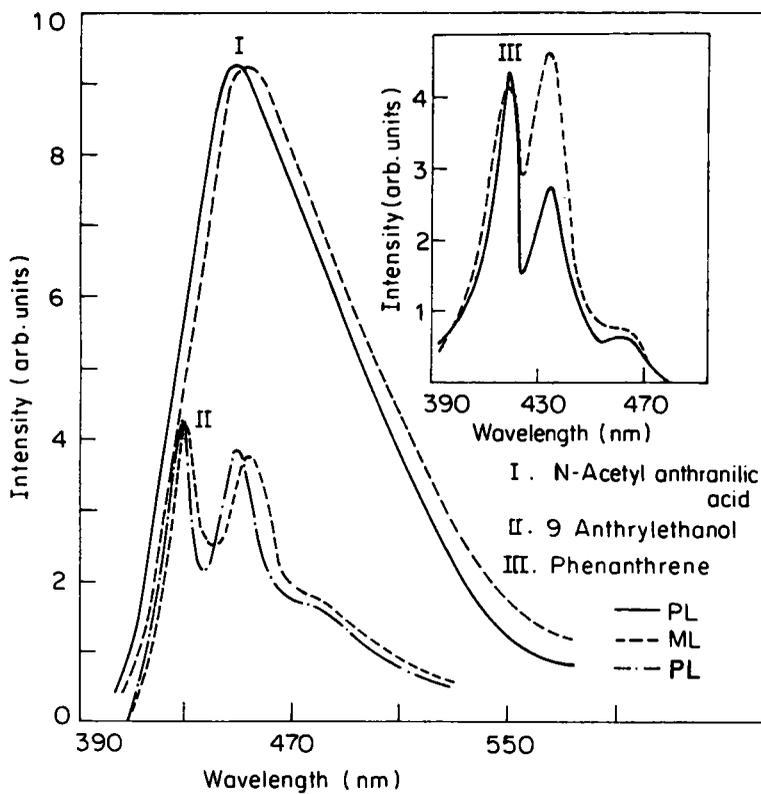


Figure 4. ML and PL spectra of N-acetyl anthranilic acid, 9-anthrylethanol and phenanthrene crystals.

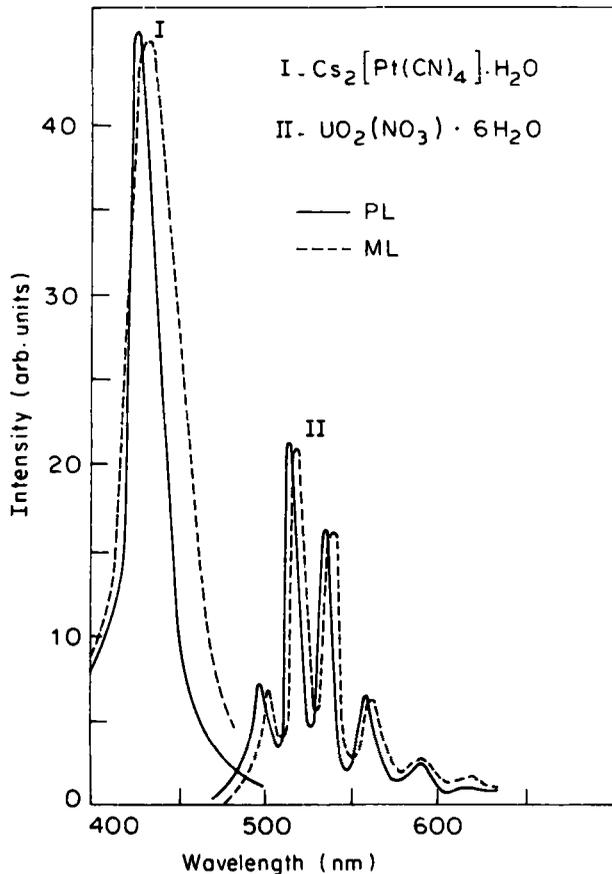


Figure 5. ML and PL spectra of  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  crystals.

the PL spectrum and 5.5:6.0:1 in the ML spectrum. Figure 5 shows the ML and PL spectra of  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  crystals. It is seen that the ML spectra of  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  shift towards higher wavelength values as compared to their PL spectra. The PL spectra of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  crystals have five main peaks at 487, 511, 535, 560 and 588 nm. There are also two more vibronic peaks at 472 and 620 nm. The ML spectra of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  crystals have all the similar peaks, but slightly shifted towards longer wavelengths side as compared to their PL spectra. The intensity of vibronic peaks is different and maximum for 512 nm.

