High pressure luminescence studies of localized excitations in ZnS doped with Pb^{2+} and Mn^{2+} [a)]

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High pressure luminescence measurements have been made on ZnS doped with Pb^{2+} and Mn^{2+}. The data include changes in peak energy and shape, integrated intensities, and lifetimes. These localized emissions are treated in terms of a single configuration coordinate model. For Pb^{2+} the emission peak shifted to lower energy by a moderate amount and narrowed. For excitation in the Pb^{2+} absorption the intensity was independent of pressure, which is consistent with the fact that the energy barrier for radiationless return to the ground state was high at all pressures. For excitation in the ZnS absorption edge the intensity decreased significantly with pressure above about 80 kbar. Data on shifts of the conduction band with pressure would indicate that one is approaching a transition from a direct to indirect transition at high pressure so that decrease in emission intensity may be associated with decreased absorption efficiency. The Mn^{2+} emission peak shifted strongly to lower energy with increasing pressure. The direction and magnitude of the shift were consistent with the predictions of ligand field theory. The intensity doubled in 100 kbar, while the lifetime decreased by roughly a factor of 2. These results could be described in terms of a model for a phonon assisted transition. In addition, peak location, intensity, and lifetime measurements were made on ZnS:Pb:Mn. There is clear evidence of energy transfer by exchange, but in addition there is a nonradiative process in the doubly doped crystal which affects both intensities and lifetimes.

INTRODUCTION

The effect of pressure has been measured on the luminescence of ZnS doped with Pb^{2+} and with Mn^{2+}. The measurements include emission peak location, half-widths and asymmetry, emission intensity and lifetimes. Some measurements were also made on ZnS doped with both Pb^{2+} and Mn^{2+} to study Pb^{2+} to Mn^{2+} energy transfer. The methods of sample preparation, the high pressure luminescence techniques, and methods of data processing are discussed in references given in the first paper of this series.[1]

These impurities when introduced into the host lattice occupy zinc sites and require no charge compensation. Whereas the optical properties of those phosphors discussed in the previous papers were largely determined by the host, the luminescence behavior of these materials is strongly dependent on the nature of the impurity ion. Luminescence in these systems involves optical transitions within the electronic levels of the impurity. Excitation can be achieved either through host absorption or direct absorption by the impurity ion. In the latter case the degree of absorption depends on the oscillator strength of the impurity in the tetrahedral environment. The pressure-dependent configuration coordinate model[2-4] provides the basis for the analysis of these deep levels.

RESULTS

Excitation of the ZnS : Pb phosphor was achieved through host lattice absorption (298 nm Hg line) and also by direct excitation of the Pb^{2+} ion (405 nm Hg line). The absorption process is the $6s^2 \rightarrow 6sp$ electronic transition. A constant excitation rate was assured in the former case since the flat portion of the fundamental absorption always overlapped the exciting line. Direct excitation at 405 nm is believed to involve the $B(^1S_0 \rightarrow {}^3P_2)$ and C band $(^1S_0 \rightarrow {}^1P_1)$ absorptions.[5] Excitation spectra yielded a fairly broad absorption peak centered at 430 nm which is insensitive to pressure. The resulting green luminescence occurs via the $^3P_2 \rightarrow {}^1S_0$ electronic transition. A detailed study and assignment of energy levels of the Pb^{2+} center in cubic zinc sulfide is given by Uehara.[5]

Figure 1 shows data for ZnS : Pb for both the emission peak shift and half-width change with pressure. In contrast to the donor–acceptor type luminescences where the emission bands exhibited a large blue shift with increasing pressure the Pb^{2+} emission band shows a shift to lower energy. A least squares fit of this data gives the following relation for the band shift (in cm^{-1}) as a function of pressure;

$$\Delta(h\nu_e) = -16p + 0.05p^2 . \qquad (1)$$

The data for the observed half-width change are fit linearly from 20–120 kbar. The half-width data obtained from 0–20 kbar required the resolution of two peaks and probably do not reflect the true bandwidth variation over this pressure range. The additional peak was due to an SA (self-activated) band introduced by chlorine which was present during firing. This band was quenched at pressures greater than 20 kbar. At 20 kbar the Pb^{2+} bandwidth was approximately 0.22 eV. The observed half-width change with pressure obeyed the following relation:

$$(\delta E_{1/2})_e = -5.8p , \qquad (2)$$

where $(\delta E_{1/2})_e$ is in cm^{-1}.

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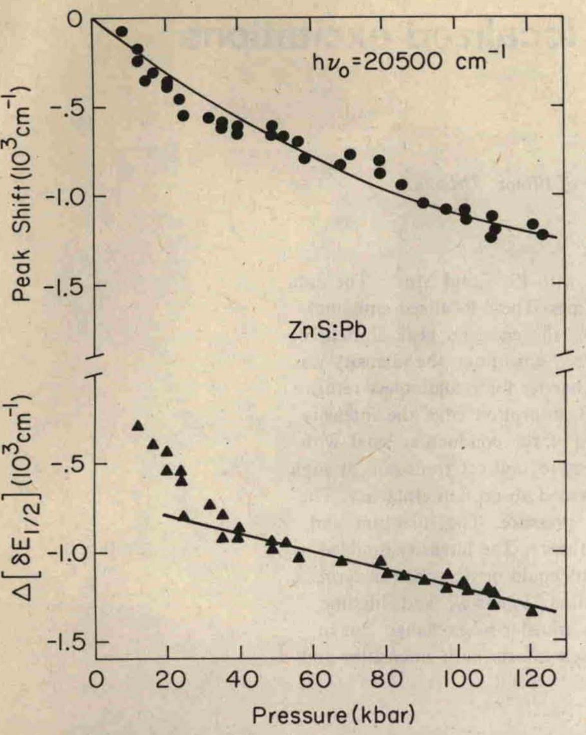

FIG. 1. Emission peak shift and half-width change versus pressure for ZnS : Pb $(\delta E_{1/2})_0 = 2390$ cm^{-1} by extrapolation of the fit curve to $p = 0$.

