defined. Experimental results of Era *et al.*[20] and the theoretical work of Hagston[21] suggest a random distribution of impurities rather than the preferential pairing offered by Prener and Williams.[15] The random distribution function has the form[21]

$$G(r) \propto r^2 \exp\left(-\tfrac{4}{3}\pi N r^3\right) , \tag{5}$$

with N, the acceptor concentration, being approximately 2×10^{18} cm^{-3}. This function serves to weigh statistically the expression for the radiative transition probability. The function $f(E_D, r)$ of Eq. (4) may be expressed[28] as

$$f(E_D, r) = \left[1 + \frac{W(E_D, r)}{g\sigma(r)}\right]^{-1} , \tag{6}$$

where g is a measure of the excitation rate (high in this case since the absorption is large and the number of active centers small) and σ is a capture cross section. As $W(E_D, r)$ becomes small the above function approaches unity. If it is assumed that the second term is small initially, then $f(E_D, r)$ is a constant. The extra r^2 in the integral of Eq. (3) arises from the variance of the pair capture cross section on r.[19] As the pressure is increased the donor level becomes more localized, and consequently the pairs contributing to the observed emission are those at the closest distances. Since the pair distances are constraints on the lattice, the observed light output (intensity) decreases. At a constant excitation rate conservation requires that a nonradiative process become important. The nonradiative processes presumably occur at lattice defects and isolated donors. As the radiative probability decreases due to a decrease in donor–acceptor overlap, the nonradiative probability will be enhanced due an increased electron-phonon coupling at the deeper donor levels. The crystal lattice vibrations provide a means of thermally dissipating the electronic energy, allowing the electron to relax nonradiatively to the valence band.

We apply these relationships first to the system ZnS : Cu : Al, where the assumptions involved are most clearly valid. Changes in r are related to the compressibility of zinc sulfide; from 0–100 kbar there is only a ~5% change in the lattice constant. Pressure, however, affords the means of varying the positions of electronic energy levels in the crystal. Changes in the binding energy of donor or acceptor levels will therefore affect both the energy and intensity of the emitted light. The effect of pressure on the ionization energies of impurity levels in semiconductors has been examined for Si, GaAs, and CdS.[22–25] In n-type CdS donor ionization energies were found to change by approximately 8×10^{-3} eV/kbar at low pressure.

The donor level (Al) in ZnS : Cu : Al is much shallower than the acceptor (Cu) level at 1 atm pressure; therefore, the parameter N in Eq. (4) is then inversely proportional to the square root of the donor binding energy E_D. Changes in the value of E_D are therefore expected to affect the radiative transition rate far more than similar changes in E_A, the acceptor binding energy. The data of Fig. 1 show that the emission maximum has a measurably smaller pressure coefficient than that of band gap. Therefore, the ionization energy of the donor

and/or acceptor must be changing with increasing pressure. Determination of the extent to which each level is affected by pressure was achieved by the following experiments: Changes in donor binding energies were estimated from thermoluminescence data.[26] Results indicated that the trap depths (presumably isolated donors) increase by approximately 4×10^{-3} eV/kbar for the samples coactivated with aluminum. This value is on the same order as that obtained for donors in n-type CdS (8×10^{-3} eV/kbar).[24]

Determination of the influence of pressure on acceptor levels in these materials was achieved through studying luminescence temperature quenching as a function of pressure. Temperature quenching in zinc sulfide phosphors is believed to occur by thermal excitation of valence electrons into acceptor levels.[13] We discuss here results for ZnS : Ag : Cl and ZnSe : Cu : Cl (Figs. 7 and 8). Similar data were obtained for ZnS : Cl(SA).

It is seen that there is a relative shift of the quenching curve to lower temperature with increasing pressure for both materials. This implies a decrease in the activation energy associated with the acceptor level. If it is assumed that this variation is linear with pressure, then using the temperature at the midpoint of the intensity versus temperature curve gives a temperature shift of approximately -1 °K/kbar. From the small temperature coefficient it would appear that a quantum-mechanical tunneling process is important if not dominant. In 50 kbar the maximum possible decrease in the acceptor binding energy is estimated to be roughly 500–600 cm^{-1}. For the calculations which follow the value of E_A the acceptor binding energy is assumed constant.