The effect of hydrostatic pressure on the emission energy was investigated by measuring high pressure PL. Figure 6 shows that energy,  $E_{\text{max}}$  of ZnS:Cu, Cl, ZnS:Ag, Cl, ZnS:Au, Cl and (Zn, Cd):S:Ag, Cl phosphors increases with increasing pressure on the phosphors. The pressure coefficients for the increase in  $E_{\text{max}}$  are found to be 38, 33, 36 and 49  $\text{cm}^{-1}/\text{kbar}$  for ZnS:Cu, Cl, ZnS:Ag, Cl, ZnS:Au, Cl and (Zn, Cd):S:Ag, Cl phosphors respectively. The  $E_{\text{max}}$  of ZnS:Mn phosphor decreases with the increasing pressure on the phosphor and the pressure coefficient for the decrease in  $E_{\text{max}}$  is found to be  $-33 \text{ cm}^{-1}/\text{kbar}$ . The effect of pressure on  $E_{\text{max}}$  of the PL on N-acetylanthranilic acid, 9-anthrylethanol,  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  and  $\text{Mn}(\text{Ph}_3\text{PO})_2\text{Br}_2$  crystals are shown in figure 7. It is seen from figure 7 that the energy corresponding to the peak of PL

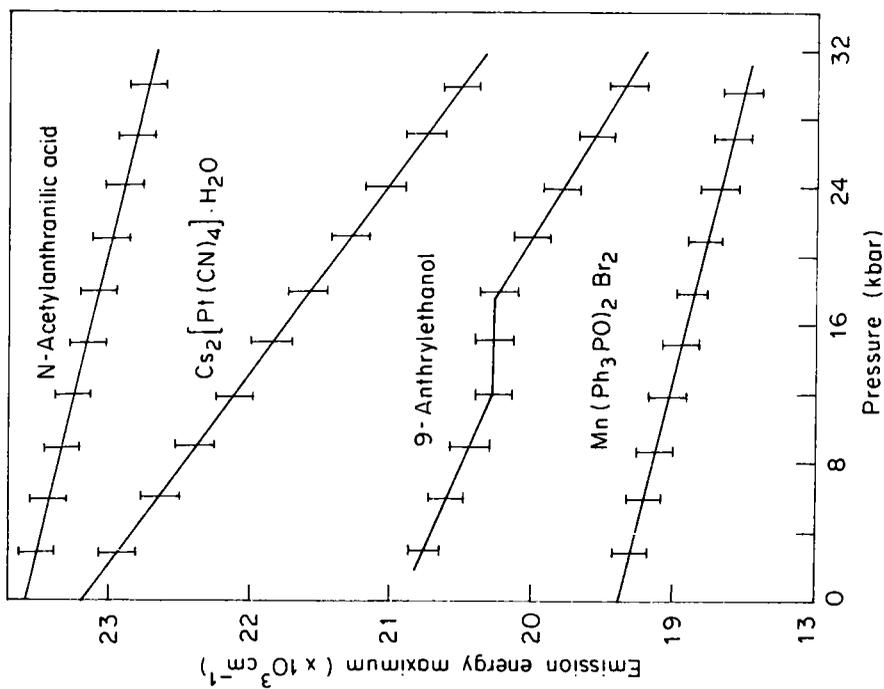


Figure 7. Pressure dependence of  $E_{\text{max}}$  of 9-anthrylethanol,  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$ , N-acetyl anthranilic acid and  $\text{Mn}(\text{Ph}_3\text{PO})_2 \text{Br}_2$  crystals.