The band location at 1 atm and the observed peak shift and half-width change were independent of the exciting wavelength. Absorption by the host and direct excitation of Pb^{2+} ion yielded identical results.

Figure 2 gives the steady state intensity and the observed lifetime of the ZnS : Pb phosphor as a function of pressure. In the case of Pb^{2+} excitation there is little change in the intensity over the entire pressure range. Excitation in the fundamental lattice absorption band, however, yields a different effect. Here the intensity stays constant up to about 80 kbar at which point a decline begins. The observed decay function is exponential as would be expected by the first order kinetics predicted for a localized center. The measured lifetime is seen to be independent of exciting wavelength and shows a modest increase in the first 30 kbar before leveling at 250 nsec.

The orange luminescence of ZnS : Mn arises from an optical transition with the Mn^{2+} ion. The Mn^{2+} has a $3d^5$ electron configuration with a spherically symmetric ground state $^6S(^6A_1)$—all spins unpaired. The lowest excited state (one spin paired) of this ion is the ^4G excited state band comprised of the $^4T_1$, $^4T_2$, and $^4A_1 + {}^4E$ excited states. The observed emission occurs from the lowest energy excited state $^4T_1$ to the $^6A_1$ ground state;[6] the transition is forbidden by spin and parity selection rules. These rules become relaxed through perturbations due to one or a combination of the following sources: crystal field, spin–orbit interaction, exchange coupling of Mn^{2+} pairs, or phonon coupling. In the case of phonon coupling it is the breathing mode about the impurity ion that is responsible for the phonon assistance.[7] The ground state of the manganese ion in zinc sulfide has been estimated to be anywhere from 3 to 6 eV below the top of the valence band. Klick and Schulman[8] provide further discussion of the luminescence properties of divalent manganese in solids. Their paper shows the applicability of the configuration coordinate model to this center and also includes causes for band asymmetry.

The data of Fig. 3 show the large pressure shift to lower energy for the ZnS : Mn phosphor. The accompanying half-width dependence over this pressure range appears in the top part of Fig. 4. The bandwidth at 1 atm and room temperature was 0.27 eV. As is known the manganese emission band is asymmetric.[8] A plot of the pressure dependence of this asymmetry is shown in the lower portion of Fig. 4. It is observed that at about 120 kbar the band assumes a Gaussian distribution [$R \rightarrow 1$ in Eq. (3) below]. It is also interesting to note that in each set of data of Figs. 3 and 4 there is a measurable change in the data at approximately 40 kbar.

The final sets of data on the ZnS : Mn system appear in Fig. 5. Plotted here are the steady state intensity and the observed lifetime(s) as a function of pressure. The emission intensity increases by a factor of 2 over the pressure range studied. The decay function was fit to the sum of two exponentials. The 1 atm, room temperature values of the decay constants were 180 and 650 msec. The 650 msec decay is believed due to the phonon-assisted electronic transition within the manganese ion, while the shorter decay is ascribed to a trapping state.[7,9] As can be seen the longer decay constant shows a gradual decrease with pressure while the faster one stays approximately constant.

DISCUSSION

The influence of high pressure on the optical properties of localized centers in ZnS : Pb and ZnS : Mn is un-

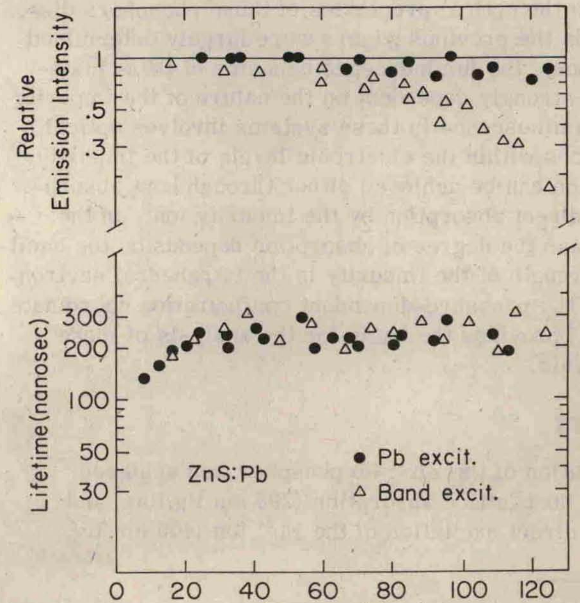

FIG. 2. Relative emission intensity and lifetime versus pressure for ZnS : Pb.

