

## Electronic Transitions in the Luminescence of Zinc Sulfide Phosphors

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The electronic transitions involved in the processes of (1) absorption, (2) excitation, (3) emission, (4) trapping, and (5) photoconductivity, at room temperature, have been measured for zinc sulfide phosphors, without added impurity, and with silver, copper, and manganese impurity.

Three types of excitation transitions are found: (1) from the filled band to the conduction band, (2) from an impurity level above the filled band to the conduction band, and (3) from a ground-state level to an excited-state level of an impurity ion. The first two transitions result in trapping and photoconductivity; the third does not.

Emission transitions occur from a level below the bottom of the conduction band to a level above the filled band.

The same five major trap depths are common to all zinc sulfide phosphors regardless of the nature of the impurity. Optical trap emptying by visible light, like thermal trap emptying, involves a process of stimulation in which trapped electrons are raised into the conduction band before returning to luminescence centers to produce emission.

A tentative energy-level diagram is constructed from the data obtained.

### INTRODUCTION

ONE of the primary goals in the understanding of luminescence is the description of luminescence phenomena in terms of an energy-level diagram. This description involves the determination of the location of energy levels, and the identification of transitions between energy levels. The required information for such a description can be largely obtained from measurements of absorption, excitation, emission, trapping, and photoconductivity.

(1) Measurements of absorption allow the determination of the width of the forbidden gap between filled and conduction bands. (2) A correlation of measurements of absorption and excitation allow the determination of the magnitude of the excitation transition. If trapping and photoconductivity result from excitation, the termination of the excitation transition may be identified as the conduction band. If excitation does not produce trapping and photoconductivity, the termination of the excitation transition is probably an excited state of the activator ion or complex. (3) Measurements of emission give the magnitude of the emission transitions. Location of the levels involved in the emission transition may be obtained from measurements of emission intensity as a function of temperature. (4) Glow curve measurements give the data from which the location of the trapping levels may be determined.

Many types of such measurements have been previously reported, both for ZnS phosphors and for other luminescent materials. Various transitions in ZnS phosphors have been studied by Kroeger,<sup>1,2</sup> Garlick,<sup>3-5</sup>

Klick,<sup>6</sup> Piper and Williams,<sup>7</sup> and Klasens.<sup>8</sup> Similar studies with the same purpose have been reported for CdS by Klick<sup>9</sup> and Broser and Warminsky.<sup>10</sup> Theoretical studies on the development of energy band diagrams for phosphors have recently been reported by Klick<sup>11</sup> and Williams.<sup>12,13</sup>

It is the purpose of this paper to present a summary of measurements, of the different types enumerated above, obtained with a series of ZnS phosphors prepared from the same pure material and prepared under identical conditions. This procedure allows a distinction to be made between effects which are essentially due to changes in impurity, and other effects which are caused by variations in preparation technique.

The results presented here (1) confirm many previously reported observations, and (2) provide additional quantitative data on these and other related phenomena.

### EXPERIMENTAL

Most of the measurements described in this paper have been made with (1) hex.-ZnS phosphor prepared without additives; (2) hex.-ZnS, [NaCl(2)];<sup>14</sup> (3) hex.-ZnS:Ag(0.01), [NaCl(2)]; (4) hex.-ZnS:Cu(0.01), [NaCl(2)]; and (5) hex.-ZnS:Mn(0.01), [NaCl(2)]. These phosphors were prepared<sup>15</sup> from triply-purified ZnS, for which spectrographic analysis<sup>16</sup> showed the

<sup>5</sup> G. F. J. Garlick and D. E. Mason, *J. Electrochem. Soc.* **96**, 90 (1949).

<sup>6</sup> C. C. Klick, *J. Opt. Soc. Am.* **41**, 816 (1951).

<sup>7</sup> W. W. Piper and F. E. Williams, *Phys. Rev.* **86**, 659 (1952).

<sup>8</sup> Klasens, Ramsden, and Quantie, *J. Opt. Soc. Am.* **38**, 60 (1948).

<sup>9</sup> C. C. Klick, *Phys. Rev.* **86**, 659 (1952).

<sup>10</sup> I. Broser and R. Warminsky, *Ann. Physik* **7**, 289 (1950).

<sup>11</sup> C. C. Klick, *Phys. Rev.* **85**, 154 (1952).

<sup>12</sup> F. E. Williams, *J. Chem. Phys.* **19**, 457 (1951).

<sup>13</sup> S. Roberts and F. E. Williams, *J. Opt. Soc. Am.* **40**, 516 (1950).

<sup>14</sup> Proportions of additives are given in weight percent throughout the paper.

<sup>15</sup> Phosphors prepared by P. R. Celmer.

<sup>16</sup> Spectrographic analysis by S. Larach.

<sup>1</sup> F. A. Kroeger, *Luminescence in Solids Containing Manganese* (Van Campen, Amsterdam, 1940), pp. 44-57.

<sup>2</sup> F. A. Kroeger and J. A. M. Dikhoff, *J. Electrochem. Soc.* **99**, 144 (1952).

<sup>3</sup> G. F. J. Garlick and A. F. Gibson, *Nature* **161**, 359 (1948).

<sup>4</sup> G. F. J. Garlick and A. F. Gibson, *J. Opt. Soc. Am.* **39**, 935 (1949).

absence of all cation impurities, except for faint traces of Mg and Na. In particular, the analysis showed that Cu was absent, at least for proportions greater than  $10^{-6}$  percent. All of these phosphors were prepared by heating in covered crucibles in air for five minutes at  $1250^{\circ}\text{C}$ . After heating and cooling, the core of each sample was washed with triple-distilled water before being used for measurement.

In addition to these phosphors, a hex.-ZnS:Cu(0.03), [NaCl(2)]; a hex.-ZnS:Mn(1.0), [NaCl(2)]; and a hex.-ZnS:Mn(1.0) phosphor were prepared under similar conditions for use where a higher proportion of impurity was necessary.<sup>17</sup> For the ZnS:Mn phosphor prepared with chloride, the Mn was added as the chloride; for the ZnS:Mn phosphor prepared without chloride, the Mn was added as the nitrate.

For future reference in the remainder of this paper, it will be assumed that the phosphor under discussion has been prepared with chloride unless the absence of chloride in the preparation is specifically mentioned.

Because of the number of different types of measurements that were used in this study, the experimental technique will be described in the same section as the experimental results. Excitation sources were as follows: a 250-watt GE Purple-X lamp for Fig. 1(c); a 100-watt C-H4 mercury spot-projector lamp with Corning 5860 filter (3.2-3.9 ev) for Fig. 3(a), Fig. 4, and Fig. 6; an 8-volt miniature lamp, GE 1183, without filters for Fig. 1(a) and 1(b), and with the Corning 5860 or Farrand filters (half-width of about 0.04 ev at 5000A, and 0.07 ev at 4000A) for Fig. 3(b), Fig. 5, Fig. 7, Fig. 10, Fig. 11, and the data of Table VI.

## RESULTS

### Absorption

Measurements of absorption were made by measuring the diffuse reflectivity from a layer of phosphor with an effectively infinite thickness. In order to detect the absorption in spectral regions where the absorption was low, e.g., the fine structure caused by impurity absorption in ZnS:Mn, a method was used, utilizing an integrating sphere of  $\text{MgCO}_3$ , in which the incident radiation was reflected at least twice from the sample before detection. The intensity of the reflected light was measured with a recording grating spectroradiometer, designed and constructed by Shrader, which will be described in another publication.

