

order of experimental error) and of opposite sign to that observed in fluorescence. The phenomenon must thus be due to the centers themselves.

The fact that natural light produces polarized emission shows that the elementary oscillators cannot be randomly oriented.<sup>1</sup> Following the dipole theory as applied to the fluorescence in alkali halides<sup>2-4</sup> and diamond,<sup>5</sup> we can try to represent the centers as an array of oscillators all aligned along some direction in the crystal. The polarization depends then upon the elements of a polarizability tensor. It can be shown quite generally that such a model cannot account for the observed results.

We can also discard the possibility of the dipoles being oriented along the 12 equivalent directions in the wurtzite lattice. Such an array of dipoles would give rise to a nonvanishing mean square dipole moment only along the  $c$  axis and hence would lead to preferential polarization along  $c$ . A similar result is obtained in case of centers having the  $c$  axis as one of the principal axes of their polarizability tensor (common  $\alpha_{zz}$  components) but randomly oriented principal axes in the  $x$ - $y$  plane. None of these models can be salvaged by assuming that the exciting radiation is subject to a dichroic absorption by the lattice.

It is possible that experimental results can be accounted for by the introduction of separate absorption and emission oscillators, such as have been postulated by Feofilov<sup>2</sup> and others,<sup>1-6</sup> in order to explain the dispersion of  $p$ . Nevertheless, for a fixed excitation wavelength anisotropic (in particular linear) oscillators are sufficient to explain the results in the halides. The centers in ZnS and CdS must therefore have essentially different features. Our results are qualitatively very similar to those obtained by Dutton<sup>7</sup> on the polarization of edge luminescence in CdS. We have also observed that the green electroluminescence (involving band to band recombination<sup>8</sup>) of CdS crystals is polarized preferentially perpendicular to  $c$ . Values of  $p$  up to -0.3 have been measured although the instability of emission makes it very difficult. As shown by Birman in the accompanying Letter,<sup>9</sup> the polarization in all these cases is consistent with the Lambe-Klick model of luminescence.

More detailed work on the effect of crystal structure, crystal disorder, and type and level of doping on the polarization of fluorescence is under way. It is becoming evident that it may

provide fundamental information on the nature of luminescent centers and processes.

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<sup>9</sup>J. L. Birman, following Letter [*Phys. Rev. Lett.* **2**, 157 (1959)].

#### POLARIZATION OF FLUORESCENCE IN CdS AND ZnS SINGLE CRYSTALS

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The polarization of the fluorescence at 6200Å in CdS and at 4500Å and 5800Å in ZnS is reported in the accompanying Letter,<sup>1</sup> along with the failure of various simple dipole theories to account for these results. Since a dipole-type model was able to account for color centers in the halides, and the localized centers in diamond, it was indicated that the CdS and ZnS centers in question may be of an essentially different type.<sup>1</sup> We shall suggest that the 6200Å emission in CdS, and probably the 4500Å in ZnS, be interpreted on the basis of the Lambe-Klick model<sup>2</sup> and shall make certain predictions based on this explanation which, if verified, will substantiate the interpretation. The 5800Å Mn emission in ZnS apparently requires a more complex interpretation, which is not surprising in view of the complexity of the ground and excited states of  $Mn^{++}$ .

In Fig. 1 we show valence and conduction bands for zinc blende (ZB) and wurtzite (W) structures

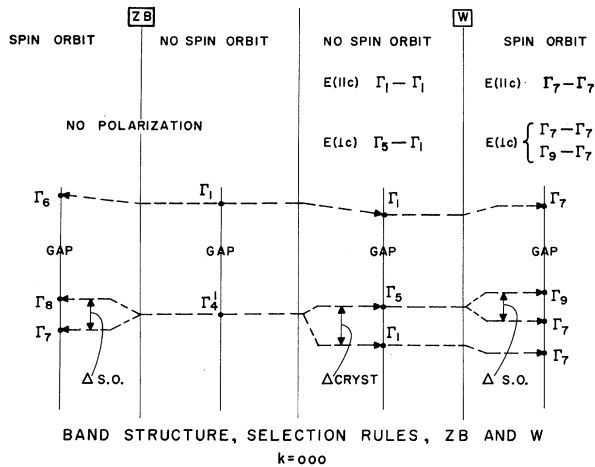


FIG. 1. Band structure and selection rules for ZB and W structures. Crystal splittings and spin-orbit splittings are indicated schematically. Transitions which are allowed for various polarizations of photon electric vector with respect to crystal "c" axis are indicated.