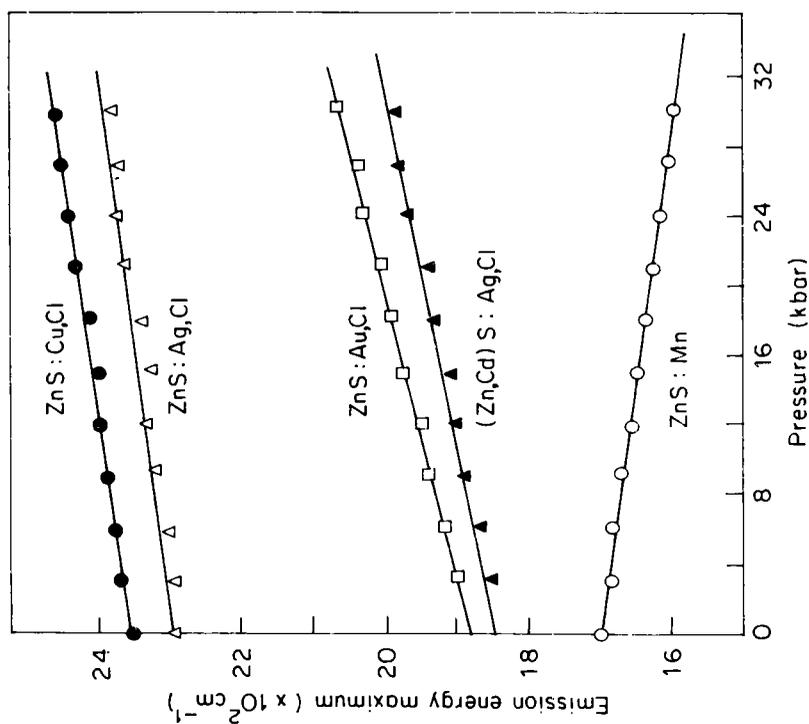


Figure 6. Pressure dependence of  $E_{\text{max}}$  of phosphors.

spectra of N-acetylanthranilic acid crystals decreases with the applied pressure and the pressure coefficient for the decrease in  $E_{\max}$  is found to be  $63.1 \text{ cm}^{-1}/\text{kbar}$ . Figure 7 shows that for 9-anthrylethanol the  $E_{\max}$  versus pressure curve has 3 different regions. Region I from 2 kbar to about 12 kbar shows a linear decrease in the energy of the  $E_{\max}$  and the pressure coefficient is  $-54 \text{ cm}^{-1}/\text{kbar}$ . Region II between 12 and 18 kbar does not indicate any measurable change in emission energy. Region III (18 to 30 kbar) indicates a linear decrease in emission energy and the pressure coefficient is  $-74 \text{ cm}^{-1}/\text{kbar}$ . In the case of  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  the  $E_{\max}$  of PL decreases with the applied pressure (figure 7). The pressure coefficient for the decrease in energy is highest and it is of the order of  $-92 \text{ cm}^{-1}/\text{kbar}$ . Figure 7 also shows the  $E_{\max}$  of the PL of  $\text{Mn}(\text{Ph}_3\text{PO})_2\text{Br}_2$  decrease with the applied pressure. The pressure coefficient is found to be  $-30 \text{ cm}^{-1}/\text{kbar}$ . For other Mn(II) complexes  $E_{\max}$  is also found to decrease with the applied pressure. The pressure coefficients are found to be  $-41$  and  $-28$  for  $(\text{MePh}_3\text{P})_2\text{MnCl}_4$  and  $(\text{Et}_4\text{N})_2\text{MnBr}_4$  crystals respectively. The pressure dependence of  $E_{\max}$  of PL for the three bands of phenanthrene is shown in figure 8. Band 3 indicates a  $-46 \text{ cm}^{-1}/\text{kbar}$  linear decrease in the energy of the emission maximum with pressure. The pressure dependence of band 1 is nearly  $-56 \text{ cm}^{-1}/\text{kbar}$  and that of band 2 is nearly  $-23 \text{ cm}^{-1}/\text{kbar}$ . The pressure dependence of bands 1 and 2 is distorted. This distortion may be due to the eventual convergence of the two bands at 42 kbar. Figure 9 shows the effect of pressure on the energies corresponding to the PL peaks at 487, 512, 535 and 560 nm of  $\text{UO}_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}$  crystals. The pressure coefficients for the decrease in energy are 11.2, 5.3, 4.3 and  $3.7 \text{ cm}^{-1}/\text{kbar}$  for the PL peaks at 487, 512, 535 and 560 nm, respectively.