Figure 1 shows the reflectivity curves obtained at room temperature with the ZnS phosphors of this study. In order to obtain impurity absorption effects for the ZnS:Mn phosphor comparable in magnitude to those found for the ZnS:Ag(0.01) and ZnS:Cu(0.01) phosphors, it is necessary to use an impurity proportion

<sup>17</sup> The proportion of Cu in the ZnS:Cu phosphors of this study was less than that required to produce the blue emission associated with a Cu proportion higher than 0.03 percent.

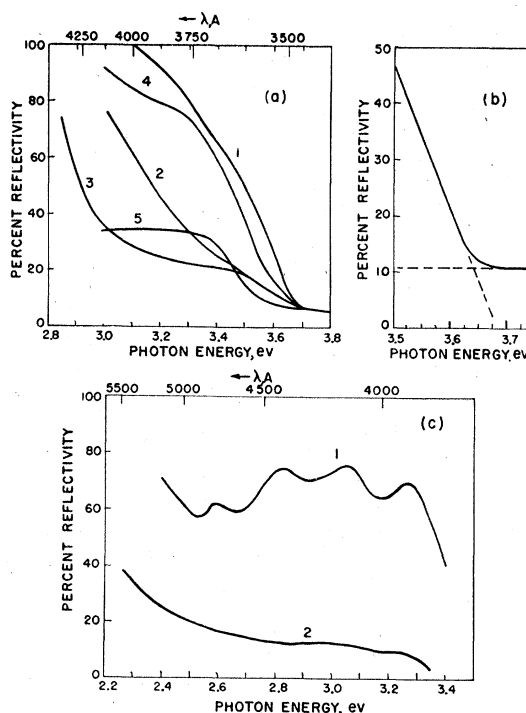


FIG. 1. Diffuse reflectivity spectra of ZnS phosphors. (a) Obtained with single reflection. (1) ZnS; (2) ZnS:Ag(0.01); (3) ZnS:Cu(0.01); (4) ZnS:Mn(1.0); (5) ZnS:Mn(1.0), no chloride. (b) Obtained with single reflection. ZnS. (c) Obtained with multiple reflection. (1) ZnS:Mn(1.0); (2) ZnS:Mn(1.0), no chloride.

100 times as large; measurements were made with ZnS:Mn(1.0) phosphor.

Table I presents a summary of the absorption data obtainable from these curves. The location of the absorption edge for the hex.-ZnS phosphor at 3.64 ev is in good agreement with the value of  $3.67 \pm 0.03$  ev reported by Piper and Williams<sup>7</sup> for single crystals of ZnS, and with the values of 3.70 ev and 3.55 ev reported for ZnS phosphors prepared with the exclusion of oxygen and with 1 percent ZnO, respectively, by Kroeger and Dikhoff.<sup>2</sup>

In addition to the host-crystal absorption, there are absorption bands associated with the Ag, Cu, and Mn impurities. A pronounced difference in absorption is found with the ZnS:Mn(1.0) phosphor depending on whether chloride is present in the preparation.

### Excitation

The excitation spectra of the ZnS phosphors of this study were measured with the assistance of DeVore using the monochromator arrangement previously described by him.<sup>18</sup> The luminescence emission was detected with a 1P21 phototube through suitable filters.

Figure 2 shows the excitation spectra obtained in this manner at room temperature, and a summary of the

<sup>18</sup> H. B. DeVore and J. W. Dewdney, Phys. Rev. **83**, 805 (1951).

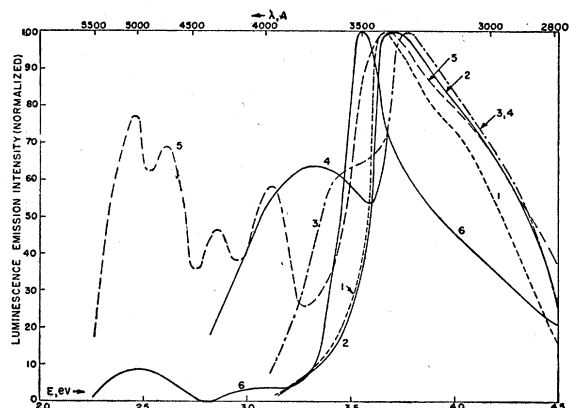


Fig. 2. Excitation spectra of ZnS phosphors. (1) ZnS, no chloride; (2) ZnS; (3) ZnS:Ag(0.01); (4) ZnS:Cu(0.03); (5) ZnS:Mn(1.0); (6) ZnS:Mn(1.0), no chloride.

excitation data is given in Table I, where it is compared with the absorption data. Each phosphor has an excitation peak at about the same energy as the absorption edge. In addition, each absorption peak due to an impurity has a corresponding excitation peak at approximately the same energy.

Although the absorption for the ZnS:Mn phosphor prepared without chloride is greater in the energy range from 2.0 to 3.5 eV than the absorption for the ZnS:Mn phosphor prepared with chloride, the excitation spectra show that the excitation process is much less efficient in the phosphor prepared without chloride. These observations are similar to previously reported results: (1) the presence of chloride in the preparation was found to decrease the absorption of ZnS phosphor,<sup>19</sup> and (2) the presence of gallium in the preparation was found to increase the luminescence efficiency of ZnS:Cu and ZnS:Mn phosphors, prepared in H<sub>2</sub>S, for photo-excitation.<sup>20</sup>

### Emission

The emission spectra for the ZnS phosphors of this study at room temperature, as measured with an

TABLE I. A summary of absorption and excitation data.

Phosphor	Process associated with	Absorption edge or max. ev	Excitation max. ev
ZnS	Host crystal	3.64	3.70
ZnS:Ag(0.01)	Host crystal	3.69	3.77
ZnS:Ag(0.01)	Ag impurity	3.50 <sup>a</sup>	3.42
ZnS:Cu(0.01)	Host crystal	3.69	3.77
ZnS:Cu(0.01)	Cu impurity	3.18 <sup>a</sup>	3.30
ZnS:Mn(1.0)	Host crystal	3.64	3.65
ZnS:Mn(1.0)	Mn impurity	3.18	3.12
		2.92	2.87
		2.67	2.60
		2.52	2.45
ZnS:Mn(1.0) (No chloride)	Host crystal	3.57	3.55

<sup>a</sup> Values obtained by taking ratios of reflectivity of ZnS:Ag and ZnS:Cu to the reflectivity of ZnS phosphor.

<sup>19</sup> R. H. Bube, J. Chem. Phys. **20**, 708 (1952).

<sup>20</sup> R. H. Bube and S. Larach, J. Chem. Phys. **21**, 5 (1953).

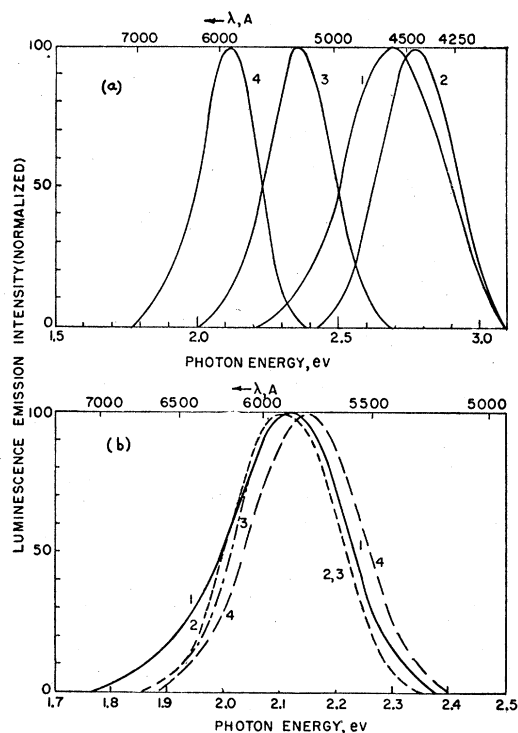


Fig. 3. Emission spectra of ZnS phosphors. (a) Excitation by ultraviolet of energy 3.2-3.9 eV. (1) ZnS; (2) ZnS:Ag(0.01); (3) ZnS:Cu(0.01); (4) ZnS:Mn(1.0). (b) Excitation of ZnS:Mn(1.0) with various excitation energies. (1) 3.2-3.9 eV; (2) 3.18 eV; (3) 2.87 eV; (4) 2.48 eV.

automatic recording spectroradiometer,<sup>21</sup> are given in Fig. 3(a). Table II presents a summary of the energies for peak emission intensity and of the half-widths of the emission spectra.

