Some Optical Properties of Zinc Sulfide Phosphors Doubly Activated with Copper and Manganese[*]

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Introduction

The sensitized luminescence in doubly activated phosphors has been one of the most interesting problems in the field of solid-state luminescence in recent years. In these phosphors two kinds of activating impurity, called " sensitizer " and " activator ", are incorporated. The activator is sensitized to emit luminescence as a result of the absorption of excitation energy by the sensitizer and of the subsequent radiationless transfer of this energy from the sensitizer, in such a spectral region that the activator has no appreciable absorption band unless the sensitizer is incorporated. In most cases the sensitizer causes also the luminescence of its own, so that these phosphors show two

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[*] A part of this work was read at the Symposium on Photochemistry held by the Chemical Society of Japan on Sept. 25, 1954, and at the 8th Annual Meeting of this Society on Apr. 1, 1955, and was briefly reported in *J. Chem. Phys.* **23**, 1173, 1976 (1955).

kinds of emission band.

Generally, the sensitizer is an atom or ion of heavy metals such as lead, thallium, copper, antimony and other metals, while the activator is an ion of transition metals such as manganese and samarium. Manganese incorporated as a divalent ion is most popular as the activator, and known to be apt to show a strong luminescence by sensitization because the optical transition involved which leads to the luminescence is a forbidden one[1].

The sensitized phosphors recently developed and investigated are confined almost entirely to non-photoconductive phosphors such as $CaSiO_3:(Pb+Mn)$[2,3,4], $Ca_3(PO_4)_2:(Ce+Mn)$[4,5], $3Ca_3(PO_4)_2\text{-}Ca(Cl, F)_2:(Sb+Mn)$[6], and $CaF_2:(Ce+Mn)$[7]. On the other hand, the investigation for photoconductive ones such as the sulfide type are rather few except those by Makishima[8] for calcium sulfide type, CaS:(Bi+Sm), CaS:(Pb+Sm), CaS:(Bi+Mn) and others, and those by the author[9] for self and manganese-activated zinc sulfide.

The theory of sensitization mechanism has been developed by Botden[5] and more fundamentally by Dexter[10], and it was concluded that the resonance transfer of excitation energy from sensitizer to activator is responsible for the sensitization process in non-photoconductive phosphors. However, in photoconductive phosphors the possibility of sensitization due to the mechanism which will be described below may be also taken into consideration, namely the mechanism by the transfer of photoelectrons through the conduction band simultaneously accompanied by the migration of holes through the filled band[11,12,13].

The present work was undertaken in order to investigate the sensitization process in photoconductive phosphors and to discuss the mechanism by which the process is governed. Zinc sulfide doubly activated with copper and manganese was taken up as an example to be investigated, and its optical properties, the emission, absorption and excitation spectra, thermoluminescences and photoconductivities, were measured. This phosphor seems to be suitable for the present purpose, since zinc sulfide singly activated with copper and that with manganese are both very familiar and their properties are well-known. The results presented below will show that in this phosphor, manganese emission is really sensitized by copper incorporated as a sensitizer, and that some interesting phenomena characteristic of sensitized luminescence take place.

Experimental

1 Preparation of the Samples.—The preparation of the samples was carried out according to the method currently used. Several series of the samples were prepared, in which the copper concentration was fixed to be constant, 3×10^{-5}g./g.ZnS*, and the manganese concentration was varied from zero to 3×10^{-3}g./g.ZnS. These were fired at 1200°C for one hour in air with the flux of sodium or potassium chloride (0.02–0.05g./g.ZnS). Each series was fired at one time so as to keep the firing condition completely constant.

2 Emission.—As is well konwn, copper-activated zinc sulfide phosphor and that which is manganese- activated show the yellow green and orange luminescence, respectively. A series of the doubly activated ones with a constant copper concentration and varying manganese concentrations shows the luminescence with colors varying from yellow green to orange with the increase of manganese concentrations under 3650Å excitation.

The exmission spectra were measured under 3650Å excitation at room temperature with a glass monochromator of constant deviation type and a photomultiplier, RCA 931A or 1P21. The excitation source was a high pressure mercury discharge lamp, Matsuda SHL-100, with a Matsuda UV-D1 filter. The output of the photomultiplier was further amplified with either of two kinds of high sensitive amplifier, a *dc* or *ac* amplifier. The *dc* amplifier was constructed by using a vacuum tube 954 operating as an electrometer tube[14]. The current amplification was about 80–100db. In the case of the *ac* amplifier, the light emitted by the phosphor was interrupted and modulated to 200cps by means of a rotating sector set just before the entrance slit of the monochromator, and the *ac* output of the photomultiplier was amplified with the *ac* amplifier tuned to this frequency, the design of which follows closely to the one devised by Yamada et al[15]. The gain of the *ac* amplifier was almost the same as that of the *dc* amplifier. The spectral sensitivity of the photomultiplier set just behind the exit slit was determined by

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[1] C. C. Klick, *Brit. J. Appl. Phys.*, Sup. No. 4 ("Luminescence"), 74 (1955).

[2] J.B. Merril and J.H. Schulman, *J. Opt. Soc. Am.*, 38, 471 (1948).

[3] J. H. Schulman, R. J. Ginther and C. C. Klick, *J. Electrochem. Soc.*, 97, 123 (1950).

