Luminescence and Trapping in Zinc Sulfide Phosphors with and without Copper Activator*†

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A comprehensive study of ZnS:[Zn] and ZnS:[Zn]:Cu phosphors has been carried out with the use of glow curves, phosphorescence emission decay curves, and spectral distribution curves of emission during excitation by 3650A ultraviolet. The principal contributions of the study are (1) glow curves and spectral emission curves for nine samples each of cubic and hexagonal ZnS with copper activator in proportions from zero to 3000 parts per million, (2) a direct proof for ZnS-type phosphors of the equation of trap emptying proposed by Randall and Wilkins, (3) a detailed extension of the study of retrapping by the method indicated by Wilkins and Garlick, (4) a determination of the number of electron traps in ZnS as a function of heating temperature in preparation, (5) an analysis of glow and decay curves by means of the equation of Randall and Wilkins, and (6) suggestions concerning the identity of traps and luminescence centers on the basis of a study of the crystal structures of cubic and hexagonal ZnS.

I. INTRODUCTION

THERE are two basic types of *centers* involved in the luminescence process of ZnS phosphors. The first of these is the *luminescence center*, which is made up of an imperfection[1] and its surroundings in the crystal. When a luminescence center is excited, an electron is raised from a ground state to an excited state, from which the electron may make a radiative return transition at a later time. The probability that this return transition is dissipative rather than radiative increases with temperature. The second type of center is the *trapping center*. This center is also made up of an imperfection and its surroundings in the crystal, but an electron in a trapping state is effectively in an excited state from which a transition to a ground state cannot be directly made. The nature of the luminescence center determines the spectral distribution of the emission of the phosphor, whereas the nature of the trapping center (in phosphors for which a temperature-independent exponential decay is not found) is a major factor in determining how the emission will decrease with time after the cessation of excitation. In such phosphors the phosphorescence emission, i.e., the emission caused by the radiative transitions of electrons with apparent excited-state lifetimes of greater than 10^{-8} sec., is due to the thermal freeing of trapped electrons followed by their capture by a luminescence center.

Since the paper of Randall and Wilkins,[2] which contained the first quantitative analysis of glow curves (curves of thermally stimulated phosphorescence emission as a function of temperature after low temperature

excitation) together with corresponding decay curves, other measurements on trapping in ZnS phosphors have been concerned with the applicability of the equation of Randall and Wilkins, the importance of retrapping, and the connection between trapping and the preparation process.

In general, a different group of investigators has studied the luminescence emission of ZnS phosphors during excitation. Among the principal problems were the nature of the luminescence centers, and the role of chloride added in the preparation of these phosphors.

The present paper contains measurements primarily made on two series of ZnS:[Zn]:Cu phosphors,[3] all prepared in an identical manner from spectroscopically pure ZnS, in such a way that the effect of varying crystal structure and activator proportions may be obtained.

Two problems are treated in the present study. (1) Is the equation of trap emptying of Randall and Wilkins[2] applicable to ZnS:[Zn]:Cu phosphors? (2) What information can be obtained concerning the identity of trapping centers and of luminescence centers in ZnS:[Zn]:Cu from a study of glow curves, decay curves, spectral distribution curves, and crystal structure?

II. THEORY

The theory of Randall and Wilkins[2] for the emptying of traps assumes that the probability of an electron escaping from a trap is given by the equation

$$P = \nu_a e^{-\epsilon/kT}, \qquad (1)$$

where ν_a is a frequency factor, the "attempt-to-escape" frequency, and the exponential term is a Boltzmann factor involving the trap depth ϵ, and the temperature T. The attempt-to-escape frequency may be interpreted as the number of times per second that thermal quanta from crystal vibrations attempt to eject the electron

[1] The term "imperfection" is used to mean any distortion of the regular crystal configuration, whether it be caused by added impurities or by inherent crystal defects, such as interstitial or omission defects.

[2] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. A184, 366, 390 (1945).

[3] The expression [Zn] will be used to indicate the unknown activator for the blue luminescence emission of "pure" ZnS. In the author's opinion, the conventional contention that interstitial zinc is this activator has not been proven.

from the trap, multiplied by the probability of a transition from the trap to the conduction band. The Boltzmann factor is the probability of the electron having an energy sufficient to escape on any one of these attempts. The straightforward use of this equation requires the assumption that electrons freed from traps are not retrapped, that ν_a and ϵ are independent of temperature, and that freed electrons undergo radiative, rather than dissipative, transitions.

The decay equation derived from Eq. (1) gives

$$I_t = n_0 P e^{-Pt}, \tag{2}$$

where n_0 is the number of eléctrons trapped in traps of depth ϵ at $t=0$.

If β is the linear heating rate, the equation for the glow curve which results from Eq. (1) is

$$I_G = n_0 P \exp\left(-\int P/\beta dT\right). \tag{3}$$

Maximizing this equation for I_G with respect to T, gives the trap depth in terms of the temperature, T_G, for maximum I_G:

$$\epsilon = (\ln\nu_a) k T_G (1+f) \tag{4}$$

in terms of the quantity f which is given by

$$f = \ln(T_G{}^2 k/\beta\epsilon)/\ln\nu_a. \tag{5}$$

This theory has been extended by Garlick et al.[4] to cases where retrapping does occur. In particular, calcu-

lations were made for the case in which the probability of an electron being retrapped was equal to the probability of an electron being captured by a luminescence center.

For this case, the equivalent equation to Eq. (2) for the decay is

$$I_t = n_0 P / [1 + Pt]^2 \tag{6}$$

if the traps have been saturated. For long times of decay, this becomes approximately

$$I_t \approx n_0 / Pt^2. \tag{7}$$

The glow curve equation for this case, equivalent to Eq. (3) is

$$I_G = n_0 P \bigg/ \left[1 + \int P/\beta dT\right]^2. \tag{8}$$

III. EXPERIMENTAL

Eighteen samples of cubic and hexagonal ZnS: [Zn]: Cu(0.0–0.3) [5] with logarithmically increasing proportions of copper make up the phosphor series with which the largest part of the experimental work was done. They were prepared[6] from the same lot of highly purified ZnS (RCA 33-Z-19),[7] in which there were no spectroscopically detectable[8] impurities. Copper, as $CuCl_2$, and two percent of a water solution of purified NaCl were added in the preparation of these phosphors. The cubic-structure samples were heated for twenty minutes at 950°C; the hexagonal-structure samples were heated for five minutes at 1250°C. Only the cores of the samples were used.

The phosphor to be tested was settled from chemically pure anhydrous methyl alcohol suspension onto the platinized bottom of a metal cup which was inside an evacuable container.[9] The other side of the bottom of this cup could be brought into contact with liquid nitrogen.

The phosphor was excited by 3650A ultraviolet from a 100-watt C-H4 mercury projector spot lamp placed approximately five centimeters from the entrance window. The emitted light was observed by a multiplier photo-tube (usually RCA 1P28) connected to a sensitive microammeter (2×10^{-8} amp. full scale). Linear heating rates were obtained by applying increasing voltages to heating coils around the metal cup at empirically determined times during the heating period.