With a knowledge of the pressure dependence of E_{gap}, E_A, and the measured peak shift one can make use of Eq. (2) to estimate the pressure dependence of the donor level. Determination of the change in the radiative transition probability with pressure can be achieved by using the pressure dependence of E_D (contained in the parameter N) in Eq. (4). Physically, changes in the donor depth E_D cannot be realized through changes in the electronic effective mass or the dielectric constant of the material. The pressure dependence of the effective mass can be determined by the relation $m_c^* \sim E_g$.[27] This predicts a change from $0.34 m_e$ to $0.44 m_e$ in 100 kbar. The pressure dependence of the static dielectric constant has been measured by Samara[28] up to 10 kbar. The following equation gives this dependence;

$$\epsilon(p) = \epsilon_0 \exp(-0.00116 p) , \tag{7}$$

where $\epsilon_0 = 8$. Use of the static dielectric constant is a questionable but not unreasonable first approximation at larger E_D where the optical dielectric constant may be more appropriate.

Assuming a constant lifetime (see Fig. 3 and Table II) Eqs. (2) and (3) were used to generate the theoretical intensity curve for the ZnS : Cu : Al system of Fig. 3. The nearest neighbor distance of 3.84 Å was used as the lower limit of the integral. The 1 atm values of E_A and E_D were 1.05 and 0.15 eV, respectively. The necessary data fitting, iterations, and integrations were ac-

complished with a computer program. Although many approximations and assumptions are required for any quantitative analysis of this system; the results are consistent with the donor–acceptor pair mechanism for the broad band luminescence. To account for the observed pressure dependence of the steady state intensity, peak shift, and lifetime of this material would be difficult with a more simplified model.

For the other ZnS systems studied the assumptions of the model may be less valid. The Cl^- donor is deeper (0.25 eV) than the Al^{3+} donor while the SA and Ag^+ levels are shallower (~0.70 eV) than the Cu^+ level; hence, the validity of Eq. (4) is less certain. In addition, the observed lifetimes were seen to decrease with pressure, implying that a competing, nonradiative process may contribute significantly to the intensity loss. Nevertheless, the similar behavior of the peak shifts and intensity changes with pressure would indicate that the same luminescence mechanism basically applies. The theoretical intensity curve of Fig. 4 for ZnS:Cu:Cl was constructed, as above, neglecting the change in lifetime. Calculations were also made for ZnSe:Cu:Cl. The values of the donor and acceptor binding energies at 1 atm were 0.20 and 0.70 eV, respectively. Integration was performed from the nearest neighbor distance to infinity. Other physical parameters were the static dielectric constant $\epsilon = 8.3$, $m^* = 0.3 m_e$ and $E_{gap} = 2.8$ eV. Again, the agreement between experiment and theory is very satisfactory as seen in Fig. 5.

Since the donor–acceptor picture suggests that both the activator and coactivator are involved in the luminescence, the pressure dependence of peak location, intensity, and lifetime of the sample might be influenced by different coactivators. Thus, a series of experiments were performed involving copper (green luminescence—5200 Å)-doped zinc sulfide phosphors coactivated with several types of ions (Al^{3+}, In^{3+}, Ga^{3+}, Cl^-). The linear pressure coefficient of the peak shift (~52.5 cm^{-1}/kbar up to 40 kbar) was found to be approximately the same for all these systems. The measured relative intensities as a function of pressure are shown in Fig. 6. It is observed that the intensity of those phosphors coactivated with trivalent cations (especially Ga^{3+} and In^{3+}) drops off more rapidly than the Cl sample. Gallium and indium coactivators are known to introduce very deep donor levels in zinc sulfide, Ga^{3+} being 0.42 eV and In^{3+} 0.50 eV.[2] The work of Williams and Apple[16] has demonstrated the participation of the ground states of these levels in the long wavelength emissions of Cu^+-doped samples. The green luminescence involves excited states of these deep levels in contrast to the shallow levels like Al^{3+} where only the ground state need be involved.

The deepening of In^{3+} level was observed experimentally. The long wavelength emission (6325 Å) due to transitions from the ground state of the indium to the copper level was found to be insensitive to pressure.

Since we have demonstrated that the Cu^+ level is relatively immobile with respect to the valence band, this indicates that the conduction band edge shifts away from the indium ground state level. The increase in the ionization energies of In^{3+} and Ga^{3+} levels would provide an efficient nonradiative path for de-excitation of the crystal. For ZnS:Cu:In the lifetime was virtually independent of pressure at a value of ~20 msec. As in the case of the ZnS:Cu:Al system the large decrease in intensity and the accompanying constant lifetime imply both a change in the radiative and nonradiative rate processes in the crystal.

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