High pressure studies of interimpurity (donor–acceptor) luminescence in ZnS and ZnSe phosphors[a]

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The effect of pressure has been measured on the emission peak location, half-width, integrated intensity, and lifetime for a series of ZnS phosphors doped with Cu^+ or Ag^+ with Cl^-, Al^{3+}, In^{3+}, or Ga^{3+} as coactivator, as well as on self-activated (SA) ZnS and on ZnSe:Cu:Cl. The emission peaks shift to higher energy with increasing pressure, but less strongly than does the absorption edge of the host. The peak intensities decrease rapidly with increasing pressure. The intensity changes could be accounted for quantitatively in terms of the donor–acceptor pair model. The shift of the luminescence peak with respect to the absorption edge is attributed to the pressure coefficient of the donor binding energy E_D. The observed intensity changes with pressure could be related directly to changes in E_D.

INTRODUCTION

High pressure studies have been made on a series of ZnS phosphors doped with Cu^+ or Ag^+ with Cl^-, Al^+, Ga^{3+}, and In^{3+} as coactivators. Studies were also made on self-activated ZnS : Cl and on ZnSe : Cu : Cl. The starting material was luminescent grade powder obtained from Research Organic/Inorganic Corp. The methods of sample preparation follow those of Clieren and van Gool[1] and Hoogenstraaten.[2] Although the firing temperatures were below the cubic–hexagonal transformation temperature, there were traces of the wurtzite phase in the materials as prepared. X-ray analysis showed that the material converted irreversibly to the cubic phase by 2 kbar.

The measurements included emission peak location and half-width, integrated intensity, and lifetimes. The high pressure luminescence techniques, pressure calibration, and methods of data treatment have been presented elsewhere.[3] Some data were obtained as a function of temperature at various pressures using a technique developed by Tyner.[4] The lifetime measurements were made on the apparatus developed by Klick.[5] Most of the data were taken in the quasihydrostatic cell using NaCl as a pressure transmitting medium. The changes obtained were reversible. In addition, runs were made to 12 kbar in a cell using hexane as a medium. These results agreed with those obtained in the quasihydrostatic cell over the same pressure range.

Initial investigations of the pressure effect on the emission bands in ZnS phosphors were carried out by Ortman and Treptow.[6] Pressures of 6 kbar were attained. More recent studies by Koda and colleagues[7] have extended this range to 40 kbar. In both of these investigations the spectral location as a function of pressure was determined. The shift of the fundamental absorption edge of ZnS as a function of pressure has not been established on thin crystals by modern techniques over a large range of pressures. Early experiments on thick crystals using a pressure calibration which is now outdated gave a value of approximately $6-6.5 \times 10^{-3}$ eV/

kbar for ZnS with the shifts for ZnSe and ZnTe some 10%–20% greater in magnitude. Recent calculations by Cohen[8] give for ZnSe a shift of the direct gap of 11×10^{-3} eV/kbar, which agrees closely with the experimental value.[9] Very recent experiments by Weinstein[10] on ZnTe give for the absorption edge

$$E = 2.55 + 0.0115p - 5 \times 10^{-5}p^2 , \qquad (1)$$

where E is in eV and p in kbar. Thus, ZnSe and ZnTe agree closely in the linear terms. A reasonable estimate of ZnS would then be $9-10 \times 10^{-3}$ eV/kbar. Over the range of 1.7 kbar Piper *et al.*[11] obtain experimentally 9×10^{-3} eV/kbar. For the calculations in this work we use the value of 9×10^{-3} eV/kbar for ZnS. An error of up to 10% in this value would result in changes well within the limits of accuracy of some of the other parameters used in the analysis.

There have been a variety of treatments of ZnS phosphors containing these dopants,[12–16] each of which accounts for some aspects of the behavior of these complex phosphors. We have used here the interimpurity or donor–acceptor model first proposed by Prener and Williams.[15] The necessary features are presented in the discussion.

RESULTS

Smoothed experimental data for peak location, half-width, and relative intensity appear in Table I and lifetime data in Table II. We outline the major features exhibited by these measurements in this section, presenting figures only to illustrate specific points or where they are compared with theory later in the paper.