at  $\vec{k} = (000)$ . We have indicated "crystal" and spin-orbit splittings, and the parentage of various states in terms of the familiar ZB levels.<sup>3</sup> Bands are shown in a normal order, and various "electric dipole" selection rules are indicated.<sup>4</sup> The relative magnitudes of crystal and spin-orbit splittings are unknown for ZnS and CdS but one expects  $\Delta_c > \Delta_{s.o.}$ . In general, the more ideal is the W structure the smaller we expect  $\Delta_c$  to be<sup>5</sup> (hence smaller in ZnS than in CdS), while the  $\Delta_{s.o.}$  should depend primarily on the anion and hence be about the same for ZnS and CdS. In Fig. 2 we show the Lambe-Klick model of fluorescence in the sulfides, indicating the appropriate complexity of valence band structure. We shall assume that  $\Delta_c > \Delta_{s.o.}$  in W and shall neglect the lower  $\Gamma_7$  band. Hence to account for the 6200Å CdS emission we assume that (a) the incident radiation creates electrons and holes, (b) the latter reach equilibrium between bands  $\Gamma_9$  and  $\Gamma_7$ , (c) then the bound electron at the center and free hole recombine, and (d) radiation  $\nu_3 + \nu_4$  is emitted. It is assumed that the bound electron is in a state whose wave function has symmetry  $\Gamma_7$  (or close enough to it) so that selection rules for edge emission and luminescence are the same. The fluorescence is polarized, and the degree of its polarization is temperature dependent, as was already shown by Hopfield<sup>6</sup> for the edge emission, following the law

$$I_{\perp}/I_{\parallel} = a \exp(\Delta_{s.o.}/kT) + b, \quad (1)$$

where  $a$  and  $b$  are ratios involving matrix elements and effective masses. The explanation of

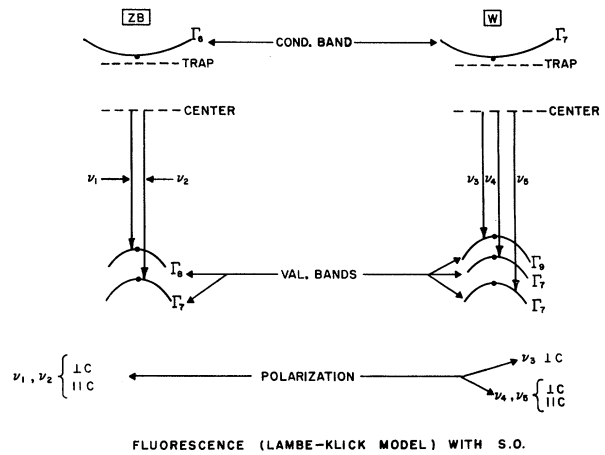


FIG. 2. Lambe-Klick model of fluorescence in ZB and W structures (schematic). The bands are labelled including spin-orbit and, in W, crystal splittings. Polarization rules follow assuming the "center" state has essentially the conduction band symmetry (edge emission is assumed to involve transitions from the shallow "trap" state to the valence band). Valence band maxima are probably not exactly at  $k = (000)$  since both structures do not have inversion symmetry, but are so indicated for purposes of simplicity.

edge emission in CdS is substantially the same as the preceding, although the initial state is, in this case, a shallow trap rather than a deep center.<sup>6</sup> Hence the model leads us to make the following predictions:

- (1) Polarization of both edge emission and 6200Å fluorescence in CdS should obey Eq. (1).
- (2) Excitation spectrum of 6200Å emission in CdS using polarized light should be identical to that of edge emission.<sup>7</sup>
- (3) The 6200Å emission, like edge emission, should be polarized independently of polarization of exciting radiation (this is observed<sup>1</sup>).
- (4) The 6200Å emission can be resolved into two bands, one totally polarized ( $\nu_3$ ) and the other not polarized.

We believe that (1) and (2) above are true tests of the model.

The 4500Å ZnS emission might be accounted for on substantially the same (Lambe-Klick) model but with additional complexity due to crystal disorder (faulting) and mixed (ZB+W) crystals. The admixture of cubic (ZB) with hexagonal (W) regions in the "single" crystals would result in regions in which the emission was governed by selection rules appropriate to ZB (Fig. 2, left-hand side), i.e., was unpolarized, as well as regions where the emission was polarized (Fig. 2, right-hand side). The depolarization of 4500Å emission in ZnS would be a sensitive func-

tion of crystal disorder and it would be necessary to obtain a homogeneous hexagonal (*W*) single crystal of ZnS to test whether the Lambe-Klick model is appropriate for ZnS edge and 4500A luminescence.

