Studies on Luminescent Materials. III. On the Photoconductivity and the Molecular Vibration Structure of Fluorescence Spectra of the Zinc Sulphide Crystal Phosphors.*

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Theory of Photoconductivity of ZnS phosphors. Pure ZnS phosphor containing no activator impurities as well as ZnS phosphors activated by Cu or Ag can emit a remarkable fluorescence by the exitation of ultraviolet ray or cathode ray.

It was pointed out by the author(1),(2) that the resonance radiation, in its wide meaning, in the activation centre is responsible for the fluorescence of these phosphors.

Fig. 1 shows the energy level diagràm of the pure ZnS and ZnS/Cu phosphors schematically.

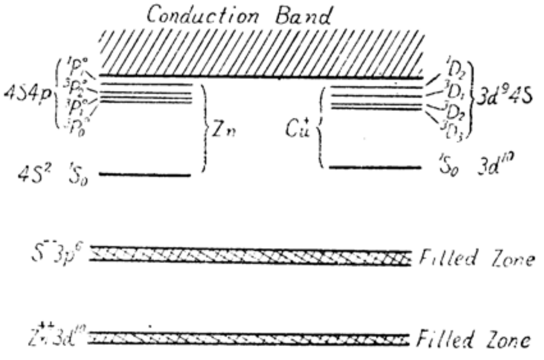

Fig. 1. Energy level diagram of the pure ZnS and the ZnS/Cu phosphor.

If the ZnS phosphors absorb the excitation energy, an electron of the impurity atom such as Zn atom or Cu^+ ion in the activation centre makes a transition from the ground state to excited states. When this electron in an exited state absorbs the heat energy from the crystal lattice, it can make a transition to the conduction band and be free to move in the crystal phosphor.

When the temperature is so low that the electron in the excited states cannot make a transition to the conduction band by absorbing heat energy, photoconductivity should disappear.

We wish to calculate the temperature dependence of photoconductivity of ZnS phosphors by the similar method as the theory of photoconductivity of F-centre of the alkalihalide crystals, proposed by N. F. Mott.(3),(4)

As quoted above, an electron in the levels of $^1D_2$, $^3D_1$, $^3D_2$, $^3D_3$ of Cu^+ ion or $^1P_1$, $^3P_2$, $^3P_1$, $^3P_0$ of Zn Atom in the activation centre can make

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[*] Read before at the Monthly Meeting of the J. Chem. Soc. Japan, September, 16, 1939 and reported on the *J. Chem. Soc. Japan*, **60**, (1939), 1293.

(1) Y. Uehara, This Bulletin, **14** (1939), 539.

(2) Y. Uehara, *ibid.*, **15** (1939), 214.

(3) N.F. Mott, *Proc. Roy. Soc.*, (London), **50** (1938), 196.

(4) N.F. Mott, *Trans. Faraday. Soc.*, **34** (1938). 506.

a transition to the conduction band by absorbing elastic (or molecular) vibration energy.⁽¹⁾

For the sake of simplicity, we assume only on energy level of excited state which represents all four levels of excited states.

Suppose that the activation energy necessary to free the electron from this exicited states is ΔE, then the probability per unit time that the electron is released, will be approximately

$$A\,e^{-\Delta E/kT} \tag{1}$$

k = Boltzmann's constant,
T = Absolute temperature,

with A of the order of magnitude of the elastic vibrations which is about 3.66×10^{12} sec.$^{-1}$, as we shall see in the following sections. Let B be the probability per unit time that an electron in the excited state drops back into the ground state, either with the emission of fluorescence or by giving up it's energy as elastic vibration energy to the lattice. Then the quantum yield η that an electron in the exicited state makes a transition to the conduction band is given by

$$\eta = \frac{A\,e^{-\Delta E/kT}}{A\,e^{-\Delta E/kT}+B} = \frac{1}{1+B/A\,e^{\Delta E/kT}} \tag{2}$$

We can express the electric conductivity in the crystal as follows,

$$J = Ne\omega$$

with e = electronic charge,
N = total number of the electrons in the unit volume,
ω = mobility of the electrons.

