Dependence of the Forbidden Gap and Luminescence Ground-State Energies of (ZnCd)S:Ag on the Concentration of CdS†

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A series of (ZnCd)S:Ag:Cl phosphors have been studied to determine the effect of increased CdS content on the forbidden gap and on the energy of the ground states associated with luminescence. This work is correlated with that of other workers to confirm the presence of two separate ground states and to show that the luminescence of this material may be adequately explained by the Klasens model. Also the uniform translation of the spectral peaks (while retaining their shape) emphasizes the long-range order aspects of these phosphors.

INTRODUCTION

THE dependence of the forbidden energy gap on the composition of a semiconductor has been reported for solid solutions of CdS-CdSe[1] and ZnS-ZnSe[2] and for the mixed phosphors of ZnS-CdS activated with silver[3,4] and copper.[5] In the works dealing with phosphors, the luminescence emission is most frequently considered to result from the capture of an electron from the conduction band (or from an excited state near this band) by a hole in an energy level near the valence band. This model (due to Klassen[6]) is illustrated in Fig. 1.[7] This picture must be complicated somewhat in order to explain the double maximum found in the ZnS, CdS:Ag phosphors particularly at low temperatures (196°K).[3,4] Here one must consider two different luminescence centers; namely, the usual impurity ion center credited with the long-wavelength
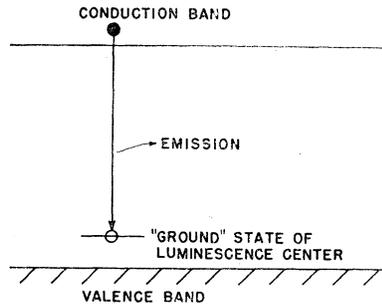
FIG. 1. Energy level diagram for ZnS:Ag:Cl phosphor after Klasens.[6]

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[1] Khansevarov, Ryvkin, and Ageeva, Zhur. Tekh. Fiz. **28**, 480 (1958) [translation: Soviet Phys. (Tech. Phys.) **3**, 453 (1958)].
[2] Larach, Shrader, and Stocker, Phys. Rev. **108**, 587 (1957).
[3] Tehv, Friedman, Studer, and Fonda, J. Opt. Soc. Am. **42**, 917 (1952).
[4] W. V. Gool, *Semiconductors and Phosphors* (Interscience Publishers, New York, 1958), p. 602.
[5] G. F. J. Garlich and A. F. Gibson, J. Opt. Soc. Am. **39**, 935 (1949).
[6] J. Klasens, Electrochem. Soc. **100**, 72 (1953).
[7] A model proposed by J. Lambe and C. C. Klick [Phys. Rev. **98**, 909–914 (1955)] ascribes the luminescence of CdS:Ag to the capture of holes by states near the conduction band. The author feels that, while the Lambe and Klick model offers a simpler description of the photoconductivity and luminescence in the sulfides, the Klasens model is adequate for the present discussion and is more commonly used and understood.

peak and another center described below to account for the short-wave peak.

For the short-wavelength emission from ZnS:Cu:Cl Kroger and co-workers[8,9] have proposed a luminescent consisting of a substitutional Cu ion associated with an interstitial Cu atom. They credit the blue emission occurring with excessive copper to this type of center. That a similar situation exists for ZnS:Ag:Cl is shown by Gool[4] in that the short-wavelength emissions for ZnS:Ag and mixed ZnS, CdS:Ag occur significantly only when excessive Ag doping is used and particularly when the coactivator content (in many cases Cl) is exceeded by the Ag. This latter condition limits the amount of Ag^+ which can be incorporated in the lattice and results in the inclusion of some silver Ag^0 atoms. One must, therefore, consider two ground states:

$$Ag^+Ag^0 \quad \text{and} \quad Ag^0.$$

The present work shows the variation in the location of the latter of these two silver bands with the concentration of CdS for mixtures of ZnS and CdS, whereas most previous measurements have applied only to pure ZnS or CdS hosts.