[4] Th. P.J. Botden and F.A. Kröger, *Physica*, 18, 553 (1948).

[5] Th. P.J. Botden, *Philips Res. Rep.*, 7, 197 (1952).

[6] H.G. Jenkins, A.H. McKeag and P.W. Ranby, *J. Electrochem. Soc.*, 96, 1 (1949).

[7] R.J. Ginther, *J. Electrochem. Soc.*, 101, 248 (1954).

[8] S. Makishima, Doctral Thesis (1945).

[9] S. Shionoya, *Bull. Fac. Eng.*, Yokohama Natl. Univ. 3, 97 (1954).

[10] D.L. Dexter, *J. Chem. Phys.*, 21, 836 (1953).

[11] N.F. Mott and R.W. Gurney, "Electronic Processes in Ionic Crystals", (1940), p. 207.

[12] M. Schön, *Z. Phys.*, 119, 463 (1942).

[13] H.A. Klasens, W. Ramsden and C. Quantie, *J. Opt. Soc. Am.*, 38, 60 (1948).

* Concentrations of activating impurities are given in weight ratios, g./g.ZnS, throughout this paper.

[14] H. Matsuda and K. Ogata, *J. Appl. Phys. Japan*, 20, 229 (1951).

[15] M. Yamada, K. Mitsuhashi and K. Akagi, *Tech. J. Japan Broadcasting Corp.*, 13, 29 (1953).

measuring the emission spectrum of a tungsten-incandescent lamp having the approved true temperature, including not only the spectral sensitivity of the photomultiplier itself but also the variation of the dispersion of the monochromator with wavelength and the absorption by glass.

Some typical results are shown in Fig. 1. The emission of manganese increases with the increase of its concentration, the emission of the copper decreasing simultaneously. Because of the overlap of the copper band with the manganese band, the samples showing both the copper and manganese emissions have broad bands, which are divided graphically into the copper and manganese bands as shown in the figure. The samples containing less than 1×10^{-4} manganese show the manganese emissions scarcely observable, those containing $2\text{-}8\times10^{-4}$ show distinctly both the copper and manganese emissions and those containing more than 1.5×10^{-3} show the predominant manganese emissions, while the copper emissions almost disappear. These concentrations of manganese are varied slightly by the firing conditions.

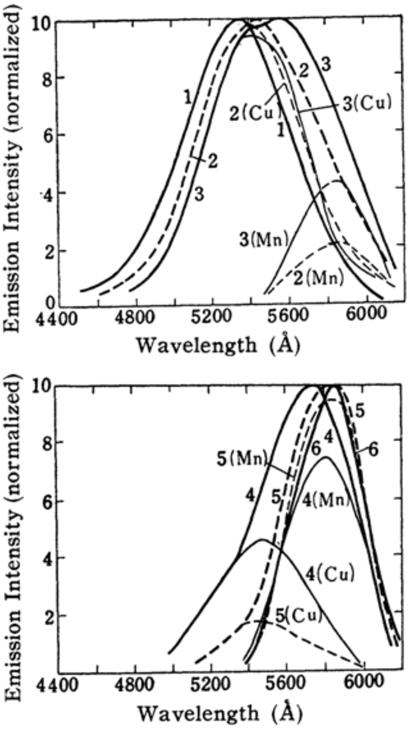

Fig. 1. Emission spectra of (1) ZnS : Cu and (2)-(6) ZnS : (Cu+Mn) under 3650 Å excitation. The Mn concentrations are (2) 2×10^{-4}, (3) 4×10^{-4}, (4) 8×10^{-4}, (5) 1.5×10^{-3} and (6) 3×10^{-3}. The Cu concentration is always 3×10^{-5} for all of the samples in this paper.

The emission peaks of copper and manganese are located at 5350-5450 Å and about 5850 Å, respectively, both being almost unchanged from those of the case where each of them is singly incorporated[16]. The copper peak has a tendency to shift slightly towards longer wavelength with the increase of manganese concentration. The reason for this effect is considered to be that since manganese is incorporated substitutionally into zinc sulfide, forming a solid solution[17] and causing the expansion of the lattice, the forbidden gap of the host lattice is made smaller, and then the energy of the copper emission becomes smaller.

3 Absorption.—The measurements of absorption were made by measuring the diffuse reflectivity from a layer of phosphor with an effectively infinite thickness. A Hitachi's quartz monochromator of Littrow type and an integrating sphere, which was set behind the exit slit, were used. The excitation source was a tungsten incandescent lamp. The intensity of the reflected light was measured with a photomultiplier, 1P28, attached to the *dc* amplifier mentioned above, and the reflectivity was determined as the ratio to that of magnesium oxide powder. An ultraviolet transmitting filter, Corning No. 9863 or Matsuda V-V1, was inserted between the integrating sphere and the photomultiplier so as to separate the reflected light from the luminescence, in the spectral region 3200-4800 Å where the incident light excites the phosphor.

