Studies on Luminescent Materials. Part 2. On the Fluorescence Spectra of Zinc Sulphide-Copper Crystalphosphors at −185°, 20°, and 150°C*.

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1. Introduction. In the previous paper(1), the author reported the theory of fluorescence, photoconductivity and the other properties of ZnS/Cu phosphors, based on the quantum mechanical theory of solid state. By the theory of the author, we can expect two fluorescence bands corresponding to the electronic transitions

$$^3D_2 \rightarrow {}^1S_0$$

$$^3D_3 \rightarrow {}^1S_0$$

of the Cu^+ ion in the activation centre of the ZnS/Cu phosphors.

In order to prove this expectation, the author carried out measurements of the fluorescence spectra of ZnS/Cu phosphors at −185°, 20°, and 150°C.

2. Experiments. (A) *Preparation of phosphors.* As raw materials, Kahlbaum's sample (guaranteed reagents for analytical purpose) were always used. These materials were purified by repeated recrystalizations or distillations. Zinc sulphide precipitate was prepared by a method similar to that of K. Mamm(2) and it was washed about fifty-times with distilled water. Then it was dried at 70°C. in an electric air bath with automatic regulator.

The resulting product is perfectly white fine powder. KCl was used as a flux and cupric sulphate water solution was added as an activator.

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* Read before the Annual Meeting of the Chem. Soc. Japan, April 5, 1939 and reported on the *J. Chem. Soc. Japan*, **60** (1939), 675.

(1) Y. Uehara: *Bull. Chem. Soc. Japan*, **14** (1939), 539; *J. Chem. Soc. Japan*, **60** (1939), 133.

(2) K. Kamm: *Ann. Physik*, **30** (1937), 333.

Finely ground mixtures whose compositions are shown in Table 1, were placed in a white alumina crucible which was placed in a larger crucible. They were heated in the sulphur vapour at 1100° ± 10°C. in an electric furnace with automatic regulator for 15 minutes and they were cooled rapidly.

Table 1. Composition of pure ZnS and ZnS/Cu phosphors.

No. of Sample	Activator	Flux
	Cu (gram atom)	KCl (mol)
ZnS—1	0	0
ZnS—2	0	1/10
ZnS—3	1×10^{-3}	1/10
ZnS—4	1×10^{-4}	1/10
ZnS—5	1×10^{-5}	1/10
ZnS—6	1×10^{-6}	1/10
ZnS—7	1×10^{-5}	0

(B) *Observation of fluorescence spectra.* In the measurements of fluorescence spectra, ZnS phosphor coated on a quartz tube, i.e. an inner tube in the Fig. 1, was irradiated by Hg 3650 Å (triplet) line and the emitted fluorescence light was introduced in about right angle in a spectrograph.

For the measurement at −185°C., the quartz tube covered with the phosphor was placed in a larger quartz tube and sealed with Apiazon W-wax at *D* in Fig. 1. After the space between the inner and the outer tube was evacuated, liquid air was poured into the inner tube.

For the experiments at 150°C., a furnace shown in Fig. 2 was used. In Fig. 2, *E* is ZnS phosphor placed in a quartz tube *C*, *F* and *D* are

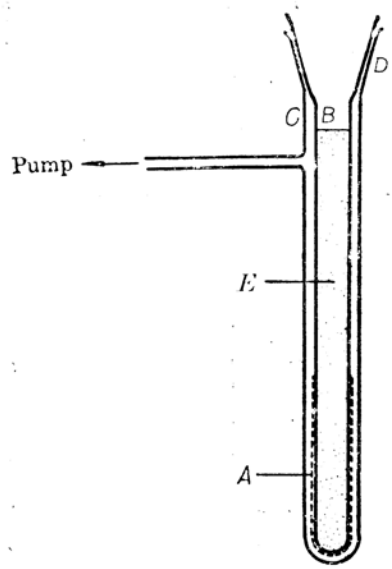

Fig. 1. Quartz tube for the measurements of the fluorescence spectra of ZnS phosphors. *A*: ZnS phosphor, *B*: inner quartz tube, *C*: outer quartz tube, *D*: Apiezon W-wax seal. *E*: liquid air.

