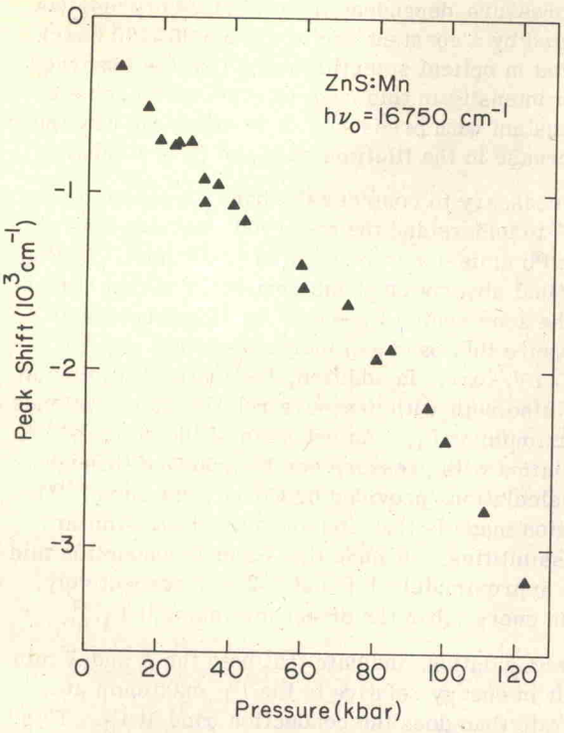

FIG. 3. Emission peak shift versus pressure for ZnS : Mn.

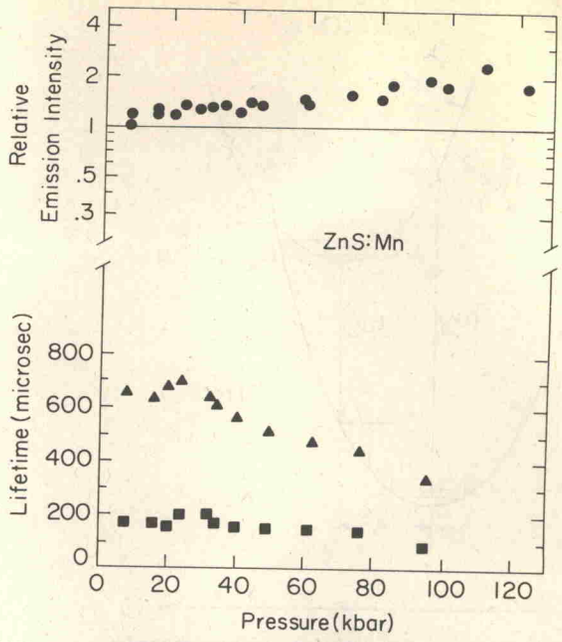

FIG. 5. Relative emission intensity and lifetime versus pressure for ZnS : Mn.

derstood in terms of a single configuration coordinate analysis.[2-4] Pressure-induced changes in the emission peak location and half-width are used to determine parameters characteristic of the model. These parameters provide the basis necessary to understand the other experimental results.

The fits of the data for ZnS : Pb [Fig. 1, and Eqs. (1) and (2)] related the emission peak shift and half-width change to the pressure variable. We use the equations

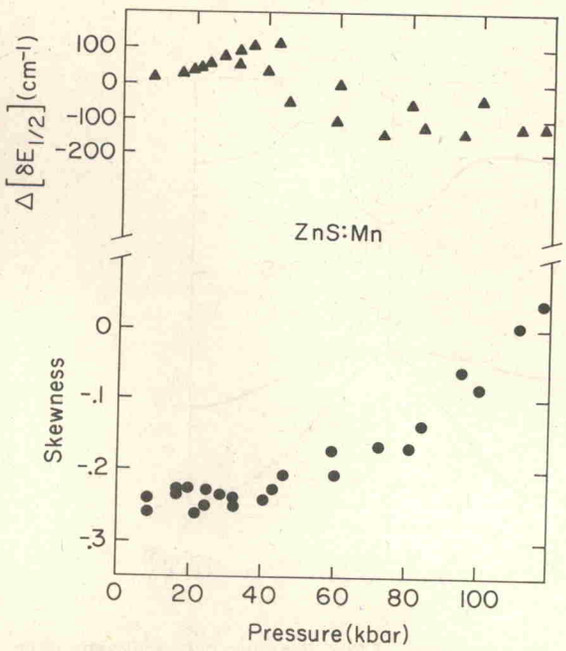

FIG. 4. Emission half-width change and skewness versus pressure for ZnS : Mn $(\delta E_{1/2})_0 = 2200$ cm^{-1}.