Essentially the same emission spectrum is obtained for the ZnS phosphors regardless of whether the excitation energy is absorbed by the host crystal or by the activator. In particular, the emission spectra for ZnS:Mn(1.0) phosphor obtained for different excitation energies are given in Fig. 3(b). The principal difference between the spectra is that a secondary emission band with peak at 1.85 eV (not resolved in Fig. 3(b), but clearly resolved in other measurements), found for ultraviolet excitation in the host-crystal absorption band, is absent for excitation in the activator bands, as it is also for cathode-ray excitation.

TABLE II. Summary of peak emission energies and half-widths.

Phosphor	Emission associated with	Energy for peak emission, ev	Emission half-width, ev
ZnS	Perturbed S	2.68	0.40
ZnS:Ag(0.01)	Ag impurity	2.77	0.31
ZnS:Cu(0.01)	Cu impurity	2.35	0.27
ZnS:Mn(1.0)	Mn impurity	2.12	0.23

<sup>21</sup> V. K. Zworykin, J. Opt. Soc. Am. **29**, 84 (1939).

TABLE III. Relative peak emission intensities of ZnS:Mn phosphors.

Crystal structure	% Mn	2% NaCl	Ultraviolet (3.2-3.9 ev), excitation <sup>a</sup>		6-kv cathode-ray excitation <sup>b</sup>	
			Blue (host-crystal) emission	Orange (Mn) emission	Blue (host-crystal) emission	Orange (Mn) emission
cubic	0.01	Yes	122	0	134	0
cubic	0.01	No	0	0	0	5
hexagonal	0.01	Yes	48	0	75	0
hexagonal	0.01	No	22	0	48	0
cubic	0.1	Yes	43	4.7	27	0
cubic	0.1	No	0	0	0	27
hexagonal	0.1	Yes	12	14	12	0
hexagonal	0.1	No	3.4	3.4	2.5	1.2
cubic	1.0	Yes	0	36	0	1.6
cubic	1.0	No	0	2.6	0	21
hexagonal	1.0	Yes	0	70	0	9.3
hexagonal	1.0	No	0	17	0	7.5
cubic	10.0	Yes	0	50	0	2.5
cubic	10.0	No	0	0	0	1.4
hexagonal	10.0	Yes	0	3.4	0	0
hexagonal	10.0	No	0	2.5	0	0

<sup>a</sup> hex.-ZnS:Ag(0.02):Cu(0.01), (RCA 33Z22A), standard equal to 100 for ultraviolet excitation.

<sup>b</sup> hex.-Zn<sub>2</sub>SiO<sub>4</sub>:Mn(0.3), (RCA 33W2A), standard equal to 100 for cathode-ray excitation

ZnS, ZnS:Ag, and ZnS:Cu phosphors are much more efficient for both ultraviolet and cathode-ray excitation if they are prepared with halide, particularly for low preparation temperatures. ZnS:Mn phosphors are, in general, more efficient for photoexcitation if prepared with halide (an especially prominent effect for excitation in the activator bands, as shown in Fig. 2), and more efficient for cathode-ray excitation if prepared without halide.<sup>22</sup> Table III compares the peak emission intensity of various ZnS:Mn phosphors to demonstrate these effects quantitatively.

Although cubic ZnS, ZnS:Ag, and ZnS:Cu phosphors have their emission maximum at a lower energy than the corresponding hexagonal phosphors, the emission maximum for ZnS:Mn phosphors is independent of

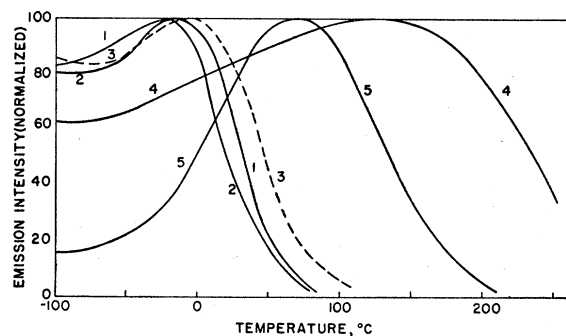


FIG. 4. Luminescence emission intensity as a function of operating temperature for ultraviolet excitation, 3.2-3.9 ev. (1) ZnS, no chloride; (2) ZnS:Ag(0.01); (3) ZnS:Cu(0.01); (4) ZnS:Cu(0.01); (5) Orange band of ZnS:Mn(0.01).

<sup>22</sup> H. W. Leverenz, *An Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950), p. 89.

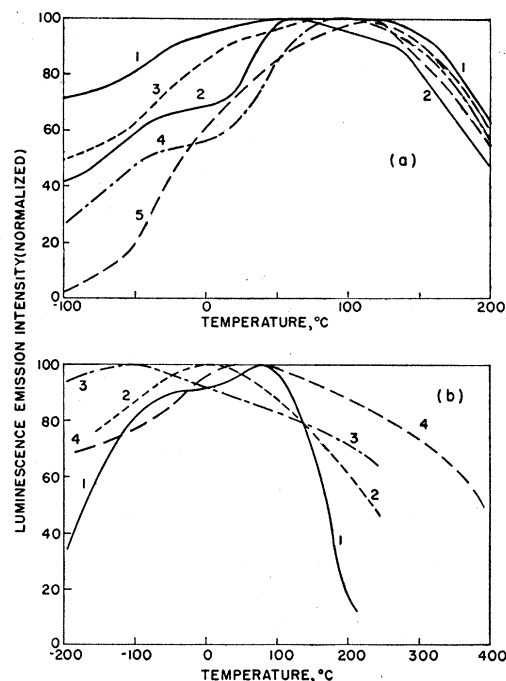


FIG. 5. (a) Luminescence emission intensity as a function of operating temperature for ZnS:Cu(0.01) for various excitation energies. (1) 3.2-3.9 ev; (2) 3.18 ev; (3) 2.97 ev; (4) 2.87 ev; (5) 2.75 ev. (b) Luminescence emission intensity as a function of operating temperature for ZnS:Mn(1.0) for various excitation energies. (1) 3.2-3.9 ev; (2) 3.18 ev; (3) 2.87 ev; (4) 2.48 ev.

crystal structure. The location of the emission for ZnS:Mn phosphors is also independent of the presence or absence of halide in the preparation, and of the type of excitation. Among all the phosphors listed in Table III, the location of the emission maximum varies by only 0.05 ev, and by only 0.02 ev if similar cubic and hexagonal phosphors are compared.

The variation of emission intensity with operating temperature for the ZnS phosphors of this study are given in Figs. 4 and 5. Table IV lists the temperatures for which maximum emission intensity occurs, and the

TABLE IV. Summary of data on variation of emission intensity with operating temperature.