Peak location and half-width

In general, the luminescent peak shifts to higher energy with increasing pressure, but not so rapidly as the absorption edge. This is illustrated in Fig. 1 for ZnS : Cu : Al and in Fig. 2 for ZnSe : Cu : Cl. The results for the other dopants are qualitatively similar except that the shift for the self-activated material is somewhat larger than the others. This is possibly due to the vacancies introduced in preparing self-activated ZnS.

The half-widths either were constant with pressure or

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TABLE I. Measured parameters versus pressure for ZnS and ZnSe phosphors Pressure (kbar).

Compound	0	5	10	15	20	30	40	50	60	70	80
ZnS:Cu:Cl											
$h\nu_e$	18.50	18.75	19.02	19.30	19.60	20.13	20.62	21.04	21.40	21.70	21.94
$\delta E_{1/2}$	3.10	3.085	3.00	3.00	3.00	3.00	3.00	...	...	...	...
I	1.00	0.89	0.73	0.60	0.49	0.29	0.18	0.11	0.073	0.048	0.031
ZnS(SA)Cl											
$h\nu$	21.30	21.70	22.12	22.52	22.41	23.62	23.97	24.26	24.50	24.73	24.93
$\delta E_{1/2}$	3.78	3.73	3.68	3.63	3.60	3.53	3.52	...	...	...	...
I	1.00	0.78	0.66	0.59	0.50	0.34	0.22	0.14	0.078	0.036	0.014
ZnS:Ag:Cl											
$h\nu$	21.50	21.82	22.08	22.38	22.90	23.14	23.60	24.02	24.40	24.74	25.06
$\delta E_{1/2}$	3.10	3.06	3.02	2.98	2.94	2.86	2.78	2.70	2.62	2.50	2.46
I	1.00	0.94	0.92	0.89	0.81	0.64	0.45	0.27	0.14	0.06	0.024
ZnSe:Cu:Al											
$h\nu$	18.50	18.78	19.05	19.39	19.60	20.13	20.13	20.60	21.00	21.34	...
$\delta E_{1/2}$	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	...	...
I	1.00	0.90	0.77	0.64	0.51	0.30	0.17	0.094	0.048	...	...
ZnS:Cu:In											
$h\nu$	18.50	18.72	19.06	19.51[a]	20.16[b]						
$\delta E_{1/2}$	3.10	3.10	3.10	3.10[a]	3.10[b]						
I	1.00	0.60	0.33	0.13[a]	0.042[b]						
ZnS:Cu:Ga											
$h\nu$	18.50	18.68	18.81	19.27[a]	19.91[b]						
$\delta E_{1/2}$	3.40	3.40	3.40	3.40[a]	3.40[b]						
I	1.00	0.74	0.31	0.16[a]	0.047[b]						

$h\nu$ = peak location (10^3 cm^{-1}); $\delta E_{1/2}$ = half-width (10^3 cm^{-1}); I = intensity relative to one atmosphere at room temperature.

[a]16 kbar.   [b]24 kilobars.

decreased. The decrease is especially noticeable for ZnS : Ag : Cl and ZnS(SA)Cl (see Table I).

Intensities

The intensity of the emission peak decreases drastically with increasing pressure, in some cases by almost two orders of magnitude in 80 kbar. Figures 3–5 illustrate these results for ZnS : Cu : Al, ZnS : Cu : Cl, and ZnSe : Cu : Cl, respectively. The solid curves la-

TABLE II. Lifetime versus pressure for several of the donor-acceptor type ZnS phosphors.[a]

	Cu:Cl		Cu:Al		Cu:In	SA	
P	τ_1	τ_2	τ_1	τ_2	τ	τ_1	τ_2
0	32	300	11	109	23	6	50
8	17	185	11	110	22	4.8	41
16	11	98	12	110	21	4.2	36
24	9.7	85	11	105	19	...	...
28	...	...	...	...	...	3.1	37
32	5.3	110	11	110	19	...	...
40	4.1	57	10	102	18	2.6	...