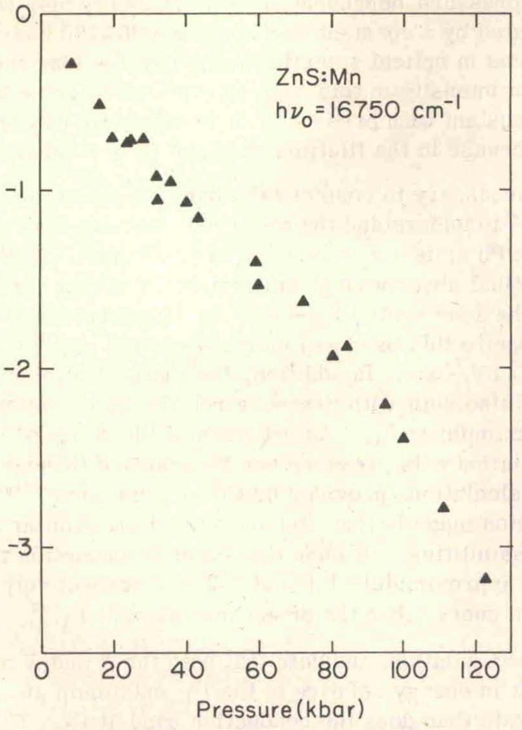

FIG. 3. Emission peak shift versus pressure for ZnS : Mn.

derstood in terms of a single configuration coordinate analysis.[2-4] Pressure-induced changes in the emission peak location and half-width are used to determine parameters characteristic of the model. These parameters provide the basis necessary to understand the other experimental results.

The fits of the data for ZnS : Pb [Fig. 1, and Eqs. (1) and (2)] related the emission peak shift and half-width change to the pressure variable. We use the equations

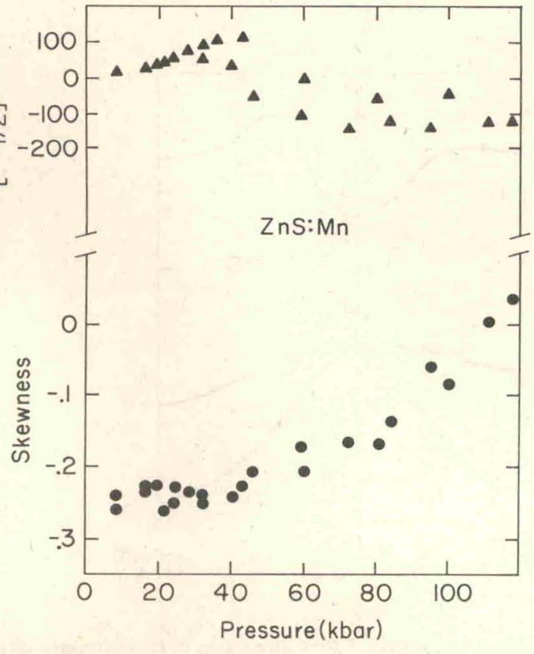

FIG. 4. Emission half-width change and skewness versus pressure for ZnS : Mn $(\delta E_{1/2})_0 = 2200$ cm^{-1}.

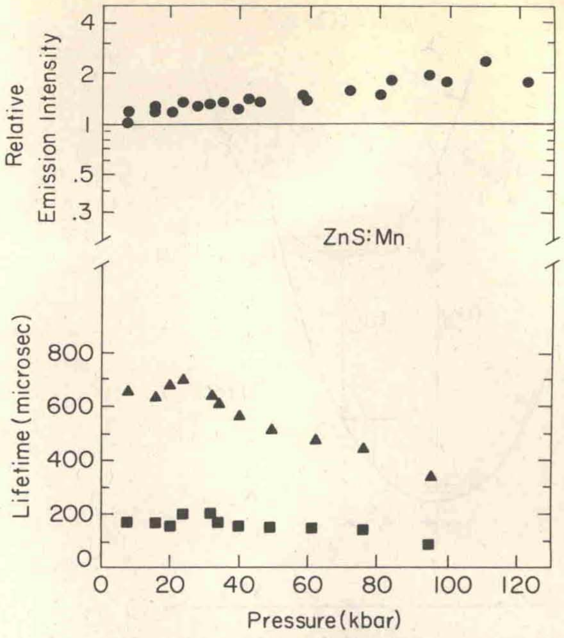

FIG. 5. Relative emission intensity and lifetime versus pressure for ZnS : Mn.

of Refs. 2–4. If one assumes that ω^2, the ground state force constant, is independent of pressure, these expressions are for the emission peak shift

$$\Delta(h\nu_e) = \frac{p\Delta_0}{R} + \frac{(R-1)p^2}{2R^2\omega^2}, \tag{3}$$

and for the emission band half-width

$$(\delta E_{1/2})_e = N\left|\frac{\omega\Delta_0}{R^{1/2}} + \frac{p(R-1)}{\omega R^{3/2}}\right|, \tag{4}$$

where Δ_0 is the value of Δ (the relative displacement of the potential wells along the configuration coordinate of interest) at zero pressure, $R = (\omega'/\omega)$ is the ratio of force constants for the potential wells, and N is a normalization factor (32 cm^{-1} at 25 °C). The other parameters we define in Fig. 6. These equations contain the same pressure dependences as the observed data and, by equating like powers of p in Eqs. (3) and (4), one can make use of the numeric coefficients of Eqs. (1) and (2) to calculate ω^2, R, and Δ_0. These quantities were found to be

$$\omega^2 = 2.17 \text{ kbar}^2/\text{cm}^{-1}, \tag{5}$$

$$R = 1.44, \tag{6}$$

$$\Delta_0 = -2.55 \text{ cm}^3/\text{mole}. \tag{7}$$

The observed steady state intensity change with pressure was seen to depend on the excitation wavelength (Fig. 2). This intensity was essentially independent of pressure when excitation was achieved by direct excitation of the Pb^{2+} ion; host lattice excitation showed a rapid decrease in intensity at pressures above 80 kbar. It is possible to understand the insensitivity of the intensity to pressure in the former case by considering the analysis below. One solves the configuration coordinate equations for the quantity of importance, the quenching energy E_q, which is the energy measured