Phosphors	Excitation by, ev	Temp. of int. max, °C	Temp. for int. of 80% max, °C
ZnS			
(No chloride)	3.2-3.9	-20	16
ZnS	3.2-3.9	-20	4
ZnS:Ag(0.01)	3.2-3.9	-5	27
ZnS:Cu(0.01)	3.2-3.9	120	199
ZnS:Mn(0.01)			
(Orange band)	3.2-3.9	70	107
ZnS:Cu(0.01)	3.17	(140)	151
	2.98	100	172
	2.87	100	168
	2.76	120	160
ZnS:Mn(1.0)	3.2-3.9	80	118
	3.17	0	118
	2.87	-100	112
	2.48	80	246

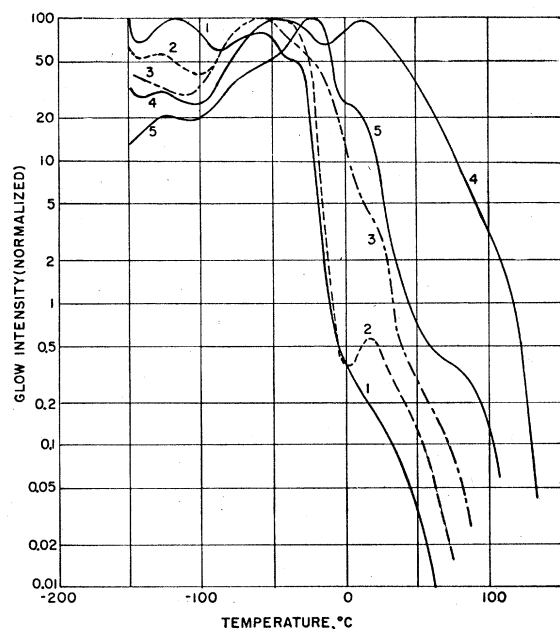


FIG. 6. Glow curves for ZnS phosphors after excitation at  $-160^{\circ}\text{C}$  with ultraviolet, 3.2–3.9 ev. (1) ZnS, no chloride; (2) ZnS; (3) ZnS:Ag(0.01); (4) ZnS:Cu(0.01); (5) Orange band of ZnS:Mn(0.01).

temperature for which the intensity has decreased to 80 percent of the maximum.

Figure 5 shows the variation of emission intensity with operating temperature for the ZnS:Cu(0.01) and ZnS:Mn(1.0) phosphors for various excitation energies. The curves of Fig. 5(a) below the temperature breakpoint, and curve 1 of Fig. 5(b) below  $0^{\circ}\text{C}$ , may not be considered accurate indications of the variation of emission intensity at these temperatures, since the temperature was raised at a rate which probably did not allow complete equilibrium to be established between low intensity excitation and trapping processes. The significant result, however, is that the temperature breakpoint and the decrease of intensity beyond the

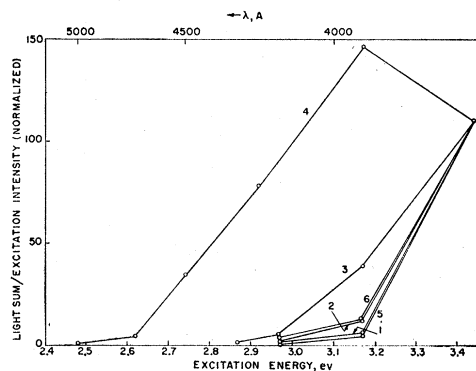


FIG. 7. Light sums, corrected for excitation intensity, measured with thermal stimulation, for ZnS phosphors, as a function of excitation energy. (1) ZnS, no chloride; (2) ZnS; (3) ZnS:Ag(0.01); (4) ZnS:Cu(0.01); (5) ZnS:Mn(0.01); (6) ZnS:Mn(1.0).

breakpoint is relatively independent of the excitation energy for ZnS:Cu, but very dependent on the excitation energy for ZnS:Mn.

### Trapping

The variation of trap distribution with impurity for the series of ZnS phosphors was obtained with measurements of glow curves using the apparatus described in past publications.<sup>23</sup> The glow curves of Fig. 6 show that there are five major glow peaks which are common to all the ZnS phosphors regardless of the impurity. Since these phosphors were prepared in an atmosphere containing oxygen, the effects of oxygen as reported by Kroeger and Dikhoff<sup>23</sup> may be expected. The results presented here show that trap depths are characteristic of defects in the ZnS host crystal. Kroeger and Dikhoff suggest that at least the four deepest trap depths are in some way associated with incorporated oxygen. Previous work by the author<sup>19,23</sup> has suggested a correlation between traps and omission defects, the formation of which may be oxygen dependent.

The five glow peaks are located at about  $-120^{\circ}$ ,  $-60^{\circ}$ ,  $-25^{\circ}$ ,  $15^{\circ}$ , and  $90^{\circ}\text{C}$ . The principal reason for the deep traps being more prominent in the Cu and

TABLE V. Time constant as a function of temperature and excitation energy for ZnS:Mn(1.0) phosphor.

Temperature, $^{\circ}\text{C}$	Time constant, millisecc			
	3.2–3.9 ev	3.18 ev	2.87 ev	2.48 ev
$-150$	400	1.4	1.8	2.3
25	9.2	1.5	1.6	2.3
100	4.0	1.8	1.7	2.6

Mn phosphors than in the others is probably simply the higher luminescence efficiency of the Cu and Mn phosphors at these temperatures.

The number of traps which are filled in a given length of time is a function of the excitation energy. The light sums, corrected for differences in excitation intensity with energy, are plotted in Fig. 7 as obtained from glow curves. Light sums for each phosphor are relative to the light sum obtained for excitation with the 5860 filter (which is set equal to 100 and plotted at 3.44 ev, the peak of the 5860 filter transmission). A comparison of the results with Fig. 2 shows that excitation in the Cu and Ag impurity bands produces trapping, whereas excitation in the Mn impurity band does not.

As an additional check on the difference between excitation in the host-crystal region and excitation in the impurity bands of ZnS:Mn phosphor, the time constant of the decay of phosphorescence emission was measured as a function of temperature for these different types of excitation. Table V summarizes the results for the ZnS:Mn(1.0) phosphor. The time constant was measured as the reciprocal of the frequency for which the percent modulation of the emission with chopped-

<sup>23</sup> R. H. Bube, Phys. Rev. **80**, 655 (1950).

light excitation was down to  $100/e$ . Because of the difficulty in separating the exciting light and the emitted light for the lower energy excitations, values of the time constant should probably be considered to have a possible error as high as 25 percent for these excitations. The results indicate the complete absence of trapping for temperatures at least below  $100^\circ\text{C}$  for excitation in the Mn bands, whereas trapping is found over this temperature range for excitation in the host-crystal band.

Although no change in trap depths was previously detected for ZnS:Cu phosphors as a function of Cu proportion up to 0.3 percent Cu,<sup>23</sup> a change in trap depths with Mn proportion is found for the ZnS:Mn phosphors, where glow curves may be obtained for 10 percent Mn. Figure 8 shows the variation of glow peak location for the four shallowest trap depths as a function of Mn proportion. The decrease in trap depth is about 0.1 eV for a change in Mn proportion from 0.001 percent to 10.0 percent.

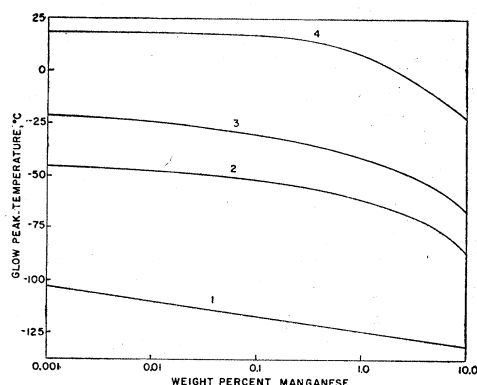


FIG. 8. Variation of location of glow peak with proportion of Mn in ZnS:Mn phosphors for four different trap depths.