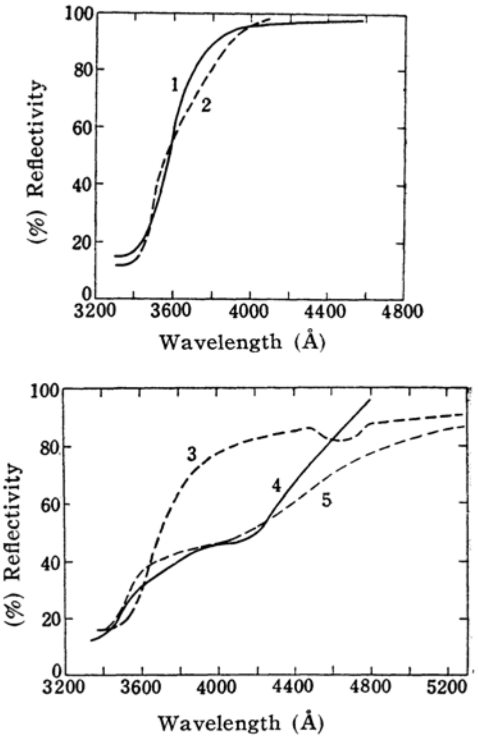

Fig. 2. Reflection spectra of (1) ZnS unfired, (2) ZnS fired without any activating impurities, (3) ZnS : Mn (Mn : 1×10^{-2}), (4) ZnS : Cu and (5) ZnS : (Cu +Mn) (Mn : 8×10^{-4}).

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[16] R.H. Bube, *Phys. Rev.*, **90**, 70 (1953).

[17] F.A. Kröger, *Z. Krist.*, **100**, 543 (1939).

Results of reflection spectra at room temperature are shown in Fig. 2, including those for ZnS unfired, ZnS fired without activating impurities and ZnS: Mn (Cu not in corporated). The long wavelength threshold of the fundamental absorption of zinc sulfide host crystal is located at about 3400Å which is nearly in agreement with the value reported by Piper[18] for single crystals of zinc sulfide. In the long wavelength region beyond the fundamental absorption, the absorption bands due to copper and manganese appear. The copper band seems to be located from 3600 to 4200Å. The manganese band has a small peak at 4600–4700Å.

4 Excitation. — The excitation spectra were measured with the same quartz monochromator and the excitation source as used in the case of absorption. The phosphor sample was coated uniformly on a glass plate in a thin layer of the thickness, 2.5mg./cm², by means of the sedimentation method, and was set just behind the exit slit. The intensity of the emission was measured through suitable filters with the photomultiplier, 1P21, set behind the plate of the phosphor, the output photocurrent being amplified by the *dc* amplifier. The copper and manganese emissions were isolated from each other with filters, namely Matsuda V-Y1 plus V-B2 for copper and V-O2 or V-R3 for manganese.

Results at room temperature are shown in Fig. 3, including those for ZnS: Mn (Cu not incorporated). All of the samples have a strong excitation peak near 3400Å. This corresponds to the fundamental absorption edge of the host crystal as seen at a glance by comparing it with the reflection spectra, so that this peak is regarded as the one due to the absorption of the host crystal. ZnS: Cu has, in addition, the broad excitation band the peak of which seems to be located at about 3800Å. This band is regarded as the one due to the absorption of copper impurity by comparing it with reflection spectra. These results are nearly in agreement with those of Bube[16]. While manganese in ZnS: Mn has only the excitation band due to the host crystal, manganese in ZnS: (Cu+Mn) has, in addition, the excitation band regarded as the one due to copper. It is no doubt obvious that this additional band is attributed to the absorption of copper, since its shape is very similar to that for copper in ZnS: Cu. This result shows that manganese emission is really sensitized by copper behaving as a sensitizer.

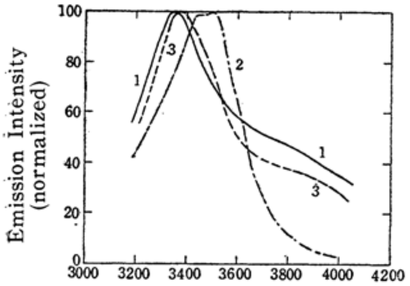

Fig. 3. Excitation spectra for (1) Cu emission of ZnS: Cu, (2) Mn emission of ZnS: Mn (Mn: 1×10^{-2}) and (3) Mn emission of ZnS: (Cu+Mn) (Mn: 8×10^{-4}).

According to Bube[16], the excitation spectrum of manganese in ZnS: Mn shows, in addition to the host excitation band, four excitation peaks due to the forbidden transition within Mn^{+2} ion itself in the wavelength region 3900–5100Å, namely 3980, 4320, 4770 and 5060Å peaks. However, they were not found in the present phosphors, and this fact seems to be probably due to the effect of impurity, especially oxygen.

As thus found, ZnS: (Cu+Mn) has two kinds of excitation band, one due to the host crystal and the other due to the copper sensitizer. Then a new problem arises whether the emission spectra are different under the host or copper excitation. As the excitation source to be used for these excitations, an ordinary 100 W. tungsten incandescent lamp was used, selecting only the necessary wavelength region for each of these excitations with suitable filters; namely Matsuda UV-D1 plus nickel sulfate solution filter (the concentration: $NiSO_4\cdot7H_2O$, 100g./*l.*; the optical path: 5 cm) for the host xcitation, and Matsuda UV-D1 plus V-B2 for the copper excitation. The transmission spectra of these filters are shown in Fig. 4. Since this excitation source was too weak to measure the emission spectra, only the ratios of the emission peak intensities of manganese to those of copper, *R*, were determined by separating these two kinds of emissions with filters.