The spectral distributions of the eighteen sample phosphors were measured at room temperature with an automatic recording spectroradiometer.[10] Excitation was by a 100-watt C-H4 mercury projector lamp 15-cm distant, through two Corning 5840 filters.
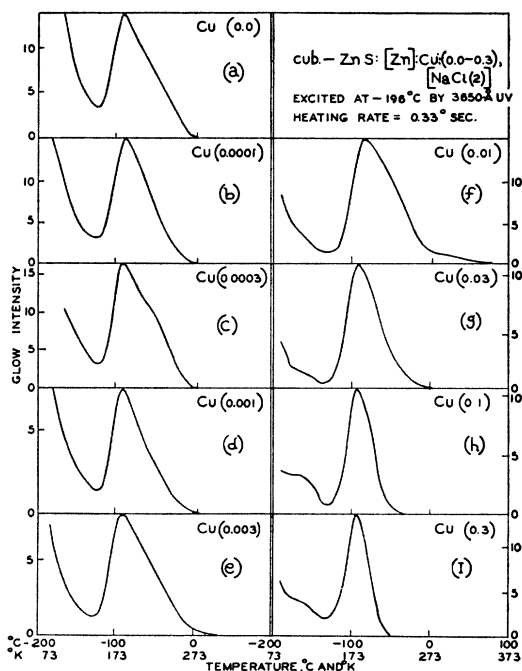

FIG. 1. Glow curves for cub.—ZnS:[Zn]:Cu(0.0–0.3) phosphors after excitation at −196°C by 3650A ultraviolet. Heating rate of 0.33°C/sec.

[4] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. London 60, 574 (1948).

[5] Proportions of activator are given in weight percent.
[6] Prepared by P. R. Celmer of these laboratories.
[7] H. W. Leverenz, An Introduction to Luminescence of Solids (John Wiley and Sons, Inc., New York, 1950).
[8] Spectrographic analysis by S. Larach of these laboratories.
[9] Apparatus originally designed by R. E. Shrader and F. E. Williams.
[10] V. K. Zworykin, J. Opt. Soc. Am. 29, 84 (1939).

Glow curves obtained at slow warming rates and measurements of phosphorescence emission decay at long times of decay were measured using a special apparatus with an especially well-insulated inner chamber.[11]

IV. RESULTS: PART I. GLOW AND DECAY CURVES

Glow Curves

The glow curves of the cubic and hexagonal ZnS: [Zn]:Cu(0.0–0.3) phosphors excited at −196°C by 3650A ultraviolet and heated at a rate of 0.33°C/sec. are given in Figs. 1 and 2. The glow curves are plotted with equal peak values because the effort to obtain phosphor layers of uniform thickness[12] was only ap-
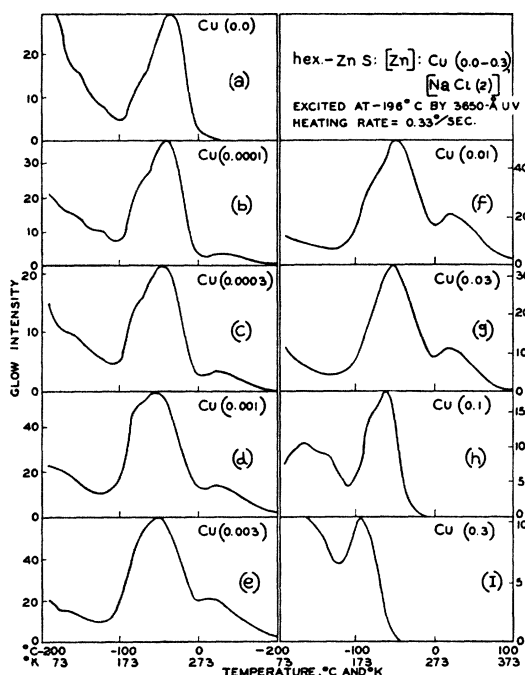
FIG. 2. Glow curves for hex.—ZnS:[Zn]:Cu(0.0–0.3) phosphors after excitation at −196°C by 3650A ultraviolet. Heating rate of 0.33°C/sec.

proximately successful. Small differences in the intensities recorded are not significant.

These curves show that (1) a large fraction of the traps[13] found in ZnS:[Zn]:Cu phosphors are present in the phosphors with no added copper, (2) the incorporation of copper affects the shape of the glow curve for hexagonal phosphors more than for cubic phosphors, (3) the incorporation of copper up to a critical proportion causes the appearance of deep traps, and (4) the incorporation of copper in proportions greater than

[11] Apparatus designed by H. W. Leverenz.
[12] The thickness affects the over-all intensity observed.
[13] When the total number of traps, regardless of depth, is under discussion, the plural "traps" will be used. When the number of different trap depths is under discussion, the term "trap depth" will be used. For example, the number of traps is very large, but the number of trap depths may be small.
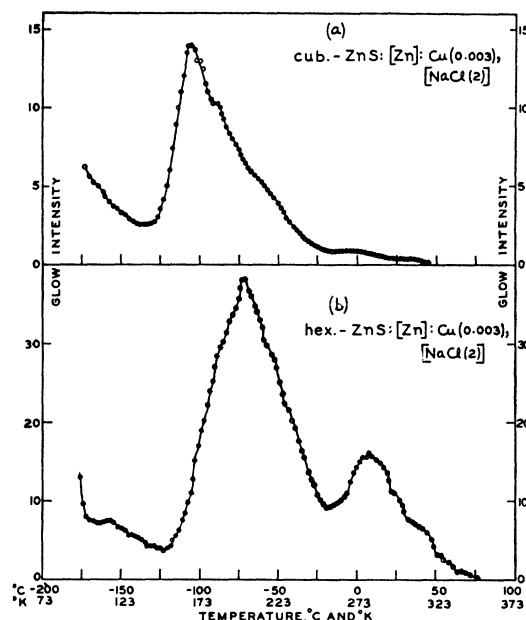
FIG. 3. Glow curves for cubic and hexagonal ZnS:[Zn]:Cu(0.003) phosphors after excitation at −175°C by 3650A ultraviolet. Heating rate of 0.033°C/sec.

this critical proportion causes the disappearance of the deep traps caused by copper, and also of some of the deeper traps present before the addition of any copper.

Both blue and green emission, corresponding to the blue and green emission bands found during excitation (see Results: Part II, Fig. 13) are found during the glow experiment for low copper proportions. Only the emission of the green band, however, is found in glow curves for copper proportions equal to or greater than 0.003 percent. All quantitative analyses of glow curves and decay curves are based on phosphors which give only green phosphorescence emission.

The shapes of the glow curves, especially for high copper proportions where deep traps disappear, suggest the presence of a limited number of component glow curves, each being caused by traps of one depth.

Glow Curves with Slower Heating Rate

One method of testing for such component glow curves is to measure glow curves at a slower heating rate, for which an increase in resolution is obtained by a decrease in the width of a glow curve. Figure 3 gives examples of glow curves obtained at a heating rate of 0.033°C/sec. for cubic and hexagonal ZnS:[Zn]:Cu-(0.003) phosphors. These curves are reproducible in general shape, but peak intensities differ by as much as 15 percent.

