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.
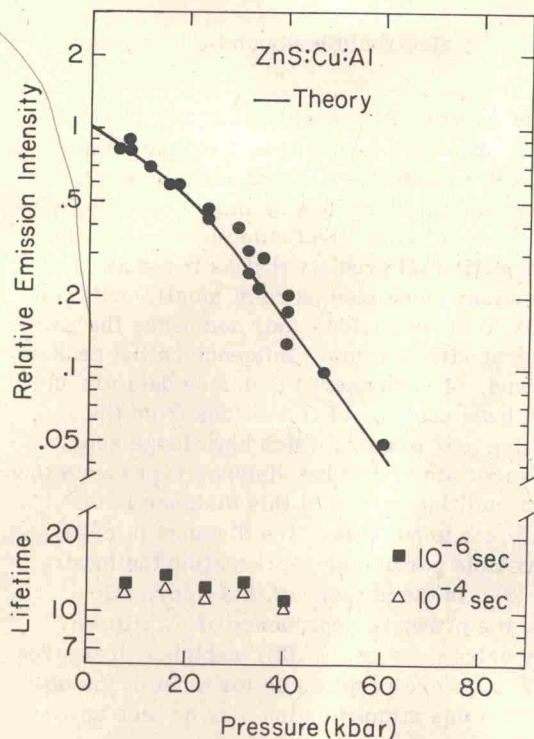
Intensities were measured as a function of temperature at different pressures for several compounds. The results are illustrated in Figs. 7 and 8 for ZnS : Ag : Cl and ZnSe : Cu : Cl, respectively. The effect of pressure on the temperature coefficient is small, a fact which enters into our discussion 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.
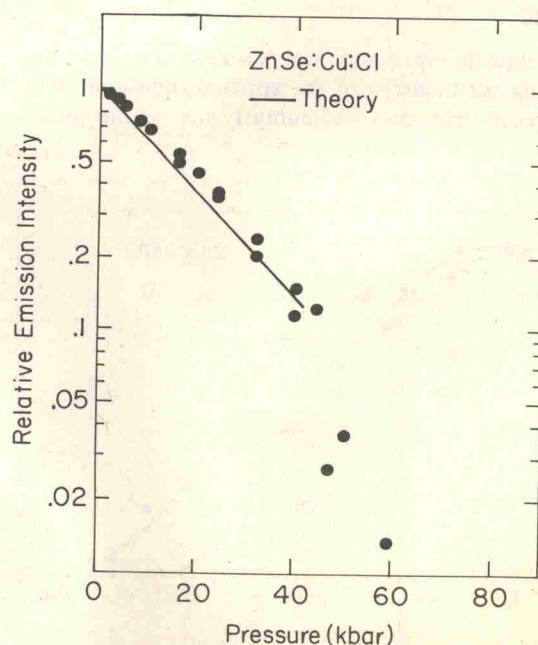

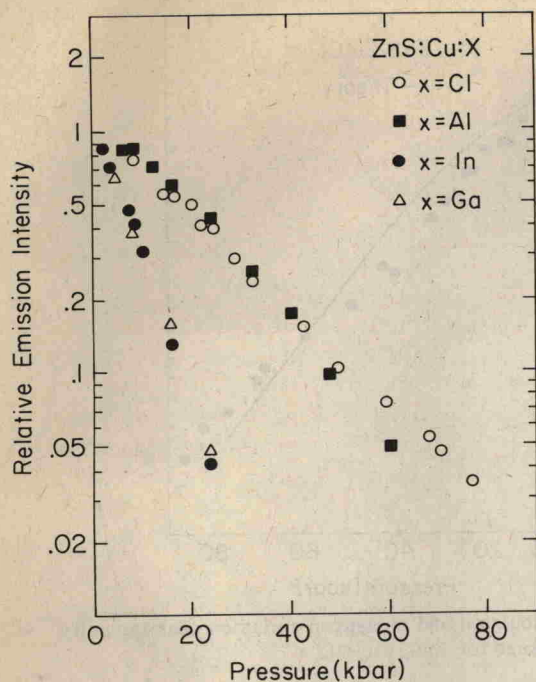FIG. 5. Relative emission intensity versus pressure for ZnSe : Cu : Cl.

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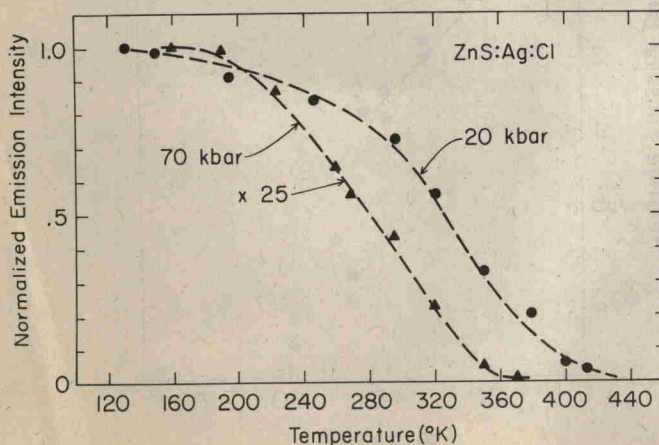
FIG. 7. Intensity versus temperature for two pressures for ZnS:Ag:Cl.

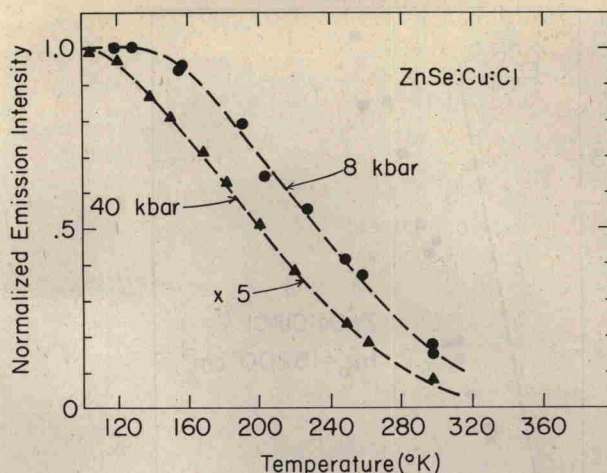FIG. 8. Intensity versus temperature at two pressures for ZnSe:Cu:Cl.

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

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

and for the total intensity

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

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

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

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