The mobility of the electrons in the polar crystals is given as follows, by the theory of Fröhlich and Mott,⁽⁵⁾

$$\omega = 2\sqrt{\frac{3}{\pi m k\Theta}}\cdot e\cdot a_0\cdot(e^{\Theta/T}-1)\cdot\frac{\varepsilon-\varepsilon_0+1}{\varepsilon-\varepsilon_0} \tag{4}$$

$$\equiv C(e^{\Theta/T}-1)$$

$$C \equiv 2\sqrt{\frac{3}{\pi m k\Theta}}\cdot e\cdot a_0\cdot\frac{\varepsilon-\varepsilon_0+1}{\varepsilon-\varepsilon_0}$$

with m = mass of the electron,
Θ = characteristic temperature of the crystal,
a_0 = radius of the Bohr orbit of hydrogen,
ε = dielectric constant in the static field,
ε_0= contribution to the dielectric constant for the polarisability of the ions.

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(5) H. Fröhlich, N. F. Mott, *Proc. Roy. Soc.*, (London), **171** (1939), 496.

Then the photoconductivity σ is given as follows

$$\begin{aligned}\sigma &= Ne\omega\eta \\ &= NeC(e^{\Theta/T}-1)\cdot\frac{1}{1+B/A\,e^{\Delta E/kT}} \\ &\equiv K\cdot\frac{1}{1+B/A\,e^{\Delta E/kT}}\cdot(e^{\Theta/T}-1)\end{aligned} \qquad (6)$$

$$K \equiv NeC = 2N\sqrt{\frac{3}{\pi mk\Theta}}\cdot e^2\cdot a_0\cdot\frac{\varepsilon-\varepsilon_0+1}{\varepsilon-\varepsilon_0} \qquad (7)$$

or

$$\log\sigma = \log K+\log\left\{\frac{1}{1+B/A\,e^{\Delta E/kT}}\,(e^{\Theta/kT}-1)\right\} \qquad (8)$$

With $\Theta = 175$ for Zincblende,(6) we get the following values, to obtain a good fit between the calculated values from eq. (9) and the observed values by Lentz(7) for Zincblende,

$$\left.\begin{aligned} B/A &= 2.13\times10^{-3}, \quad (A = 3.66\times10^{12}\ \text{sec}^{-1}) \\ \Delta E &= 0.081\ eV \end{aligned}\right\} \qquad (10)$$

We can now get $1/B = 1.28\times10^{-10}$ sec. This value obtained above is reasonable for the mean time in the excited state.**

Fig. 2 shows the photoconductivity curve visa temperature calculated from eq. (9) with the values of (10) and also the observed values by Lentz. The coincidence between these two values is satisfactory.

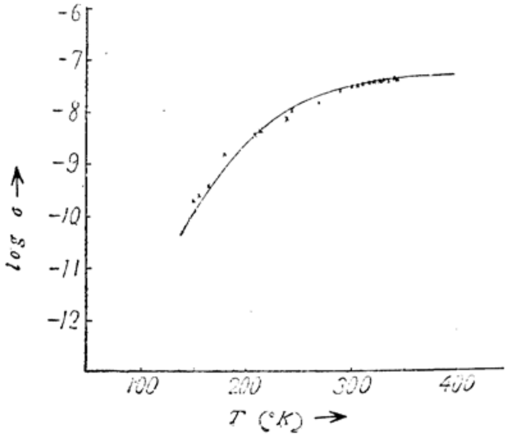

Fig. 2. Temperature dependence of the photoconductivity of ZnS phosphor; thick line (theoretical curve), cross (observed value).

As the results, we can say that the resonance radiation, in the wide meaning, in the activation centre is responsible for the fluorescence of ZnS phosphors. If it is the case, we can expect that the molecular vibration structure should be observed in the fluorescence spectra of ZnS phosphors.

In facts, the author could observe the molecular vibration structure in the fluorescence spectra, as we shall see in the following sections.

Observation of the fluorescence spectra. The fluorescence of ZnS phosphors excited by Hg 3650 A line was photographed by means of Zeiss three glass prism spectrograph.

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(6) K. Försterling, *Z. Physik*, **8** (1922), 251; **3** (1920), 9.

(7) H. Lentz, *Ann. Physik*, **77** (1925), 449.