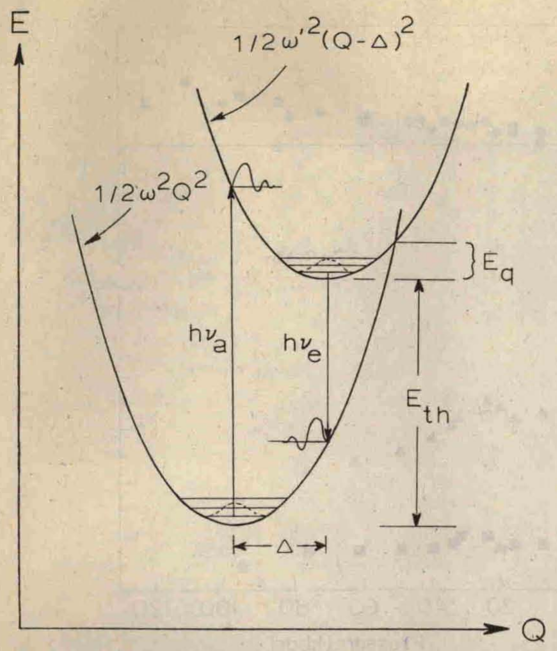

FIG. 6. Schematic configuration coordinate diagram.

from the lowest vibrational level of the excited state to the point of intersection of the potential wells (see Fig. 6). This energy represents the classical energy necessary for an electron to surmount the potential E_q and crossover nonradiatively to the ground state well. The probability n_q of this occurrence is generally expresed in the following fashion:

$$n_q \propto e^{-E_q/kT} , \tag{8}$$

where $kT \cong 200\ \mathrm{cm}^{-1}$ at room temperature. Using the value of Q obtained above one can then use the following relations, assuming $R=1$ (linear coupling with $\Delta = \Delta_0$), to obtain a relationship for the pressure dependence of the quenching energy:

$$h\nu_e = h\nu_{e0} + p\Delta = E_0 + p\Delta - \tfrac{1}{2}\omega^2\Delta^2 , \tag{9}$$

$$E_q = \tfrac{1}{2}\omega'^2(Q_q - \Delta)^2 . \tag{10}$$

The resulting expression is

$$E_q = \frac{1}{2\omega^2\Delta^2}(h\nu_{e0} + p\Delta)^2 . \tag{11}$$

Although this equation is strictly valid for linear coupling, the previously determined configuration coordinate parameters, based on $R \neq 1$, will not introduce much error in the argument. Using values of $h\nu_{e0}$ of 20 000 cm^{-1}, $\Delta = -2.55\ \mathrm{cm}^3/\mathrm{mole}$ and ω^2 of $2.17\ \mathrm{kbar}^2/\mathrm{cm}^{-1}$, one obtains a value of roughly 10 000 cm^{-1} for E_q at 1 atm. This value compares favorably with the 12 000 cm^{-1} value obtained by Mita[10] for the ZnS : Pb yellow emission. Hence, at room temperature and atmospheric pressure there is a very low probability of classically surmounting E_q. It is known that there is little temperature quenching of this phosphor below 100 °C.[10] At 100 kbar the quantity $(h\nu_{e0} + p\Delta)^2$ is reduced by only 20% or $E_q = 8000\ \mathrm{cm}^{-1}$, hence, the effect of pressure on the quenching energy is slight over the range of pressures studied. It is seen then that in the absence of any competing, pressure-dependent, nonradiative process (as is indicated by a constant lifetime from 30–120 kbar) or changes in optical selection rules that the observed emission intensity in this case is expected to remain fairly constant with pressure. It is uncertain why there is an increase in the lifetime over the first 30 kbar.

It is necessary to consider the band structure diagram of Fig. 7 to understand the observed intensity loss of the ZnS : Pb emission when excited in the host. In Fig. 7 the optical absorption of interest is the direct transition at the zone center $\Gamma_{15} - \Gamma_1$. As stated before at low pressure this band gap increases at the rate of 9.0×10^{-3} eV/kbar. In addition, the indirect minima at L and X also shift with pressure relative to the valence band maximum at Γ_{15}. An estimate of the shifts of these minima with pressure can be achieved through use of calculations provided by Cohen[11] for ZnSe. The assumption made is that Zns and ZnSe have similar compressibilities. In ZnSe the X and L conduction minima are approximately 1.9 and 1.2 eV, respectively, higher in energy than the direct minimum at Γ_1.[12]