The interpretation of the 5800A Mn emission in ZnS is probably of a different nature. We expect the analysis to require an understanding of the effect of uniaxial field (caused by both pure *W* and [111] faulted *W* or *ZB*) upon the ground and excited states of the  $Mn^{++}$  center, which is commonly believed to be a tightly bound center,<sup>8</sup> not involving conduction or valence band transitions in emission. Such a model is beyond the scope of this note.

This work is continuing.

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<sup>3</sup>R. H. Parmenter, Phys. Rev. **100**, 573 (1955).

<sup>4</sup>G. Dresselhaus, Phys. Rev. **100**, 580 (1955); Phys. Rev. **105**, 135 (1957). The latter paper contains a number of errors which have been corrected in Figs. 1 and 2.

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## COLLECTIVE DESCRIPTION OF ELECTRON INTERACTIONS WITHOUT SUBSIDIARY CONDITIONS

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The Bohm-Pines collective description<sup>1</sup> uses an extended Hamiltonian involving extra degrees of freedom and associated subsidiary conditions which are not easily satisfied in practical calculations. In this Letter a different approach<sup>2</sup> is used to obtain (1) similar results without in-

troducing additional degrees of freedom, and (2) the Bohm-Pines extended Hamiltonian with additional degrees of freedom but without requiring subsidiary conditions.

The basic Hamiltonian for a system of electrons in a uniform background of positive charge is<sup>1</sup>

$$H = \sum_i (p_i^2/2m) + \frac{1}{2} \sum_{\mathbf{k} \neq 0} (\rho_{\mathbf{k}} \rho_{\mathbf{k}}^* - n) v_{\mathbf{k}}, \quad (1)$$

where  $\rho_{\mathbf{k}} = \sum_i \exp(-i\mathbf{k} \cdot \mathbf{r}_i)$ ,  $n$  is the number of electrons in the system, taken to be of unit volume, and  $v_{\mathbf{k}} = 4\pi^2/k^2$ .

We now define

$$\sigma_{\mathbf{k}} = i \sum_i (e^{i\mathbf{k} \cdot \mathbf{r}_i/2} \mathbf{k} \cdot \mathbf{p}_i e^{i\mathbf{k} \cdot \mathbf{r}_i/2}) / nk^2, \quad (2)$$

and assume the validity of the following approximate relations:

$$[\rho_{\mathbf{k}}, \sigma_{\mathbf{k}'}] \approx i\hbar \delta_{\mathbf{k}\mathbf{k}'}, \quad k < k_c \quad (3a)$$

$$[\sum_i p_i^2, \sigma_{\mathbf{k}}] \approx 0, \quad k < k_c \quad (3b)$$

where  $k_c$  is an arbitrary cutoff parameter. Equation (3a) is valid in the random phase approximation; Eq. (3b) is valid to the lowest order in the electron-plasmon coupling constant. These assumptions simplify the presentation of our general method, but are not essential.

From the relations (3) we obtain the equations of motion for the plasmon creation and annihilation operators:

$$[H, (\rho_{\mathbf{k}} + i\omega_p \sigma_{\mathbf{k}}^*/v_k)] = \hbar\omega_p (\rho_{\mathbf{k}} + i\omega_p \sigma_{\mathbf{k}}^*/v_k), \quad (4a)$$

$$[H, (\rho_{\mathbf{k}}^* - i\omega_p \sigma_{\mathbf{k}}/v_k)] = -\hbar\omega_p (\rho_{\mathbf{k}}^* - i\omega_p \sigma_{\mathbf{k}}/v_k), \quad (4b)$$

where the zero-order plasmon frequency  $\omega_p = (nk^2 v_k/m)^{1/2}$ . We now define the "intrinsic" Hamiltonian

$$H_{\text{int}} = H - \frac{1}{2} \sum_{0 \neq k < k_c} v_k (\rho_{\mathbf{k}} + i\omega_p \sigma_{\mathbf{k}}^*/v_k) \times (\rho_{\mathbf{k}}^* - i\omega_p \sigma_{\mathbf{k}}/v_k). \quad (5)$$

Let  $\psi_{0n}$  be any eigenfunction of  $H$  describing a state with no plasmons present; that is,  $(\rho_{\mathbf{k}}^* - i\omega_p \sigma_{\mathbf{k}}/v_k) \psi_{0n} = 0$  for all  $k < k_c$ . Then

$$H_{\text{int}} \psi_{0n} = H \psi_{0n} = E_n \psi_{0n}. \quad (6)$$

From Eqs. (4) and (5),  $H_{\text{int}}$  commutes with all the  $\rho_{\mathbf{k}}$ 's and  $\sigma_{\mathbf{k}}$ 's for  $k < k_c$ . Thus if  $F(\rho_{\mathbf{k}}, \sigma_{\mathbf{k}})$  is an arbitrary function of these variables, then