Studies on Luminescent Materials. Part 1. Theory of Zinc Sulphide-copper Crystal Phosphor.

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Introduction. Crystals which can emit all kinds of excitation energy which they absorbed as the light energy, are called crystal phosphors. Of such phosphors, especially zinc sulphide phosphors have been extensively investigated, since they are theoretically important as well as technically. Most of the studies on the zinc sulphide phosphors, however, were restricted in the description of the properties of the phosphors and they have not been able to give a fairly complete picture of the mechanism of fluorescence and photoconductivity, and of many other behaviours of the phosphors.

In the present paper, the author wish to propose a picture of the zinc sulphide-copper crystal phosphor, based on the quantam mechanical theory of solid state, which can explain the mechanism of fluorescence and phosphorescence, the distribution of fluorescence- and excitation-bands, photoconductivity, and many other behaviours of the phosphors.

The treatment is similar in some way to that of F. Seitz[1] which was reported while this paper was written, but the mechanism of fluorescence and the interpretation of the properties of the phosphors,

(1) F. Seitz: *J. Chem. Phys.*, **6** (1938), 454; **6** (1938), 150.

proposed by the author, are different from that of F. Seitz, as we shall see in the following sections.

Theory. (a) Energy levels in the zinc sulphide-copper crystal phosphor. Let us consider electrons moving in the self-consistent field $V(\mathfrak{r})$ in the crystal which has the same periodicity and symmetry with the crystal lattice. If we assume that $V(\mathfrak{r})$ is large near the lattice point (and falls rapidly with distance, we can solve the Schrödinger equation) by the Wilson-Bloch's method.[2]

We shall first deal with the state whose wave function of atom $\phi(\mathfrak{r})$ is spherically symmetrical. For the energy value, we can obtain the following results.

In a simple cubic lattice

$$E = E_0 - \alpha - 2\gamma(\cos \bar{\mathfrak{k}}_x a + \cos \bar{\mathfrak{k}}_y a + \cos \bar{\mathfrak{k}}_z a),$$

in a body-centred cubic lattice

$$E = E_0 - \alpha - 8\gamma\left(\cos \frac{1}{2}\bar{\mathfrak{k}}_x a + \cos \frac{1}{2}\bar{\mathfrak{k}}_y a + \cos \frac{1}{2}\bar{\mathfrak{k}}_z a\right),$$

in a face-centred cubic lattice

$$E = E_0 - \alpha - 4\gamma\left(\cos \frac{1}{2}\bar{\mathfrak{k}}_y a \cos \frac{1}{2}\bar{\mathfrak{k}}_z a + \cos \frac{1}{2}\bar{\mathfrak{k}}_z a \cos \frac{1}{2}\bar{\mathfrak{k}}_x a + \cos \frac{1}{2}\bar{\mathfrak{k}}_x a \cos \frac{1}{2}\bar{\mathfrak{k}}_y a\right)$$

with $-\alpha = \int \phi_{\mathfrak{g}}^*(\mathfrak{r})\{V(\mathfrak{r}) - U_{\mathfrak{g}}(\mathfrak{r}-\mathfrak{g})\}\phi_{\mathfrak{g}} d\tau$,

$-\gamma = \int \phi_{\mathfrak{h}}^*(\mathfrak{r})\{V(\mathfrak{r}) - U_{\mathfrak{g}}(\mathfrak{r}-\mathfrak{g})\}\phi_{\mathfrak{g}} d\tau$,

$\bar{\mathfrak{k}}$ = wave number, $\mathfrak{g}, \mathfrak{h}$ = lattice vector,

a = lattice constant,

ϕ = eigenfunction of the isolated atom,

$U_{\mathfrak{g}}$ = potential function of the isolated atom.

By the same method, we can obtain the energy value in the crystal for the wave function of p- or d-state.

As the results, we can say that the energy of an electron in the crystal consists of a constant term $E_0 - \alpha$, together with a term which depends on the wave number. E_0 is the electronic energy of an isolated atom. α is the mean value of the potential energy which is due to all the neighbouring atoms, and it is approximately given by the Madelung energy, in the ionic crystals, if we neglect the polarisation energy. γ which is represented by the exchange integral, defines the breadth of

(2) Hand. d. Physik, 24/2 (1933), 394.

the energy band and it will be greater the more the wave functions overlap.

Thus we see that, if we consider the forces due to the neighbouring atoms, each energy level of the electron splits into a number of levels forming a band in the crystal.