** Mott got the valeus for the quantities for the colour centre of NaCl, $E=0.075$ eV, $1/B=0.7\times10^{-10}$ sec.

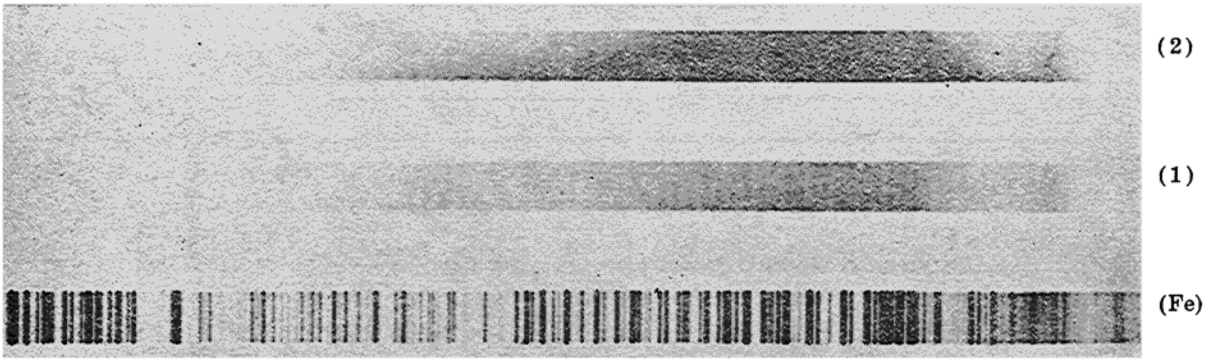
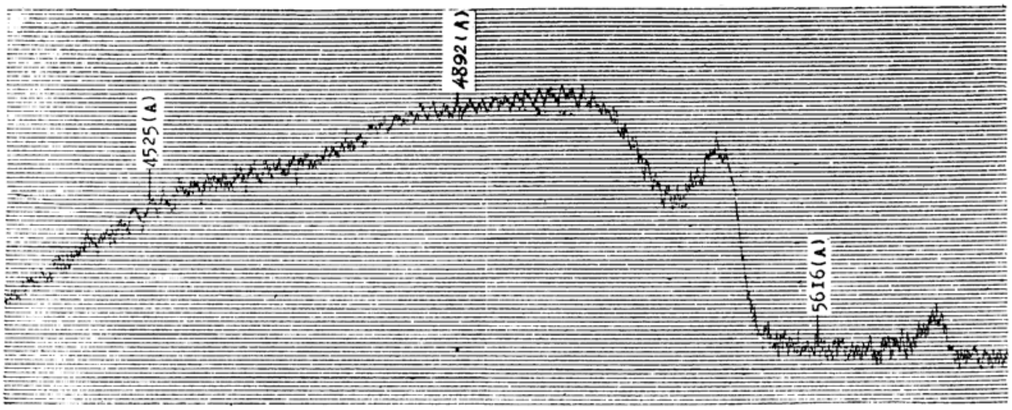
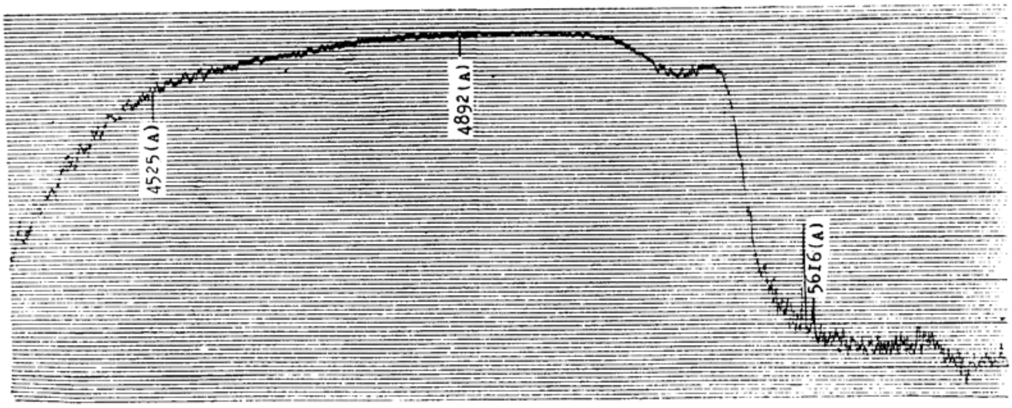


Fig. 3. Fluorescence spectra of (1) pure ZnS and (2) ZnS/Cu at +150°C.



(1)



(2)

Fig. 4. Microphotometer curves of fluorescence spectra of (1) pure ZnS and (2) ZnS/Cu at +150°C.

