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The phosphorescence and thermoluminescence of zinc sulfide phosphors are governed by the mechanism of electron trapping in the phosphor crystal lattice. Experiments have been carried out to find the effect of phosphor constitution and method of preparation on the numbers and the energy distribution of electron traps. In order to investigate the traps, use has been made of the thermoluminescence *vs.* temperature characteristics of the phosphors.

These experiments show that pure zinc sulfide and zinc sulfide activated by silver and manganese possess similar "shallow" electron trap configurations after preparation and that these configurations are not markedly dependent on the particular activator. However, the introduction of copper impurity to zinc sulfide causes a marked change in the number and distribution of electron traps and is responsible for the long afterglow of these phosphors. Investigations of the effect of firing temperature and crystal form on the electron traps show that below the blende-wurtzite transition temperature (1020°C)

the proportion of deep traps increases with firing temperature but that above this temperature the trap distribution is independent of the firing temperature or of fluxes and excess of sulfur. Experiments attempting to show that these traps were due to stoichiometric excess of zinc gave inconclusive results, but it is clear that the deep electron traps which produce the long afterglow characteristics of zinc sulfide are due both to the presence of copper impurity and to some change produced in the zinc sulfide lattice at high temperature without copper being present.

Other studies have been made of the effect of the mixed crystal proportions in the ZnS-CdS-Cu phosphor system on the electron traps. At high CdS contents some relatively deep electron traps are produced. Measurements of the fluorescence *vs.* temperature characteristics of the above phosphors show how the phosphor constitution and firing temperature affect the temperature at which the thermal quenching of fluorescence becomes appreciable.

INTRODUCTION

WHEN electrons are raised into the conduction levels of an insulating crystalline solid they frequently become trapped in special positions where localized energy levels, called electron traps, exist just below the conduction levels. Trapped electrons may be raised to the conduction levels by thermal energy and may, in luminescent solids, then produce phosphorescence and thermoluminescence by return to their original ground states in the luminescence centers. Trapped electrons also produce optical absorption and thus often are known as color centers![1] Capture of electrons by traps is shown clearly by studies of photo-conductivity.[2]

In the alkali halides the color centers which constitute the electron traps exist in the localized regions where a halogen ion is missing from the crystal lattice. The chemical nature of trapping centers in other solids is, however, largely unknown, and the present work is an attempt to determine the nature of electron traps in zinc sulfide phosphors. The research was carried out in 1940–41 for the Ministry of Home Security, and though never completed it is of interest as being the first study of zinc sulfide constitution using the "thermal glow curve" technique (Randall and Wilkins[3]) in which the phenomenon of thermoluminescence is used to analyze the distribution of trap energy levels.

THE MODE OF PREPARATION OF PHOSPHORS

The basis of all the phosphors was pure precipitated zinc or cadmium sulfide obtained from Messrs. Levy and West. Heavy metal impurity atoms were added by mixing the sulfide to a paste with a solution of a salt of the heavy metal in redistilled water (Pyrex still); fluxes, such as sodium chloride, were "Analar" chemicals, and these were dissolved in the paste. The mixture was dried on a watch glass in a steam oven and then ground and thoroughly mixed in an agate mortar. The phosphor was then fired in an electric furnace in a silica ignition tube sealed at one end. (The tube was 12 inches long with $\frac{1}{2}$-inch bore, and the mixture occupied approximately 2 inches of the tube length.) The open ends of the tubes were placed in the cold furnace, the temperature raised gradually over a period of one to three hours, and the tubes removed when the required temperature was attained. Experiments were also made with phosphors heated in sealed bulbs made from $\frac{1}{2}$-inch bore silica tubing. The bulbs were outgassed by heating to approximately 1000°C on the pump. Water and sulfur, etc., were removed from the precipitated zinc sulfide by heating to a few hundred degrees centigrade in the bulb in vacuum, and the bulb was then sealed while still connected to the pump.

METHOD OF PRESENTATION OF EXPERIMENTAL RESULTS

Throughout the following sections the results of experiments show how the mode of preparation and chemical constitution of the phosphor affect the energy level distributions of electron traps and therefore the phosphorescence characteristics. In

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[1] R. W. Pohl, Proc. Phys. Soc. 49 (extra part), 3 (1937).
[2] B. Gudden and R. W. Pohl, Zeits. f. Physik 17, 340 (1923).
[3] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. A184, 366 (1945).