The presence of retrapping in the course of the glow curve measurement has been found for ZnS:Mn phosphors, in a similar way to its occurrence for ZnS:Cu phosphors.<sup>23</sup> Figure 9(b) gives the relative intensities of the glow peaks at  $-60^\circ$ ,  $-25^\circ$ , and  $15^\circ\text{C}$  compared to the intensity of the glow peak at  $-120^\circ\text{C}$ , as a function of the percent of the total number of traps which are filled at the beginning of the glow curve measurement, as measured with ZnS:Mn(0.01). The variation in these relative intensities is caused by the retrapping of electrons, freed from shallow traps in the course of the glow curve measurement, by empty deeper traps. The result is that high temperature glow peaks are most prominent relative to glow peaks at lower temperatures, for excitation conditions such that few electrons are initially trapped.

Figure 9(a) shows another effect for ZnS:Mn(0.01) phosphor which is dependent on the number of electrons trapped before the start of the glow curve measurement: the ratio of blue emission (host-crystal) intensity in the glow curve to the orange emission (Mn) intensity.

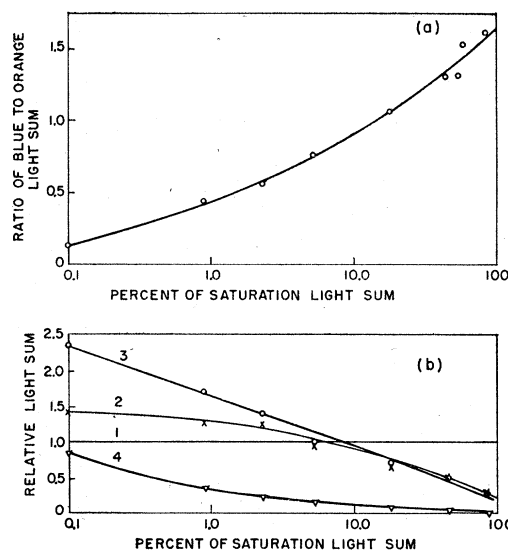


FIG. 9. (a) Variation of the ratio of blue to orange thermally-stimulated light sum of ZnS:Mn(0.01) with the percent of the saturation light sum. (b) The light sum of glow peaks at  $-60^\circ\text{C}$ , curve (2);  $-25^\circ\text{C}$ , curve (3); and  $15^\circ\text{C}$ , curve (4); relative to the glow peak at  $-120^\circ\text{C}$ , curve (1); as a function of the percent of saturation light sum.

Light which does not produce trapping may be used to remove electrons from traps to which they have been excited by previous irradiation. Table VI presents a summary of the percent of traps emptied in a ten-minute interval by light of various energies, but of equal intensity, for the phosphors of this study. The process of trap emptying is relatively independent of impurity or irradiating energy over the range studied.

In order to investigate the nature of the transition involved in the optical emptying of traps, the optically-stimulated light sum obtained by irradiation by 2.00 eV light at  $-160^\circ\text{C}$  (after all traps had been filled by ultraviolet excitation) was compared with the difference in thermally-stimulated light sums for the case in which a glow curve was measured without previous 2.00-eV irradiation, and the case in which the glow curve was measured after irradiation. The data presented in Fig. 10 shows that at least 70 percent of the electrons optically freed from traps undergo radiative transitions. From Fig. 10(b) it is seen that the glow intensity for very shallow traps is greater for the curve obtained after irradiation. This is true in general, also for trap-emptying measurements with higher energy

TABLE VI. Summary of trap emptying as a function of impurity and irradiating energy.

Phosphor	Percent of traps emptied in a 10-minute irradiation			
	3.18 eV	2.87 eV	2.43 eV	2.00 eV
ZnS	32	52	46	29
ZnS:Ag(0.01)	20	46	48	25
ZnS:Cu(0.01)	...	...	42	8
ZnS:Mn(0.01)	36	31	23	35

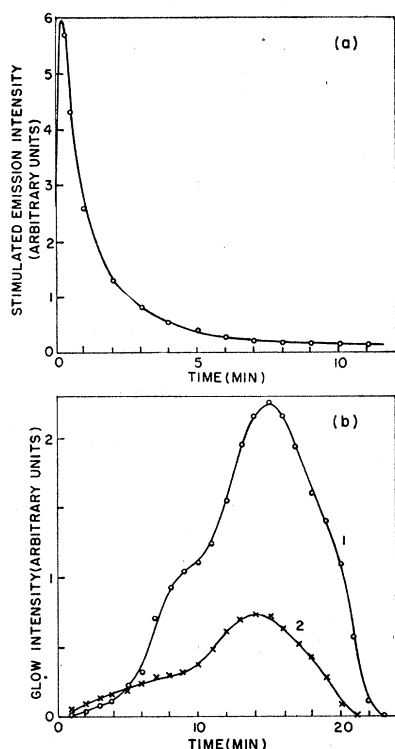


FIG. 10. (a) The photostimulated emission of ZnS phosphor at  $-160^{\circ}\text{C}$ , after trap-filling with excitation energies 3.2–3.9 ev, for irradiation with light of energy 2.00 ev. (b) (1) Glow curve obtained for ZnS phosphor after 5 minutes of excitation followed by 15 minutes of decay; (2) glow curve obtained after 5 minutes of excitation followed by 15 minutes of irradiation with light of energy 2.00 ev.

irradiating light. The effect is caused by the retrapping in shallow traps of electrons optically freed from deeper traps.

### Photoconductivity

The photoconductivity of the series of ZnS phosphors was measured at room temperature as a function of excitation energy. A photoconductivity cell was made by painting a thin paste of phosphor powder in castor oil over a conducting transparent coating on glass. A copper weight, resting on top of the paste, was the second electrode. A comparison of the results shown in Fig. 11 with Fig. 7 and Fig. 2, indicates that excitation in the Ag and Cu impurity bands produces photoconductivity as well as trapping, whereas excitation in the Mn impurity bands produces neither photoconductivity nor trapping.

## DISCUSSION

### Absorption and Excitation Processes

The following conclusions may be drawn from the above data as far as the excitation processes are concerned:

(1) Excitation of the host-crystal emission in ZnS phosphors is the result of an excitation transition from

the top of the filled band to the bottom of the conduction band. The excitation process is most efficient when the excitation energy is about the same as the energy of the forbidden gap, but excitation still occurs for larger excitation energies, being about 20 percent of its maximum efficiency for an excitation energy 1 ev larger than the forbidden gap for all the phosphors prepared with halide. The decrease in excitation efficiency for excitation energies larger than the forbidden gap may be attributed to an increased host-crystal absorption, resulting in dense excitation of surface layers with only a small number of active centers. For excitation energies less than the forbidden gap, the excitation efficiency falls off much more rapidly, being decreased to 20 percent of the maximum for an excitation energy of about 0.15 ev less than the forbidden gap. Excitation produces both trapping and photoconductivity.

(2) Excitation of the emission of ZnS:Ag phosphors can occur either by a transition from the filled band to the conduction band, if the excitation energy is greater than about 3.50 ev, or by direct excitation from the Ag level to the conduction band for excitation by lower energy. The unexcited Ag level is located at about 0.22 ev above the top of the filled band. For both types of excitation transitions, trapping and photoconductivity result. Excitation of Ag centers for the transition from filled band to conduction band is probably associated with the migration of holes in the filled band to Ag centers.

(3) Excitation of the emission of ZnS:Cu phosphors is similar to that described for ZnS:Ag phosphors. The unexcited Cu level is located at about 0.34 ev above the top of the filled band. Trapping and photoconductivity occur for excitation absorbed by the host crystal and for excitation absorbed by Cu centers themselves. Excitation of Cu centers for the transition from filled band to conduction band is probably also associated with the migration of holes to Cu centers.