DISCUSSION

The location of the ground states associated with the two emission bands influences the temperature dependence of luminescence band[10] efficiency of each band according to the expression:

$$\frac{L}{L_0} = \frac{1}{1 + A\,\exp(-\Delta E/kT)},$$

where L is the intensity of luminescence at temperature T, L_0 that at a low temperature (80°K), and ΔE the energy gap between the ground state for the emission in question and the valence band. A is a constant for the material involved and k is Boltzmann's constant. By plotting (for the long- and short-wave bands

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[8] Kröger, Hellingman, and Smit, Physica **15**, 990 (1949).
[9] F. A. Kröger and N. W. Smit, Physica **16**, 317 (1950).
[10] H. A. Klasens and M. E. Wise, J. Opt. Soc. Am. **38**, 226 (1948).

separately)

$$\ln[(L_0/L)-1] \ vs \ 1/T,$$

one obtains values for ΔE for each emission band.

Values of ΔE obtained in the present work are shown in Table I along with values obtained by other workers. Also shown are values of the appropriate luminescence transition energies (E_{LT}) and total band gaps (E_G). Measurements of the energy of these ground states (relative to the valence band) have been made for a series of mixed ZnS; CdS:Ag:Cl phosphors. The results obtained are compared with published values for the pure ZnS:Ag and CdS:Ag phosphors. The energy differences between the various states associated with luminescence processes in this class of phosphors are shown to decrease monotonically as the forbidden band gap is decreased (with increased CdS concentration).

TABLE I. Energy levels and transition energies in (ZnCd)S:Ag phosphors for various proportions of CdS. (See Fig. 3 for clarification of terms.)

Atom parts CdS	ΔE (Ag$^+$) (ev)	E_{LT} (Ag$^+$Ag^0) (ev)	E_{LT} (Ag$^+$) (ev)	E_G (ev)
0	0.55[a] 0.53[b]	3.2[c]	2.8[a,b,c]	3.77[a]
0.22	0.48[b]	2.8[c]	2.4[c] 2.5[b]	
0.30	0.51[b]	2.7[c]	2.3[c] 2.4[b]	
0.46	0.46[b]	2.5[c]	2.2[c]	
0.63	0.46[b]	2.3[c] 2.2[b]	2.0[c]	
0.72		2.2[b,c]	1.8[c]	
1.00	0.43[c]	2.0[b,c]	1.7[c]	2.4[d]

[a] R. Bube, Phys. Rev. 90, 70–80 (1953).
[b] This article.
[c] See reference 4.
[d] See reference 1.

PREPARATION

The phosphors used in this study were prepared from luminescent pure ZnS and CdS (RCA), NaCl, and Ag$_2$NO$_3$. The proportions used were:

10 g ZnS (or mixed ZnS-CdS),

2 g NaCl,

0.016 g Ag$_2$NO$_3$.

The materials were wet-mixed using triply distilled water, air dried at $\sim 120°C$, then fired in air in covered (not sealed) Vycor crucibles for 10 minutes at $780°C$ in a preheated furnace. Only the core of each sample was used in this study as the outer layers were contaminated (presumably by O$_2$ since they showed a long time phosphorescence). The specimens thus prepared were painted onto the sample holder with a solution of 10% Duco cement in ethyl acetate.
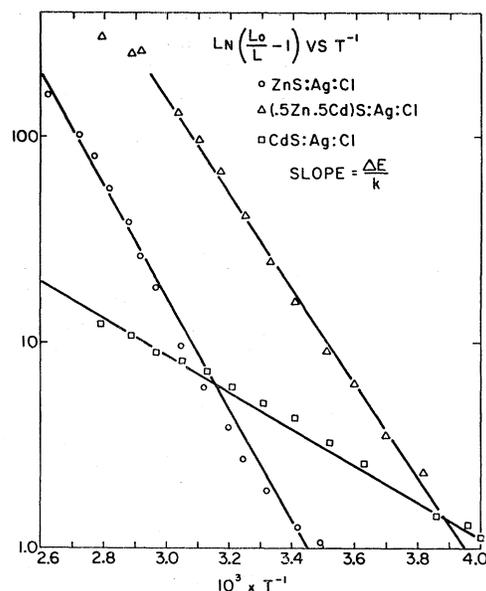
FIG. 2. Graph showing typical values of $[(L_0/L)-1] \ vs \ T^{-1}$ for three (ZnCd)S:Ag:Cl type phosphors.