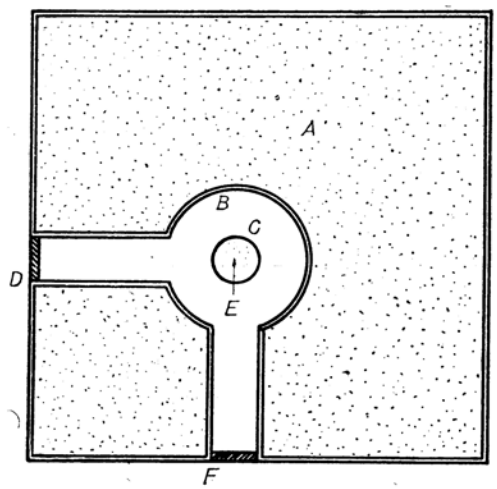

Fig. 2. Electric furnace for the measurements of Fluorescence spectra of ZnS phosphors at 150°C. *A*: electric furnace, *B*: aluminium metal wall, *C*: quartz tube, *E*: ZnS phosphor, *D*, *F*: quartz plate window.

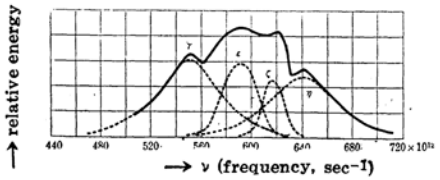

Fig. 3. Fluorescence spectra of ZnS—I (Cu=0, KCl=0) at −185°C.

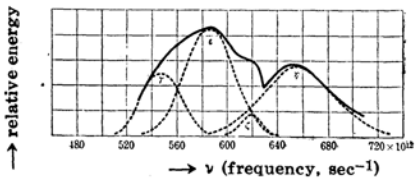

Fig. 4. Fluorescence spectra of ZnS—II (Cu=0, KCl=1/10) at −185°C.

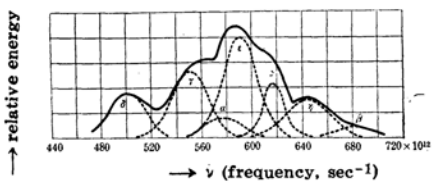

Fig. 5. Fluorescence spectra of ZnS—VII (Cu=1×10⁻⁵, KCl=0) at −185°C.

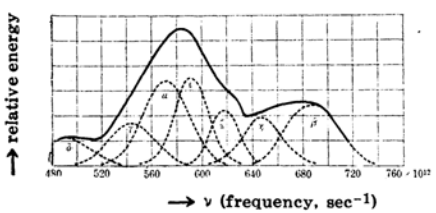

Fig. 6. Fluorescence spectra of ZnS—VI (Cu=1×10⁻⁶, KCl=1/10) at −185°C.

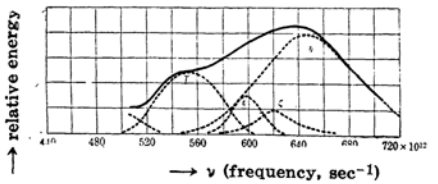

Fig. 10. Fluorescence spectra of ZnS—I (Cu=0, KCl=0) at 20°C.

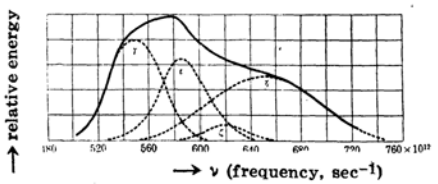

Fig. 11. Fluorescence spectra of ZnS—II (Cu=0, KCl=1/10) at 20°C.

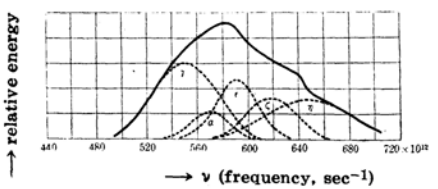

Fig. 12. Fluorescence spectra of ZnS—VII (Cu=1×10⁻⁵, KCl=0) at 20°C.

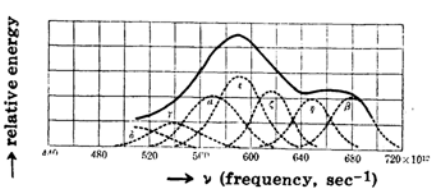

Fig. 13. Fluorescence spectra of ZnS—VI (Cu=1×10⁻⁶, KCl=1/10) at 20°C.