Let us obtain the energy value of E_0-a in the zinc sulphide crystal phosphors and of the impurity level arising from the copper which is added to the phosphors as an activator, by the following considerations.

There are two crystal forms in the zinc sulphide crystal phosphors,

(1) Zinc blende, cubic system, it is formed above the temperature of 1015° – 1024°C.[3]

(2) Wurzite, hexagonal system, it is formed below the temperature of 1015° – 1024°C.[3]

These two crystal forms of the zinc sulphide phosphors show the same properties as the luminescent materials,[4] and in fact, we can obtain the same results for the two crystal forms, in the zero order approximation, by the following calculations. Therefore we shall deal only with the zinc blende crystal.

We can consider the zinc sulphide crystals as the nearly ionic crystal, since it has "Reststrahlen" at 31μ[5] and trigonal polar axis of symmetry.[6]

In the ionic crystals, Madelung energy is given by the theory of Hund[7] as follows:

$$W = \frac{ZAe^2}{r} \qquad (4),$$

where Z is valence of ions in the lattice point, r is the shortest distance between the nearest unlike ions, and e is electronic charge.

Putting into (4) $r = 2.35$Å, $Z = 2$ and $A = 1.6831$ for the zinc blende, we obtain $W = 19.9$ eV.

As the results, the energy of electrons on positive ions is increased by the amount of 19.9 eV and that on negative ions is decreased by the same amount in the zinc blende crystal.

If we assume that the electron affinity of ions in the crystal is approximately equal to the ionization energy of the free ions,[1],[8],[9] we can obtain the energy levels of the ions in the crystal by the algebraic sum of the electron affinity and Madelung energy, i.e. by $E-a$.

The energy levels in the crystal broaden into bands by the zone-theory and we can estimate the broadening roughly. The energy levels in the zinc sulphide-copper crystal phosphors are shown in Fig. 1.

In Fig. 1 the lowest energy band is $3d^{10}$—band of Zn^{++} ions which is completely occupied by ten electrons. The energy immediately above the d-band of Zn^{++} ions is $4p^6$—band of S^{--} ions which is completely occupied by six electrons. These two bands are narrow compared with the conduction band.

(3) E. T. Allen, J. L. Creshaw: *Z. anorg. Chem.*, **79** (1920), 186.
(4) E. Tiede, A. Schleede: *Ber.*, **53** (1920), 1721.
(5) K. Forsterling: *Z. Physik*, **8** (1922), 251.
(6) P. P. Ewald: "Kristalle u. Röntgenstrahlen," Berlin, (1923), 186.
(7) F. Hund: *Z. Physik*, **34** (1925), 833.
(8) J. H. De Boer, E. J. W. Verwey: *Proc. Phys. Soc.* (*London*), **49** (1937), 59.
(9) N. F. Mott: *Trans. Faraday Soc.*, **34** (1938), 500.

Levels about 9 and 13 eV above the S^{--}-band are respectively 1st and 2nd excited levels of Zn^{++} ions. The uppermost band is 4s-band of Zn^{+} ions and its broadening can be estimated a few eV. This band corresponds to the conduction band.

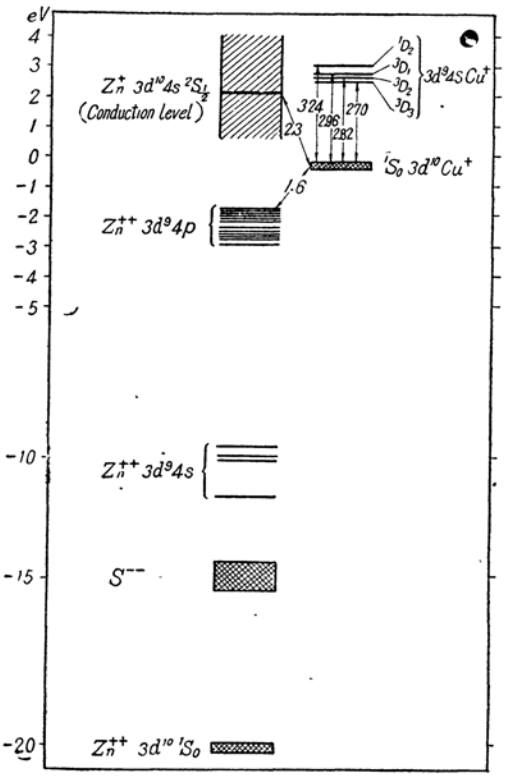

Fig. 1. Energy levels in ZnS/Cu.