Trap depth in ev	Thermal glow temperature in °K	Mean phosphorescence decay time at 291°K
0.2	100	0.0003 sec.
0.4	200	1 sec.
0.6	300	46 min.
0.8	400	100 days

order to determine the electron trap distributions, use is made of the "thermal glow" experiment as developed by Randall and Wilkins.[3] The phosphor specimen is mounted in a very thin layer on a rhodium plated copper surface forming part of the inner portion of a german-silver Dewar vessel, and is in vacuum during the experiments. The specimen is cooled to liquid air temperature, strongly excited by suitable radiation (in the following experiments filtered radiation of wave-length 0.365μ was used), and then warmed at an approximately uniform rate in the dark. The variation of thermoluminescence intensity with temperature is recorded continuously during this warming by means of an electron multiplier and galvanometer, the temperature being measured by a thermocouple attached to the copper surface, and a second galvanometer. By suitable development of technique both the thermoluminescence emission and the phosphor temperature are recorded manually on a rotating drum by one observer. The horizontal scale in the glow curve diagrams is a linear time scale marked in temperature intervals.

The theoretical interpretation of the thermal glow curve (that is, the recorded variation of thermoluminescence with temperature) has been given by Randall and Wilkins.[3] For a uniform rate of warming, and to the first degree of approximation, the thermoluminescence intensity at the absolute temperature T is proportional to the number of electrons traps of depth E (where E is the activation energy associated with the release of an electron from a trap), and E can be assumed to be proportional to the temperature T over the temperature range used. The proportionality constant between E and T depends on several factors, including the rate of warming, and for the experimental conditions described here (warming rate ~ 2.5°K sec.) the relation between E and T is such that emission at 300°K is due to electron traps of depth ~ 0.6 ev. However, in the figures given the temperature scale has been retained, but the approximate trap depths can be deduced from the above relation. Electron traps referred to as "shallow" in the text are those below 0.5 ev—that is, those contributing to thermal glow at temperatures below 250°K and "deep" traps correspond to thermal glow above 250°K. It is useful, with respect to the phosphorescence characteristics of the specimens described, to give a few relations between the thermal glow temperature, the trap depth, and the mean phosphorescence decay time at room temperature due to electron traps of "shallow" and "deep" designations. These relations are contained in Table I for the experimental conditions described above. Throughout this paper the constitution of a phosphor is given by the percent ratio of the number of metallic impurity atoms to the number of metallic matrix atoms. The crystal structure of the phosphor was determined by both x-ray diffraction and polarizing microscope.

EXPERIMENTAL RESULTS

(a) Pure ZnS, ZnS-Ag, and ZnS-Mn phosphors

If pure zinc sulfide is heated without any foreign activator metal to a temperature of about 500°C or above, a phosphor luminescing blue is produced.[4,5] The thermal glow curves of Fig. 1 show that the electron traps in this type of phosphor are distributed over a wide range; more deep traps are produced when a higher firing temperature is used between 500° and 900°C, but from 900°C to 1500°C there is no significant change in the thermal glow curve. The curves b, c, d in Fig. 1 were chosen from many dozen curves to show the extreme variation of curve which may occur. Double and single peak curves occur apparently at random, and no significant difference in this respect was found between phosphors having a zinc blende structure and those having a wurtzite structure. Attempts to "kill" the traps and the luminescence, which are both likely to be due to a stoichiometric excess of zinc, by heating the phosphor in about one-atmosphere pressure of sulfur vapor in a sealed quartz tube were unsuccessful.

Zinc sulfide activated by manganese or silver impurity gave the same type of thermal glow curve as
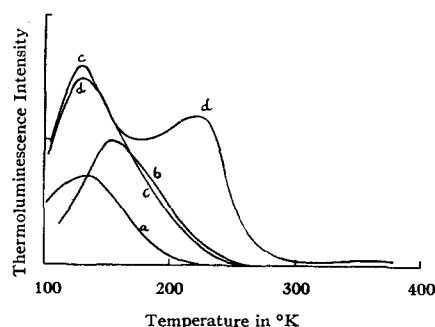

FIG. 1. Thermoluminescence characteristics of self-activated ZnS phosphors. (a) ZnS: blende lattice: made at 600°C in open tube; (b) ZnS: blende lattice: made at 930°C with sulfur vapor in sealed tube; (c) ZnS: blende lattice: made at 900°C with 10 percent NaCl in open tube; (d) ZnS: wurtzite lattice: made at 930°C in open tube.