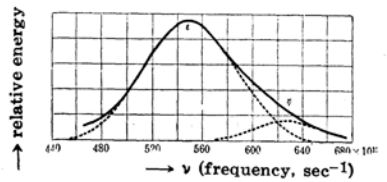

Fig. 17. Fluorescence spectra of ZnS—I (Cu=0, KCl=0) at 150°C.

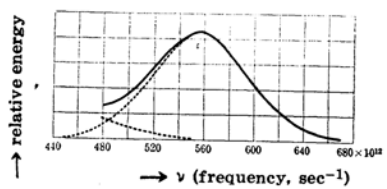

Fig. 18. Fluorescence spectra of ZnS—II (Cu=0, KCl=1/10) at 150°C.

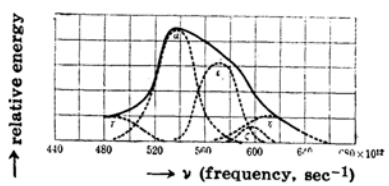

Fig. 19. Fluorescence spectra of ZnS—VII (Cu=1×10⁻⁵, KCl=0) at 150°C.

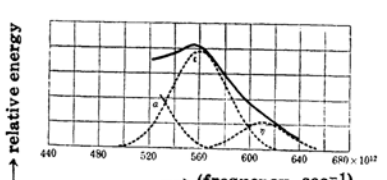

Fig. 20. Fluorescence spectra of ZnS—VI (Cu=1×10⁻⁶, KCl=1/10) at 150°C.

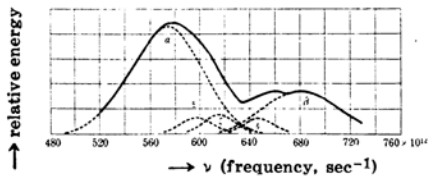

Fig. 7. Fluorescence spectra of ZnS—V (Cu=1×10⁻⁵, KCl=1/10) at −185°C.

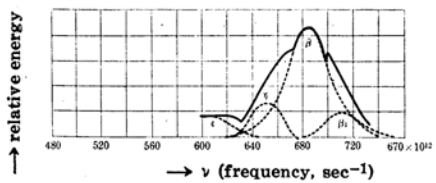

Fig. 8. Fluorescence spectra of ZnS—IV (Cu=1×10⁻⁴, KCl=1/10) at −185°C.

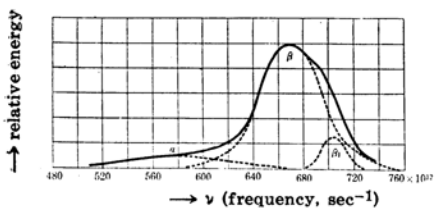

Fig. 9. Fluorescence spectra of ZnS—III (Cu=1×10⁻³, KCl=1/10) at −185°C.

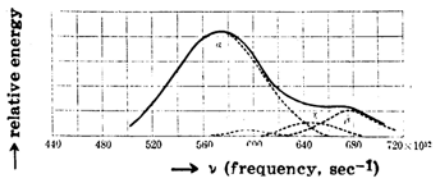

Fig. 14. Fluorescence spectra of ZnS—V (Cu=1×10⁻⁵, KCl=1/10) at 20°C.

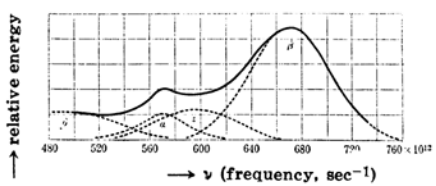

Fig. 15. Fluorescence spectra of ZnS—IV (Cu=1×10⁻⁴, KCl=1/10) at 20°C.

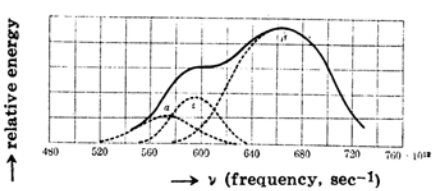

Fig. 16. Fluorescence spectra of ZnS—III (Cu=1×10⁻³, KCl=1/10) at 20°C.