For determining the pressure shift of emission energy of the non-mechanoluminescent substances, the high pressure PL was studied for  $(\text{Bu}_4\text{N})_2\text{MnI}_4$ ,  $(\text{PyN})_2 \cdot \text{MnCl}_4$ , anthracene and naphthalene crystals. The  $(\text{Bu}_4\text{N})_2\text{MnI}_4$  and  $(\text{PyN})_2 \cdot \text{MnCl}_4$  have broad PL peaks at 525 and 520 nm respectively and pressure coefficient of the

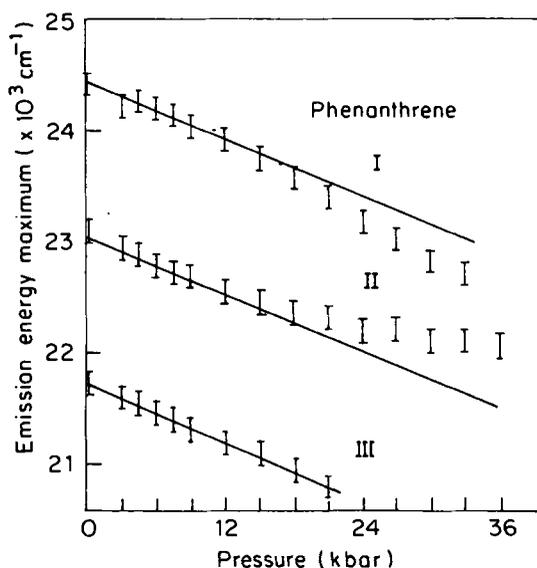


Figure 8. Pressure dependence of  $E_{\max}$  of phenanthrene crystals. (Curves I, II and III correspond to PL peaks at 410, 430 and 460 nm respectively).

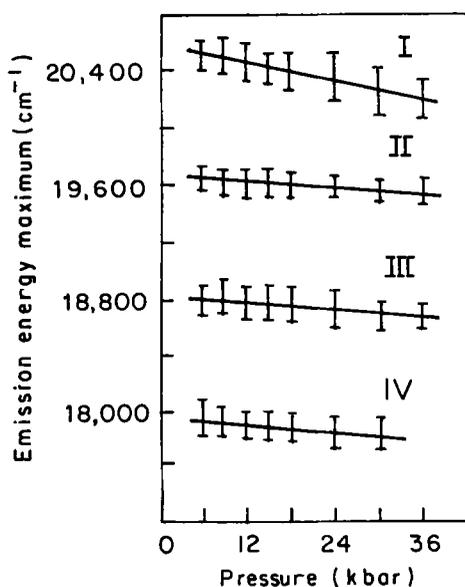


Figure 9. Pressure dependence of  $E_{\max}$  of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  crystals. (Curves I, II, III and IV corresponds to PL peaks at 487, 512, 535, 560 nm respectively).

Table 1. ML and high pressure PL of certain phosphors and crystals.

Phosphor/crystals	PL maximum (nm)	ML maximum (nm)	Pressure-coefficient of shift in emission energy ( $\text{cm}^{-1}/\text{kbar}$ )
1. ZnS:Cu, Cl	526	523	+ 38
2. ZnS:Ag, Cl	435	430	+ 33
3. (Zn, Cd)S:Ag, Cl	540	525	+ 49
4. ZnS:Au, Cl	530	526	+ 36
5. ZnS:Mn	580	585	- 33
6. $\text{Mn}(\text{PH}_3\text{PO}_2)\text{Br}_2$	500	505	- 30
7. $(\text{MePH}_3\text{P})_2\text{MnCl}_4$	505	$515 \pm 5$	- 41
8. $(\text{Et}_4\text{N})_2\text{MnBr}_4$	515	520	- 28
9. $\text{Mn}(\text{Ph}_3\text{PO})_2\text{Cl}_2$	None	516	-
10. $(\text{Bu}_4\text{N})_2\text{MnI}_4$	525	None	- 43
11. $(\text{PyN})_2\text{MnCl}_4$	520	None	- 22
12. N-acetylanthracitic	418	421	- 63.1
13. 9-Anthrylethanol	430, 450, 476	433, 453, 478	- 54, - 74
14. Phenanthrene	410, 430, 460	413, 435, 465	- 56(for 410 nm), - 23(for 430 nm), - 46(for 460 nm)
15. Anthracene	425, 445, 470	None	- 85(for 470 nm)
16. Naphthalene	325, 330, 335 340, 345, 355 360	None	- 22(for 340 nm)
17. Uranyl nitrate hexahydrate	472, 487, 512, 535 560, 588, 620	475, 490, 515 538, 563, 590 623	- 11.2(for 487 nm) - 3.3(for 512 nm) - 4.3(for 535 nm) - 5.3(for 560 nm)
18. $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$	430	438	- 92