[4] S. Rothschild, Zeits. f. Physik 108, 24 (1937).
[5] A. Schleede, Zeits. f. angew. Chemie 48, 276 (1935).

the "pure" specimens. Examples of curves for these phosphors are given in Fig. 2.

(b) Copper Activated ZnS Phosphors

The addition of copper (1 part in 10^4) to zinc sulfide may appreciably alter the electron trap distribution and also change the color of luminescence from blue to yellow-green. The mode of heating and the crystal form (i.e., blende or wurtzite or a mixture of both) can also be important factors in determining the luminescence[6] and the trap distribution. If the phosphor is prepared in an atmosphere of sulfur, the thermal glow curve, for firing temperatures between 400° and 900°C, does not differ appreciably from that of pure zinc sulfide, there being more deep traps the higher the firing temperature (as shown by the curves a, b, c, d of Fig. 3); and the sulfide crystallizes in the blende
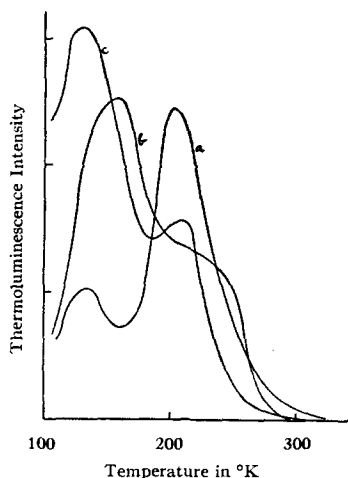
FIG. 2. Thermoluminescence curves of silver and manganese activated zinc sulfide phosphors. (a) ZnS-Ag No. 1; (b) ZnS-Ag No. 2; (c) ZnS-Mn.

form. If, however, the zinc sulfide is heated in an open tube without sulfur, some wurtzite structure is formed, and the trap distribution is quite different if copper is present (curve e; Fig. 3). The transition temperature for the blende-wurtzite structure change is given as 1020°C,[7] though it has been suggested that this temperature should be much lower.[8] The transition temperature at 1020°C was confirmed by heating fine grain wurtzite at 1000°C with sulfur or a flux, such as sodium chloride, both of which increase the rate recrystallization, blende being formed. Again, if coarsely crystalline blende or large lumps of natural zinc blende are heated for about an hour at 1040°C, wurtzite is formed though the external shape of the crystals may remain

[6] S. Rothschild, Trans. Faraday Soc. 42, 635 (1946).
[7] A. T. Allen and J. L. Greenshaw, Zeits. f. anorg. allgem. Chemie 79, 130 (1913).
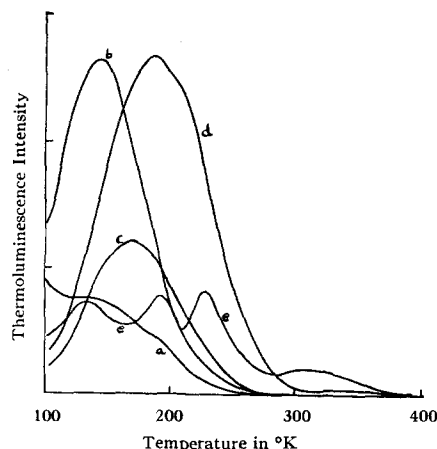[8] F. Seitz, J. Chem. Phys. 6, 454 (1938).

FIG. 3. Effect of crystal form and firing temperature on the thermoluminescence of ZnS-Cu (0.01 percent) phosphors. (a) ZnS-Cu: blende lattice, 600°C; (b) ZnS-Cu: blende made at 765°C in sealed tube; (c) ZnS-Cu: blende: made by firing for 7 hours in sealed tube with sulfur at 850°C; (d) ZnS-Cu: largely blende: made with sulfur in sealed tube at 980°C; (e) ZnS-Cu: partly wurtzite made at 765°C in open tube.

unaltered. Blende only changes to wurtzite below the transition temperature if fine-gained zinc sulfide is heated alone, and it appears that the wurtzite is formed by sublimation, the condensing wurtzite crystals being metastable.