Cohen's calculations indicate that both the L and X minima shift in energy relative to the Γ_{15} maximum at a slower rate than does the conduction band at Γ_1. This effect has been experimentally observed in many of the III–V semiconductors.[13] The calculations for ZnSe show that the X minimum shifts much more slowly to higher energy than does the L minimum. The shift of the various minima up to a 0.30 Å change in lattice constant a are nearly linear. The shift of these minima relative to the Γ_{15} valence band are

$$\frac{dE_{\Gamma_1}}{da} = 3.62\ \mathrm{eV/Å} , \tag{12}$$

$$\frac{dE_X}{da} = 1.31\ \mathrm{eV/Å} , \tag{13}$$

$$\frac{dE_L}{da} = 2.94\ \mathrm{eV/Å} . \tag{14}$$

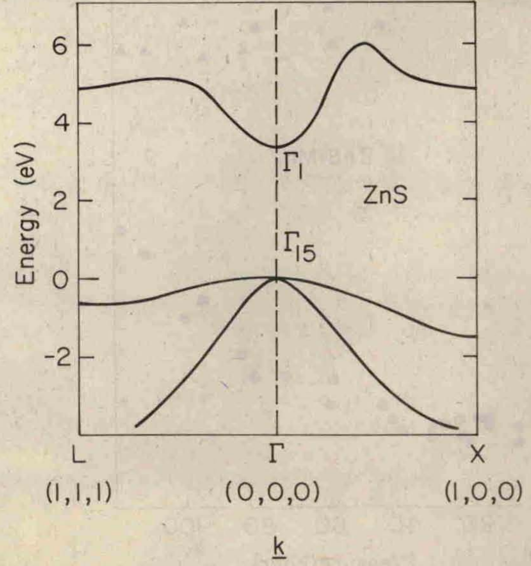

FIG. 7. Band structure of ZnS along two principal symmetry directions.

Assuming a similar dependence for ZnS and a change in lattice constant of about 0.33 Å corresponding to roughly 100 kbar one can estimate the locations of various conduction minima relative to each other. The band structure of ZnS at atmospheric pressure shows the X minimum to be at an energy of about 1 eV higher than the Γ_1 point. At 100 kbar the estimated relative position of these bands can be expressed, using Eqs. (12) and (13), as

$$(E_x - E_{\Gamma_1})_{100\ \text{kbar}} = 8000\ \text{cm}^{-1} - 0.33\ \text{Å}\left(\frac{dE_{\Gamma_1}}{da} - \frac{dE_x}{da}\right) = 1900\ \text{cm}^{-1}\ . \tag{15}$$

Physically, the material is nearly an indirect semiconductor. As the material goes indirect it is expected that the absorption coefficient will decrease since phonons of the wave vector $\mathbf{k}_p$ are required to satisfy the conservation of wave vector. Thus, it can be seen that the intensity of the Pb^{2+} emission will drop due to a reduction in the absorption coefficient of the host. In addition, the decrease in absorption strength of the host should not effect the observed lifetime of the emission.

From Fig. 2 it is noted that the intensity of the emission for excitation in the host absorption edge starts to decrease significantly near 80 kbar, which is somewhat lower than the pressure predicted for the indirect transition to become lowest in energy by Eq. (15). In view of the approximations involved in the numbers used, however, the agreement is qualitatively satisfactory. This effect is not apparent in the donor–acceptor type emissions since these materials are quenched at lower pressures.

A quantitative understanding of the pressure dependence of the emission transition energy of Mn^{2+} in ZnS : Mn may be obtained through use of crystal field theory. In considering the ${}^4T_1 \rightarrow {}^6A_1$ transition as a function of pressure one can make use of the Tanabe and Sugano diagram[14] for the $3d^5$ electron configuration. The pertinent parameters of crystal field theory are the Racah parameters B and C, which account for interelectronic repulsion in a d-electron system, and D_q, the crystal field strength. The latter parameter can be crudely approximated by a point charge model which has an r^{-5} dependence; r is the ligand-impurity ion distance. The value of D_q for Mn^{2+} in cubic ZnS : Mn has been estimated to be 410 cm^{-1}.[18] The energy diagram of Tanabe and Sugano relates the energy of the ${}^4T_1 \rightarrow {}^6A_1$ transition to B, C, and D_q. The effect of changes in these parameters on the transition energy can be extracted from the diagram. The dependence of B on pressure has been determined to be $-0.348\ \text{cm}^{-1}/\text{kbar}$.[15] The zero pressure (1 atm) value is 655 cm^{-1}.[16] The results of Zahner and Drickamer[17] show that the ratio C/B in $MnCl_2$ and $MnBr_2$ is fairly independent of pressure. Qualitatively, it is easily seen that a decrease in B and an increase in D_q will result in a decrease in the energy separation E of the ${}^4T_1$ and ${}^6A_1$ states. The zero pressure ratio D_q/B is 0.626 and the corresponding value of E/B is 16 750 $\text{cm}^{-1}/655\ \text{cm}^{-1} = 25.6$. Using the pressure dependence of B and D_q one can estimate the change in the emission transition energy with pressure. In 100 kbar (corresponding roughly to a 0.14 Å change in ligand impurity ion distance) the value of D_q/B is found to be

$$\frac{(2.34/2.20)^5 \times 410}{655 - 34.8} = 0.90\ . \tag{16}$$

In the region of interest for D_q/B $(0.5 \rightarrow 1.0)$ the energy diagram[14] has a linear slope of 10 for the ${}^4T_1$ state. Using the zero pressure values of $D_q/B = 0.626$ and $E/B = 25.6$ gives a point which falls slightly below the ${}^4T_1$ curve. Assuming a slope of 10 and using the 100 kbar value of 0.90 for D_q/B results in a graphical value of 22.8 for E/B. Since B at 100 kbar is roughly 620 cm^{-1}, the estimated transition energy is $E = 22.8 \times 620 = 14\,150$ cm^{-1}. The predicted red shift is then 2600 cm^{-1}, which agrees very well with the observed 2500 cm^{-1} peak shift of Fig. 3.