emission energy related to these peaks are  $-43$  and  $-22 \text{ cm}^{-1}/\text{kbar}$  respectively. The crystals of anthracene have PL emission peaks at 425, 445 and 470, the main peaks at one atmospheric pressure are at 425 and 445 nm, which are of nearly equal intensity. The pressure coefficient for shift in energy is  $-85 \text{ cm}^{-1}/\text{kbar}$  for the 470 nm peak. Naphthalene crystals at one atmospheric pressure have PL emission peaks at 325, 330, 335, 340, 345 and 355 nm. The main emission peak is at 340 nm, the pressure coefficient for energy shift for this PL peak is  $-22 \text{ cm}^{-1}/\text{kbar}$ .

It is to be noticed from table 1 that the pressure coefficients are of the same order for the mechanoluminescent and non-mechanoluminescent crystals. Moreover, materials of both types i.e. with pressure coefficient of energy shift positive or negative, exhibit the phenomenon of ML.

## 4. Discussion

### 4.1 Spectral shift in photoluminescence with pressure

(A) *Phosphors*: It is believed that the luminescence in ZnS:Cu,Cl and ZnS:Ag,Cl phosphors is due to the recombination of free or nearly free carriers via some localized impurity levels. The observed pressure shifts in ZnS:Ag has been found to be nearly parallel to that of the band gap energy (Edwards *et al* 1959). Furthermore, in the solid solution of (Zn,Cd)S system, the lattice parameter increases linearly with the content of Cd ions resulting in the simultaneous change in the fundamental absorption edge and the emission bands. It has been found that the peak-shift due to the lattice parameter change caused by pressure is the same as that caused by the replacement of Zn ion with Cd ion (Koda *et al* 1966). Thus from the comparison of ML and PL spectra, it seems that the emitting mechanoluminescent crystal sites are under compression during ML emission.

It is well known that the Mn-orange luminescence arises from  $\text{Mn}^{2+}$  ion, which has a  $3d^5$  electron configuration, at the substitutional site. The energy level of the  $d^5$  system in cubic crystal field has been given by Tanabe and Sugano (1954) on the basis of the crystal field theory. According to this theory each energy level is generally expressed in terms of the crystal field strength  $10Dq$  and of Racah's parameters B and C, all of which depend on the ligand configuration. Koda *et al* (1966) have studied in detail the red shift in the case of ZnS:Mn and have interpreted it to be due to the effect of the change of crystal field parameter for the  $d$ -electron system of the  $\text{Mn}^{2+}$  ion.

(B) *Tetrahedral manganese (II) complexes*: The  $d-d$  excited states of tetrahedral manganese(II) complexes have been assigned using ligand field theory (Cotton *et al* 1962; Vala *et al* 1972; Lawson 1967). The lowest energy excited state,  $4T_1$ , arises from a  $(e)^3(t_2)^2$  electronic configuration. The photoluminescence mirrors the low energy  $4T_1$  absorption band which obeys exponential intensity decay with lifetimes of the order of  $10^{-4}$  s (Vala *et al* 1972; Lawson 1967). For these reasons, the luminescence was assigned to the  $4T_1 \rightarrow 6A_1$  transition (Vala *et al* 1972). The mixed-ligand triphenylphosphine oxide complexes ( $C_{2v}$  symmetry) were treated as having approximately tetrahedral site symmetry. Their luminescences were assigned as above on the basis of the similar yellow-green colours (Goodgame and Cotton 1961). The photoluminescence and mechanoluminescence maxima of the compounds reported here are given in

table 1. All our results are consistent with the previous assignments and are thus attributed to the  $4T_1 \rightarrow 6A_1$  transition. A possible explanation for the absence of photoluminescence from  $\text{Mn}(\text{Ph}_3\text{PO})_2\text{Cl}_2$  may be that its lifetime is even longer and that radiationless processes dominate its excited state relaxation.