It is well known that the zinc sulphide-copper crystal phosphor shows the photoconductivity and fluorescence, at the same time, by the absorption of the light corresponding to its excitation bands.[10] Therefore, we can assume that the fluorescence and photoconductivity are caused from the same origin, that is to say, from the Cu^{+} ion or atom in the activation centre. As the results, we can conclude that the energy level of the activation centre must lie in the range of, at least, 3 or 4 eV below the conduction band, and such a level is that of Cu^{+} ion, as we see in Fig. 1.

The level immediately below the conduction band is $3d^{10}$-level of Cu^{+} ion which is completely occupied by ten electrons. Since it lies in the forbidden region, the broadening of the level is very narrow. The excited levels of Cu^{+} ion, that is to say, $^1D_2$, $^3D_1$, $^3D_2$ and $^3D_3$ levels lie immediately below the conduction band or on the position overlapping each other in the real crystal.

(b) Excitation bands of fluorescence. If the zinc sulphide crystal absorbs the excitation energy such as light, an electron of the Cu^{+} ion in the activation centre makes transitions from the ground state S^{--} into the excited states of $^1D_2$, $^3D_1$, $^3D_2$ and $^3D_3$. As the results, we can expect the four excitation bands of fluorescence whose maxima lie about at following wave length:

$$a_1 = 3.24\ \text{eV}, \qquad a_2 = 2.96\ \text{eV}, \qquad a_3 = 2.82\ \text{eV}, \qquad a_4 = 2.70\ \text{eV}.$$

In fact, Tomascheck[11] observed following excitation bands of fluorescence in the zinc sulphide-copper crystal phosphor,

(10) B. Gudden, R. Pohl: *Z. Physik*, **2** (1920), 181.
(11) R. Tomascheck. "Handb. d. exp. Phys"., Tell I, (1928), 392.

for α-fluorescence-band $d_1^\alpha = 430\ \mathrm{m}\mu = 2.87\ \mathrm{eV}$ $d_2^\alpha = 360\ \mathrm{m}\mu = 3.43\ \mathrm{eV}$,
$d_3^\alpha = 260\ \mathrm{m}\mu = 4.11\ \mathrm{eV}$ $d_4^\alpha = 235\ \mathrm{m}\mu = 7.22\ \mathrm{eV}$,

for β- ,, ,, $d_1^\beta = 365\ \mathrm{m}\mu = 3.37\ \mathrm{eV}$ $d_2^\beta = 270\ \mathrm{m}\mu = 4.57\ \mathrm{eV}$,

(for γ- ,, ,,) $d_1^\gamma = 470\ \mathrm{m}\mu = 2.62\ \mathrm{eV}$ $d_2^\gamma = 380\ \mathrm{m}\mu = 3.25\ \mathrm{eV}$,

for δ- ,, ,, $d_1^\delta = 425\ \mathrm{m}\mu = 2.90\ \mathrm{eV}$ $d_2^\delta = 370\ \mathrm{m}\mu = 3.37\ \mathrm{eV}$.

The author interprets these results of the observations on the excitation bands of fluorescence as follows:

$^1S_0 \rightarrow {}^1D_2$ $a_1 = 3.24\ \mathrm{eV}$ corresponds to the observed excitation bands
$d_2^\alpha = 3.43\ \mathrm{eV}$ $d_1^\beta = 3.37\ \mathrm{eV}$
$(d_2^\delta = 3.37\ \mathrm{eV})$ $(d_2^\gamma = 3.25\ \mathrm{eV})$,

$^1S_0 \rightarrow {}^3D_1$ $a_2 = 2.96\ \mathrm{eV}$ corresponds to the observed excitation bands
$d_1^\delta = 2.90\ \mathrm{eV}$,

$^1S_0 \rightarrow {}^3D_2$ $a_3 = 2.82\ \mathrm{eV}$ corresponds to the observed excitation bands
$d_1^\alpha = 2.87\ \mathrm{eV}$,

$^1S_0 \rightarrow {}^3D_3$ $a_4 = 2.70\ \mathrm{eV}$ corresponds to the observed excitation bands
$d_1^\gamma = 2.62\ \mathrm{eV})$.

We must, however, notice the following facts: We could confirm that the fluorescence spectra of zinc sulphide-copper crystal phosphors consisted of α- and β-band (and probably δ-band), and γ-band was not correlated to the Cu^+ ion, but to the Zn atom diffused in the phosphors.

The excitation bands of fluorescence above quoted have a wide broadening due to molecular and lattice vibrations in the crystal as a whole, as we see in the following sections.