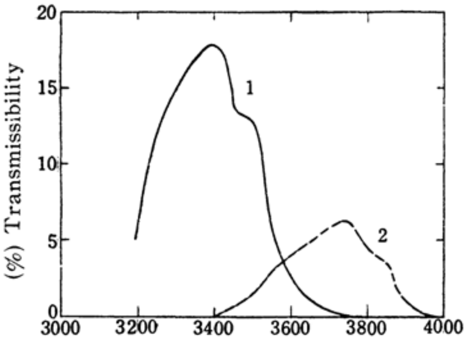

Fig. 4. Transmission spectra of filters for (1) the host and (2) Cu excitations.

It was found that the values of the ratios under the host excitation, R_{host}'s, are about 1.2 times R_{3650}'s for all the phosphors, while R_{Cu}'s are about 0.8 times R_{3650}'s. It may be suggested that the excitation energy absorbed by the host crystal is shared between copper and manganese in proportion to their capture cross sections under the host excitation, whereas under the copper excitation a part of the excitation energy absorbed by copper is transferred to manganese. This results shows that the transfer probability from copper to manganese is rather small as compared with the probability that manganese captures the

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[18] W.W. Piper, *Phys. Rev.*, **92**, 23 (1953).

host absorbed energy. R_{3650}'s shows the intermediate values between R_{host}'s and R_{Cu}'s, since 3650Å line lies just at a middle position between the two excitation peaks, and consequently causes the both kinds of excitation.

5 Thermoluminescence.—The thermoluminescence for both the copper and manganese emissions after both the host and copper excitations were measured with a specially designed Dewar vessel shown in Fig. 5, using liquid air as a coolant. The phosphors were coated with distilled water on an aluminum plate, which was attached to the copper block. The excitation source was the same as mentioned just above, the tungsten incandescent lamp with filters. The phosphors were excited up to the saturated emission intensities at a liquid air temperature, and then heated by means of nichrome wire with a constant rate, 0.22°K/sec., after allowing the emission to decay for six minutes, detecting the glow intensities with the photomultiplier attached to the *ac* amplifier mentioned in Sec. 2. The copper and manganese emissions were isolated from each other with filters.

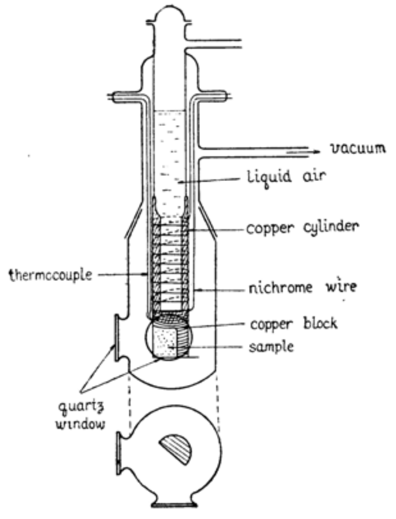

Fig. 5. An apparatus for the thermoluminescence measurement.

Examples of the results are shown in Fig. 6. Every phosphor shows the main glow peak in the temperature range 230–300°K. Low temperature peaks associated with shallow traps were not found, because the emissions were allowed to decay for six minutes after the ceasing of the excitation. In ZnS: Cu, the glow curves for the copper emission after the host and copper excitations are similar to each other, showing main glow peaks at about 240°K. On the other hand, in ZnS: (Cu+Mn) (Mn: 8×10^{-4}) with the copper and manganese emissions which are both distinct, the glow curves for the copper and manganese emissions after the copper excitation are very similar to each other having the main glow peaks at 265°K, whereas those after the host excitation are remarkably different from each other, the main glow peaks being at 295°K for the copper emission and at 235°K for the manganese emission. This result should be strongly noticed in connection with the sensitization mechanism. Also in ZnS: (Cu+Mn) (Mn: 3×10^{-3}) with the predominant manganese emission, the two manganese glow curves are different depending on either the host or copper excitation.

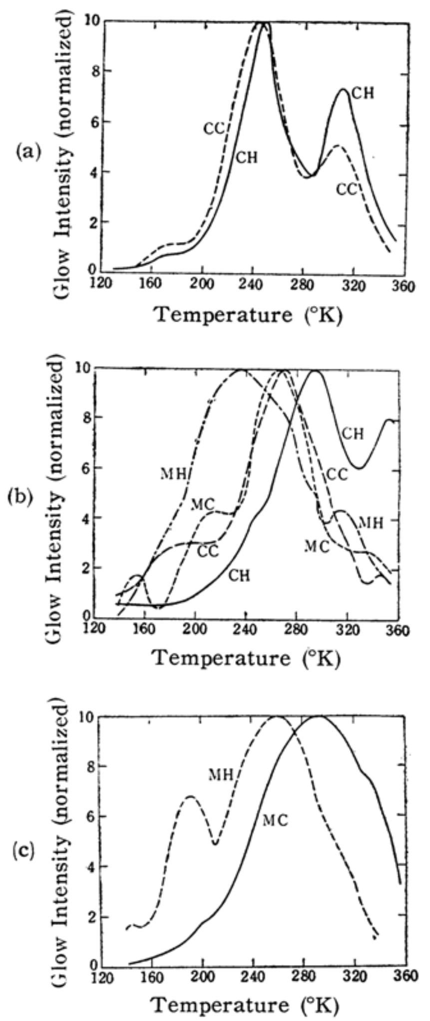

Fig. 6. Glow curve of (a) ZuS: Cu, (b) ZnS: (Cu+Mn) (Mn: 8×10^{-4}) and (c) ZnS: (Cu+Mn) (Mn: 3×10^{-3}).