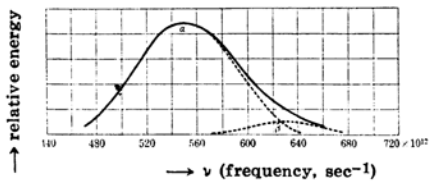

Fig. 21. Fluorescence spectra of ZnS—V (Cu=1×10⁻⁵, KCl=1/10) at 150°C.

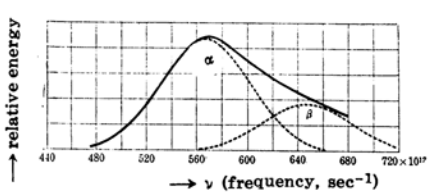

Fig. 22. Fluorescence spectra of ZnS—IV (Cu=1×10⁻⁴, KCl=1/10) at 150°C.

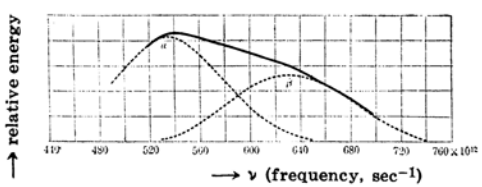

Fig. 23. Fluorescence spectra of ZnS—III (Cu=1×10⁻³, KCl=1/10) at 150°C.

quartz plate windows. The furnace in which the ZnS phosphor is contained, is kept at 150°C. by means of automatic regulator.

As the excitation light source, a high pressure mercury discharge tube in connection with a wood filter yielding practically only line of 3650 Å (triplet), was used.

Photographic spectrophotometry of the fluorescence spectra was made by means of Zeiss three glass prism spectrograph (focal length of camera lens: 27 cm.) in connection with a Zeiss fifth stepped filter and tungsten lamp as a standard light source.

The observed energy distribution curves of the fluorescence spectra were given in Fig. 3 ~ Fig. 23. In these figures thick lines show the observed energy distribution curves of the fluorescence spectra and broken lines show the energy distribution curves of the partial fluorescence bands ressolved by the similiar method to that of P. Borrissow[3], O. Schellenberg[4] and H. Nitka[5].

3. Theoretical Interpretation of the Experimental Results. (A) *Fluorescence of pure* ZnS *phosphors.* Fluorescence of pure ZnS phosphors containing no activator was observed first by A. Schleede[6] and later by N. Riehl[7] and by S. Rothschild[8]. Rothschild[8] reported that pure ZnS phosphors which contain NaCl as a flux but no activator, show only one fluorescence band with a maximum at 466 mμ. In the pure ZnS phosphors containing no flux and no activator, however, the author observed four (partial fluorescence bands with maxima at 4670 Å, 4870 Å, 5085 Å and 5455 Å at -185°C., as shown in Fig. 3. The author proposes to give a following nomenclature for these four fluorescence bands,

$$\eta = 4670 \text{ Å} \qquad \zeta = 4870 \text{ Å} \qquad \varepsilon = 5085 \text{ Å} \quad \text{and} \quad \gamma = 5455 \text{ Å}.$$

In these bands, η=4670 Å band will probably correspond to the band 466 mμ observed by Rothschild.

Tomaschek[9] observed four bands in the ZnS phosphor activated by by Cu, $\alpha = 520$ mμ, $\beta = 437$ mμ, $\gamma = 570$ mμ, and $\delta = 600$ mμ. Rothschild[8] assumed that $\gamma = 570$ mμ band observed by Tomaschek will not be due to Cu activator but to Mn activator which might be involved as impurities in this phosphor. The author, however, observed $\gamma = 5455$ Å band in the pure ZnS phosphor containing no impurities. $\gamma = 5455$ Å band will probably correspond to $\gamma = 570$ mμ band observed by Tomaschek. Then we can conclude that γ band is not due to Cu activator or Mn activator but to Zn atom activator diffused in this phosphor, as shown in our previous paper.[1]

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(3) P. Borrissow: *Ann. Physik.* **42** (1913), 1321.
(4) O. Schellenberg: *Ann. Physik.* **13** (1932), 249.
(5) H. Nitka: *Ann. Physik.* **16** (1933), 720.
(6) A. Schleede and H. Rupp: Die Leuchtmassen und ihre Verwendung, Borntraeger (1937), 153.
(7) N. Riehl: *Ann. Physik.* **29** (1937), 637.
(8) S. Rothschild: *Z. Physik.* **108** (1937), 24.
(9) R. Tomaschek: *Ann. Physik.* **65** (1931), 212.