(4) Excitation of the emission of ZnS:Mn phosphors can occur either by a transition from the filled band to the conduction band, exactly as in the case of ZnS:Ag and ZnS:Cu phosphors, or by a transition to any one of four excited states of the Mn ion.

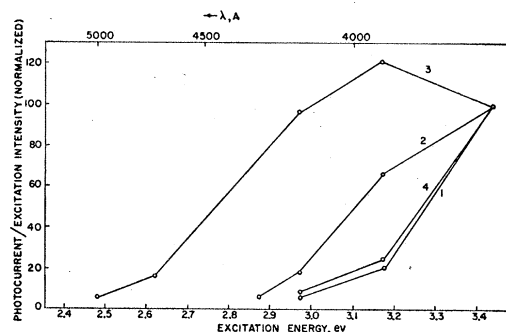


FIG. 11. Photocurrent, corrected for excitation intensity, for ZnS phosphors as a function of excitation energy. (1) ZnS; (2) ZnS:Ag(0.01); (3) ZnS:Cu(0.01); (4) ZnS:Mn(1.0).

The principal problem preventing the complete explanation of the excitation of ZnS:Mn phosphors is that involving the existence of a level associated with the Mn impurity within the forbidden gap.

That such a level may not exist is suggested by the following evidence. (1) No indication is found of an absorption or an excitation from such a level to the conduction band, resulting in trapping and photoconductivity, such as was found for the ZnS:Ag and ZnS:Cu phosphors. (2) The variation of the emission intensity with operating temperature is different for excitation absorbed by the host crystal and excitation absorbed by the Mn centers directly; a difference which does not occur in ZnS:Ag and ZnS:Cu phosphors.

On the other hand, there are a number of phenomena common to ZnS:Ag, ZnS:Cu, and ZnS:Mn phosphors, which are explained for the ZnS:Ag and ZnS:Cu phosphors in terms of hole migration to a level in the forbidden gap. (1) The relative intensity of blue and orange emission bands in a ZnS:Mn phosphor with a low Mn proportion (so that the blue host-crystal emission is still observed), is a function of the excitation intensity, higher excitation intensities making the blue emission more prominent. (2) Mn centers are excited by absorption of energy by the host crystal. (3) The orange emission associated with Mn centers increases in intensity over the temperature range for which the blue emission is decreasing. (4) The ratio of blue to orange intensity in the decay and in the glow-curve is much less than in the emission during excitation.

Although it may be possible to construct formal models to reconcile some of these observations, the lack of more positive evidence makes a hypothetical suggestion at this point of questionable value.

### Emission Processes

The fact that the energy of the emitted radiation is considerably smaller than the excitation energy used to produce it, shows that a readjustment of levels occurs as a result of the excitation process. Two energy-level diagrams are needed, therefore, to describe the luminescence processes; one for the location of levels before excitation, and another for the location of levels during excitation.

A method has been proposed by Klasens<sup>24,25</sup> by which the energy difference between the top of the filled band and the ground-state level of the excited center may be calculated from the variation of emission intensity with temperature during excitation. This method is based on the assumption that the cause of the decrease of efficiency at high temperatures is a filling of excited centers by the thermal raising of electrons from the filled band to the centers. (Another mechanism, which results in an equation between the efficiency and the temperature of exactly the same form, is the thermal

TABLE VII. Location of energy levels for excited centers.

Phosphor	$E^*$ <sup>a</sup>	$E^{**b}$
ZnS	0.55 ev	0.41 ev
ZnS:Ag(0.01)	0.55	0.32
ZnS:Cu(0.01)	0.95	0.34
ZnS:Mn(1.0)		
Host-crystal excitation	0.60	
Mn excitation	0.37	

<sup>a</sup> Energy difference between the ground-state level of the excited center and the top of the filled band; values reported by Garlick and Gibson (reference 4).

<sup>b</sup> Energy difference between the excited-state level of the excited center and the bottom of the conduction band; calculated for room temperature assuming a negligible change in the value of  $E^*$  between the temperature of the breakpoint and room temperature.

raising of electrons from the level from which the emission transition would be made, into the conduction band before such a transition has occurred. The application of this mechanism will be ruled out as a result of the following discussion.)

According to the formulation by Klasens, the efficiency,  $E$ , is expressible in terms of the activation energy,  $E^*$ , for the temperature-quenching process, and the absolute temperature,  $T$ , according to the equation:

$$E = 1/[1 + C \exp(-E^*/kT)]. \quad (1)$$

The quantity  $C$  is expressible in terms of the ratio:

$$C = F/(svJ)^{\frac{1}{2}}, \quad (2)$$

where  $F$  is the frequency-factor of the temperature-quenching transition,  $s$  is the capture cross section for the luminescence center,  $v$  is the electron velocity, and  $J$  is the number of excitations per second per cm<sup>3</sup>.

Garlick and Gibson<sup>4</sup> have used this equation to calculate  $E^*$  for ZnS:Ag, ZnS:Cu, and ZnS:Mn phosphors by plotting  $\ln(1/E - 1)$  as a function of  $1/T$  for the portion of the  $E$  vs  $T$  curve past the breakpoint. The values which they have reported are given in Table VII. There is good independent evidence which supports these values, at least in the case of the ZnS:Cu phosphor. The measurement of the decay of ZnS:Cu phosphor at high temperatures shows that for long decay times, an exponential decay is found, the slope of which is temperature dependent.<sup>28</sup> From the variation of the slope with temperature, a value of  $E^*$  of 1.0 ev and a value of  $F$  of  $3 \times 10^{10}$  sec<sup>-1</sup> were calculated. Schoen<sup>26</sup> has pointed out that the rate-controlling step in this process is very probably a raising of electrons from the filled band to the excited activator levels. It has also been reported that the stimulation spectrum of ZnS:Cu phosphors contains a peak associated with the Cu at 1.3 microns (0.95 ev),<sup>5,27</sup> and that the ratio of blue (host-crystal) to green (Cu) emission intensity during the decay becomes much larger during stimulated decay than during normal decay.<sup>28</sup> These results favor a value of  $E^* = 0.95$  ev and  $F = 10^{10}$  sec<sup>-1</sup> for the

<sup>24</sup> H. A. Klasens, Nature 158, 306 (1946).

<sup>25</sup> H. A. Klasens and M. E. Wise, J. Opt. Soc. Am. 38, 226 (1948).

<sup>26</sup> M. Schoen, Z. Naturwiss. 38, 235 (1951).

<sup>27</sup> E. F. Daly, Proc. Roy. Soc. (London) 196, 554 (1949).

<sup>28</sup> R. H. Rube, Phys. Rev. 80, 764 (1950).



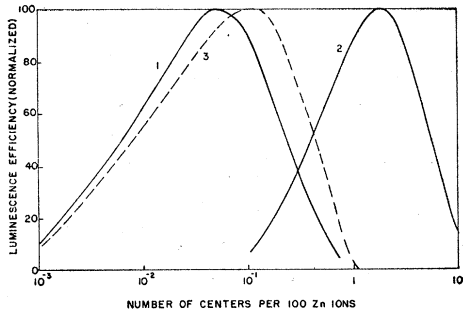


FIG. 12. The luminescence efficiency of (1) ZnS:Cu phosphors and (2) ZnS:Mn phosphors as a function of impurity proportion, assuming that a center is associated with each impurity ion; and (3) the luminescence efficiency of ZnS:Mn phosphors as a function of impurity proportion, assuming that a center is associated with each pair of Mn ions.

temperature-quenching transition in ZnS:Cu phosphors.