A comparison of the glow curves at 0.33°C/sec. and 0.033°C/sec. shows a general increase in detectable structure for the latter. Although the shifts of the major glow peaks are in agreement with the shifts predicted by the simple theory [Eqs. (4) and (5)], these results
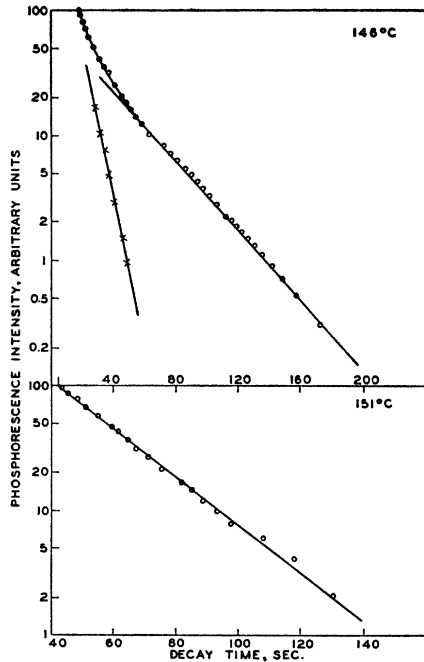
FIG. 4. Decay of phosphorescence emission for hex.—ZnS:[Zn]: Cu(0.01) at 146° and 151°C.

FIG. 6. Decay of phosphorescence emission for hex.— ZnS:[Zn]:Cu(0.01) at 75° and −9°C.

are inconclusive as far as the presence of component glow peaks is concerned.

Decay Curves

Typical decay curves for hex.—ZnS:[Zn]:Cu(0.01) at high temperatures (near the temperature at which the glow intensity becomes zero) are given in Fig. 4. The decay is exponential for long times of decay. If the final exponential portion is subtracted (Curve for 146°C), another exponential curve is found.

The agreement between the exponential decays at seven temperatures between 135° and 168°C and Eq. (2) is shown in Fig. 5. The logarithm of the decay constant is found to vary linearly with $1/T$, as predicted.

Figure 6 gives the decay curves for this same phosphor at 75° and −9°C. If the assumption is made that these
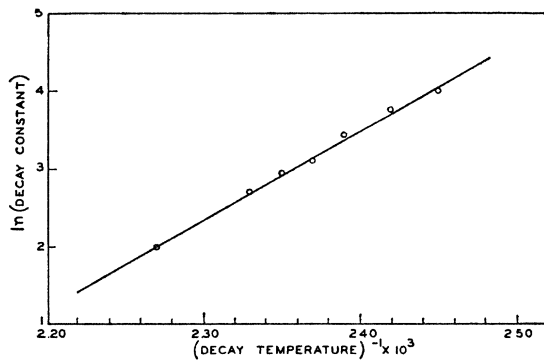
decay curves, and others like them for other temperatures, are to be analyzed into a series of exponentials, at least three exponentials are required for each decay curve. It is possible to start with the exponential found at high temperatures and by successive subtraction of exponentials to analyze the experimental curves into a set of exponentials. The analysis of the curves for 75° and −9°C in this way is shown in Fig. 6. Although the set of exponentials obtained in this way cannot be said to be unique because of the increasingly larger errors attendant on the subtractions, the least number of exponentials which would be required is estimated.

Glow Curves after Various Periods of Decay

A glow curve for traps of one depth [Eq. (3)] has the same shape and peak temperature regardless of the

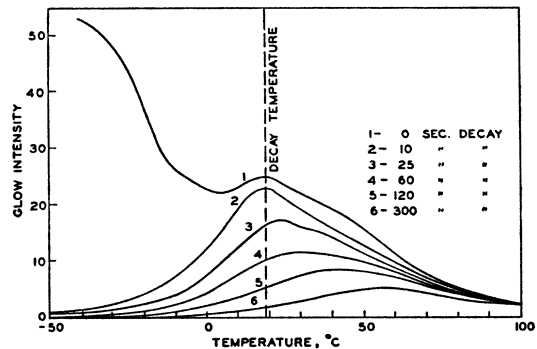FIG. 5. Plot of the log (decay constant) vs. (decay temperature)$^{-1}$ for hex.—ZnS:[Zn]:Cu(0.01).

FIG. 7. Glow curves for hex.—ZnS:[Zn]:Cu(0.01) after various times of decay at 19°C before cooling and starting the glow curve run.
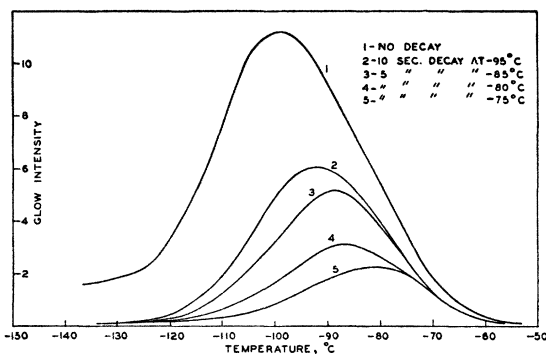
FIG. 8. Glow curves for cub.—ZnS:[Zn]:Cu(0.3) after various times of decay at temperatures between −75° and −95°C before cooling and starting the glow-curve run.

number of electrons trapped. Figures 7 and 8 show glow curves of hex.—ZnS:[Zn]:Cu(0.01) and cub.—ZnS:[Zn]:Cu(0.3) after various periods of decay at different temperatures. The phosphor was excited and then allowed to decay for the designated period. Then it was rapidly cooled to liquid nitrogen temperature, and the glow curve was measured.

The peak of the glow curve shifts continuously to higher temperatures with increasing periods of decay. The major glow peaks of Figs. 7 and 8, therefore, cannot be caused by traps of a single depth.

Glow Curves after Different Excitation Intensities and Periods; Retrapping (?)

Wilkins and Garlick[14] introduced a method for testing for the presence of retrapping. They used a hex.—ZnS:[Zn]:Cu phosphor with two distinct glow peaks: a low temperature peak caused by shallow traps and a high temperature peak caused by deep traps. When the phosphor was excited with very low intensity so that most of the traps were empty, they expected that the presence of retrapping by the deep traps of electrons freed from the shallow traps in the course of the glow curve run would make itself evident. Such retrapping would make the high temperature glow peak much more intense relative to the low temperature peak than was found in a glow curve obtained after high excitation intensity.

Measurements of this type have been extended over wide ranges of exciting intensity and periods of excitation. Figure 9 shows the results for hex.—ZnS:[Zn]:Cu(0.01) for excitation intensities varying by a factor of 10[4]. A fixed excitation period of five minutes was used. The curves are normalized in this case so that the intensity of the shallow-trap peak remains fixed.

Analogous results obtained by variation of the excitation period are shown in Fig. 10. An excitation intensity was used that was 0.3 percent of the normal intensity used in Figs. 1 and 2.