Since the Mn^{2+} ion forms a highly localized center in ZnS, the single configuration coordinate model may be applied. Assuming a linear peak shift from 0–100 kbar for the data of Fig. 3 the value of Δ_0 was determined to be $-25.6\ \text{cm}^{-1}/\text{kbar}$ or $-3.07\ \text{cm}^3/\text{mole}$. As the data of Fig. 4 show the Mn^{2+} emission band is asymmetric at pressures less than 100 kbar. There are several causes of band asymmetry: self-absorption when Δ_0 is small, low temperature freezing out of vibrational levels of the excited state which participate in the transition, and quadratic electron–phonon coupling.[17] In this investigation the first two causes can be ruled out since the oscillator strength of manganese is so low and the experimental data were taken at room temperature. Although the half-width data of Fig. 4 show a relative insensitivity to pressure (implies $R = 1$), the band skewness indicates quadratic coupling ($R \neq 1$). An estimate of R at 1 atm and room temperature can be obtained through the following relation[17]:

$$b_e(\delta E_{1/2})_{e0} = 2.8kT(R-1)/R\ . \tag{17}$$

Using this relation R was found to equal 0.55. Substitution of this value of R in Eq. (4) at $p = 0$ yields a value of $3.50\ \text{kbar}^2/\text{cm}^{-1}$ for ω^2, the ground state force constant. Implicit in the change of band asymmetry for this case is a change in R with pressure. The data indicate that R is constant up to 40 kbar at which point it varies linearly $(0.55 \rightarrow 1.0)$ up to 100 kbar. It is not clear based on the change in band asymmetry why the observed half-width is nearly constant with pressure.

The data of Fig. 5 gave the relative emission intensity and lifetime of ZnS : Mn as a function of pressure. The intensity was seen to rise by a factor of 2 in 100 kbar while the lifetime decreased by roughly that same factor over the pressure range. An understanding of the measured lifetime may be obtained through the relation given in by Klick *et al.*[18] for phonon-assisted transitions

$$1/\tau \propto (\Delta\omega)^2 kT\ . \tag{18}$$

The pressure dependence of τ is contained mainly in Δ:

$$\Delta = \Delta_0 + \frac{p}{\omega'^2}(R-1)\ . \tag{19}$$

The dependence of R on band skewness is given in Eq. (17). R remains constant (0.55) over the first 50 kbar

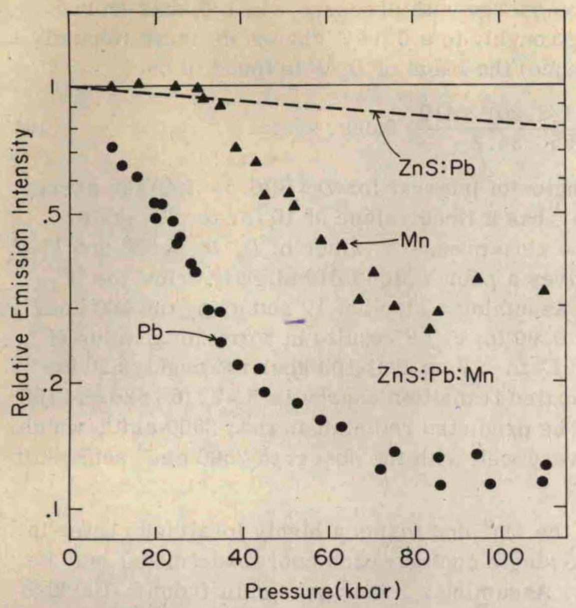

FIG. 8. Relative emission intensities versus pressure for Pb^{2+} and Mn^{2+} emissions of ZnS : Pb : Mn.

and then varies nearly linearly to 0.73 up to 90 kbar. Therefore, by Eq. (18) as Δ increases τ will decrease. The experimental data of Fig. 5 for the longer component (see previous discussion) are in good agreement with this prediction. The observed increase in the intensity may be argued by assuming the radiative process within the Mn^{2+} ion is rate controlling, i.e., those host absorptions not dissipated via a Mn^{2+} transition are thermally degraded by the crystal. If the observed rate at which the Mn^{2+} transition occurs is increased (decreasing lifetime), then, with a fixed number of Mn^{2+} centers in the region of the crystal where light is absorbed, it is expected that the number of electrons returning radiatively per unit time (intensity) will increase.

SENSITIZED LUMINESCENCE

Sensitized luminescence is known to occur in many inorganic systems.[19,20] Usually, the host must possess a large band gap and the sensitizer and activator ions must form highly localized states. It is of scientific interest to investigate the pressure dependence of this nonradiative energy transfer process as it occurs in zinc sulfide. The modest band gap (3.7 eV) restricts the availability of sensitizer and activator ions which satisfy the above requirement of localization. The ions found suitable for this study were Pb^{2+} (sensitizer) and Mn^{2+} (activator). The data presented previously on the ZnS : Pb and ZnS : Mn phosphors provided useful information on the singly doped systems. Two ZnS : Pb : Mn phosphors were prepared; one contained equal impurity concentrations of 0.15 mole% and the other had a manganese concentration 10 times greater. The experimental results are discussed qualitatively in terms of Dexter's analysis.[20] Prior study of the ZnS : Pb : Mn system has been limited to the temperature work of Shionoya *et al.*[21] In their investigation they were unable to determine if room temperature energy transfer was due to photoconductive transfer or resonance transfer.