The same apparatus and methods as that reported in the previous paper(2) were used in the present measurements. The measurements of fluorescence spectra were carried out at the temperature covering a range from $-185°C$ to $+300°C$. We could observe the molecular vibration structure of the fluorescence spectra most obviously at the temperature about $+150°C$. The fluorescence spectra of the pure ZnS phosphor and the ZnS phosphor containing 1×10^{-5} g. atom/mol. Cu as an activator were shown in the figures (1) and (2) of Fig. 3 respectively. The microphotometer curves for the fluorescence spectra of the pure ZnS and ZnS/Cu phosphors were given in the curves (1) and (2) of Fig. 4 respectively. Also the (mean) energy distribution curves of the fluorescence spectra of both phosphors were given in the curves (I) and (II) of Fig. 5 respectively. The each fluorescence band given by the curves (I) and (II) in Fig. 5 are caused from the transition $^3P_1\rightarrow{}^1S_0$ in the pure ZnS phosphor and $^3D_3\rightarrow{}^1S_0$ in the ZnS/Cu phosphor respectively, as already shown in the previous paper.(1)

The fluorescence spectra for both the pure ZnS phosphor and the ZnS/Cu phosphor have the identical structure, within the range of error, consisting of many diffused lines.

The observed values of the wave length and wave number of these spectra were shown in Table 1.

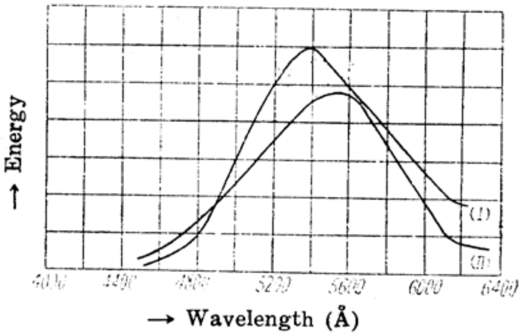


Fig. 5. Fluorescence spectra of (1) pure ZnS and (II) ZnS/Cu at +150°C.

Theoretical interpretations for the experimental results. The properties of the molecular and elastric vibrations in the polar crystals have been extensively investigated by Born, Kármán, and many other investigators. According to their theory, we can distinguish the molecular vibrations and elastic vibrations in the diatomic crystals, so far as the masses of atoms or ions constituting the binary crystals are not identical each other. Although the molecular vibration frequency of Zincblende crystal has not yet been known experimentally, its theoretical value has been obtained as follows,

from the Madelung-Einstein formula(8)

$$\lambda_M = 44.8\mu \qquad \nu_M = 223.2\ \mathrm{cm}^{-1},$$

and from the Lindemann formula(8)

$$\lambda_L = 36.9\mu \qquad \nu_L = 271.0\ \mathrm{cm}^{-1}.$$

On the other hand, F. Seitz(9) gave the following formula for the cubic crystal, from the viewpoint of quantum mechanics,

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(8) C. Schaefer, F. Mottossi "Das ultrarote Spectrum," 285, Berlin (1930).

(9) R. B. Barnes, R. R. Brattain, F. Seitz, *Phys. Rev.*, **48** (1935), 582.

$$\tilde{\nu} = \frac{1}{\sqrt{2\pi}}\left(\frac{f}{M}\right)^{1/2} \qquad (11),$$

with $f = (C_{11} + C_{44}) \times r$, $M = \dfrac{m_1 m_2}{m_1 + m_2}$

C_{11}, C_{44} = elastic constant in the terms of Voigt,
r = the shortest distance between two unlike atoms,
m_1, m_2 = mass of each unlike atom.

For Zincblende these quantities have following values,(6),

$C_{11} = 9.43 \times 10^{10}$,
$C_{44} = 4.34 \times 10^{11}$,
$r = 2.35\text{Å}$.

With these results, we can get from eq. (11)

$\nu_s = 226\ \text{cm}^{-1}$, $\lambda_s = 44.2\ \mu$.

It has been known that Zincblende shows Reststrahlen at 31 μ and the characteristic temperature of this crystal is 175.(6)

The maximum frequency $\tilde{\nu}_m$ and the corresponding wave number of the elastic vibrations are expected as

$\tilde{\nu} = 3.66 \times 10^{12}\ \text{sec},^{-1}$
$\nu_m = 122\ \text{cm}^{-1}$.

We can see that the maximum frequency of the elastic vibrations is almost equal to one half of the fundamental frequency of the molecular vibrations.

By assuming the usual formula for the diatomic molecule in this case, we can analize the observed fluorescence spectra as follows,

$$\nu = 1805 + 315\,(v' + 1/2) - 236\,(v'' + 1/2) + \cdots \qquad (12)$$

with v' = vibration quantum number for the excited state,
v'' = vibration quantum number for the ground state.

