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

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

$$= 1900 \text{ cm}^{-1} . \qquad (15)$$

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 cm^{-1}/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 16750 cm^{-1}/655 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

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

In the region of interest for D_q/B (0.5 → 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 $E = 22.8 \times 620 = 14150$ 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 cm^{-1}/kbar or -3.07 cm^3/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]:

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

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 kbar^2/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 → 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

$$1/\tau \propto (\Delta\omega)^2 kT . \qquad (18)$$

The pressure dependence of τ is contained mainly in Δ:

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

The dependence of R on band skewness is given in Eq. (17). R remains constant (0.55) over the first 50 kbar
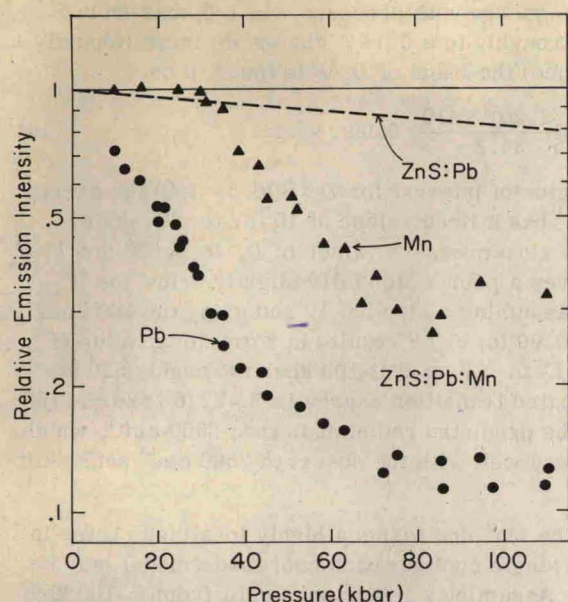
FIG. 8. Relative emission intensities versus pressure for Pb^{2+} and Mn^{2+} emissions of ZnS : Pb : Mn.

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
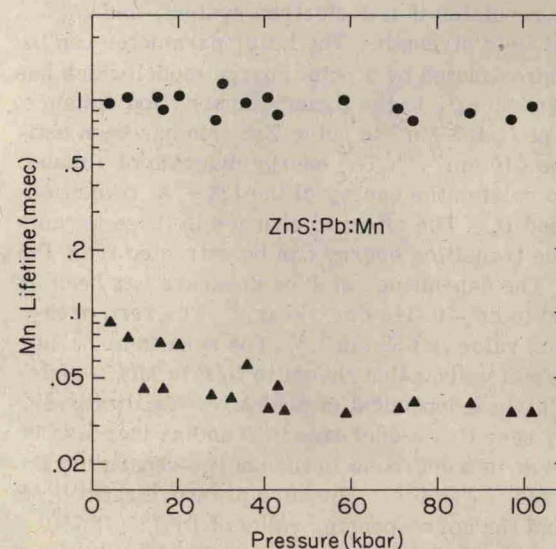

FIG. 9. Lifetimes versus pressure of the Mn^{2+} emission in ZnS : Pb : Mn.