For the sample more dilute in Mn^{2+} excitation of the Pb^{2+} ion at 405 nm yielded an emission spectrum composed of equally intense Pb^{2+} and Mn^{2+} bands. No measurable Pb^{2+} emission was evident in the sample containing the higher Mn^{2+} concentration, only an intense Mn^{2+} band was observed. The data presented in Figs. 8 and 9 refer only to the phosphor containing equal Mn^{2+} and Pb^{2+} concentrations. The steady state emission intensity changes as a function of pressure for both Pb^{2+} and Mn^{2+} are given in Fig. 8. The dashed line represents the variation of the lead emission intensity in the ZnS : Pb phosphor over this pressure range. The observed pressure effect on the ZnS : Pb : Mn phosphor is to decrease substantially the Pb^{2+} emission intensity over the first 70 kbar. Over this same pressure range the Mn^{2+} intensity stays constant to 30 kbar, then behaves similarly to the Pb^{2+} emission. The sample containing the higher Mn^{2+} concentration exhibited an initial rise in intensity about a factor of 2 to 30 kbar, then remained fairly constant in intensity at the higher pressures (data not shown).

Excitation at 405 nm eliminated the possibility of photoconductive energy transfer. Thermal ionization of the Pb^{2+} was felt to be negligible since the Pb^{2+} excited state lies 0.40 eV below the bottom of the conduction band[21]; at higher pressures this ionization energy is even larger as indicated by the red shift of the Pb^{2+} emission band relative to the large blue shift of the conduction band edge. Further experimental confirmation of this neglect of thermal ionization was obtained from a ZnS : Pb phosphor also possessing a self-activated (SA) band due to chlorine. Excitation in the host showed the presence of both bands while direct excitation of Pb^{2+} at 405 nm yielded only Pb^{2+} emission.

Figure 9 gives the change of the Mn^{2+} lifetime with pressure for the ZnS : Pb : Mn phosphor. The faster component (0.07 msec at zero pressure) is believed due to the Mn^{2+} decay. This initial (zero pressure) lifetime

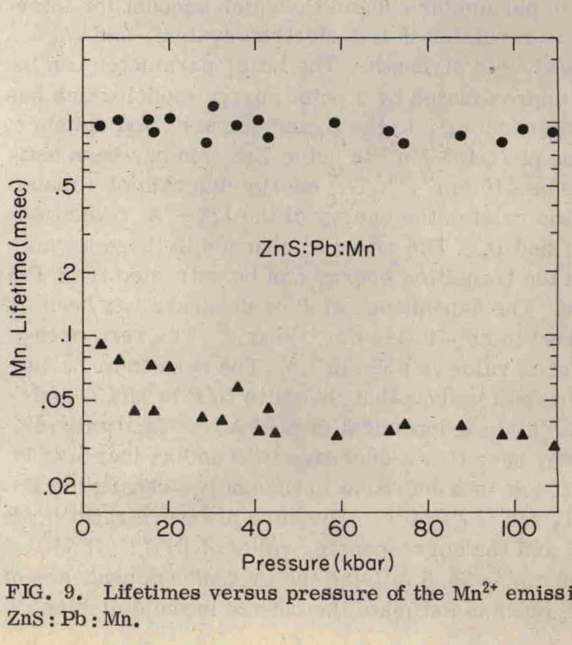

FIG. 9. Lifetimes versus pressure of the Mn^{2+} emission in ZnS : Pb : Mn.

is seen to be much faster than that of ZnS : Mn. This decrease in the Mn^{2+} decay constant is not expected in the doubly doped crystal since energy transfer should not alter the lifetime of the activator. It appears that a nonradiative process may be enhanced when both impurities are present. Decay constants for the Pb^{2+} emission in ZnS : Pb : Mn were too rapid for measurement. Addition of Mn^{2+} is expected to decrease the sensitizer lifetime [see Eq. (22)] but not to the extent observed. It appears that desensitization of the Pb^{2+} ion by modes other than radiative recombination or energy transfer to Mn^{2+} are important. The data for the Mn^{2+} decay as a function of pressure indicate an enhancement of nonradiative processes.

The optical transition involved in the excitation of the Mn^{2+} ion is presumed to be the $^6S \rightarrow {}^4G$ crystal band. The cascade process, i.e., absorption of photons emitted by the Pb^{2+} center, will not be efficient since the Mn^{2+} absorption is both spin and parity forbidden. The bright Mn^{2+} emission observed in the ZnS : Pb : Mn system indicates that sensitization of Mn^{2+} by Pb^{2+} does occur; excitation of the ZnS : Mn phosphor at these excitation wavelengths yielded virtually no emission at any Mn^{2+} concentration. Due to the forbidden nature of the Mn^{2+} absorption it is apparent that the dominant transfer process is by exchange. In Dexter's treatment of exchange[20] the expression for the energy transfer probability is

$$P_{SA}(\mathrm{ex}) = \frac{2\pi}{h} Z^2 \int f_S(E) f_A(E)\, dE \ . \tag{20}$$

In this equation

$$Z^2 = K^2 \exp(-2R/L) \ . \tag{21}$$

Z is an asymptotic form of an exchange integral for the sensitizer–activator pair; the exponential dependence arises from the fact that the electronic wavefunction generally declines exponentially. K has the units of energy and L is a constant termed the effective Bohr radius. The spectral overlap condition is given by the integral, where $f_S(E)$ and $f_A(E)$ are the normalized sensitizer emission band and activator absorption band, respectively.