It is pointed out by Seitz[10] that the presence of excess of Zn atom is responsible for the fluorescence of pure ZnS phosphors. But Seitz's mechanism of fluorescence of pure ZnS phosphors is different from that of the author, as shown already in the previous paper.[1]

The author has pointed out in the previous paper[1] that the resonance radiation (in its wide meaning) in the activation centre is responsible for the fluorescence of pure ZnS phosphors as well as ZnS phosphors activated by Cu. Fig. 24 shows schematically the energy levels of pure ZnS phosphors and of ZnS phosphors activated by Cu. (cf. Uehara.[1])

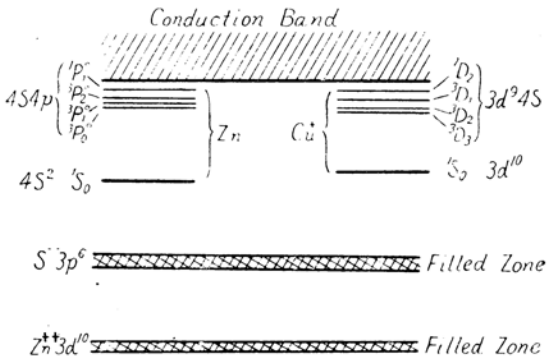

Fig. 24. Energy level diagram of the pure ZnS and ZnS/Cu phosphor.

The energy levels of normal Zn atom lies in the forbidden region between conduction band and S^{--} $3p^6$ band. The energy levels of excited Zn atom lies immediately below the conduction band or on the position overlapping partially each other. Fig. 25 show the potential curve of Zn atom in the activation centre schematically. *A* represents an equilibrium position of the normal Zn atom in the activation centre. After an electron in this position has absorbed light quanta, it makes a transition to one of the excited states of Zn atom. Then it moves into a new equilibrium position of the excited states. The transition of the electron from the excited states to the ground state gives rise to the four fluorescence bands in the pure ZnS phosphors. But it is very difficult to predict which of these transitions corresponds to each band of these four fluorescence bands. Therefore, we assume that the four fluorescence bands observed by the author may be correlated with following electronic transitions, (cf. Fig. 25),

$$^1P_1 \rightarrow {}^1S_0 \ (a \rightarrow i) = 4670 \text{ Å} = \eta$$

$$^3P_2 \rightarrow {}^1S_0 \ (b \rightarrow h) = 4870 \text{ Å} = \zeta$$

$$^3P_1 \rightarrow {}^1S_0 \ (c \rightarrow g) = 5085 \text{ Å} = \varepsilon$$

$$^3P_0 \rightarrow {}^1S_0 \ (d \rightarrow f) = 5455 \text{ Å} = \gamma \ .$$

The reason for this assumption will be given to some extent in the following discussion about the fluorescence of ZnS/Cu phosphors.

By using this mechanism of the fluorescence of pure ZnS phosphors, the author could calculate theoretically the temperature dependence of the photoconductivity and of the intensity of the fluorescence of pure ZnS phosphors as well as ZnS phosphors activated by Cu, as we shall see in the following paper.

(B) *Fluorescence of* ZnS/Cu *phosphors.*

As we see in Table 2 ~ Table 4, there exists three fluorescence bands α, β and β_1 due to activator in the ZnS phosphors activated by Cu, Fig. 26

(10) F. Seitz: *J. Chem. Phys.* **6** (1938), 150.

Table 2. Fluorescence band of pure ZnS and ZnS/Cu phosphors at −185°C. (Wave length unit Å)

Activator	Flux	Fluorescence bands							
Cu (gr atom)	KCl (mol)	β_1	β	η	ζ	ε	α	γ	δ
0	0	—	—	4670	4870	5085	—	5445	—
0	1/10	—	—	4585	4840	5120	—	5475	—
1×10^{-5}	0	—	4410	4660	4870	5085	5300	5455	6120
1×10^{-6}	1/10	—	4380	4645	4870	5085	5270	5535	6120
1×10^{-5}	1/10	—	4410	4645	4885	5050	5225	—	—
1×10^{-4}	1/10	4225	4375	4615	—	—	—	—	—
1×10^{-3}	1/10	4265	4480	—	—	—	—	—	—
	Mean	4245	4410	4635	4865	5085	5260	5480	6120