of Refs. 2–4. If one assumes that ω^2, the ground state force constant, is independent of pressure, these expressions are for the emission peak shift

$$\Delta(h\nu_e) = \frac{p\Delta_0}{R} + \frac{(R-1)p^2}{2R^2\omega^2} , \tag{3}$$

and for the emission band half-width

$$(\delta E_{1/2})_e = N\left|\frac{\omega\Delta_0}{R^{1/2}} + \frac{p(R-1)}{\omega R^{3/2}}\right| , \tag{4}$$

where Δ_0 is the value of Δ (the relative displacement of the potential wells along the configuration coordinate of interest) at zero pressure, $R = (\omega'/\omega)$ is the ratio of force constants for the potential wells, and N is a normalization factor (32 cm^{-1} at 25 °C). The other parameters we define in Fig. 6. These equations contain the same pressure dependences as the observed data and, by equating like powers of p in Eqs. (3) and (4), one can make use of the numeric coefficients of Eqs. (1) and (2) to calculate ω^2, R, and Δ_0. These quantities were found to be

$$\omega^2 = 2.17 \text{ kbar}^2/\text{cm}^{-1} , \tag{5}$$

$$R = 1.44 , \tag{6}$$

$$\Delta_0 = -2.55 \text{ cm}^3/\text{mole} . \tag{7}$$

The observed steady state intensity change with pressure was seen to depend on the excitation wavelength (Fig. 2). This intensity was essentially independent of pressure when excitation was achieved by direct excitation of the Pb^{2+} ion; host lattice excitation showed a rapid decrease in intensity at pressures above 80 kbar. It is possible to understand the insensitivity of the intensity to pressure in the former case by considering the analysis below. One solves the configuration coordinate equations for the quantity of importance, the quenching energy E_q, which is the energy measured

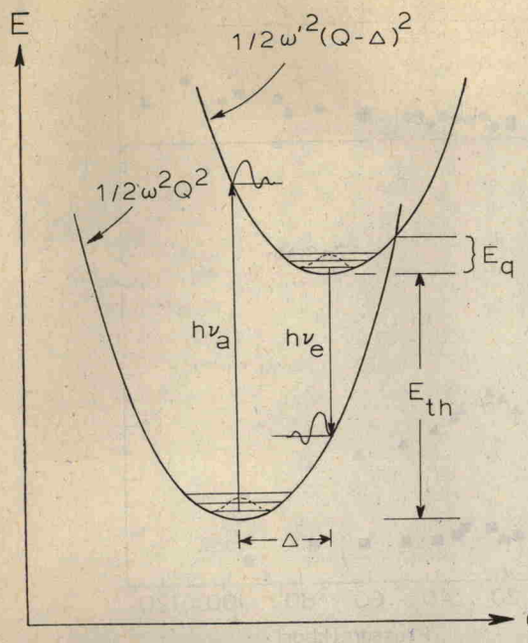

FIG. 6. Schematic configuration coordinate diagram.

from the lowest vibrational level of the excited state to the point of intersection of the potential wells (see Fig. 6). This energy represents the classical energy necessary for an electron to surmount the potential E_q and crossover nonradiatively to the ground state well. The probability n_q of this occurrence is generally expresed in the following fashion:

$$n_q \propto e^{-E_q/kT} , \tag{8}$$

where $kT \cong 200$ cm^{-1} at room temperature. Using the value of Q obtained above one can then use the following relations, assuming $R = 1$ (linear coupling with $\Delta = \Delta_0$), to obtain a relationship for the pressure dependence of the quenching energy:

$$h\nu_e = h\nu_{e0} + p\Delta = E_0 + p\Delta - \tfrac{1}{2}\omega^2\Delta^2 , \tag{9}$$