CH: Cu glow after the host excitation
CC: Cu glow after the Cu excitation
MH: Mn glow after the host excitation
MC: Mn glow after the Cu excitation

Analyses for the main glow peaks were carried out in the usual manner. The thermoluminescence is produced when the trapped electrons are released by the thermal energy and recombine with the holes in the ground states of the luminescence centers. In the photoconductive phosphors such as zinc sulfide, it is suggested that this process is governed by the bimolecular mechanism. However, Randall and Wilkins[19,20] found that the phosphorescence and thermoluminescence in the sulfide type phosphors can be explained by the monomolecular mechanism rather than by the bimolecular one. Also, Williams and Eyring[21] established fairly conclusively that the rate-determining process for the glow emission of ZnS : Cu is predominantly monomolecular, based on the analysis of the shape of the glow curve. The reason for these results appears to be that the number of electrons escaping from traps is much smaller than the number of holes in luminescence centers, and so the thermoluminescence process is determined by the rate at which electrons escape from traps, or in other words that the time necessary for the release of electrons from traps is much larger than that during which electrons stay in the conduction band. Furthermore, the effect of the retrapping of thermally released electrons should be also taken into consideration in the photoconductive phosphors. However, Randall and Wilkins[19,20] showed that the retrapping is a negligible process during luminescence, although an empty luminescence center and an empty electron trap have similar cross-sections for electron capture.

Therefore, the analyses were done assuming the monomolecular kinetics and the negligible retrapping. The distribution of trap depth was also ignored. In the case of the monomolecular kinetics, the intensity of the glow emission, I, is given by

$$I=-\alpha\mathrm{d}n/\mathrm{d}t=akn, \qquad (1)$$

where n is the number of electrons in the trap at any instant and k is the specific rate constant for the thermal release of trapped electrons. The rate constant is expressed by

$$k=s\exp(-E/\boldsymbol{k}T), \qquad (2)$$

where s is the frequency factor and E is the activation energy, i. e. the trap depth. Integrating Eq. (1),

$$n=n_0\exp\left(-\int_{t_0}^{t}k\mathrm{d}t\right) \qquad (3)$$

where n_0 is the number of electrons in the trap at time t_0. Introducing the heating rate, $\beta=\mathrm{d}T/\mathrm{d}t$,

$$n=n_0\exp\left(-\frac{1}{\beta}\int_{T_0}^{T}k\mathrm{d}T\right). \qquad (4)$$

The emmission intensity is given by inserting Eq. (4) into Eq. (1),

$$I=\alpha n_0 k\exp\left(-\frac{1}{\beta}\int_{T_0}^{T}k\mathrm{d}T\right). \qquad (5)$$

From Eq. (4),

$$k=\frac{\mathrm{d}}{\mathrm{d}T}\left[-\beta\ln\frac{n}{n_0}\right]=\beta\frac{\mathrm{d}}{\mathrm{d}T}\left[-\ln\left(1-\frac{n_0-n}{n_0}\right)\right]. \qquad (6)$$

Assuming that the number of trapped electrons which undergo radiationless transition is negligible, n_0 and (n_0-n) can be expressed in terms of the light sums, i. e.

$$n_0=\frac{1}{\alpha\beta}\int_{T_0}^{\infty}I\,\mathrm{d}T \quad\text{and}\quad n_0-n=\frac{1}{\alpha\beta}\int_{T_0}^{T}I\,\mathrm{d}T. \qquad (7)$$

Hence, the rate constant is given as a function of observables,

$$k=\beta\frac{\mathrm{d}}{\mathrm{d}T}\left[-\ln\left(1-\frac{\int_{T_0}^{T}I\,\mathrm{d}T}{\int_{T_0}^{\infty}I\,\mathrm{d}T}\right)\right]. \qquad (8)$$

With this equation both the frequency factor and activation energy can be calculated, although absolute intensities are not observed.

In Table I, The calculated values for the main peaks of the glow curves shown in Fig. 6 are given. The trap depth for the copper main peaks are 0.21–0.23 e. V., irrespective of either the host or copper excitation. The frequency factors for these are made a bit smaller by the incorporation of manganese. The trap depth for the manganese main peak of ZnS : (Cu+Mn)(Mn : 8×10^{-4}) after the copper excitation shows a similar value to that for copper, whereas that after the host excitation shows a considerably different value from that for copper, namely, a smaller one 0.15 e. V., as expected from the results of Fig. 6. Similarly for ZnS : (Cu+Mn) (Mn : 3×10^{-3}), the manganese trap depth after the host excitation is smaller than that after the copper excitation, although both show smaller values than those for ZnS : (Cu+Mn)(Mn : 8×10^{-4}). This effect of trap shallowing by the increased concentration of manganese appears to be caused by the same reason as suggested for the effect that the copper emission peak shifts towards a longer wavelength with the increase of manganese concentration.