(c) Fluorescence band. Since Cu^+ ion in the activation centre is surrounded by Zn^{++} and S^{--} ions in the crystal, the normal and excited states of the electron of Cu^+ ion can be represented as functions of a parameter (u) describing the positions of the ions.

After an electron in the equilibrium position of the normal state has absorbed the excitation energy, it makes a transition to the excited state and then it moves into a new equilibrium position of the excited state, the excess energy is taken up by the vibrations of the surrounding ions.

Fig. 2 shows the energy curve of Cu^+ ion in the activation centre. A represents an equilibrium position of the normal state of Cu^+ ion in the activation centre. After an electron in this position has absorbed light quanta, it makes a transition into one of the excited states of Cu^+ ions, for example, to C of the energy curve $^3D_2$. Then it moves into a new equilibrium position f of $^3D_2$ curve in about 10^{-13} second, mean-

while giving up the excess energy as the lattice vibrations. From f the electron makes a transition either to h of $^3D_3$ curve or to g of the ground state, in accordance with Franck-Condon principle.

The transition $f \rightarrow h$ occurs with radiation of infra-red waves or elastic vibration waves, and the latter case is more probable when the coupling between the electron and lattice vibrations is strong.

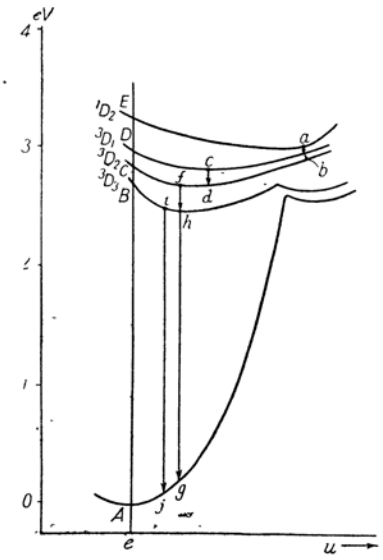

Fig. 2. Potential curves in the activation centre.

The transition $f \rightarrow g$ gives the fluorescence. The electron in h moves into the equibrium position of $^3D_3$ and then it makes a transition to j of the ground state with the radiation of the fluorescence. By such a picture, these fluorescence bands will show a wide breadth by the molecular vibrations coupled with the elastic vibrations of the lattice. In fact, the author could observe the molecular vibration structure of the fluorescence bands which will be reported in the following paper.

On the other hand, the electron which moved into the equilibrium position c from D of $^3D_1$ curve, will make a transition into d and the transition from c to the ground state will scarcely occur when the interaction between the electron and lattice vibrations is very strong. The same process is possible for the electron which has made a transition to E of the energy curve $^1D_2$.

As it can be seen in Fig. 3 and Fig. 4, the author observed two fluorescence bands at about 5250 Å and 4550 Å arising from the copper activator in the zinc sulphide phosphor. They are considered to correspond to α-and β-band respectively. The author assignes α-band to the electronic transition of $^3D_3 \rightarrow {}^1S_0$ $(i \rightarrow j)$ and β-band to that of $^3D_2 \rightarrow {}^1S_0$ $(f \rightarrow g)$ of the Cu^+ ion in the activation centre.

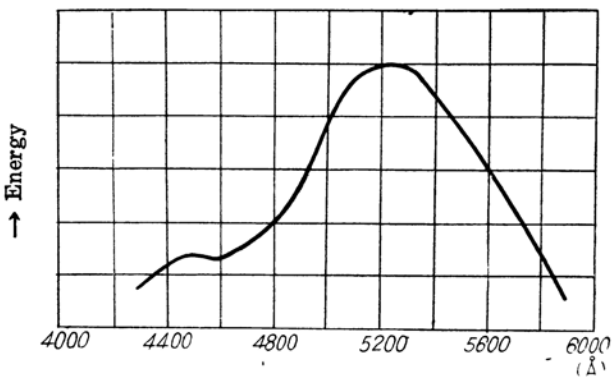

Fig. 3. Fluorescence spectrum of ZnS/Cu
Cu = 1×10^{-5} mol fraction, 25°C.

On the other hand, F. Seitz[1] reported that the activation centre of the zinc sulphide-copper phosphor consisted of the copper atom which diffused into the crystal. And he concluded that the direct transition of the electron (which is raised in the conduction band from the ground state) from the conduction band

to the ground state is responsible for the fluorescence band. If it is the case, the fluorescence spectra of zinc sulphide-copper phosphor should show a simple wide band.