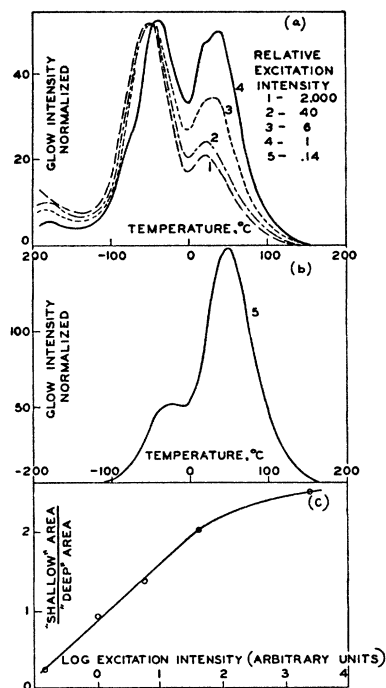For the sake of calculations, the glow curve is

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[14] M. H. F. Wilkins and G. F. J. Garlick, Nature 161, 565 (1948).

FIG. 9. Glow curves for hex.—ZnS:[Zn]:Cu(0.01) after excitation at −196°C by different excitation intensities.

divided into two major sections: (1) shallow traps between −100° and 0°C, and (2) deep traps above 0°C. The area under the glow curve for any portion of the curve is proportional to the number of electrons in traps which are responsible for the glow in that portion of the curve. Reducing the excitation intensity or the period of excitation causes an increase in the relative intensity of deep trap peaks with respect to shallow trap peaks.

Figures 9-c and 10-d show that the ratio of the areas of low temperature and high temperature glow peaks
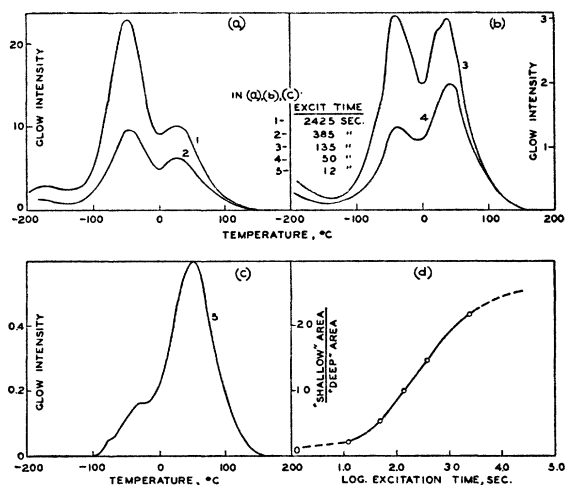

FIG. 10. Glow curves for hex.—ZnS:[Zn]:Cu(0.01) after excitation at −196°C for different excitation times.

approaches zero for low excitation intensities and short excitation periods.

V. DISCUSSION: PART I

Of fundamental importance in any discussion of glow curves and decay curves is the extent of the applicability of Eq. (1) and the equations derived from it. It is necessary to ask: (1) Is it experimentally possible to verify this equation directly? (2) What range of values may ν_a be expected to assume? (3) Can retrapping be neglected in ZnS:[Zn]:Cu phosphors?

Direct Proof of the Equation

Traps of a single depth were found in KCl:Tl by Buenger and Flechsig.[14a] They showed that the decay was exponential and that the decay constant varied with temperature in the manner expected from Eq. (2).

Traps of a single depth and with a temperature-dependent exponential decay were also found for a SrSiO$_3$:Eu phosphor by Garlick and Gibson.[4] The value of ϵ calculated from the glow curve was different, however, from the value calculated from the decay.

A direct proof of the equation for ZnS-type phosphors is demonstrated by Figs. 4 and 5. Exponential decay is found at high temperatures, for which the decay constant varies with temperature as expected from Eq. (2). The deepest trap in ZnS:[Zn]:Cu phosphors is found to have a trap depth of 1.00 ev.

Values of ν_a

The following values of ν_a have been reported in the literature: (1) 2.9×10^9 sec.$^{-1}$, Buenger and Flechsig,[14a] with traps of a single depth in KCl:Tl; (2) $10^{8\pm1}$ sec.$^{-1}$, Randall and Wilkins[2] from measurements of glow curves after various periods of decay, assuming a distribution of traps with the same ν_a, for ZnS phosphors and for calcium and strontium sulfides; (3) 10^{11} sec.$^{-1}$, Randall and Wilkins,[2] from similar measurements with cadmium borate and cadmium chlorophosphate, both with Mn activator; (4) 10^{10} sec.$^{-1}$, Mott and Gurney,[15] from the decrease of photo-conductivity at low temperatures for F-centers in alkali halides; (5) 10^{11} sec.$^{-1}$, Mott and Gurney,[15] from the cross section for luminescence capture of photo-electrons in alkali halides; (6) 6×10^6 to 2.5×10^7 sec.$^{-1}$, Garlick and Gibson,[16] from measurements of dielectric relaxation times for electrons in traps in ZnS:[Zn]:Cu and in other ZnS-type phosphors.[17]

Figure 5 of the present investigation gives a value for ν_a of 3×10^{10} sec.$^{-1}$ for the deepest trap in ZnS:[Zn]:Cu.

Subtraction of the decay of this trap depth gives the next shallowest trap depth a value of ν_a of 7×10^9 sec.$^{-1}$.

Theoretically ν_a might be expected to be larger than these values, about 10^{12} to 10^{13} sec.$^{-1}$ or the order of magnitude of the frequency of crystal vibrations. The fact that measured values are several orders of magnitude less than this indicate the presence of a small transition probability in the process of trap emptying, such as has been proposed by Mott and Gurney.[15]

An expression has been derived by Mott and Gurney[15] relating the attempt-to-escape frequency for an electron captured in a state (luminescence center or trapping state) to the cross section for capture of an electron into the state. For an equilibrium condition, the rate of capture of electrons by the state was equated to the rate of escape of electrons from the state. In this case, the relation is found:

$$\nu_a/\sigma = (2(6)^{\frac{1}{2}}\pi^{\frac{3}{2}}mk^2/h^3)T^2, \qquad (9)$$

where σ is the cross section for electron capture.

Because all of the reported values of ν_a lie above 10^6 sec.$^{-1}$, this value may be taken as a minimum to be considered for use in Eq. (1).

Importance of Retrapping

The study of glow and decay curves has led Wilkins, Garlick, Gibson, and Williams[4,14,18] to come to the conclusion that retrapping is negligible. In general their work has been non-quantitative and only partially conclusive.

The fact that the decay measured at high temperatures in the present investigation was found to be exponential, and that the decay constant varied with temperature in the manner predicted by Eq. (2), (Fig. 5), shows that at least for the deepest trap in ZnS:[Zn]:Cu retrapping is completely negligible. If retrapping did occur, a decay given by Eq. (6) would be expected, with a variation of the intensity according to t^{-2} at long decay times [Eq. (7)]. Retrapping of electrons by traps of the same depth as those from which they were freed does not occur in this case where a direct test was possible.

Figures 9 and 10 provide information on retrapping by deeper traps than those from which the electrons were freed. The relative intensity of the high temperature glow peak increases as the total number of electrons trapped decreases.

This dependence of glow-curve shape on excitation conditions could be caused by a larger probability for capture by a deep trap than by a shallow trap. Because there are many more shallow than deep traps in ZnS:[Zn]:Cu phosphors, the relative number of electrons trapped in shallow traps would increase as the total number of trapped electrons increased, and as saturation of the deep traps was approached. If the variations of glow-curve shape were caused by a larger

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[14a] W. Buenger and W. Flechsig, Zeits. f. Physik 67, 42 (1931).