If the zinc sulfide is heated with sulfur or flux to prevent the formation of wurtzite below the transition temperature, more deep electron traps are formed as the temperature is raised from 900° to 1000°C as shown in Figs. 3 and 4. The presence of these deeper traps in blende phosphors is indicated in the thermal glow curve by the development of a "tail" at the high temperature end of the curve (Fig. 4 curves a and b, Fig. 5 curve a, and Fig. 6 curve a). This tail, which is associated with an appreciable phosphorescence of many seconds at room temperature, is not present in pure zinc sulfide phosphors or in silver or manganese activated specimens and is produced by the addition of copper. The development of this tail in the thermal glow curve is continuous as the firing temperature is raised, but when approximately 1020°C is reached wurtzite is formed with a characteristic "wurtzite glow curve" (Fig. 4, curves c, e, and d), and the tail, characteristic of blende structure, changes to a large thermal glow peak with a maximum in the region of 320°K. These deep electron traps (~0.65 ev), because of the presence of copper in the wurtzite form of zinc sulfide, produce the afterglow in all commercial long afterglow zinc sulfide phosphors. If the phosphor is prepared at a temperature above 1100°C, the thermal glow curve does not alter and is independent of the presence of flux or of sulfur. It would appear, however, from the above results that the wurtzite structure is not essential for the existence of some deep traps associated with copper in
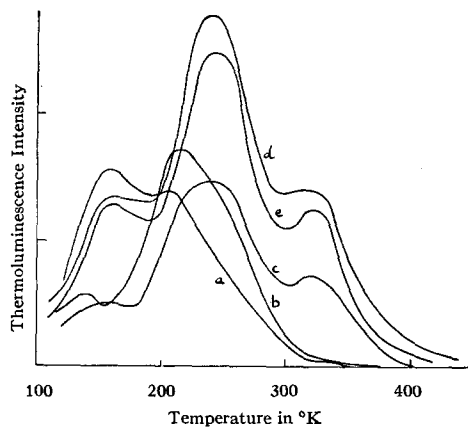
FIG. 4. Development of deep traps in ZnS-Cu phosphors with increase in firing temperature. (a) thermal glow curve of ZnS-Cu: plus 10 percent NaCl: made at 980°C: all blende; (b) thermal glow curve of ZnS-Cu: plus 10 percent NaCl: made at 1000°C: trace wurtzite; (c) thermal glow curve of ZnS-Cu: plus 10 percent NaCl: made at 1028°C: largely wurtzite; (d) thermal glow curve of ZnS-Cu: made at 1180°C; (e) thermal glow curve of ZnS-Cu: made at 1480°C wurtzite.

copper activated zinc sulfide. The blende-wurtzite transition takes place in a temperature range where the number of deep traps produced varies rapidly with the firing temperature and, as a result, a large number of deep traps is only found when the phosphor has been heated sufficiently for the blende-wurtzite transition to take place. The effect of flux below the transition temperature is shown by the thermal glow curves of Fig. 5; wurtzite with a large number of deep electron traps can be formed at firing temperatures as low as 930°C if no flux is used, such phosphors having an afterglow comparable with that of the phosphor fired at 1100° with flux.

(c) The Effect of Sulfur Concentration on Copper Activated ZnS Phosphors

The following incomplete observations have been made on the effect of sulfur vapor pressure during firing on the electron trap distributions in zinc sulfide phosphors. By analogy with oxygen deficient
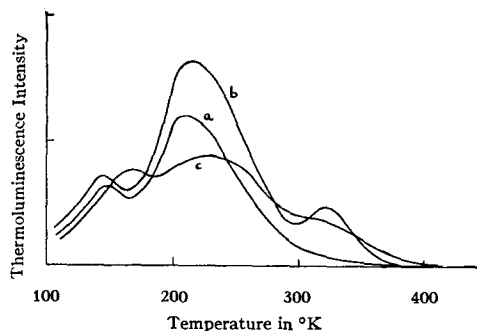