EXPERIMENTAL ARRANGEMENT

The emission spectra from the phosphors were measured with a simple prism spectrometer using a 1P21 multiplier phototube as a detector. The spectral response of the 1P21 is such that the long-wave peak of the ZnS, CdS:Ag emission was emphasized for mixtures containing up to 50% CdS, while the short-wave peak was prominent in the data for 75% and 100% CdS:Ag. This selection also is apparent in the efficiency data where those materials with less than 75% and 100% CdS show activation energies char-
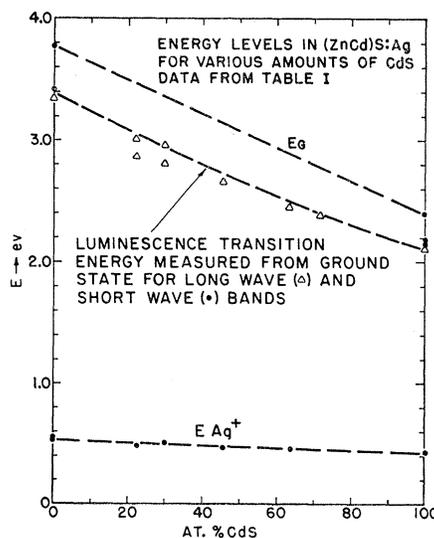
FIG. 3. Graph showing levels of conduction band and "ground states" of luminescence transitions for mixed ZnS-CdS based phosphors.

acteristic of the long-wavelength emission peak and those for 75% and 100% CdS show activation energies typical of the short-wavelength peak.

The energy gap between the valence band and the luminescence "ground" states was determined through measurement of the luminescence *versus* temperature. The slope of the $\log[(L_0/L)-1]$ *vs* $1/T$ curves (Fig. 2) for T above the breakpoint yields the activation energy for thermal quenching. The activation energies thus determined are subject to about 10% error as they depend upon the measurement of a slope in the semilog graphs and this slope is quite sensitive to small errors in L particularly for values of L near L_0. (L_0 was chosen as the value for L at 80°K.)

The chamber used in observation of the phosphors consisted of a specially constructed Dewar flask which held the specimen on a brass block which could be heated as needed. Temperatures were measured by a Cu-Constantan thermocouple calibrated at 78°K, 196°K, and 293°K. Cooling was achieved by filling the inner container of the Dewar (where the specimen was held) with liquid nitrogen.

CONCLUSION

The present paper assembles the results of several other workers and supplies additional experimental evidence to show that the band gap, the luminescent transition energies, and the activation energies (for thermal quenching) of the ZnCdS:Ag phosphors may be continuously and uniformly varied by changing the CdS content of the host material.

From the graph, Fig. 3, one may see that the starting points for both the long-wave and short-wave transitions lie within the same distance (~ 0.4 ev) of the conduction band (E_G). Thus the difference in energies of the two transitions may be explained by the difference in the two ground-state energies. The difference between the energy absorbed and energy emitted for each band may be credited to the Stokes shift associated with lattice rearrangement following both excitation and emission.

Measurements of the activation energy for quenching of the Ag^+ emission bands have been reported for both "pure" ZnS:Ag:Cl and "pure" CdS:Ag:Cl. However, the present work extends the measurements to include solid solutions of the two materials and shows that the activation energy is uniformly decreased as the CdS content increases throughout a range from 0 to 100% CdS. This uniform shift in activation energy along with the steady shift in wavelength of the emission peaks is indicative that the characteristics of the luminescent centers are results of long-range effects in the crystals— at least beyond nearest neighbors. If short-range order were the predominant factor, one would expect separate emission bands to occur for each component; *viz.*, CdS:Ag:Cl and ZnS:Ag:Cl.