$$E_q = \tfrac{1}{2}\omega'^2(Q_q - \Delta)^2 . \tag{10}$$

The resulting expression is

$$E_q = \frac{1}{2\omega^2\Delta^2}(h\nu_{e0} + p\Delta)^2 . \tag{11}$$

Although this equation is strictly valid for linear coupling, the previously determined configuration coordinate parameters, based on $R \neq 1$, will not introduce much error in the argument. Using values of $h\nu_{e0}$ of 20 000 cm^{-1}, $\Delta = -2.55$ cm^3/mole and ω^2 of 2.17 kbar^2/cm^{-1}, one obtains a value of roughly 10 000 cm^{-1} for E_q at 1 atm. This value compares favorably with the 12 000 cm^{-1} value obtained by Mita[10] for the ZnS : Pb yellow emission. Hence, at room temperature and atmospheric pressure there is a very low probability of classically surmounting E_q. It is known that there is little temperature quenching of this phosphor below 100 °C.[10] At 100 kbar the quantity $(h\nu_{e0} + p\Delta)^2$ is reduced by only 20% or $E_q = 8000$ cm^{-1}, hence, the effect of pressure on the quenching energy is slight over the range of pressures studied. It is seen then that in the absence of any competing, pressure-dependent, nonradiative process (as is indicated by a constant lifetime from 30–120 kbar) or changes in optical selection rules that the observed emission intensity in this case is expected to remain fairly constant with pressure. It is uncertain why there is an increase in the lifetime over the first 30 kbar.

It is necessary to consider the band structure diagram of Fig. 7 to understand the observed intensity loss of the ZnS : Pb emission when excited in the host. In Fig. 7 the optical absorption of interest is the direct transition at the zone center $\Gamma_{15} \rightarrow \Gamma_1$. As stated before at low pressure this band gap increases at the rate of 9.0×10^{-3} eV/kbar. In addition, the indirect minima at L and X also shift with pressure relative to the valence band maximum at Γ_{15}. An estimate of the shifts of these minima with pressure can be achieved through use of calculations provided by Cohen[11] for ZnSe. The assumption made is that Zns and ZnSe have similar compressibilities. In ZnSe the X and L conduction minima are approximately 1.9 and 1.2 eV, respectively, higher in energy than the direct minimum at Γ_1.[12]

Cohen's calculations indicate that both the L and X minima shift in energy relative to the Γ_{15} maximum at a slower rate than does the conduction band at Γ_1. This effect has been experimentally observed in many of the III–V semiconductors.[13] The calculations for ZnSe show that the X minimum shifts much more slowly to higher energy than does the L minimum. The shift of the various minima up to a 0.30 Å change in lattice constant a are nearly linear. The shift of these minima relative to the Γ_{15} valence band are

$$\frac{dE_{\Gamma_1}}{da} = 3.62 \text{ eV/Å} , \tag{12}$$

$$\frac{dE_X}{da} = 1.31 \text{ eV/Å} , \tag{13}$$

$$\frac{dE_L}{da} = 2.94 \text{ eV/Å} . \tag{14}$$

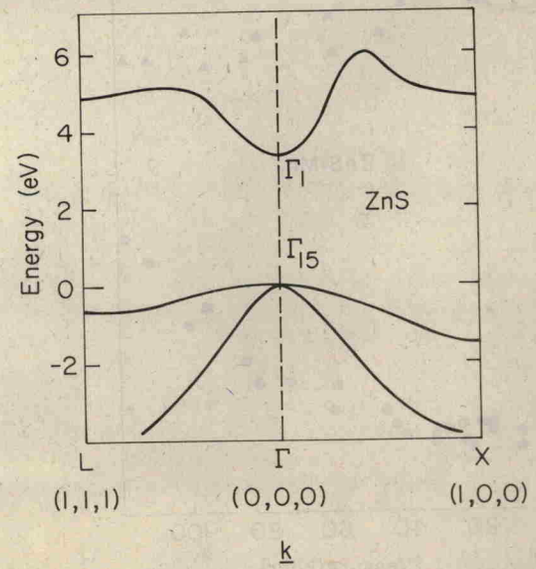

FIG. 7. Band structure of ZnS along two principal symmetry directions.