FIG. 5. Effect of flux on thermoluminescence characteristics of ZnS-Cu phosphors. (a) ZnS-Cu (0.01 percent) +10 percent NaCl: blende lattice: made at 980°C; (b) ZnS-Cu (0.01 percent) no flux: wurtzite lattice: made at 980°C; (c) ZnS-Cu (0.01 percent) no flux: largely wurtzite lattice: made at 930°C.
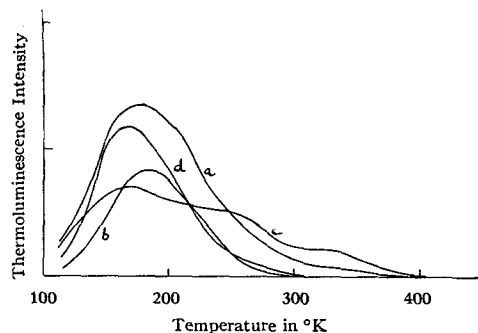

FIG. 6. Suppression of traps by sulfur treatment in blende and wurtzite ZnS-Cu phosphors as shown by thermal glow curves. (a) ZnS-Cu+5 percent MgCl$_2$ fired at 950°C for 20 min. in open tube: blende; (b) ZnS-Cu+5 percent MgCl$_2$+S: fired at 950°C for 4 hr. in sealed tube: blende; (c) ZnS-Cu made at 1030°C (wurtzite) refired at 850°C for 1 hour in sealed tube with sulfur; mainly wurtzite (d) ZnS-Cu made at 1030°C (wurtzite) refired at 850°C with sulfur for 6 hours in sealed tube: blende.

zinc oxide and other excess semiconductors, one would expect that the blue luminescence of pure zinc sulfide and the shallower electron traps in copper activated zinc sulfide might be associated with sulfur deficiency in the sulfide lattice.[9] Experiments designed to test this hypothesis gave no very definite evidence for or against it. In fact, it is not easy to carry out experiments to test the effect of variation in sulfur concentration on the electron trap distribution. It must be recognized that ZnS-Cu phosphors are normally produced in a cloud of sulfur vapor (also sulfur dioxide) resulting from the evaporation of sulfur contained in the original zinc sulfide precipitate. In experiments with phosphors made in sealed quartz tubes the pressure could be increased to one to five atmospheres, but any really effective attempt to remove sulfur vapor also removed the green luminescence characteristic of the copper impurity (and, if anything, also reduced the blue emission). Phosphors prepared by heating in vacuum luminesce a pale blue and cannot be reactivated by adding copper afterwards at 600°C. The same applies to copper activated zinc sulfide phosphors fired in crucibles at temperatures above 1500°C. It appears that copper escapes from the zinc sulfide lattice under these conditions, and some permanent change is produced in the lattice which prevents copper from re-entering. The recent significant observations of Rothschild[6] on the role of halides in zinc sulfide phosphors may lead to an explanation of some of these observations.

A number of experiments were carried out which appeared at first sight to indicate that the deep electron traps in ZnS-Cu phosphors were due to sulfur deficiency. Copper activated phosphors fired at 1100°C did not alter their trap distribution if refired at 1100°C in a closed tube containing a few

[9] J. T. Randall, Trans. Faraday Soc. 35, 85 (1939).

atmospheres of sulfur vapor but, if refired at 800°–900°C for as long as six hours with sulfur, the deep traps were "killed" (compare curves c and d, Fig. 6). Heating at 900°C for only one hour did not, however, alter the phosphor and hence, if sulfur deficiency is associated with traps, it would appear that sulfur cannot readily diffuse into the zinc sulfide lattice. After one hour of firing at 850°C the coarsely crystalline phosphor was inappreciably recrystallized, but after six hours the phosphor was entirely converted into plate-like blende crystals. In all experiments which showed sulfur "killing" of electron traps a new recrystallized phosphor was produced at a lower temperature than the original, and it was immaterial whether the constituent atoms of this phosphor were derived from the original phosphor or from unheated zinc sulfide. It appears that sulfur is effective in "killing" deep electron traps only because it is an effective recrystallizing agent or flux. It is clear that an increase of 50°C in the firing temperature (especially in the range 950°C to 1050°C) produces a noticeable increase in the number of deep traps, but an increase in the sulfur vapor pressure, while tending to decrease the number of deep traps, never produces such a clear-cut change as does this small increase in temperature. In no case was it possible (without additional impurity inclusions such as nickel) to produce wurtzite phosphors with the luminescence characteristic of copper but possessing no deep traps. Possibly, if copper activated zinc sulfide phosphors were fired at temperatures slightly in excess of 1020°C with several hundred atmospheres of sulfur vapor, this result could be achieved.