[15] N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Oxford University Press, London, 1940).

[16] G. F. J. Garlick and A. F. Gibson, Proc. Roy. Soc. 188, 485 (1947).

[17] Omitted from this lisi of reported values for ν_a are the much lower values reported in reference 18. These are obtained by the rather arbitrary analysis of a glow curve tnto four component curves.

[18] F. E. Williams and H. Eyring, J. Chem. Phys. 15, 298 (1947).

capture probability for deep traps, the ratio of high temperature glow-peak area to low temperature glow-peak area should approach a constant value for low intensities and short excitation periods. This constant value would be the ratio of the capture probabilities multiplied by the ratio of the number of traps. The measurements of Figs. 9-c and 10-d show that a value of zero is the probable lower limit of the ratio of high temperature to low temperature glow-peak area. This result means that a simple difference in capture probabilities is not the cause of the changes in glow-curve shape with excitation conditions, unless the probabilities are different by a factor of 20 or more.

The glow-curve variations could be caused alternatively by the retrapping by non-filled deep traps of electrons freed from shallower traps in the course of the glow curve run. A certain area, corresponding to the number of electrons retrapped, would be displaced from the low temperature glow peak.

The glow-curve difference could not be caused by a larger probability of escape for electrons in shallow traps as compared to deep traps during excitation, because both the shallow traps and the deep traps have glow peaks far above the excitation temperature of $-196°C$.

If it is assumed that the whole dependence of the glow-curve intensities on excitation conditions is due to retrapping, a measure of the maximum amount of retrapping which could occur is obtained.

The glow curve for a high excitation intensity and long excitation period is used as a standard. Excitation for still longer times or at still higher intensities does not appreciably change the glow intensity or the relative intensities of high and low temperature glow peaks. Let the area measured under the low temperature glow peak for high excitation intensity and long excitation periods be L, and for a lower intensity and shorter period L'. Similarly let the respective high temperature glow-peak areas be H and H'. L is the number of shallow traps. H is the number of deep traps. R is the number of electrons retrapped, and is found from

$$(L'+R)/(H'-R)=L/H.$$

The number of electrons initially available for retrapping will be $(L'+R)$. The number of deep traps initially empty will be $[H-(H'-R)]$. The proportion of freed electrons retrapped, P_r, is $R/(L'+R)$. The number of initially empty deep traps per retrapped electron is $[H-(H'-R)]/R$.

A plot of P_r as a function of the number of deep traps initially empty is given in Fig. 11-b for the hex.—ZnS:[Zn]:Cu(0.01) phosphor of Figs. 9 and 10, and in Fig. 11-a for a cub.—ZnS:[Zn]:Cu(0.01) phosphor. The actual proportion of electrons retrapped is much less in cubic than hexagonal phosphors, because there are many less deep traps in the cubic phosphor.

The proportion of electrons retrapped is small until 80 or 90 percent of the deep traps are initially empty.
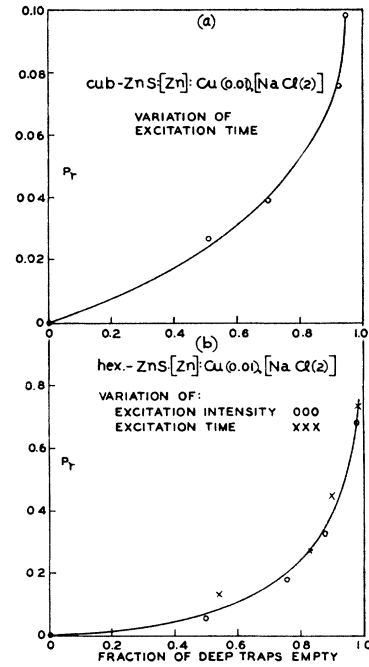

FIG. 11. Proportion of electrons freed from shallow traps which are retrapped by deep traps in the course of the glow-curve run as a function of the number of deep traps initially empty, for cubic and hexagonal ZnS:[Zn]:Cu(0.01).

The curve of Fig. 11-b shows that the proportion of electrons retrapped does not depend on whether changes in the number of electrons initially trapped were achieved by low excitation intensities or low excitation times.

The number of empty deep traps (at the start of the glow-curve run) per retrapped electron may be calculated for further information about the importance of retrapping. For excitation conditions such that less than 75 percent of the deep traps are initially empty, less than 20 percent of the freed electrons are retrapped. Over this range of excitation conditions, there are between 4 and 7 deep traps initially empty for every electron retrapped by these deep traps. For excitation conditions such that about 97 percent of the deep traps are initially empty, there are about 30 empty deep traps for every retrapped electron.

Although retrapping may occur, therefore, if a sufficient number of empty traps are present in which electrons may be stably retrapped,[19] retrapping does not play a role in the normal measurements of glow and decay curves for ZnS:[Zn]:Cu phosphors where initial excitation conditions are such that the number of empty traps is very small.

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[19] The retrapping of electrons by empty shallow traps (still deep enough, however, to empty slowly at the operating temperature) after the electrons had been freed from deep traps by infrared has been reported by Garlick and Mason, J. Electrochem. Soc. 96, 90 (1949), and D. Curie, Comptes Rendus 230, 1400 (1950).
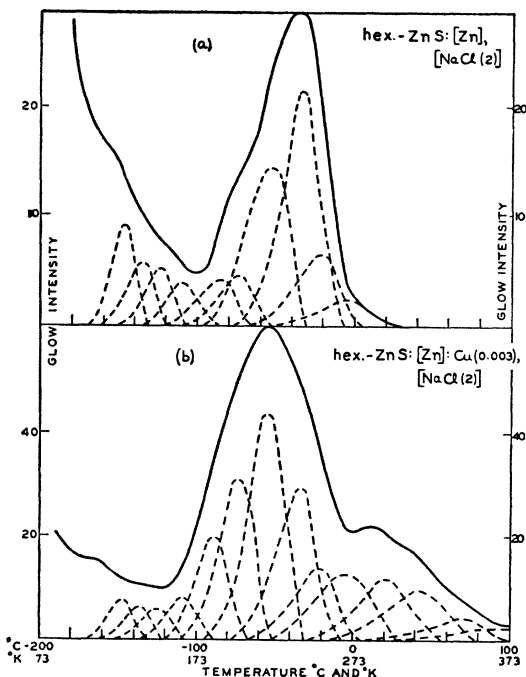
Fig. 12. Analysis of glow curves for hexagonal ZnS:[Zn] phosphor and for hex.—ZnS:[Zn]:Cu(0.003), using Eq. (3) for the shape of the component glow curves.

Analysis of Glow and Decay Curves

These results justify the use of Eq. (1) with a value of ν_a of greater than 10^6 sec.$^{-1}$.

Correlation between glow curves and decay curves for KCl:Tl was obtained (for decay curves near room temperature) by Randall and Wilkins[2] using Eq. (1) with the assumption of a narrow distribution of trap depths.