Since the energy transfer process competes with the normal sensitizer emission, the observed lifetime of the sensitizer will be altered by the presence of the activator. A relationship has been derived which describes this effect in the case of exchange interaction.[22] The time dependence of the sensitizer decay as a function of activator concentration c may be expressed as

$$\phi(t) = \exp[-t/\tau_0 - \gamma^{-3} c/c_0\, g(e^{\gamma} t/\tau_0)] \ , \tag{22}$$

$$g(x) = 6 \sum_{m=0}^{\infty} \frac{(-x)^m}{(m+1)^4 m!} , \tag{23}$$

where $\gamma = R_0/L$, R_0 being a critical transfer distance, where for an isolated sensitizer–activator pair is the separation distance at which energy transfer occurs at the same rate as spontaneous deactivation of the sensitizer. C_0 is defined as $3/(4\pi R_0^3)$ and τ_0 is the inverse of the rate of spontaneous deactivation of the sensitizer. The short range nature of this process is evident in the exponential factor contained in Eqs. (20) and (21). It is expected that appreciable transfer by exchange will occur from the sensitizer ion to only nearest or next nearest neighbor cation sites. If it is assumed that the Pb^{2+} and Mn^{2+} ions are randomly distributed (there should be no electrostatic interactions since they replace Zn^{2+}), then the fraction of Pb^{2+} ions having as a nearest cation neighbor Mn^{2+} is[23]

$$f(c) = 1 - (1-c)^{12} \ , \tag{24}$$

where c is the mole fraction Mn^{2+} in the sample. For $c_1 = 0.0015$, $f_1(c) = 0.018$ or 1.8%; for $c_2 = 0.015$, $f_2(c) = 0.165$ or 16.5%. If one includes next nearest neighbors, the fraction of Pb^{2+} having a Mn^{2+} at a nearest neighbor or next nearest neighbor will be much higher. It is seen then that at the lower activator concentration where equally intense Pb^{2+} and Mn^{2+} bands were observed at zero pressure the impurity ions are probably closer than a random distribution would predict. It is not obvious based on simple size effects why this should occur. The ionic radius of Mn^{2+} (0.80 Å) is very similar to that of Zn^{2+} (0.74 Å), while that of Pb^{2+} (1.20 Å) is much larger. Perhaps the lattice strain introduced by the incorporation of Pb^{2+} is reduced by having a Mn^{2+} nearby. In the case of the higher Mn^{2+} concentration there is no Pb^{2+} emission. This indicates that most of the Pb^{2+} ions have a nearest or next nearest neighbor cation Mn^{2+} and that the energy transfer process is an efficient one. Dexter[20] has given a typical transfer time for exchange of 10^{-11} or 10^{-12} sec for nearest neighbors. This transfer time is much more rapid than either the sensitizer lifetime (10^{-7} sec) or nonradiative thermal transitions which also have 10^{-7} sec time scale.

It is difficult to account for the results in Fig. 8 simply in terms of Dexter's equation (20). The spectral overlap given by the integral is certainly influenced by pressure. It has already been shown that the spectral locations of the Mn^{2+} emission and the Pb^{2+} emission in the singly doped crystals are shifted with pressure. The Pb^{2+} band shifts -12.5 cm^{-1}/kbar while the Mn^{2+} emission shifts at a more rapid -25.0 cm^{-1}/kbar. Transfer is assumed to occur to the Mn^{2+} ^4G band and it is likely this band exhibits a pressure dependence much like that of the Mn^{2+} emission. Based on these data and the zero pressure spectral locations of the sensitizer and activator bands it would seem that the spectral overlap should increase as the Mn^{2+} ^4G band overtakes the Pb^{2+} emission band. The observed intensity decrease of the Pb^{2+} emission in ZnS : Pb : Mn over the 0–70 kbar range are highly supportive of this argument. The Mn^{2+} data however do not reflect any enhancement of the Mn^{2+} emission intensity. The constant Mn^{2+} intensity from 0–30 kbar followed by a decrease up to 70 kbar imply that a nonradiative process is important since both emissions are being quenched over this latter pressure range. Any energy transfer process, as observed via the Mn^{2+} data, has superimposed upon it some quenching process. The fast component of the lifetime in Fig. 9 is seen to be much shorter than the ZnS : Mn lifetime discussed previously. This is not expected since the activator lifetime should be unaffected by the presence of the sensitizer. This fact alone implies that a competitive, nonradiative process has been introduced by simultaneous incorporation of these ions into the crystal. In addition, this lifetime is seen to decrease by a factor of 3 over the pressure range.

It may be concluded from the data that the Pb^{2+} ion when introduced in ZnS : Mn does sensitize the Mn^{2+} ion and that the dominant mode of energy transfer is by exchange. The large intensity loss with pressure of the Pb^{2+} emission is not accompanied by a corresponding increase in the Mn^{2+} emission. It is apparent that a quenching process of unknown origin influences both the Pb^{2+} and Mn^{2+} emissions.

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