Table 3. Fluorescence bands of pure ZnS and ZnS/Cu phosphors at 20°C. (Wave length unit Å)

Activator	Flux	Fluorescence bands						
Cu (gr atom)	KCl (mol)	β	η	ζ	ε	α	γ	δ
0	0	—	4645	4855	5035	—	5455	—
0	1/10	—	4600	4840	5120	—	5475	—
1×10^{-5}	0	—	4645	4855	5085	5270	5455	—
1×10^{-6}	1/10	4410	4645	4870	5085	5265	5555	—
1×10^{-5}	1/10	4445	4645	—	5050	5245	—	—
1×10^{-4}	1/10	4480	—	—	5040	5265	—	6120
1×10^{-3}	1/10	4520	—	—	5050	5265	—	—
	Mean	4465	4635	4855	5065	5260	5485	6120

Table 4. Fluorescence bands of pure ZnS and ZnS/Cu phosphors at +150°C. (Wave length unit Å)

Activator	Flux	Fluorescence bands				
Cu (gr atom)	KCl (mol)	β	η	ζ	ε	α
0	0	—	4840	—	5475	—
0	1/10	—	—	—	5415	—
1×10^{-5}	0	—	4920	5035	5265	5595
1×10^{-6}	1/10	—	4920	—	5355	—
1×10^{-5}	1/10	4760	—	—	—	5455
1×10^{-4}	1/10	4645	—	—	—	5300
1×10^{-3}	1/10	4760	—	—	—	5595
	Mean	4755	4895	5035	5375	5485

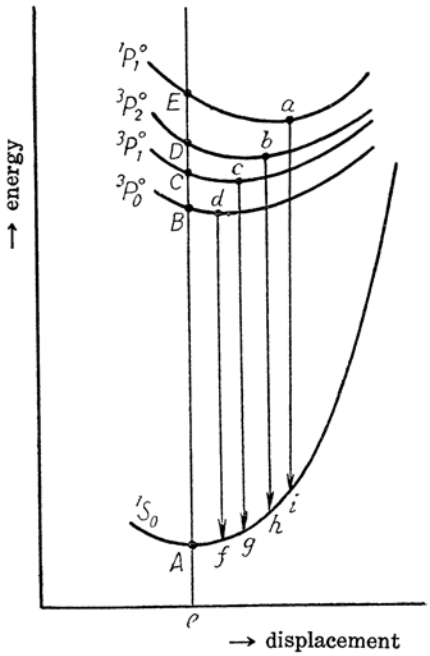

Fig. 25. Potential curve of Zn atom in the activation centre of the pure ZnS phosphor.

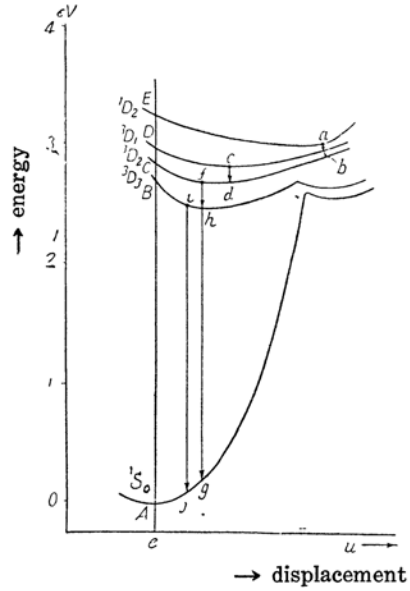

Fig. 26. Potential curve of Cu^+ ion in the activation centre of the ZnS/Cu phosphor.

shows the potential curve of Cu^+ ion in the activation centre, which has been already given by the author.[1] When an electron in the equilibrium position of one of the excited states of Cu^+ ion in the activation centre makes a transition to the ground state of Cu^+ ion, fluorescence will be observed. For example, the electronic transitions $f \rightarrow g$ or $i \rightarrow j$ give rise to fluorescence. On the other hand, the transition $f \rightarrow h$ will occur with radiation of elastic vibration wave and this transition will be more probable compared with the transition $f \rightarrow g$, when the coupling between the electron and lattice vibrations is strong.