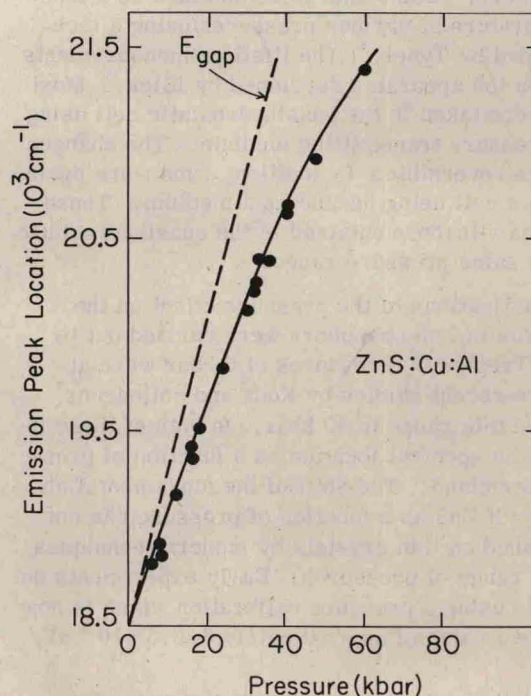[a]All components fit to exponential functions. Time constant τ in msec.

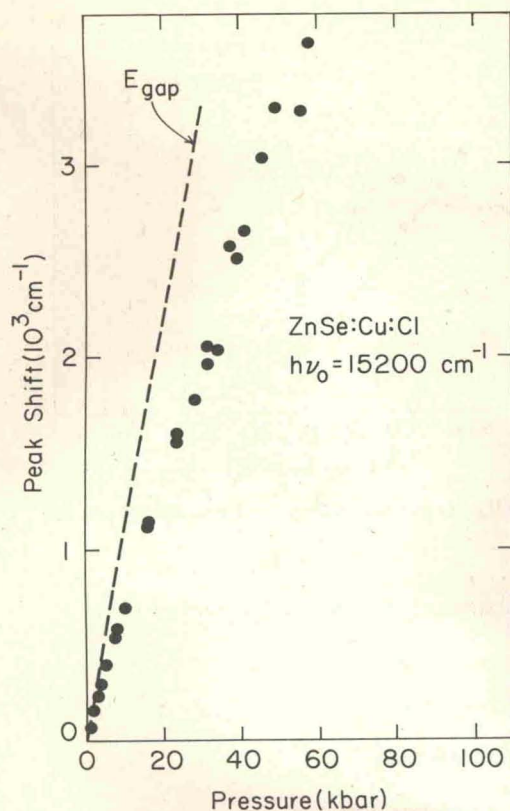FIG. 1. Emission peak location versus pressure for ZnS : Cu : Al.

FIG. 2. Emission peak shift versus pressure for ZnSe : Cu : Cl.

FIG. 4. Calculated and measured emission peak intensity versus pressure for ZnS : Cu : Cl.

beled "Theory" are discussed in the latter part of the paper. The rate of decrease in intensity depends on the coactivator, particularly for the series of coactivators Al^{3+}, In^{3+}, Ga^{3+} as illustrated in Fig. 6.
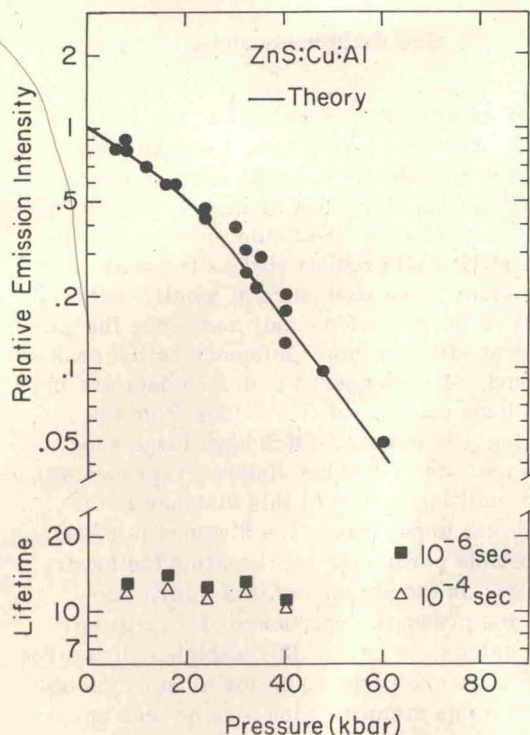
Intensities were measured as a function of temperature at different pressures for several compounds. The results are illustrated in Figs. 7 and 8 for ZnS : Ag : Cl and ZnSe : Cu : Cl, respectively. The effect of pressure on the temperature coefficient is small, a fact which enters into our discussion below.