TABLE I

TRAP DEPTHS AND FREQUENCY FACTORS FOR THE MAIN PEAKS OF THE GLOW CURVES

Phosphor	Emission	Excitation	Trap Depth e. V.	Frequency Factor (sec^{-1})
ZnS : Cu	Cu	host	0. 23	4×10^2
		Cu	0. 23	6×10^2
ZnS : (Cu+Mn) (Mn : 8×10^{-4})	Cu	host	0. 21	2×10
		Cu	0. 21	6×10
	Mn	host	0. 15	1×10
		Cu	0. 23	2×10^2
ZnS : (Cu+Mn) (Mn : 3×10^{-3})	Mn	host	0. 14	2
		Cu	0. 18	7

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[19] J. T. Randall and M. H. F. Wilkins, *Proc. Roy. Soc.* (London), **A184**, 347, 365, 390 (1945).

[20] G. F. J. Garlick, "Luminescent Materials", Oxford Press (1949), Chap. II.

[21] F. E. Willams and H. Eyring, *J. Chem. Phys.*, **15**, 289 (1947).

The values of Table I are characterized by the unusually low values of frequency factors, resulting from the fact that the width of the main glow peaks are rather broad. The neglect of trap depth distribution seems predominantly responsible for this result. If the trap depth were not a single one, but had a distribution, or two or more traps which could not be resolved by the heating rate used were involved, the broad glow peak would result, which would give the apparent low value of the frequency factor by the analysis on the assumption of the single trap depth. The ignoring of the effect of the retrapping can be also considered as the cause of the low frequency factor. It was shown by Randall and Wilkins[19,20] that when retrapping is present the half-width of the peak for the same values of trap depth and frequency factor becomes much larger. Therefore, if retrapping were involved, it would give the apparent low value of the frequency factor similarly to the trap depth distribution.

The aforementioned results may be reasonably explained by the following inference, if an assumption is made that two kinks of main traps are involved in these phosphors, the deep one associated with copper and the shallow one associated with manganese, as indicated in Fig. 8 in Discussion 2. Under the copper excitation, the freed electron from the copper center enters only into the copper associated trap, and the thermal release from it is the rate-determining step for both of the copper and manganese main glow peaks. On the other hand, under the host excitation, the freed electron from the host lattice enters, probably through the conduction band, into either of the copper and manganese associated traps, and the thermal release from either of them is the rate-determining step for each of the copper and manganese main glow peaks. On the nature of these traps nothing can be discussed here from only this experiment.

6 Photoconductivity.—Only a preliminary experiment was done on the photoconductivity. Cells were made by packing the phosphor powder between a conductive glass and an aluminum plate in the thickness of 1mm. Photocurrents induced by applying *dc* electric field of 280V./cm. under 3650Å excitation were detected by means of a sensitive amplifier constructed with a Matsuda UX-54 vacuum tube and a galvanometer.

In Fig. 7 the relative photoconductive response of a series of ZnS: (Cu+Mn) with a constant copper concentration and varying manganese concentrations are given as the function of manganese concentrations. The response of the samples with higher manganese concentrations are by far smaller than those with lower concentrations. Comparing this with the results of emission spectra, it is shown that the photoconductive response changes abruptly to the smaller value at the manganese concentration at which the manganese emission becomes distinct.

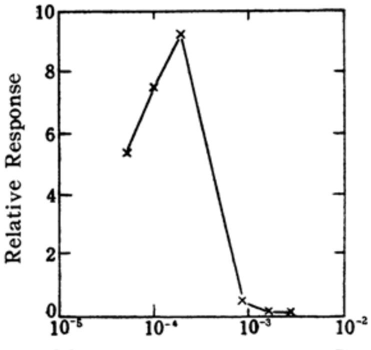

Fig. 7. The relative photoconductive response of a series of ZnS: (Cu+Mn) as the function of the manganese concentration.

Discussion

1 The Range of Energy Transfer from Copper to Manganese.—As mentioned in Experimental 4, the manganese emission in zinc sulfide phosphor is really sensitized by copper behaving as a sensitizer. In other words, a part of the excitation energy absorbed by copper is transferred to manganese to give rise to its emission. The extent of the range surrounding the sensitizer where this energy transfer takes place can be estimated from the relation between the concentrations and luminescent intensities of the sensitizer and activator, based on the assumption that they are distributed at random over the whole lattice sites[9].

Defining z as the number of lattice sites (substitutional or interstitial, or both) surrounding a given sensitizer, it is assumed that if any one of these z sites is occupied by an activator the sensitization can take place with the probability of unity, but that if none of them is occupied by an activator the emission of the sensitizer itself is caused. Then, the mole fraction of the sensitizer incapable of the sensitization and responsible for its own emission is given by

$$C_s(1-C_a)^z, \tag{9}$$

where C_s and C_a are the mole fraction of the sensitizer and activator, respectively. Therefore, the mole fraction of the sensitizer capable of the sensitization, which corresponds to the mole fraction of the activator to be sensitized, is given by

$$C_s[1-(1-C_a)^z]. \tag{10}$$

Under the excitation by the sensitizer absorption, the emission of both the sensitizer and activator are caused only by the light absorption of the sensitizer. Accordingly, the ratio of the number of the quanta emitted by the activator, N_a, to that emitted by the sensitizer, N_s, is expressed by the ratio of Eq. (10) to (9), i.e.

$$B=\frac{N_a}{N_s}=\frac{1-(1-C_a)^z}{(1-C_a)^z}=\frac{1}{(1-C_a)^z}-1 \tag{11}$$

This equation holds if only the following three conditions are satisfied; the first is that no transfer of the excitation energy between the sensitizers takes place, the second is that the concentrations of both the sensitizer and activator are so low that we may permit the concentration quenching of luminescences among themselves to be neglected, and the third is that the radiationless transition of excitation energy does not occur. It is known[22,23] that for both copper and manganese in zinc sulfide the temperatures at which the radiationless transition begins to occur are higher than room temperature. Then, the value of z is calculated by

$$z = -\frac{\log(B+1)}{\log(1-C_a)}. \qquad (12)$$

The values of B can be estimated by the shapes of the emission bands and the peak intensities for the sensitizer and activator.