If the deep electron traps in ZnS-Cu phosphors are not associated with excess or deficiency of sulfur, it is possible that they might be due to disorder in the crystal lattice produced at the high firing temperatures and frozen in by rapid cooling. Rapid cooling or slow annealing (six hours to fall in

FIG. 8. Thermoluminescence characteristics of ZnS-CdS-Cu phosphors made at 1100°C. (a) ZnS (85 percent)-CdS (15 percent) no copper; (b) ZnS (85 percent)-CdS (15 percent)-Cu (0.01 percent); (c) ZnS (55 percent)-CdS (45 percent)-Cu (0.01 percent; (d) ZnS (45 percent)-CdS (55 percent)-Cu (0.01 percent) curve increased in height approx. 10 times.

temperature from 1050° to 950°C), however, did not alter the trap distribution in the phosphor.

Further light is cast on the nature of deep traps in ZnS-Cu phosphors by experiments in which the zinc sulfide was heated to a high temperature without copper and the copper added in a subsequent refiring at 400°–600°C. The effect of this refiring on the glow curve is shown by curves a and b of Fig. 7. (The small thermal glow between 300° and 400° on curve a is due to small traces of copper—probably 0.001–0.0001 percent). The phosphor produced in this way was almost identical in characteristics with that produced by firing the zinc sulfide together with copper impurity at the high temperature. It is clear that high temperature treatment of the zinc sulfide produces some change in the crystal lattice and that the copper impurity may afterwards diffuse into the lattice at a much lower temperature. The presence of copper and the change in the lattice together produce the deep electron traps.

Curve c of Fig. 7 shows the "killing" effect of a small amount of nickel impurity on the trap distribution of ZnS-Cu phosphor. Independent measurements of dielectric changes in nickel-killed phosphors, made by Garlick and Gibson (1947)[10] show that the deep traps are destroyed by the nickel and not merely inhibited from supplying electrons to
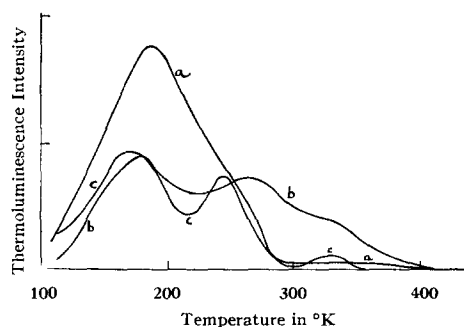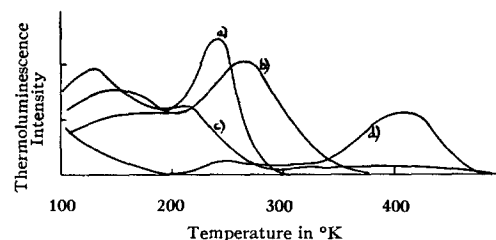

FIG. 7. Effect of copper addition to pure ZnS phosphor at relatively low temperature and destruction of traps by addition of Ni as shown by thermoluminescence curves. (a) pure ZnS phosphor made at 1050°C: wurtzite: blue luminescence; (b) phosphor a reheated at 425°C with 0.01 percent Cu: green luminescence; (c) ZnS-Cu phosphor (wurtzite) heated at 1100°C with 0.0005 percent Ni.
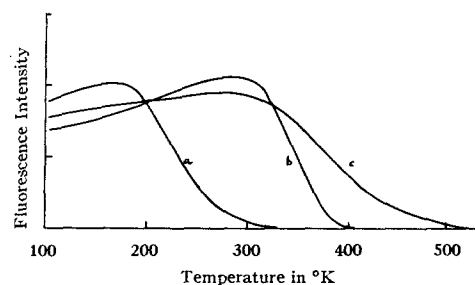

FIG. 9. Fluorescence $vs.$ temperature curves for pure ZnS and ZnSAg phosphors excited by 3650A radiation of constant intensity. (a) pure ZnS made at 500°C: blende; (b) pure ZnS made at 1000°C: blende; (c) ZnS-Ag made at 1000°C: blende.