Lifetimes

The intensity was measured as a function of time at different pressures for four ZnS phosphors. The time dependence is complex. The curves (except for ZnS : Cu : In) were fit with two exponentials. The lifetimes τ_1 and τ_2 are listed in Table II. The use of two
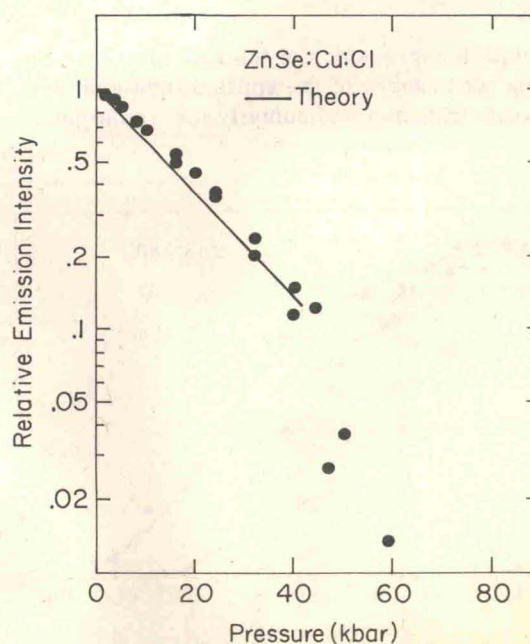
FIG. 3. Relative emission intensity and observed lifetime versus pressure for ZnS : Cu : Al.

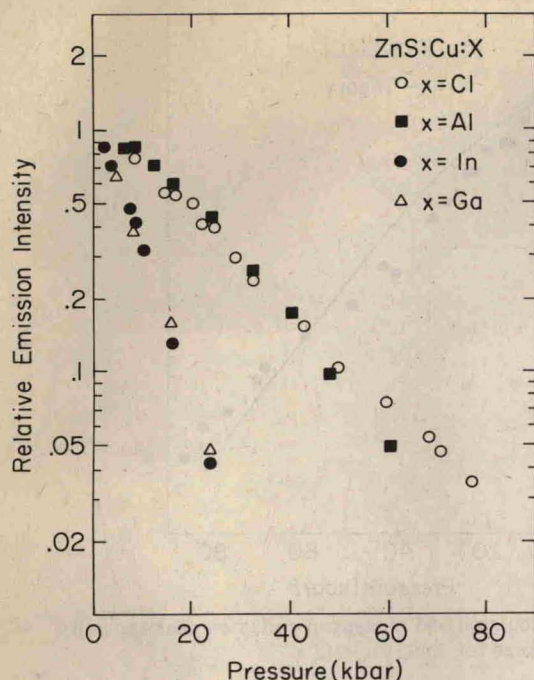FIG. 5. Relative emission intensity versus pressure for ZnSe : Cu : Cl.

FIG. 6. Relative emission intensity versus pressure for a Cu$^+$-doped ZnS with different coactivators.

exponentials is regarded as a convenient approximate way of describing the data. No doubt the actual process is more complex.[17,18] For ZnS : Cu : Al both τ_1 and τ_2 were independent of pressure (see also Fig. 3). For the other materials there was a distinct decrease in both time constants with increasing pressure. The analysis we use below implies that the lifetime should not be pressure dependent, so it is a better approximation for ZnS : Cu : Al than for the other systems, although it would appear to describe their behavior satisfactorily also.