The energies of the photoluminescence of all the manganese complexes show an appreciable red shift as a function of increasing pressure (figure 7). The decrease in the energy of the lowest energy  $d-d$  transition with increasing ligand field strength is unique to high spin  $d^5$  complexes. As the pressure increases,  $Dq$  increases and the crystal field stabilization energy of the excited state increases and approaches the spin-pairing energy. At large  $Dq$  values, the CFSE becomes greater than the pairing energy and the low-spin configuration becomes the ground state. Because Tanabe-Sugano diagrams for both tetrahedral and octahedral symmetries are identical for  $d^5$  manganese(II), similar pressure effects occur for octahedral complexes. A decrease in absorption energy with increasing pressure was observed by Zahner and Drickamer (1961) in octahedral complexes of  $\text{MnCl}_2$  and  $\text{MnBr}_2$ .

(C) *Organic molecular crystals*: The ( $\pi \leftarrow \pi^*$ ) transition is responsible for the PL and in turn also for the ML emission of N-anthranilic acid crystals.

The  $\pi \leftarrow \pi^*$  transitions generally exhibit a large shift to lower energy as pressure increases. Shifts of  $2700\text{--}8100\text{ cm}^{-1}$  over 100 kbar have been observed for the transition in many aromatic hydrocarbons and related compounds (Drickamer 1965). Since  $\pi$  orbitals usually exhibit considerably less overlap at atmospheric pressure than  $\sigma$  orbitals, they are much more pressure sensitive. As pressure is applied, the  $\pi^*$  orbital is pushed closer in energy to the  $\pi$  orbital so that in some cases it is sufficient to give thermal occupation of the  $\pi^*$  state.

Plots of energy of the peak maximum versus pressure up to 40 kbar usually give a straight line. Exceptions to this are evident in the case of phase transitions. Instead of one straight line, the plot gives two straight line portions of different slopes. At the point of the transition, slope changes sharply. This behaviour is to be expected since different phases most likely do not couple to pressure in the same manner.

(D) *Cesium platino-cyanide* ( $\text{Cs}_2\text{Pt}(\text{CN})_4 \cdot \text{H}_2\text{O}$ ): An interpretation of pressure tuning of the PL spectra of tetracyanoplatinates may be given on the basis of a simple band model. Because of the exceptional arrangement of the molecular units in crystals with column structure, the intermolecular coupling within every column is much stronger than the coupling between different column (Yersin and Gliemann 1978). If the Pt-Pt spacing  $R$  decreases, orbitals of neighbouring molecular units will show increasing overlap, especially those orbitals pointing directly to the adjacent metal ions. It has been reported that the orbitals (Pt  $6P_z$ , CN  $\pi^*$  and Pt  $5d_{z^2}$ , 6s) have relatively a strong overlap and therefore, a relatively broad band splitting results. For this reason the upper region of the (Pt  $5d_{z^2}$ , 6s) band forms the edge of the valence band, whereas the conduction band is derived from the coupled (Pt  $6P_z$ , CN  $\pi^*$ ) states. With increasing pressure values,  $R$  decreases causing increase in the band splitting, which in turn, decreases the gap energy. As such the peak of the spectra shifts towards longer wavelength side with increasing values of the applied pressure.

(E) *Uranyl nitrate hexahydrate*: The luminescence of uranyl salts has been exhaustively investigated at least for a century. The yellow-green fluorescence of uranyl ion ( $\text{UO}_2^{2+}$ )

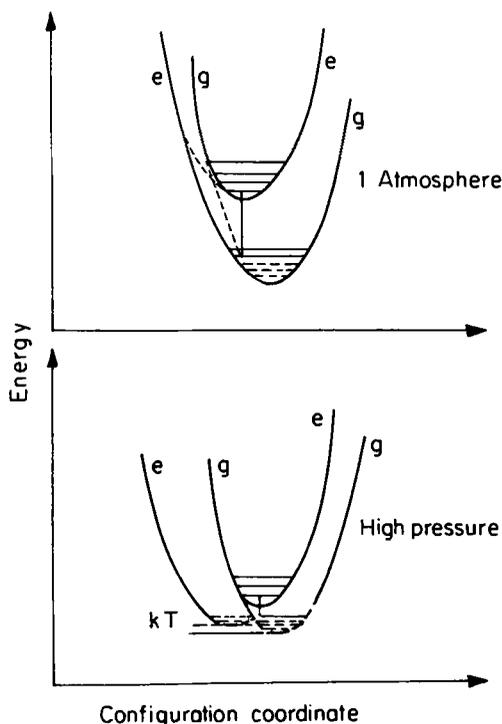
in many compounds is well known. Uranyl nitrate, sulphate, and phosphate crystals, for example, fluoresce strongly and many substances are made fluorescent when doped with uranium. The photoluminescence of  $\text{UO}_2(\text{NO}_3)\cdot 6\text{H}_2\text{O}$  is characteristic of the hydrated  $\text{UO}_2$  ion. The PL spectra are independent of the wavelength of absorbing light and the quantum yield is nearly equal to one. The prominent vibronic peaks in the spectrum, spaced at an average interval of  $84\text{ cm}^{-1}$  arise from coupling with the symmetric  $0\text{-U-}0$  stretch  $\sigma_g^+$  (Chandra 1983).