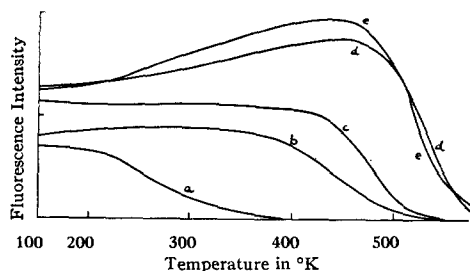[10] G. F. J. Garlick and A. F. Gibson, Proc. Roy. Soc. A188, 485 (1947).

FIG. 10. Fluorescence (green band only) vs. temperature curves for ZnS-Cu phosphors excited by constant intensity 3650A radiation. (a) ZnS-Cu made at 500°C; (b) ZnS-Cu made at 700°C; blende; (c) ZnS-Cu made at 900°C: blende; (d) ZnS-Cu made at 1000°C: blende (some wurtzite); (e) ZnS-Cu made at 1160°C: wurtzite.

luminescence centers, as suggested by some workers (cf. Klasens 1946).[11]

Experiments were made to find the effect of oxygen in the air on the phosphors during firing (phosphors being fired in nitrogen, specially exposed to air, and in the normal manner). No clear effect was found, but it must be remembered that all the phosphors probably contained oxide from the hydroxide present in the original zinc sulfide precipitate.

(d) Zinc Sulfide-Cadmium Sulfide Phosphors Activated by Copper

Except for specimens of high ZnS content, the mixed crystal system ZnS-CdS has always the wurtzite structure, but the lattice dimensions depend on the ZnS:CdS ratio. The effect of this ratio on the trap distributions in ZnS-CdS-Cu phosphors all made at the same temperature, and with the same copper concentration, is shown in the four curves of Fig. 8. As shown by curves a and b of this figure, the introduction of copper into ZnS-CdS phosphors gives rise to deep traps as in ZnS-Cu phosphors. As the cadmium sulfide content increases, for constant copper concentration, marked changes in the trap distributions take place. For phosphors with less than 45 percent CdS the increase in CdS content tends to suppress the deep traps, but for higher CdS concentrations (curve d) very deep traps are produced. It is not possible to compare the relative heights of the curves of Fig. 8 as the emission color shifts from green to red with increase in CdS content, and the curves have not been corrected for the rapid decrease in sensitivity of the recording electron multiplier with increase in wave-length of the impinging radiation. Thus the high temperature glow peak of curve d may represent a considerable number of deep traps. It is possible that the change in the trap distribution with increasing cadmium content is simply a shift of the distribution towards lower values of trap depth

and this, like the corresponding shift of the luminescence spectrum, is to be accounted for by the progressive shift of lattice energy zones relative to impurity levels.

(e) Fluorescence vs. Temperature Characteristics and Phosphor Constitution

Measurements of the variation of the fluorescence intensity with temperature under constant high intensity excitation by ultraviolet radiation of 3650A wave-length were made for the phosphors described in the above sections. Experimental curves for representative specimens are given in Figs. 9 and 10. As shown by curves a and b of Fig. 9 for self-activated "pure" zinc sulfide phosphors, the firing temperature has a marked influence on the upper limit of temperature at which the fluorescence is "quenched." In general, for ZnS with any activator for firing temperatures up to 1000°C the quenching temperature for the fluorescence increases with firing temperature and for higher firing temperatures remains unaltered. Curves a and b may be supplemented by Randall's[12] observations on pure unheated zinc sulfide which is non-fluorescent under intense excitation at room temperature but shows emission when excited at liquid oxygen temperature (90°K). The addition of silver impurity with subsequent firing at 1000°C (curve c, Fig. 9) causes an extension of the fluorescence vs. temperature curve to higher temperature. This is a general result for the addition of activating impurities to zinc sulfide.

Measurements of the temperature variation of "green band" fluorescence from copper activated zinc sulfides made at different temperatures are represented by the curves of Fig. 10. As for the specimens of Fig. 9, increase in firing temperature improves the fluorescence efficiency at higher temperatures, but the characteristics change little with firing temperature above 1000°C. For ZnS-Cu phosphors prepared by heating ZnS to a high temperature and adding the copper subsequently at a low temperature the fluorescence temperature curve is the same as that for a ZnS-Cu phosphor fired with impurity at the high temperature. The blue band of emission in ZnS-Cu varies with temperature in the same way as the blue emission of self-activated ZnS.

[11] H. A. Klasens, Nature 157, 306 (1946).

[12] J. T. Randall, Trans. Faraday Soc. 35, 2 (1939).