The calculated values from eq. (12) were given in Table 1 together with the wave number difference ($\Delta\nu$) between the calculated values and the observed values. The molecular vibration structure of ZnS phosphor activated by Cu is identical with that of pure ZnS, as mentioned above. This fact can be explained as follows. The molecular vibration will be influenced by the presence of atoms of other kinds only in the magnitude of second order.(10) Since Cu atom has almost the same mass as Zn atom especially in our case, the variation of the frequency of the molecular vibrations caused by the substitution of Zn atom by minute amount of Cu atom (of the order of 10^{-5}) is very small, as we can evaluate it from the Madelung-Einstein, Lindemann or Seitz formula.

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(10) J. Frenkel, *Rhys. Rev.*, **37** (1931), 17.

Table 1. Fluorescence spectra of the pure ZnS phosphor (at+150°C).

$\lambda_{obs.}$ (Å)	$\nu_{obs.}$ (cm^{-1})	$\nu_{calc.}$ (cm^{-1})	$(v'v'')$	$\Delta\nu$	$\lambda_{obs.}$ (Å)	$\nu_{obs.}$ (cm^{-1})	$\nu_{calc.}$ (cm^{-1})	$(v'v'')$	$\Delta\nu$
5754	17379	17392	(0 5)	−13	5103	19596	19596	(4 1)	0
5731	17449	17471	(1 6)	−22	5083	19673	19675	(5 2)	− 2
5705	17528	17550	(2 7)	−22	5062	19755	19754	(6 3)	+ 1
5675	17621	17628	(0 4)	− 7	5041	19837	19832	(4 0)	+ 5
5654	17687	17707	(1 5)	−20	5021	19916	19911	(5 1)	+ 5
5625	17778	17786	(2 6)	− 8	5001	19996	19990	(6 2)	+ 6
5600	17857	17864	(0 3)	− 7	4982	20072	20069	(7 3)	+ 3
5574	17940	17943	(1 4)	− 3	4965	20141	20147	(5 0)	− 6
5551	18015	18022	(2 5)	− 7	4946	20218	20226	(6 1)	− 8
5527	18095	18100	(0 2)	− 5	4924	20309	20305	(7 2)	+ 4
5502	18175	18179	(1 3)	− 4	4903	20396	20384	(8 3)	+12
5479	18252	18258	(2 4)	− 6	4886	20467	20463	(9 4)	+ 4
5453	18339	18336	(0 1)	+ 3	4868	20542	20541	(7 1)	+ 1
5429	18420	18415	(1 2)	+ 5	4849	20623	20620	(8 2)	+ 3
5406	18498	18494	(2 3)	+ 4	4831	20700	20699	(9 3)	+ 1
5384	18574	18572	(0 0)	+ 2	4813	20777	20778	(10 4)	− 1
5360	18657	18651	(1 1)	+ 6	4794	20859	20857	(11 5)	+ 2
5339	18730	18730	(2 2)	0	4776	20938	20936	(12 6)	+ 2
5318	18804	18809	(3 3)	− 5	4759	21013	21014	(10 3)	− 1
5292	18896	18887	(1 0)	+ 9	4742	21088	21093	(11 4)	− 5
5270	18975	18966	(2 1)	+ 9	4725	21164	21172	(12 5)	− 8
5250	19048	19045	(3 2)	+ 3	4707	21245	21251	(13 6)	− 6
5230	19120	19124	(4 3)	− 4	4690	21322	21329	(11 3)	− 7
5209	19198	19202	(2 0)	− 4	4672	21404	21408	(12 4)	− 4
5188	19275	19281	(3 1)	− 6	4655	21482	21487	(13 5)	− 5
5167	19354	19360	(4 2)	− 6	4638	21561	21566	(14 6)	− 5
5142	19448	19439	(5 3)	+ 9	4621	21640	21644	(12 3)	− 4
5122	19524	19517	(3 0)	+ 7	4605	21716	21723	(13 4)	− 7

Thus we can confirm that the resonance radiation in the activation centre is responsible for the fluorescence of ZnS phosphors and the breadth of the fluorescence bands of ZnS phosphors is caused by the molecular vibration structure of the fluorescence spectra.

In conclusion, the author wishes to express his sincere thanks to Vice-Director B. Imamura of this institute for his generous help, and also to Prof. S. Mizushima of Tokyo Imperial University for his kind advices and encouragement.

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