The emitting state of uranyl ion has not been clearly assigned. The molecular orbital (MO) calculations on the linear  $0\text{-U-}0^{+2}$  ion indicates four different orbital orderings (McGlynn and Smith 1961; Newman 1967; Boring *et al* 1975; Ellis *et al* 1975). All the results agree with a  $^1\Sigma_g^+$  ground state and indicate that the lowest energy symmetry allowed transition is  $^3\pi_u \rightarrow \Sigma_g^+$ . However, different MO ordering and role of  $j\text{-}j$  coupling have allowed various assignments of the observed transition. Regardless of the electronic state assignments, the uranyl emission, is a spin forbidden transition involving metal  $d$  or  $f$  orbitals. The lifetime of the emission in the order of  $10^{-2}\text{ s}$  indicates the phosphorescent nature of the emission (McGlynn and Smith 1961). Independent of orbital orderings, emission occurs from a molecular orbital which is predominantly  $U(5f)$  orbitals. The different vibronic peaks suggest that at very high pressure some of the bands may overlap and many merge into each other.

#### 4.2 Pressure-induced thermal population of excited states

The first step related to the pressure-induced thermal population of excited state mechanism is considered in figure 10. At 1 atm, the ground and excited electronic state potential energies are shown at some displacement along a configuration co-ordinate. Distortion of the potential wells is a consequence of configuration interaction between the two states. In the solid state, vibrations are available to mix approximately the two states of any symmetry. At high pressure, the difference in energy between the two states decreases, allowing thermal electron transfer to a new potential energy well minimum. The high pressure ground state is the result of mixing of the 1 atm ground and excited state potential wells. The thermal population of the new ground state may occur even though the optical Frank-Condon transitions observed in absorption and emission at high pressure are much greater than  $kT$ . Several examples of this process are known. The pressure induced polymerization of pentacene crystals has been attributed to the population of a highly reactive state produced by the mixing of  $\pi$  and  $\pi^*$  states (Drickamer *et al* 1972). Pressure induced high spin to low spin ground state transitions are observed in  $\text{Fe}(\text{phen})_2\text{X}_2$  complexes ( $\text{phen} = 1, 10\text{-phenanthroline}$ ,  $\text{X} = \text{halide}$ ) as well as low to high spin transitions in  $\text{Fe}(\text{phen})_3$  (Drickamer and Frank 1973; Fisher and Drickamer 1971). Over forty examples of a ferric to ferrous ground state reduction are known at high pressure (Drickamer *et al* 1970) as well as pressure induced reductions of ferrate salts (Panyushkin and Drickamer 1969). These reductions are attributed to thermal charge transfer from a ligand non-bonding orbital to a  $-\pi-$  bonding metal orbital (Drickamer and Frank 1973).

The second step of this mechanism is somewhat more speculative. Given that a new ground state is produced at high pressure by thermal electron transfer, upon sudden release of this pressure the electron can either relax to the 1 atm ground state, or remain in the excited state potential well long enough to relax to 1 atm and



**Figure 10.** Model for pressure-induced thermal population of excited state ( $g$  and  $e$  represent ground and excited states respectively: solid line shows the potential energy after mixing of states by configuration interaction).

radiatively transfer back to the ground state. This latter process is unprecedented but provides an attractive ML mechanism consistent with the observation that the emission occurs from a molecule at or near atmospheric pressure.

The PL spectra of some of the phosphors and crystals decrease in emission energy with increasing pressure which is in accord with the thermal population mechanism. However, the following experimental results do not support this mechanism of the ML excitation.

