On the Lowering of the Luminescence Yield of Phosphors in Intense Excitation

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It is shown that the lowering of the luminescent output of ZnS-Cu and ZnS-Cu, Co phosphors with intense excitation is conditioned to a considerable degree by the illuminating action of the exciting light and by the fact that the recombination of optical electrons or "holes" results in radiationless transitions. The same causes result in the fact that the total illumination, as determined from the curve of increasing illumination, turns out to be considerably smaller than the total illumination as determined from the curve of the extinction process.

1. INTRODUCTION

IT is known that minute quantities of impurities frequently act as extinguishers of luminescence of crystal phosphors. The ZnS-Cu phosphor with traces of the iron group elements is a classic example. In spite of the great number of published works in this field[1-11] no definite results have yet been obtained in the understanding of the mechanism of extinction by impurities in typical phosphors – i.e., in luminescent substances which exhibit the phenomenon of recombination. This is apparently due to the fact that the authors of the referenced works have not taken into consideration certain, only recently investigated phenomena in the field of luminescence [for example: the luminescent action of the exciting light and the possible difference in the effectiveness of irradiation for recombination of thermal and optical, (i.e., liberated by light) electrons][12-16].

In this work, using phosphors ZnS-Cu and ZnS-Cu, Co, we show that with high degree of excitation, these phenomena can substantially influence the magnitude of the luminescent output and determine the relation between the output and the intensity of the exciting light. By taking these phenomena into account it is possible to explain why, with excitation of high intensity, the total light output as determined from the curve of increasing luminescence turns out to be considerably smaller than the total light output determined from the curve of extinction.

2. INVESTIGATION OF THE DEPENDENCE OF LIGHT OUTPUT ON THE INTENSITY OF THE EXCITING LIGHT

In the investigation of the equilibrium luminescent output q of ZnS-Cu phosphor for different intensities E of the exciting light we have established together with Alentsev[17] that q is constant only for moderate values of E ("plateau" region); for this case $q \sim 1$. Outside the "plateau" the value of q falls both in the direction of increasing and decreasing E. The fall of q at high values of E was explained by the increase of that portion of the excitation energy which is absorbed by the localized electrons and the ionized luminescent centers (the luminescent action

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of the exciting light), the concentration of which increases with the increase of E. This in turn leads to an increase in the number of electrons and "holes" the recombination of which does not produce any radiation[3]. The reduction of q for low values of E was explained by the accompanying increase of the role of external quenching which is a linear reaction (proportional to the concentration of the ionized centers n) while the luminescent processes are reactions of the second order (proportional to n^2).

We have conducted similar investigations of the dependence of q on E for ZnS-Cu,Co phosphors. We have measured not the quantity q itself but the intensity of equilibrium luminescence which is a quantity proportional to q.

$$I_\infty = aq. \tag{1}$$

Since the introduction of Co does not result in any change of the absorption in the region of excitation, a = constant.

The results turned out to be similar to those obtained with pure phosphors of ZnS-Cu, i.e., there is a plateau with a drop in q to the right and to the left of it. It can therefore be considered that the cause of the drop in q outside the plateau for the ZnS-Cu,Co phosphor is the same as for the ZnS-Cu phosphor. Besides the similarity, there is also a difference in that, even in the plateau region, $q \ll 1$. The reason for this general reduction in the values of the ordinates in the q vs. E curve will be discussed by us in a later paper.

In the previously mentioned work, the dependence of q on E for the ZnS-Cu phosphor was investigated at various temperatures in order to prove the correctness of the assumptions made concerning the general lowering of the value of q. As expected, it turned out that the heating results in the displacement of the plateau into the region of higher values of E. It can be shown that the same data also give certain quantitative support to these assumptions.

Indeed, the lowering of q with increase of E begins at the moment ($E \simeq E'$), when the probability of the optical liberation of the electron (or "hole") $w_E = \alpha E$ (α = constant) becomes comparable with that of thermal liberation $w_T = w_0 \exp\{-\epsilon/kT\}$ (w_0 = const., ϵ = binding energy of the electron, k = Boltzman's constant) i.e., when

$$\alpha E' \sim w_0 e^{-\varepsilon/kT} \tag{2}$$

It follows from (2) that

$$\lg \frac{E_2'}{E_1'} \approx \frac{\varepsilon}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \tag{3}$$

where indexes 1 and 2 refer to two different temperatures. If we make use of the data for $T_1 = 20\,^\circ\mathrm{C}$ and $T_2 = 100\,^\circ\mathrm{C}$ taken from the work of Alentsev et al[17], we obtain

$$\epsilon \sim 0.3 \text{ ev}. \tag{4}$$

This result agrees with values ϵ(ϵ = 0.3 – 0.5 ev), for the phosphor ZnS-Cu obtained by other methods[18].