DISCUSSION

The quantitative expressions of interest are those relating the observed energy of the emitted light and the intensity of that light to experimentally accessible quanti-
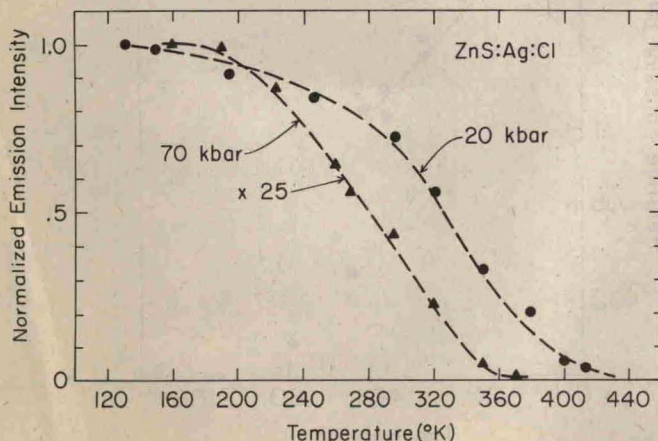

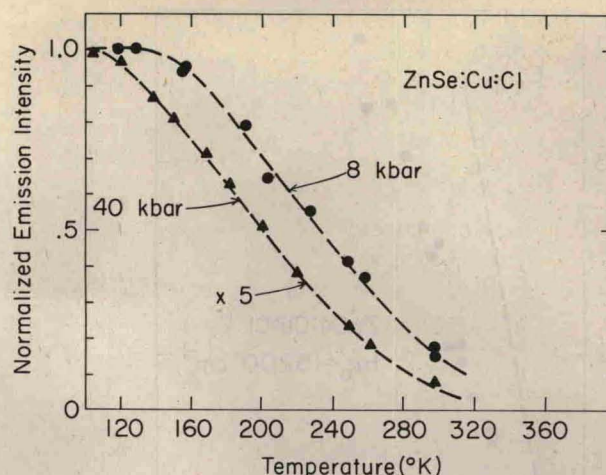
FIG. 7. Intensity versus temperature for two pressures for ZnS : Ag : Cl.

FIG. 8. Intensity versus temperature at two pressures for ZnSe : Cu : Cl.

ties. These expressions are for the energy of the emitted light[2]

$$E(r) = h\nu = E_{gap} - (E_A + E_D) + \frac{e^2}{\epsilon r} \tag{2}$$

and for the total intensity

$$I(r) \propto \frac{1}{\tau} \int r^2 W(r) G(r) F(r) \, dr , \tag{3}$$

where $W(r)$, the radiative recombination rate, is given by

$$W(r) = \text{const} x (r/a^*)^{2(N-1)} \exp(-2r/Na^*) . \tag{4}$$

Here

$$N = \left(\frac{E^*}{E_D}\right)^{1/2} , \quad E^* = \frac{e^2}{2a^*\epsilon} , \quad a^* = \frac{h^2\epsilon}{m^*e^2} .$$

m^* is the effective electronic mass and ϵ is the dielectric constant.

The form of the transition probability [Eq. (4)] by Thomas et al.[19] becomes a poorer approximation at larger E_D. If one considers pairs at large r (e.g., emitting pairs separated by 20 Å or more), use of Eq. (2) is straightforward since the Coulomb term may be neglected. Equation (4) predicts that as the shallower level becomes more localized pairs at small r will contribute mainly to the emission band, and hence the pair interaction term will have more influence on the peak energy of the band. The measured emission data are in the form of a band made up of transitions from the closest emitting pair to pairs which have large separations. It is uncertain as to what distance represents that of the closest emitting pair or if this distance is the same for different impurities. The distance is essentially an adjustable parameter representing the lower limit in Eq. (3). In the absence of this information estimation of the pressure dependence of E_D will be simplified by using $r \to \infty$ in Eq. (2); at higher pressures where closer pairs are responsible for most of the observed emission this simplification may be less appropriate.

To make use of Eq. (3) a distribution function must be

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]

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

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

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

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 $(8 \times 10^{-3}$ 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;

$$\epsilon(p) = \epsilon_0 \exp(-0.00116 p) , \qquad (7)$$

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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