- (i) The measurements of the pressure-coefficient of shift of the energy corresponding to the peak of the PL, suggests that the ground and excited states will be within  $kT$  at hydrostatic pressure ranging from 500 to 700 kbar. However, the stress near the tip of mobile crack in a solid is only of the order of 5 kbar.
- (ii) There is no systematic correlation between the extrapolated pressure at which thermal population can occur and the presence or absence of ML in crystals. In other words, the PL of mechanoluminescent crystals is not more sensitive to pressure than that of non-mechanoluminescent crystals. This finding is strong evidence against the proposed thermal mechanism of ML.
- (iii) The ML spectra of ZnS:Cu, ZnS:Ag and (Zn, Cd)S:Cu phosphors shift towards higher energy with increasing value of the applied pressure. If thermal population mechanism is operative, then these phosphors should be non-mechanoluminescent. However, these phosphors exhibit intense ML.

(iv) It is known that the ML emission of many phosphors contain the emission from the absorbed or adsorbed molecules of the surrounding gases. Such emission cannot be explained by an intramolecular pressure mechanism.

Thus, the high pressure spectroscopy indicates that the ML should be attributed to the crystal property rather than to the electronic property of the molecule. It seems that if by any means the product of pressure-coefficient of energy shift and stress at the mobile crack-tip can be increased 50 to 100 times, then the thermal population of the excited states may take place. In recent years the investigations on material science are exploring new substances where a particular property can be enhanced to a greater extent. Thus, it seems undoubtedly that the investigation of the mechanoluminescence capable of thermal population of excited state is in the realm of possibility.

#### 4.3 Evaluation of the stress near the tip of mobile cracks from mechanoluminescence experiments

Generally ML spectra shift either towards higher wavelength side or towards lower wavelength side as compared to the corresponding PL spectra. Several compounds have been tested and more differences between ML and PL spectra have been found for (Zn, Cd)S:Ag, Cl phosphors and  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  crystals.

As the coefficients of pressure shift are  $49 \text{ cm}^{-1}/\text{kbar}$  for (Zn, Cd) S:Ag and  $92 \text{ cm}^{-1}/\text{kbar}$  for  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$ , the observed shifts of 15 nm and 8 nm for these two specimens give the stress of 10.8 and 4.8 kbar near the tip of mobile cracks in (Zn, Cd)S:Ag, Cl phosphors and  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  crystals. The theoretical estimation suggests that the stress near tip of mobile cracks should be of the order of  $E/10$  (where  $E$  is Young's modulus of elasticity), which is also in the range of 10 kbar (Cottrell 1960). Practically the crystals of (Zn, Cd)S:Ag and  $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  get fractured for an applied stress of the order  $10^6 \text{ Newton M}^{-2}$ . However, the ML experiment indicates that the stress near the tip of mobile cracks should be of the order of  $10^9 \text{ Newton M}^{-2}$ . This observation indicates the stress application of the order of one thousand near the tip of mobile cracks.

It is found that in some of the crystals the ML spectra resemble the PL spectra which indicates that the emission takes place nearly at one atm pressure. This means that the emission in such crystals should be taking place after the relaxation of the stress to lower values.

In the materials where pressure-coefficients are remarkably different for different vibronic peaks, the comparison of the intensity ratio observed in the ML spectrum with that of PL at high pressure, may also give indication of the stress near the mobile crack-tip. Using this procedure, Zink *et al* (1980) have shown that the stress near the tip of a mobile crack in  $[(\text{CH}_3)_3\text{NH}]_3\text{Mn}_2\text{Cl}_7$  crystals is of the order of  $2 \pm 1 \text{ kbar}$ .

Conclusively it can be said that the usual pressure coefficient of energy shift of the order of  $50\text{--}100 \text{ cm}^{-1}/\text{kbar}$  and the stress at the crack tip of the order of  $5\text{--}10 \text{ kbar}$  are not sufficient to cause the thermal population of the excited state. If by any means the product of pressure coefficient and the stress at the mobile crack-tip can be increased 50 to 100 times, then the thermal population of excited states may take place. It has been found that certain metal complexes have comparatively higher pressure-coefficient of the energy shift and the fracture-stress increases remarkably in mixed crystals and in reinforced materials. Investigation of ML in the mixed crystals

of metal complexes or in reinforced materials may be interesting. In this regard, the ML studies in ruby and diamond like materials may also be meaningful. The investigation of materials having thermal population of excited states is exciting and challenging.

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