Because the glow curve of a ZnS phosphor was found by Randall and Wilkins to have an approximately exponential variation with temperature at room temperature, a continuous distribution of traps was assumed at room temperature such that the number of traps of a given depth decreased exponentially with increasing depth. Calculation using Eq. (1) showed that such a distribution of traps should give rise to a power-law decay. General agreement between glow curves and decay curves at this temperature was reported. Exact power-law decay is not found experimentally for any of the phosphors described in the present paper (an exponential variation of the glow curve with temperature was not found either), but approximate power-law decay is found for many temperatures for which the variation of the glow curve with temperature is not even approximately exponential.

The only previously reported separation of the glow curve into component curves where separate peaks are not found in the glow curve, was that done by Williams and Eyring[19] on the basis of absolute rate theory.[20] This

[20] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

theory gives an equation of exactly the same form as Eq. (1). A glow curve for a ZnS:[Zn]:Cu phosphor was approximately fitted by four component glow curves. Correlation with decay curves was not checked. This analysis gave low values of ν_a.

An analysis of the glow and decay curves of the present paper with the use of Eq. (1) gives the following results:

(1) Extremely low values of ν_a would be necessary to fit the experimental glow curves with two simple component curves calculated from Eq. (3). A reasonable fit between $-110°$ and $30°C$ may be obtained using $\nu_a = 10$ sec.$^{-1}$, but calculated decay curves do not agree with experimental decay curves.

(2) An estimate of the least number of component glow curves that would be needed to fit the experimental curve and still have ν_a be at least 10^6 sec.$^{-1}$ is obtained by dividing the widths of the experimental glow curves by the width of the calculated glow curve for $\nu_a = 10^6$ sec.$^{-1}$. At least three component curves would be needed to fit the principal central peak, and at least three or four component curves would be needed to fit the high temperature peak. Allowing for three or four subsidiary component curves to fill in the edges gives a total of at least 10 component curves.

(3) Figures 7 and 8 show that the glow maximum shifts to increasingly higher temperatures with increasing periods of decay before the glow-curve measurement. At least three component curves with $\nu_a = 10^6$ sec.$^{-1}$ would be required to fit the region over which the peak shifts in Fig. 7, and similarly at least two component curves would be required to explain Fig. 8.

(4) Glow curves measured at slow heating rates (Fig. 3) show no great increase in resolution of component detail, as might be expected if the number of component curves were small.

(5) Every measured decay curve (except at very high temperatures) must be analyzed into at least three exponentials, if it is to be analyzed into exponentials at all. Each exponential is attributable to a certain trap depth. It is possible for two exponentials at two different temperatures to refer to the same trap depth (since the decay constant is temperature dependent), but even allowing for such identities, at least about 12 different trap depths are required to describe the decay curves between $-83°$ and $200°C$.

(6) The glow curves of Figs. 1 and 2 have been analyzed into a set of twelve component curves with $\nu_a = 10^8$ sec.$^{-1}$ for temperatures above $-100°C$. These curves were chosen, first by noting (a) the apparent maxima and (b) gross inconsistencies with the asymmetry required by the calculated glow curves, and then by filling in with other curves required to make a good fit with the experimental curve (Fig. 12). It is possible to analyze all the curves of Figs. 1 and 2 into the same set of 12 component curves. Too much significance cannot be attached to the exact details of these analyses.

Until clearly distinct peaks are observed in the glow

curves, however, or until some means of resolving separate trap depths is found, it may only be said that the presence of a series of discrete trap depths in ZnS:[Zn]:Cu phosphors is plausible. The possibility remains that a continuum of trap depths followed by one or two discrete deep trap depths might also describe the experimental results.

VI. RESULTS: PART II

Emission Spectra

The spectral emissions of cubic and hexagonal ZnS:[Zn]:Cu(0.0–0.3) phosphors excited by 3650A ultraviolet at 24°C are given in Fig. 13. The curves are plotted to scale.

The emission of the ZnS:[Zn] phosphors without added copper is blue. Incorporation of copper up to a certain critical proportion causes the appearance of a green emission, and a decrease in intensity of the blue emission. Further incorporation of copper causes a blue band to appear. At very high copper proportions all visible emission disappears except a broad green band.

Spectrographic analysis[21] shows that the amount of copper added in the preparation of each phosphor is present in the phosphor sample. This means that changes in the spectral emission are not caused by differences between the amount of copper actually in the phosphors and the amount added in the preparation.

Of special interest is the emission for the highest proportion of copper used. Figure 14 is a tracing of the actual pen-drawing of the automatic recording spectroradiometer for the spectra of the cubic and hexagonal
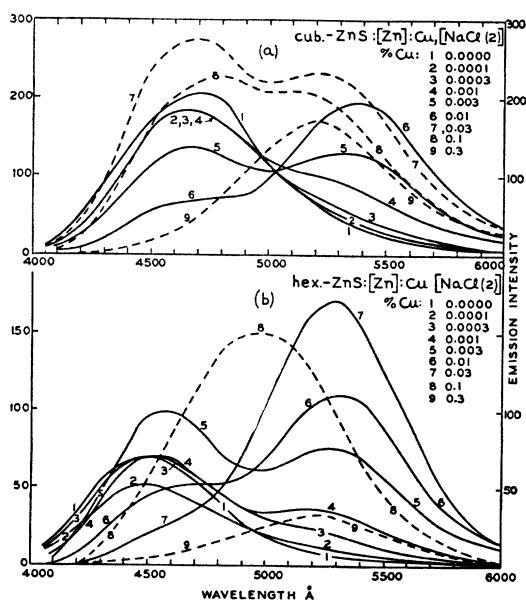

Fig. 13. Luminescence emission spectra for cubic and hexagonal ZnS:[Zn]:Cu(0.0–0.3) during excitation by 3650A ultraviolet at 24°C.

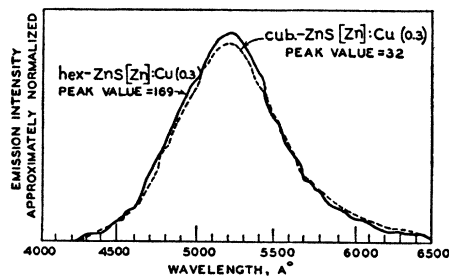[21] Spectrographic analysis by S. Larach.

Fig. 14. Trace of the pen-drawing of the automatic recording spectroradiometer for the spectral curves of cubic and hexagonal ZnS:[Zn]:Cu(0.3).

ZnS:[Zn]:Cu(0.3). Although the actual intensity of the cubic emission is about five times greater than that of the hexagonal emission, the gain was adjusted so that both curves were drawn to about the same scale. The spectral curves are strikingly similar.

Effects of Chemical and Physical Variations on Emission and Glow Curves

One of the principal correlations found is that a decrease in the ratio of green to blue intensity during excitation, caused by some chemical or physical change, is accompanied in general by an increase in the glow intensity for shallow traps for temperatures −170° to −100°C, and a decrease in the glow intensity for deep traps at higher temperatures. This change is caused by heating or preparing phosphors in an atmosphere containing hydrogen. Another way of causing this change is to recrystallize a cubic ZnS:[Zn]:Cu(0.01) phosphor to form a hexagonal ZnS:[Zn]:Cu(0.01) phosphor. The change, in this case, is stopped by the addition of sufficient chloride in the recrystallization.