In Table II, the values of z calculated for a series of ZnS:(Cu+Mn) with a fixed copper concentration and varied manganese concentrations under the copper excitation are given. The sensitization is shown to take place over the range of 400–500 lattice sites.

TABLE II

THE CALCULATION OF THE VALUES OF z FOR ZnS:(Cu+Mn) UNDER THE COPPER EXCITATION

R: The ratio of the peak intensity of manganese to that of copper.

B: The ratio of the number of quanta emitted by manganese to that emitted by copper.

Mn conc. (g./g. ZnS)	R	B	z	
1×10^{-4}	0.13	0.095	500	Mean 440
2×10^{-4}	0.18	0.13	360	
4×10^{-4}	0.37	0.28	350	
8×10^{-4}	1.3	0.96	470	
1.5×10^{-3}	4.3	3.2	530	

The values of z were already estimated for several non-photoconductive phosphors, such as $CaSiO_3$:(Pb+Mn)[3,9], $Ca_3(PO_4)_2$:(Ce+Mn)[5], and CaF_2:(Ce+Mn)[7]. All of them lie between 10 and 70. The one calculated here for ZnS:(Cu+Mn) is characterized by a value one order of magnitude larger than these.

2 Sensitization Mechanism.—In the photoconductive phosphors two kinds of sensitization mechanism, the resonance transfer and the photoelectron transfer, are suggested as the possible mechanisms, as already mentioned in Discussion 1.

Dexter[10] has developed a quantum-mechanical theory of the sensitized luminescence due to the resonance transfer in non-photoconductive phosphors. He has calculated the probability of the energy transfer by the following mechanisms, i.e. the overlapping of the electric dipole fields of sensitizer and activator, the overlapping of the dipole field of sensitizer with the quadrupole field of activator, and the exchange effect, and has concluded that these mechanisms will give rise to the sensitization of about 10^3–10^4, 10^2 and 30 lattice sites surrounding each sensitizer in typical systems.

The energy levels of doubly ionized manganese in the gaseous state are ^6S, ^4G, ^4P, ^4D and ^4F starting with the lowest term[24]. Based on the experimental results of magnetic susceptibility change accompanying the optical excitation for ZnF_2:Mn[25] and ZnS:Mn[26] and on the comparision of the excitation spectra of phosphors containing manganese with the energy levels in the gaseous state[27], it is indicated[1] that the excited state leading to the luminescence of divalent manganese has four of the 3d electrons with parallel spins and one anti-parallel, while the ground state has all electrons with parallel spins. The luminescence may be suggested to correspond to $^4G\rightarrow{}^6S$ transition.

Although it seems difficult to determine whether the dipole-quadrupole or the exchange transfer is responsible for the sensitized luminescence of divalent manganese in non-photoconductive phosphors, the experimentally derived values of z for these phosphors agree with the theoretical one for the exchange transfer, giving a suggestion that this transfer might be the case. The value of z for ZnS:(Cu+Mn) here calculated is too large to assume the exchange transfer, and still large even for the dipole-quadrupole transfer. This result seems to preclude these mechanisms. However, this value is the one calculated from the assumption that sensitizers and activators are distributed at random, so that the true value might be much smaller if they had a tendency to approach to each other in the host crystal.

Manganese will be distributed at random, since it is incorporated substitutionally forming a solid solution, but copper would not be so. The author has shown[28] in the

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study of the diffusion of copper into zinc sulfide crystal that copper seems to diffuse, not through the perfect lattice, but along the internal surface, grain boundary or dislocation line. Diemer[29] has studied light patterns in electroluminescent zinc sulfide single crystals activated by the diffusion of copper, and shown that at temperatures a little above room temperature copper diffuses into the bulk of the crystal along certain imperfections which are supposed to be screw dislocations. Therefore, it is likely that copper incorporated as an activating impurity is situated at the vicinity of crystal imperfections. Substitutionally incorporated manganese will give rise to a small disturbance of lattice. Hence, the above assumption that copper and manganese have a tendency to approach to each other might be rather reasonable.

According to Bube[16] zinc sulfide activated with copper shows a photoconductivity by the absorption of copper as well as by the host absorption. Therefore, there is a possibility that the sensitization by photoelectron transfer may occur. This mechanism is shown schematically in Fig. 8. As a result of the excitation of the copper sensitizer, the electron is raised directly or thermally into the conduction band (process 1). The hole left in the ground state of the sensitizer is released thermally (2), migrates through the lattice (3), and is trapped at the ground state of the manganese activator (4). The electron in the conduction band is transferred to the excited state of the activator (5), and then recombines with the hole producing the luminescence of the activator (6).