Using the values of  $E^*$  as reported by Garlick and Gibson, and assuming that  $F$  is of the order of  $10^{10} \text{ sec}^{-1}$  for ZnS and ZnS:Ag as well as for ZnS:Cu, the data of Fig. 4 may be used to calculate the capture cross section for the luminescence centers. (The method used by Garlick and Gibson to calculate  $E^*$ , being very dependent on the exact shape of the  $E$  vs  $T$  curve, is not applicable to the data of Figs. 4 and 5, which were obtained with nonmonochromatic excitation and with a thick sample. The location of the temperature breakpoint is a more simply determinable quantity.) The capture cross section is calculated by inserting into Eq. (1) the value of  $T$  for which  $E$  is 80 percent of its maximum value, as given in Table IV, known values of  $E^*$  and  $F$ , and an estimated value of  $J$ . Measurements with a CsSb cell gave a value of  $5 \times 10^{14}$  photons per second incident on the sample which had an area of  $6 \text{ cm}^2$ . If it is assumed that the ultraviolet penetrates about  $10^{-4} \text{ cm}$ , the value of  $J = 10^{18}$  excitations per second per  $\text{cm}^2$  is obtained. The value of  $s$  is found to be about  $10^{-24} \text{ cm}^2$ , approximately the same for ZnS, ZnS:Ag, and ZnS:Cu. This value is much smaller than the atomic cross section, but is of about the order of magnitude of cross sections calculated from measurements of photoconductivity on many different materials, such as PbS, CdS, and ZnS, as summarized by Rose.<sup>29</sup>

The ratio of the frequency-factor for transitions out of a given energy level, and the cross section for capture into that energy level, is a constant at a given temperature. Mott and Gurney<sup>30</sup> have calculated this ratio:

$$F/s = 2(6)^{\frac{1}{2}}(\pi)^{\frac{1}{2}}mh^{-3}(kT)^2, \quad (3)$$

which for room temperature gives a value of  $1.5 \times 10^{26}$ . Rose<sup>29</sup> has shown how this same value for the ratio may be obtained by simple considerations involving the Fermi-limit concept. The value of  $s$  calculated

above is for capture into the excited-state energy level of the excited center lying below the bottom of the conduction band. The frequency-factor for thermal excitation from this level to the conduction band may then be calculated to be about  $10^2 \text{ sec}^{-1}$ . This very low value of the frequency-factor, compared to the value of  $10^{10} \text{ sec}^{-1}$  found for thermal excitation from the filled band, is possibly explainable in terms of a difference in coupling between isolated impurity ions and the crystal vibrations, and host-crystal ions and the crystal vibrations.

The capture cross section of a hole in the filled band for an electron is found to be  $10^{-16} \text{ cm}^2$  by calculation from Eq. (3), or about the order of magnitude of the atomic cross section.

The discussion of the temperature-quenching process thus far has assumed that the transition involved is that from the filled band to excited centers. Garlick and Gibson, however, have suggested that the activation energies they measured are for the thermal excitation from excited-state level into the conduction band. That the latter process can have no effect in the observed process of temperature-quenching may be shown in the following way. Measurements of Strange and Henderson<sup>31</sup> have shown that the initial decay in ZnS phosphors has a time constant of at most about  $10^{-5} \text{ sec}$ . If the probability of a transition from the excited-state level into the conduction band is calculated at temperatures near the observed temperature breakpoint, for the  $E^*$  of Garlick and Gibson and  $F = 10^{10} \text{ sec}^{-1}$ , it is found that the probability of such transitions is of the order of one per sec, or a factor  $10^5$

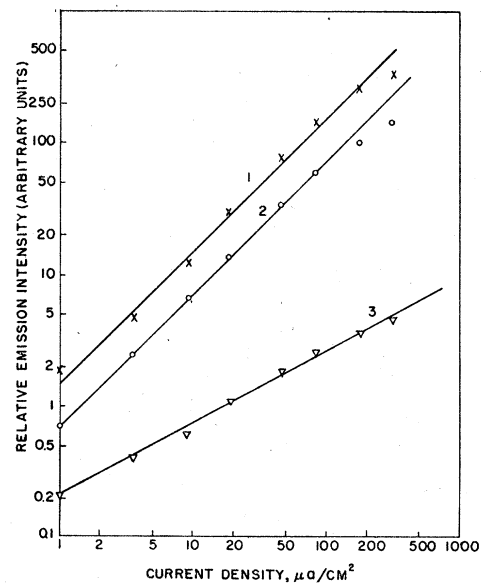


FIG. 13. The relative cathodoluminescence emission intensity of (1) ZnS:Ag(0.01); (2) ZnS:Cu(0.01); and (3) ZnS:Mn(1.0) as a function of current density for 4-kv cathode-ray excitation.

<sup>29</sup> A. Rose, RCA Rev. 12, 362 (1951).

<sup>30</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 108.

<sup>31</sup> J. W. Strange and S. T. Henderson, Proc. Phys. Soc. (London) 58, 369 (1946).

times smaller than would be necessary to make the raising of an electron in the excited-state level into the conduction band more probable than the return of the electron to the ground state with radiation.

For ZnS, ZnS:Ag, and ZnS:Cu phosphors, the ground-state level of the center was raised relative to the filled band as a result of excitation. The explanation of the effect of excitation on the levels of ZnS:Mn phosphor is made much more complicated by the fact that the value of  $E^*$  determined for ZnS:Mn is dependent on whether the excitation is absorbed by the host crystal or by the Mn centers directly. Values reported by Garlick and Gibson are included in Table VII.

One of the outstanding characteristics of ZnS:Mn phosphors is that the luminescence properties of ZnS:Mn(1.0) are comparable to properties obtained with ZnS:Ag or ZnS:Cu phosphors with only 0.01 percent impurity. It is reasonable to believe that there are the same number of active centers in ZnS:Mn and ZnS:Ag or ZnS:Cu phosphors with equal emission intensity. Leverenz,<sup>32</sup> for example, has reported that the saturation characteristics of ZnS:Mn(1.0) are quite different from those of Zn<sub>2</sub>SiO<sub>4</sub>:Mn(1.0), but are similar to those of ZnS:Ag(0.01) or ZnS:Cu(0.01). Figure 12 shows the variation of luminescence efficiency as a function of the impurity proportion of ZnS:Cu and ZnS:Mn phosphors. An explanation is required that will not only indicate why a certain fraction of the Mn ions incorporated do not act as effective centers, but which will also indicate why this fraction varies in an apparently irregular way experimentally found as a function of Mn proportion. The simple assumption that centers in ZnS:Mn phosphors are associated, not with isolated Mn ions, but with pairs of Mn ions, is able to furnish such an explanation to a first approximation, as is demonstrated by the dashed curve 3 of Fig. 12. Calculations of the number of pairs as a function of Mn proportion was obtained from the probability curves based on a random distribution of Mn ions, published by Leverenz.<sup>33</sup>

The fundamental difference between ZnS:Mn and ZnS:Ag or ZnS:Cu phosphors may also be demonstrated by measuring the luminescence emission intensity as a function of current density for 4-kv cathode-ray excitation below saturation. The results shown in Fig. 13 indicate that the emission intensity for ZnS:Ag and ZnS:Cu varies very closely to linearly with current density, but the emission intensity of the ZnS:Mn phosphor increases as the square-root of the current density. The square-root relationship indicates that the probability of exciting centers decreases as the number of excited centers increases, even below normal saturation, for ZnS:Mn.

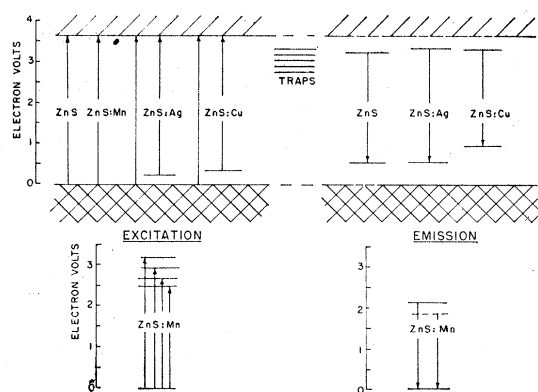


Fig. 14. A tentative energy-level diagram for the excitation and emission transitions in ZnS phosphors. Impurity levels for the ZnS:Mn phosphor are presented separately because of uncertainty about the nature or existence of the ground-state level in the forbidden gap, as discussed in the text.