Although the use of chloride in the preparation of phosphors was found to increase the number of traps and the intensity of the excited emission, and to affect the ratio of shallow to deep traps, it was also found that the presence of chloride or other halide is not essential for the presence of luminescence emission or trapping (Fig. 15). "Pure" ZnS, the same as was used in the preparation of the ZnS:[Zn]:Cu series, was heated at various temperatures from 950° to 1340°C with no additives whatsoever. Figure 15 shows that the logarithm of the number of traps increases linearly with the reciprocal of the heating temperature. (The number of traps is proportional to the area under the glow curve.) The intensity of the blue emission also increases as the heating temperature of the phosphor increases.

VII. GENERAL DISCUSSION

Nature of Crystal Defects in ZnS

Because a large number of traps are found in the same energy range both for ZnS:[Zn]:Cu phosphors and for ZnS:[Zn] phosphors without added Cu, these traps are the result of crystal defects in ZnS. It is also true that the activating impurity must occupy either an

interstitial or substitutional position in the crystal. A study of the types of defects in ZnS crystals is useful.

There are two different types of interstitial positions and two different types of substitutional positions in cubic and hexagonal ZnS.[22] The interstitial positions are pictured diagrammatically in Fig. 16. The small black dots at the centers of the respective crystal diagrams represent the interstitial positions. None of the interstitial positions is the same in cubic and hexagonal ZnS.

A Zn substitutional position in cubic ZnS, however, is identical with a Zn substitutional position in a hexagonal ZnS out to third nearest neighbors; similarly for S substitutional positions.

This striking difference between interstitial and substitutional positions naturally leads to a new analytical approach: Luminescence phenomena caused by impurities in interstitial positions will be different when observed in cubic and hexagonal ZnS phosphors, whereas luminescence phenomena caused by impurities in substitutional positions will be identical or practically identical whether observed in cubic or hexagonal ZnS phosphors. The validity of this approach depends on the assumption that simple defect formation does not alter symmetry relations in the crystal.

Use of the Analytical Approach

The use of this approach together with the experimental results of this paper leads to the following set of hypotheses which are able to explain all of the results found in this study.

(1) Trapping centers are located at substitutional sites, principally omission defects, in ZnS phosphors.

The general variation of glow with temperature is the same for all the curves of Figs. 1 and 2. The shallowest traps give a glow with a minimum at −120°C, the central peak is the principal peak and extends from −120° to 0°C or a little above, and the deep traps caused by copper extend from 0° to over 100°C. As a special example, the principal glow peaks for cubic and hexagonal ZnS:[Zn]:Cu(0.3) are almost identical.

The same set of component glow curves describes all of the curves of Figs. 1 and 2.

The variation of the number of traps with heating temperature (Fig. 15) for "pure" ZnS is exactly the same as the variation of the number of omission defects.[15] A reasonable value of 2.2 ev is found for the activation energy for omission-defect formation. (It is true that the number of interstitial defects varies with heating temperature in the same way, but with an activation energy of 4.4 ev.)

(2) The luminescence emission for which the Cu is responsible depends on the position of Cu in the crystal structure.

Because Fig. 13 has shown that the spectral curves for low copper proportions have different blue and green

[22] P. P. Ewald and C. Herman, *Strukturbericht* (Akademische Verlagsgesellschaft mbH, Leipzig, 1931), pp. 76–79.
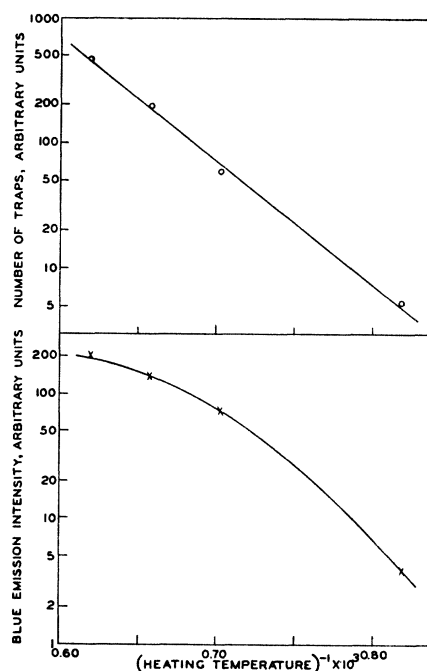

FIG. 15. The variation of the number of traps and of the blue emission intensity with preparation heating temperature for "pure" ZnS:[Zn].

bands for cubic and hexagonal phosphors, the impurities responsible for these emissions are located at interstitial sites. This agrees with the findings of Riehl and Ortmann,[23] and Seitz.[24,25]

The work of other investigators has included measurements on the spectra of ZnS:[Zn]:Cu phosphors up to the proportion of Cu for which a blue band reappears.
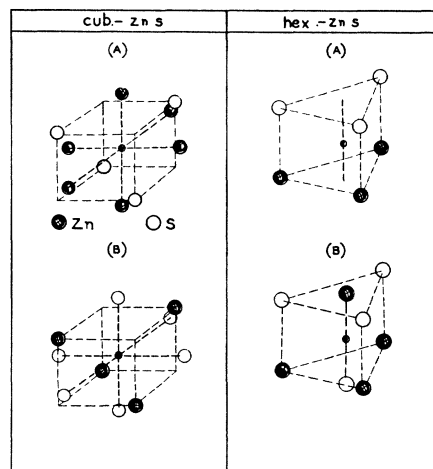

FIG. 16. Types of interstitial positions in cubic and hexagonal ZnS crystals. The small black dots represent the interstitial positions.

[23] N. Riehl and G. Ortmann, Zeits. f. physik. Chemie **188**, 109 (1941).
[24] F. Seitz, Trans. Faraday Soc. **35**, 74 (1939).
[25] F. Seitz, J. Chem. Phys. **6**, 454 (1938).

But, previous to this present paper, there has been no mention[26] to the knowledge of the author of the return of the emission to a broad green band for very high copper proportions, which band (Fig. 14) is almost identical for cubic and hexagonal ZnS:[Zn]:Cu(0.3). This identity of the emission bands for cubic and hexagonal phosphors means that the copper responsible for this emission is located in substitutional sites.

The reappearance of a blue band in the curves of Fig. 13 at a critical copper proportion marks the entrance of copper into substitutional sites. At low copper proportions, copper is located predominantly in interstitial positions and is responsible for a green emission. At some critical proportion, more copper is located in substitutional sites and is responsible for a blue emission. At very high copper proportions, only a broad green emission caused by pairs of substitutionally located copper ions is found.

(3) The effect of Cu on traps depends on the position of Cu in the crystal structure.

A comparison of Figs. 1 and 2 and Fig. 13 shows that deep traps are caused by copper when it is responsible for a green emission. The effect of interstitial copper is to perturb neighboring omission defects and cause deeper trap depths.

When copper gives rise to a blue emission, and for all larger proportions of copper, traps are destroyed. When copper enters substitutional positions, it destroys the traps which existed previously at those omission defects.

Shallow traps are located at sulfur omissions because these are the most likely to form. Because the entrance of copper into substitutional positions occurs at Zn positions, however, neighboring zinc and sulfur omission defects are indicated as trapping centers of intermediate depth.

