

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 ${}^6\text{S} \rightarrow {}^4\text{G}$ 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 exchange²⁰ the expression for the energy transfer probability is

$$P_{\text{SA}}(\text{ex}) = \frac{2\pi}{h} Z^2 \int f_{\text{S}}(E) f_{\text{A}}(E) dE. \quad (20)$$

In this equation

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

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 $f_{\text{S}}(E)$ and $f_{\text{A}}(E)$ 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

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

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

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+} is²³

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

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. Dexter²⁰ 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 $-12.5 \text{ cm}^{-1}/\text{kbar}$ while the Mn^{2+} emission shifts at a more rapid $-25.0 \text{ cm}^{-1}/\text{kbar}$. Transfer is assumed to occur to the $\text{Mn}^{2+} {}^4\text{G}$ 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 $\text{Mn}^{2+} {}^4\text{G}$ 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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