But it is well known that the fluorescence spectra of zinc sulphide-copper phosphor consist of a few bands.[11] In fact, the author could confirm that the fluorescence spectrum of zinc sulphide phosphor is consists of two fluorescence bands of α and β and each fluorescence band shows the molecular vibration structure.

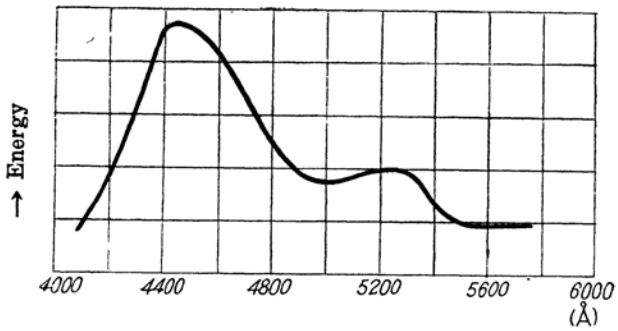

Fig. 4. Fluorescence spectrum of ZnS/Cu
Cu = 1×10^{-4} mol fraction, 25°C.

Therefore we can not adopt the Seitz's model of the zinc sulphide-copper phosphor. And it will be a reasonable picture that the electronic transition from the excited states to ground state of Cu^+ ion is responsible for the fluorescence. In other words, the resonance radiation, in the wide meaning, in the activation centre is responsible for the fluorescence of the zinc sulphide crystal phosphor.

The same picture will be possible in the case of the excitation bands of fluorescence and photoconductivity.

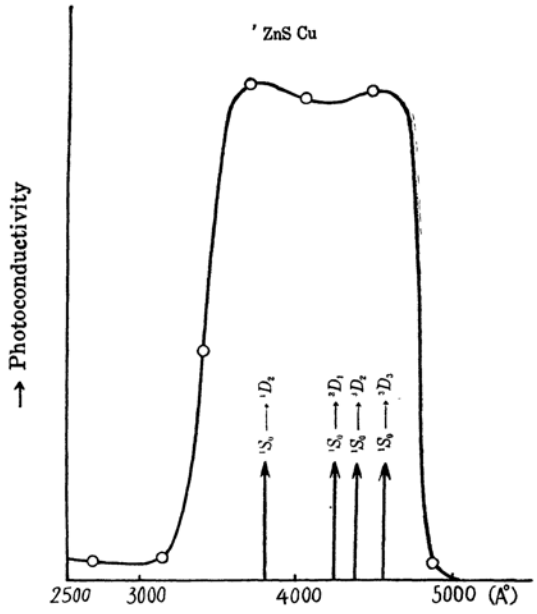

Fig. 5. Photoconductivity of ZnS/Cu

If the electron in the excited states of Cu^+ ion in the activation centre, absorbs the heat energy, it can make a transition to the conduction band and be free to move in the crystal phosphor.

Therefore we can expect that the zinc sulphide-copper crystal phosphor has photoconductivity at room temperature or at enough high temperature, if it absorbs the light corresponding to the excitation bands of fluorescence.

Fig. 5 shows excitation band of the photoconductivity observed by Gudden and Pohl[10] and in this figure the arrows show the maxima of the excitation bands obtained theoretically by the author.

In the above quoted picture, the photoconductivity will decrease with decreasing temperature. In fact, it is the case by the observation of the photoconductivity of zinc sulphide crystal by Lentz.[12] And the author could calculate theoretically the temperature dependence of the photoconductivity of zinc sulphide phosphor by using the above quoted mechanism of the photoconduction, and the results coincide with the experiment of Lentz[12] very good, as we shall see in the following paper.

Summary.

In this paper, the author has attempted to interpret the properties of the zinc sulphide-copper crystal phosphor from the view point of zone-theory.

(1) It was pointed out that the activation centre of zinc sulphide-copper phosphor consists of Cu ion surrounded by the ions of Zn and S.

(2) The transition of electron of Cu^+ ion from the ground state $^1S_0$ to the conduction band is responsible for the excitation bands of fluorescence.

(3) The two fluorescence bands with maxima at 5250 Å and 4550 Å in this phosphor may be correlated with the electronic transitions

$$^3D_3 \rightarrow {}^1S_0 \ (\alpha\text{-band}),$$

$$^3D_2 \rightarrow {}^1S_0 \ (\beta\text{-band}).$$

(4) If the electron in the excited states of Cu^+ ion absorbs heat energy, it makes a transition to the conduction band and be free to move in the phosphor, then the phosphor will show a phenomenon of the photoconduction.

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