(4) The role of the chloride, or other halide, in ZnS phosphors is to assist the temperature-dependent formation of defects.

An increase in the number of traps and of the intensity of the luminescence emission, which may be achieved by the use of chloride in the preparation, can be achieved also by merely raising the heating temperature of phosphor formation sufficiently (Fig. 15).

The use of chloride, bromide, or iodide in ZnS phosphors all give rise to the same spectral distribution of the emission.[27] This would hardly be expected if the chloride were an inherent part of the emission center, as was originally proposed by Kroeger et al.[28,29] Recently Kroeger[30] has altered this view in favor of one more com-

patible with these results. If the effect of the chloride were simply to increase the formation of defects, however, the luminescence emission would be characteristic of the defect and its surrounding in the crystal, and would not be dependent on the way it had been formed.

The emission change from green to blue and the destruction of deep traps when cub.—ZnS:[Zn]:Cu(0.01) is recrystallized into hex.—ZnS:[Zn]:Cu(0.01) indicates the entrance of copper into substitutional positions. The addition of chloride in the recrystallization prevents this by acting to keep copper in interstitial positions.

VIII. CONCLUSIONS

A large number of traps are present in ZnS:[Zn] phosphors with no added impurity. The incorporation of copper up to 0.01 percent causes the appearance of traps which are deeper than those present before the addition of copper. Incorporation of copper in amounts of more than 0.01 or 0.03 percent causes the traps due to copper, and also some of the deeper traps present before the addition of copper, to disappear. In proportions up to 0.01 percent, the copper is found to be responsible for a green luminescence emission. At about the proportion for which the deep traps start to disappear, a blue band is found. For very high proportions of copper, a green band is found that is almost identical for both cubic and hexagonal phosphors. These results may be explained by assuming a transition from interstitial copper to substitutional copper.

Equation (1) of Randall and Wilkins[2] was proven directly for a ZnS-type phosphor from measurements of decay at high temperatures. The deepest traps in ZnS:[Zn]:Cu phosphors have a single trap depth of 1.00 ev, and an attempt-to-escape frequency of 3×10^{10} sec.$^{-1}$. Subtraction of this decay yields for the next deepest trap depth, a single depth of 0.89 ev, and an attempt-to-escape frequency of 7×10^9 sec.$^{-1}$.

The present measurements, together with previously published results of other investigators, favor the assumption that the probable range of values for the attempt-to-escape frequency is between 10^8 and 10^{10} sec.$^{-1}$, with a minimum of about 10^6 sec.$^{-1}$.

The agreement of the decay with Eq. (1) at high temperatures, indicates that retrapping of electrons by traps of the same depth as those from which they were freed does not occur. If retrapping did occur, the shape of the decay curve would be given by Eq. (6) instead of by an exponential.

The other possibility of retrapping is that freed electrons may be retrapped in deeper traps than those from which they were freed. It is shown for the hexagonal ZnS:[Zn]:Cu phosphors, assuming the maximum amount of retrapping possible, that there are at least four to seven empty deep traps for every electron retrapped. Normal measurements, therefore, which are

[26] Except reference 7.

[27] Spectral curves obtained by the Chemico-Physics Section of the RCA Laboratories show that spectral distributions are the same whether chloride, bromide, or iodide is used, although the efficiencies are slightly different.

[28] F. A. Kroeger and J. E. Hellingman, J. Electrochem. Soc. 93, 156 (1948); 95, 68 (1949).

[29] Kroeger, Hellingman, and Smit, Physica 15, 990 (1949).

[30] F. A. Kroeger and J. Dikhoff, Physica 16, 297 (1950). From the sizes of the ionic radii, it would be expected that a change from interstitial to substitutional Cu would also mean a change from

Cu$^+$ to Cu^{++}. Kroeger has proposed that the presence of Cl$^-$ aids the formation of Cu$^+$ on the basis of charge compensation.

obtained after excitation by high intensity and for a long time, at least for ZnS:[Zn]:Cu phosphors, are not affected by retrapping.

The existence of a series of discrete trap depths, at least 12 in number between $-100°$ and $200°C$, appears plausible. Definite evidence, however, was not obtained that a continuous distribution of trap depths, followed by one or two discrete depths, could not give an alternative description of the observed results.

A study of the crystal structure of ZnS indicates that interstitial positions are all different in cubic and hexagonal ZnS, whereas substitutional positions are the same out to third nearest neighbors. A new analytical approach was indicated, therefore, which states that, if formation of simple defects does not alter symmetry relations, luminescence phenomena caused by impurities in interstitial positions should be different when observed in cubic and hexagonal ZnS phosphors, but that luminescence phenomena caused by impurities in substitutional positions should be the same or practically the same when observed in cubic and hexagonal ZnS phosphors.

The similarity in trap depths found for cubic and hexagonal phosphors leads to the hypothesis that trapping centers are located in substitutional sites, primarily omission defects. This hypothesis and the previously mentioned analytical approach may be used to interpret many observations of luminescence emission and glow curves.

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Quantum Electrodynamics of Charged Particles without Spin

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Feynman's formulation of quantum electrodynamics is shown to be equivalent to the Schwinger-Tomonaga theory also for spinless charged particles (mesons) as developed by Kanesawa and Tomonaga. The divergencies of the scattering matrix are analyzed to all orders in the fine-structure constant and it is found that mass and charge renormalizations do *not* remove all divergencies, unlike the electron case. The remaining divergence is associated with the meson-meson interaction and occurs in all orders of radiative corrections except the lowest (second) order in which the process can exist. In order to make the scattering matrix completely finite a direct interaction term $\lambda\phi^*(x)\phi^*(x)\phi(x)\phi(x)$ in the Hamiltonian must be postulated. The infinite coupling constant λ is to be renormalized by an infinite renormalization. One obtains a finite amount of direct interation which must be determined from experiment. The identical cancellation of certain divergencies to all orders of the fine-structure constant and valid for spin 0, $\frac{1}{2}$, and 1 is proven in the Appendix.

I. INTRODUCTION

THE theory of the interaction of elementary particles has been formulated in two equivalent ways by Schwinger and Tomonaga, and by Feynman. So far the equivalence has been proven explicitly only for the interaction of electrons with the electromagnetic field,[1] but there seems to be little doubt that it holds also for the interaction of the electromagnetic field with particles of other spin and for nuclear interactions as described by meson theories. Also, a consistent separation and removal of divergencies to all orders in the coupling constant has so far been shown possible only

for the quantum electrodynamics of the electron. Dyson[2] showed that this could be achieved by a consistent procedure of mass and charge renormalization. The resultant finite effects as far as they have been calculated seem to agree well with experiments. This theory is therefore outstanding as the only one both as to finiteness to all orders and correctness.[3]

This success of the theory of the interaction of electrons, positrons, and photons warrants a similar investigation for other elementary particles. As a first step

[1] F. J. Dyson, Phys. Rev. 75, 486 (1949). In the following quoted as I.

[2] F. J. Dyson, Phys. Rev. 75, 1736 (1949). In the following quoted as II.

[3] For an extension of these results to the interaction of spinless mesons with nucleons see P. T. Matthews, Phil. Mag. 41, 185 (1950) and Phys. Rev. (to be published).