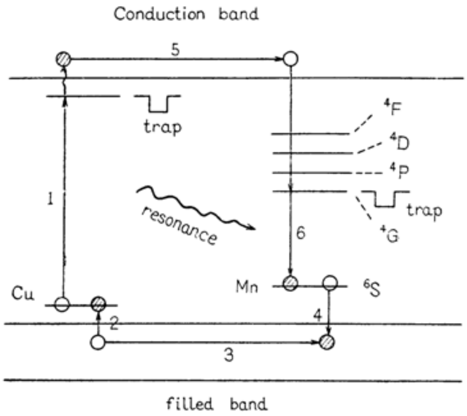

Fig. 8. An energy level diagram for ZnS:(Cu+Mn).

For the occurrence of this mechanism, it is needed that the thermal energy for the process 2 is supplied, and that the hole in the filled band has an appreciable mobility. This thermal energy will be so little, the order of 10^{-1} e. V. or less, as to be easily supplied, because the energy for the process 1 is 3.3 e. V. (3800 Å) and that for the host absorption which corresponds to the band gap is 3.6 e. V. (3400 Å). Nothing is yet known for the mobility of holes in zinc sulfide. It was shown in the measurement of thermoelectric effect[22] and in the study of the modulation of luminescence by an *ac* electric field[30] that the dominant charge carriers in zinc sulfide are electrons, and not holes. If the hole mobility were very small, the sensitization by photoelectron transfer mechanism would not occur with an appreciable probability.

In the continuation of this study, it was examined whether heavy metals other than copper which are capable of having luminescence of their own caused by allowed transitions when incorporated in zinc sulfide can act as effective sensitizers for divalent manganese[31]. The results of the study were that lead can sensitize manganese whereas silver or bismuth cannot. This gives a suggestion for the sensitization mechanism. Silver in zinc sulfide is known[16] to show a photoconductivity by the absorption of its own likewise to copper. Also in the case of lead or bismuth the sameness may be expected. If the photoelectron transfer mechanism is the case, any sensitizer which has a photoconductivity in its own absorption band should alway be able to sensitize manganese although the sensitization probability may vary with the kinds of sensitizer used. The above fact that silver and bismuth cannot sensitize manganese at all seems to argue against this mechanism. Thus it appears reasonable to conclude tentatively in the present situation that the resonance transfer rather than the photoelectron transfer is the predominant mechanism. The different behavior of silver and bismuth from that of copper and lead might be attributed to the difference of the electronic state between these two groups.

The results of thermoluminescence are considered to be favorable to the resonance transfer mechanism. If it is assumed that the manganese thermoluminescence after the copper excitation is caused by the photoelectron transfer, it would show the same glow curve as after the host excitation, since

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electrons raised into the conduction band seem to behave irrespectively of their history, whether they have originated from the host crystal or the coppzer sensitizer. Therefore this assumption appears inconsistent with the experimental results. On the assumption of the resonance transfer, however, the experimental results that the thermoluminescence of copper and manganese after the copper excitation are very similar to each other may be reasonably understood.

The results of photoconductivity measurement might also present a support for the occurrence of sensitized luminescence by the resonance transfer. As mentioned in Experimental 6 the photoconductive response for ZnS: (Cu+Mn) decreases with the increase of the manganese concentration. The similar experiment was done for ZnS: (Ag+Mn), but such an effect was not observed. This difference between copper and manganese seems to be correlated with the different behavior as a sensitizer between them. This effect in the case of copper is explained as follows if the resonance transfer is assumed. The life-time of the excited electron of copper sensitizer, which, it is considered, gives rise to photoconductivity owing to the thermal excitation, will be made shorter by the sensitization of manganese, so that the photoconductive response should becomes smaller with the increase of manganese concentrations.

A tentatively determined energy level diagram for ZnS: (Cu+Mn) is given in Fig. 8. As already mentioned in Experimental 4 manganese in ZnS: Mn has four excitation peaks due to the forbidden transitions within Mn^{+2} ion, i. e. 5060, 4770, 4320 and 3980 Å peaks, which were found by Bube[16]. They are considered to correspond to the excitation from ^6S ground state to ^4G, ^4P, ^4D and ^4F excited states, respectively. Since the energy of the manganese ground level is not yet determined, its position is written arbitrarily. If the resonance transfer is responsible for the sensitized luminescence, the overlap of the emission band of sensitizer with the excitation band of activator is required essentially, and the sensitization probability is proportional to this overlap[10]. Since the emission peak of copper is located at 5350–5450 Å, the excitation energy will be transferred directly to ^4G state of manganese, the lowest excited state from which the luminescence is emitted.

Summary

Optical properties of ZnS: (Cu+Mn) phosphors have been extensively studied with the purpose to investigate the phenomena of sensitized luminescence in photoconductive phosphors. Spectra of emission, absorption and excitation, thermoluminescence and photoconductivity were measured. It was confirmed from the measurement of excitation spectra that the manganese emission is really sensitized by copper behaving as a sensitizer. Some interesting phenomena ascribed to this sensitization were found in the measurements of thermoluminescence and photoconductivity. The mechanism of the sensitization was discussed exhaustively. It appears reasonable to conclude tentatively in the present situation that the resonance transfer rather than the photoelectron transfer is the predominant mechanism.

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