The results obtained in this manner can serve as a new confirmation of the theory that the lowering of q outside the "plateau" region is connected with the luminescent action of the exciting light. However, with the action of the exciting light, there is associated not only the lowering of q in the plateau region but also, as will be shown later, a decrease in total illumination, as determined from the curve of increasing luminescence, compared with that determined from the extinction curve.

3. DEPENDENCE OF THE RATIO OF TOTAL LIGHT OUTPUTS DETERMINED FROM THE CURVES OF RISE AND EXTINCTION OF LUMINESCENCE ON THE INTENSITY OF THE EXCITING LIGHT

The total light output determined from the curve of rising luminescence is given as

$$L_p = \int_0^\infty (I_\infty - I_\vartheta)\, d\vartheta, \tag{5}$$

where ϑ = time elapsed from the beginning of excitation and I_ϑ = intensity of light at the time ϑ.

The total light output, evaluated from the curve of extinction of luminescence, is equal to

$$L_3 = \int_0^\infty I_t\, dt, \tag{6}$$

where t = time elapsed from the cessation of excitation. It is generally assumed that

$$L_p / L_3 = 1. \tag{7}$$

However, such equality requires that the following conditions be fulfilled:

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1) that the light output associated with recombination of electrons and "holes"

$$q = \text{constant} \tag{8}$$

during the time of increasing luminescence, as well as during the time of extinction of luminescence even if quenching exists.

2) that the ionization per unit time remains constant during the excitation time.

Tolstoi[19] has shown that with external quenching which follows the first order kinetic law

$$L_p / L_3 > 1. \tag{9}$$

The inequality of L_p and L_3 in this case is associated with the nonfulfillment of condition (8).

By measuring L_p and L_3 for phosphors ZnS-Cu, and ZnS-Cu,Co, we have obtained the following results: Under weak excitation, when the effect of the extinction is present, inequality (9) is confirmed (Table I). Under strong excitation (Table II) the opposite is true.

TABLE I. Values of L_p/L_3 at weak excitation and $T = 80\,°C$ for phosphors ZnS-Cu and ZnS-Cu,Co (thin layer).

E (Rel. Intensity of exciting light)	Cu (3×10^{-5}), Co (0)	Cu (3×10^{-5}), Co (10^{-6})
11	—	1.43
2.4	1.64	2.50
1.0	2.17	3.00

TABLE II. Values of L_p/L_3 at intensive excitation and $T = 20\,°C$ for phosphors ZnS-Cu and ZnS-Cu,Co (thin layer).

E	Cu (3×10^{-5}), Co (0)	Cu (3×10^{-5}), Co (10^{-7})	Cu (3×10^{-5}), Co (10^{-6})
800	—	—	0.41
200	0.38	0.33	—
3.5	—	—	0.73
1.0	0.73	0.60	—

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$$L_p / L_3 < 1. \tag{10}$$

This result can be explained as follows: Inasmuch as L is relatively high at high values of E, and the action of the exciting light plays an important role in the kinetics of phosphorescence (a portion of the excitation energy is captured by the localized electrons or "holes"), the results are that:

1. During the excitation of the phosphor, as L is increasing, its optical characteristics may change, which may result in the violation of condition (2).

2. Optical electrons and "holes" which appear during excitation enter into recombination which, in the case of phosphors ZnS-Cu and ZnS-Cu,Co, does not result in radiating transitions. This results in the violation of condition (8), since there are no such losses during the extinction in view of the absence of electrons and "holes".

RESULTS

The results obtained indicate that:

1. The causes of the decrease in the light output outside the "plateau" region for the ZnS-Cu,Co phosphor are the same as for the ZnS-Cu phosphor. At low intensities of the exciting light, this decrease is caused by the rising role of the external quenching, at high intensities – by the luminescent action of the exciting light and by the fact that only recombination of thermal electrons produces radiation.

2. As a result of the phenomena described the ratio of light outputs $L_p/L_3 < 1$ for high intensity of excitation.

3. In all works on investigation of the nature of the extinction process of ZnS-Cu phosphor by the elements of the iron group*, in which the phenomena associated with the luminescent action of the exciting light have not been considered, the interpretation of the results may be more or less incorrect.

* Preliminary experiments have shown that the action of Ni and Fe are very similar to the action of Co, but there is also a considerable difference. For example, while infra-red radiation of wavelengths $\lambda = 0.8$ and $\lambda = 1.3\,\mu$ quenches the luminescence of ZnS-Cu,Co, in the case of ZnS-Cu, Ni only radiation $\lambda = 1.3\,\mu$ produces quenching, and radiation $\lambda = 0.8\,\mu$ produces a noticeable intensification.

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