Therefore, the transition $f \rightarrow g$ will become more probable compared with the transition $i \rightarrow j$, when the amplitude of the elastic vibrations in the activation centre becomes small. In other words, the lower the temperature is, the stronger the fluorescence band corresponding to the transition $f \rightarrow g$ becomes. As we see in Fig. 4 ~ Fig. 23, when the temperature decreases the blue β (and β_1) band becomes stronger compared with the green α band. Therefore, we can say that α and β band may be correlated with the following transitions.

$$^3D_2 \rightarrow {}^1S_0 \ (f \rightarrow g) = \beta$$

$$^3D_3 \rightarrow {}^1S_0 \ (i \rightarrow j) = \alpha$$

By the same reason, the transition $^3D_1 \rightarrow {}^1S_0$ may be responsible for the band β_1, which has the shortest wave length. $\delta = 6120$ Å band

observed by the author in some of the ZnS/Cu phosphors will probably correspond to the $\delta = 600$ mμ band observed by Tomaschek. But nothing can be predict about the origin of the δ band at present, for the measurements of the fluorescence spectra of the other phosphors have not yet been carried out thoroughly in this region of the spectrum.

(C) *Effect of the amount of activator on the fluorescence spectra.* The ionic radius of Cu^+ ion is smaller than that of S^{--} ion. Hence the larger the amount of the Cu activator is, the smaller becomes the overlapping of their eigenfunctions in the activation centre. Therefore, when a large amount of Cu^+ activator is introduced in the phosphor, the coupling between the excited states of Cu^+ ion and lattice vibrations will become weaker: Then β-band should occur more intensively, when the amount of Cu activator becomes larger. In fact, it is the case in our observations, as seen in Fig. 4 ~ Fig. 23.

(D) *Effect of the flux on the fluorescence spectra.* It could not be observed any appreciable variations of the wave length of the maxima of the partial fluorescence band between the ZnS phosphors containing no flux and that of ZnS phosphors containing KCl as a flux. But relative intensity of each fluorescence band varies very much by adding KCl as a flux. As the results, the energy distribution curves of the fluorescence spectra vary remarkably by the influence of the flux.

From these results, we can consider that K^+ (or Cl^-) ion may diffuse into the crystal lattice and it changes the transition probability of the electron from the excited states to the ground state in the activation centre.

(E) *Temperature effect on the fluorescence spectra.* It has been already pointed out by the author that the fluorescence band of ZnS phosphors should show a wide breadth by the molecular vibrations coupled with the elastic vibrations of the lattice.[1] Therefore, the breadth of the bands should become larger when the temperature is raised, which was actually the case in the observations by the author. Further it could be confirmed experimentally that the wave length of the maxima of the partial fluorescence bands make a shift from blue to red with increasing temperature above the room temperature.

Summary.

(1) Energy distribution curves of the fluorescence spectra of pure ZnS and ZnS/Cu phosphors were measured at –185°, 20°, and 150°C.

(2) Four fluorescence bands were observed in the pure ZnS phosphors containing no activator and no flux. It was pointed out that these four fluorescence bands may be correlated with the transitions

$$^1P_1 \rightarrow {}^1S_0 = 4670\ \text{Å} = \eta$$

$$^3P_2 \rightarrow {}^1S_0 = 4870\ \text{Å} = \zeta$$

$$^3P_1 \rightarrow {}^1S_0 = 5085\ \text{Å} = \varepsilon$$

$$^3P_0 \rightarrow {}^1S_0 = 5455\ \text{Å} = \gamma$$

of the electron of the Zn atom in the activation centre.

(3) In the ZnS phosphors activated by Cu, three bands α, β and β_1 were observed. These three fluorescence bands may be correlated with the transitions

$$^3D_3 \rightarrow {}^1S_0 = 5260\ \text{Å} = \alpha$$

$$^3D_2 \rightarrow {}^1S_0 = 4410\ \text{Å} = \beta$$

$$^3D_1 \rightarrow {}^1S_0 = 4245\ \text{Å} = \beta_1$$

of the electron of the Cu^+ ion in the activation centre.

(4) The effect of the temperature and of the amount of the activator, and flux on the fluorescence spectra were discussed.

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