### Trapping Processes

Trapping in ZnS phosphors occurs for excitation transitions which raise an electron into the conduction band with accompanying photoconductivity.

Traps are characteristic of defects in the host crystal. Differences in impurity may change the relative distribution of traps of different depths to some extent, but not the trap depths themselves, except, as in the case of high proportions of Mn, when crystal spacings are altered.

Optical stimulation of trapped electrons with visible light raises the electrons from traps into the conduction band. Evidence for this conclusion is that (1) a large proportion of the freed electrons return to centers with normal luminescence emission, (2) electrons raised from deep traps by optical stimulation are retrapped by empty shallow traps, and (3) the effectiveness of trap-emptying is independent of impurity or irradiating energy.

Retrapping occurs whenever the number of empty traps becomes appreciable. Cases are found both for retrapping by deep traps of electrons freed from shallow traps, as in the case of the glow curve experiment, and for retrapping by shallow traps of electrons freed from deep traps, as in the case of optical stimulation. The retrapping process involves a raising of electrons to the conduction band, and is not the result of simple transitions between trapping levels.

No direct evidence has been found with these phosphors for transitions directly from trapping levels to the filled band.

### SUMMARY

A tentative energy-level diagram for the excitation and emission processes in ZnS phosphors at room temperature is given in Fig. 14 for ZnS, ZnS:Ag, ZnS:Cu, and ZnS:Mn phosphors. Trapping levels are

<sup>32</sup> See reference 22, p. 359.

<sup>33</sup> See reference 22, p. 478.

included at the trap depths obtained by assuming a frequency-factor for trap-emptying of  $10^{10}$  sec $^{-1}$ . Energy levels for the impurity-associated excitation and emission processes of ZnS:Mn phosphors are included below the band diagrams for the other ZnS phosphors, because of the uncertainty of the nature or even the existence of a real energy level for the Mn in the forbidden gap.

The next logical extension of these measurements is the determination of the variation in electronic transitions with temperature.

The author wishes to express his thanks to Dr. R. E. Shrader for his assistance in obtaining measurements of absorption, to Dr. H. B. DeVore for his assistance in obtaining measurements of excitation, and to Dr. A. Rose for helpful discussions.

## The Zeeman Effect in the Spectra of Tellurium

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Over one hundred lines of tellurium have been investigated in fields of approximately 36 000 gauss;  $g$  values have been established for Te I, Te II, Te III, and from one line of Te IV. Classifications already published for many of these lines are in general agreement with the Zeeman patterns given in this report. Some previously indefinite assignments of  $j$  values are established.

THE experimental data on which this paper is based were taken during the summer of 1936 on the 21-foot concave grating spectrograph which was then in existence at the Mendenhall Laboratory of Physics.

The method of excitation of the tellurium was the same as that described for the excitation of the spectra of arsenic.<sup>1,2</sup>

### TELLURIUM I

The first classification of the arc spectrum of tellurium was given by McLennan<sup>3</sup> and his co-workers and was later extended by Bartelt,<sup>4</sup> but no Zeeman effects have ever been published.

TABLE I. Zeeman effect for tellurium I.

Wave-length	Classification	Zeeman pattern	$g_1$	$g_2$
2383.27	$p^4 \ ^3P_0 - 6s(^4S) \ ^3S_1$	(0) 1.90	...	1.90
2385.78	$\ ^3P_1 - \ ^3S_1$	(0.40) 1.49 1.90	1.49	1.90
2530.73	$\ ^3P_1 - \ ^5S_2$	(0) (0.47) 1.96 2.47	1.49	1.98
2769.65	$\ ^1D_2 - \ ^3S_1$	0 0.94	?	?
2858.28		(0) 1.10		
3175.13	$\ ^1S_0 - 5d(^4S) \ ^3D_1$	(0) 1.39	...	1.39

\* Now at Operations Research Office, The Johns Hopkins University, Baltimore, Maryland.

† Deceased.

<sup>1</sup> J. B. Green and W. M. Barrows, Jr., Phys. Rev. **47**, 131 (1935).

<sup>2</sup> A word of caution should be inserted here. Tellurium, after it comes in contact with the skin, is readily absorbed by the body. It is then eliminated very slowly by means of perspiration which gets on the clothing of the unfortunate victim, or by means of expiration. The result is an aura of concentrated garlic which seems to persist for several months after only one short exposure.

<sup>3</sup> J. C. McLennan *et al.*, Phil. Mag. **4**, 486 (1927).

<sup>4</sup> O. Bartelt, Z. Physik **88**, 522 (1934).

Six lines of this spectrum were observed, five classified and one unclassified. Table I gives the results, together with the  $g$  values garnered therefrom. The classifications are those of Bartelt.<sup>4</sup> The line  $\lambda 2770$  is a fuzzy triplet, and if we omit the usual designation for polarization (there is no information on polarization), the pattern is consistent with the  $g$  value, 1.03, calculated for the  $\ ^1D_2$  level on the basis of the structure of the  $p^4$  configuration. The pattern of  $\lambda 2858$  yields no clue to its classification. In view of the  $g$  value for the  $j=1$  level of  $\lambda 3175$ , it seems inappropriate to assign  $LS$  classification to this level.

TABLE II.  $g$  values for tellurium II.

Even terms				Odd terms			
Level $j$	$g$ value	Accu- racy	Mack	Level $j$	$g$ value	Accu- racy	Mack
71 5/2	1.60	<i>c</i>	1.70	93°1/2	0.79	<i>a</i>	...
74 3/2	1.67	<i>b</i>	1.78	96°3/2	1.33	<i>a</i>	1.3
76 1/2	2.62 <sub>s</sub>	<i>a</i>	2.71	99°3/2	1.25 <sub>s</sub>	<i>a</i>	1.30
78 1/2	2.25	<i>a</i>	2.4	100°5/2	1.36 <sub>s</sub>	<i>b</i>	1.39
81 3/2	1.08	<i>a</i>	1.12	101°3/2	1.30	<i>a</i>	1.30
82 3/2	1.44	<i>a</i>	1.42	101°1/2	2.33 <sub>s</sub>	<i>a</i>	2.29
83 1/2	1.02	<i>b</i>	1.07	102°5/2	1.35	<i>b</i>	1.33
85 5/2	{ 1.35 or 0.95	<i>c</i>	...	103°7/2	1.34	<i>c</i>	1.36
85 3/2	0.86	<i>b</i>	0.8	103°3/2	1.72	<i>a</i>	1.74
85°5/2	1.47	<i>b</i>	1.49	105°3/2	1.20	<i>b</i>	1.18
86 3/2	0.93	<i>a</i>	0.99	105°5/2	1.27 <sub>s</sub>	<i>a</i>	1.29
87 5/2	1.13	<i>b</i>	...	106°1/2	0.81	<i>c</i>	...
88 3/2	1.12	<i>c</i>	1.14	107°5/2	1.15	<i>d</i>	...
117 3/2	1.62	<i>c</i>	...	112°3/2	1.10	<i>c</i>	1.12
120 5/2	1.57	<i>c</i>	...	112°5/2	1.33	<i>c</i>	...
124 5/2	1.27	<i>c</i>	1.27				
121°3/2	0.89	<i>c</i>	1.24				
123 7/2	1.28	<i>d</i>	1.24				