Investigation of the Origin of Levels of Electron Localization in Zinc Sulphide Phosphors

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The role of copper and oxygen in the formation of three bands of localization levels of electrons in ZnS-Cu phosphor is clarified by the method of temperature controlled lumines-cence. The action of iron, nickel and cobalt on the separate maxima of the temperature controlled luminescence curve is examined. It is found that Fe and Ni in small concentrations may sharply increase the intensity of luminescence.

1. INTRODUCTION

P ROLONGED emission of phosphors is caused by the freeing of electrons from special localized centers in the crystal structure, where they are trapped when the phosphor is excited. Typical phosphors generally have several kinds of energy levels of localization of electrons, differing in their depth, each of which takes part in a definite way in the process of phosphor lumines-cence. It is clear from this that the electron localization levels play an exceptionally important role in the kinetics of phosphorescence.

The question of the origin of electron localization levels has not been adequately investigated up to the present time. According to the generally accepted opinion, the places in the crystal structure which are deformed by the inclusion of the activator ions, are also the places of electron localization. However, each phosphor must be separately investigated to determine which set of levels is connected (and to what extent) with one or the other activator. Also, the influence of the other components of the phosphor and of the so-called extinguishers of luminescence, such as iron, nickel and cobalt, on the formation of localized levels is very little understood.

The most widely studied class of phosphors are the zinc sulphides which found wide practical application. It is known that a typical ZnS-Cu phosphor has three bands of electron localization of different depth. The depth of the levels in each band is characterized by a temperature at which most of the electrons stored on the levels of a given band are freed. Hereinafter, the three bands of electron localization of the ZnS-Cu phosphor will be indicated in the order of increasing depth by numbers I, II and III; the depths of these bands are characterized by temperature ranges -140 to -110° C, -60 to -40° C, +20 to +50° C, respectively.

The most thoroughly investigated is the III band of levels. According to references 1 and 2, the origin of this band is connected with the presence of copper. However, in references 3 and 4 this band is explained by the presence of oxygen in the lattice of ZnS. Wee see that there is no agreement on the nature of this most highly investigated band of electron localization. Concerning the origin of bands I and II, there are even less data available. Kreger[3] considers that the band II ($T = -50$ to $-25°$ C) originates by the penetration of copper into the lattice ZnS. According to the opinion of Hoogenstraten[4], it is caused by the presence of complex Cu^+O^{-2}. Hoogenstraten connects the origin of band I with presence of sulphur ion vacancies in the ZnS lattice if oxygen ions enter into the composition of the phosphor; in the absence of oxygen, ions of the type Cl^- are considered the cause of formation of the I band of levels.

Our work is devoted to the further clarification of influence of the components of the ZnS-Cu phosphor on the formation of its levels of localization. To carry out this work we have changed, in different respects, the composition of the investigated samples and have determined their curves of light emission as a function of temperature.

2. DESCRIPTION OF THE EXPERIMENTAL METHOD

In order to establish more accurately the composition of the investigated ZnS-Cu phosphor samples, their preparation was carried out by ourselves. For the preparation of the phosphors,

[1] G. F. Garlick, A. F. Wells and M. F. Wilkins, J. Chem. Phys. **17**, 399 (1949).

[2] R. Bube, Phys. Rev. **80**, 655 (1950).

[3] F. A. Kreger and J. A. Dikhoff, J. Electrochem. Soc. **99**, 144 (1952).

[4] W. Hoogenstraten, J. Electrochem. Soc. **100**, 356 (1953).

we had at our disposal specially purified zinc suplhide and alkaline halide melts. The copper, and also Fe, Ni and Co, used as activators were in the form of chloride salts marked "chemically pure". Quartz and ceramic vessels only were used in the preparation of the samples. Heat treatment was performed in closed quartz crucibles at a temperature of $1100°$ C for a period of 15 minutes.

For the investigation, samples $\sim 10 \mu$ thick were deposited by precipitation from alcohol on mica plates $\sim 7 \mu$ thick.

As the basic method of investigation, we chose the temperature controlled luminescence method which consists of a measurement of the intensity of the excited luminescence at low temperatures of the phosphor as a function of this temperature. A very important requirement of this method is the uniform heating of the phosphor in the process of excitation. Otherwise, the entire picture of resulting levels is distorted.

The area under the curve of the temperature controlled luminescence or the height of its maximum (if the width does not change and on the assumption that in the given range of temperatures there is no temperature extinction) is proportional to the number of localized electrons on the levels of a given depth under given conditions of excitation. The latter conclusion cannot be considered strictly true since electrons which are elevated from the levels of localization into the conduction bands may undergo secondary localization, which may disturb the proportionality between the intensity of illumination corresponding to the maximum of the temperature controlled luminescence curve and the number of electrons localized on the levels of a given depth. However, as we shall see below, a series of experiments shows that under conditions of our experiment, the above-mentioned proportionality is preserved with very good approximation. The method of temperature controlled luminescence is therefore very convenient for the study of the origin of the electron localization levels, which in this case is reduced to the determination of the cause of the formation of separate maxima in the curve of the temperature controlled luminescence.

To achieve temperature controlled luminescence, we have constructed special equipment which permits us to obtain quite accurately a linear relationship between the time of heating and the temperature of the excited phosphor. A sketch of the experimental arrangement is shown in Fig. 1. The equipment consists of a massive brass rod with a cavity for the sample. The sample was fastened by a special movable holder. The

temperature of the phosphor was measured by a thermocouple. The heating wire was wound over the entire surface of the rod. The rod was placed in a Dewar vessel with windows for excitation of the sample under observation.

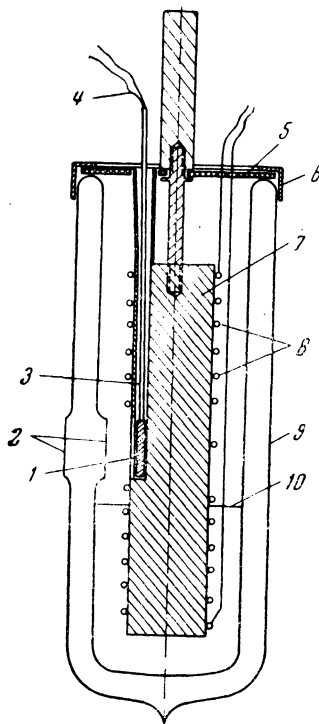For the purpose of cooling the sample prior to

FIG. 1. Experimental equipment for obtaining thermoluminescence. 1. Sample, in holder; 2. Windows of the Dewar vessel; 3. Copper tube for the thermocouple wires; 4. Thermocouple output; 5. Textolite cover; 6. Metal collar; 7. Brass rod; 8. Heater; 9. Dewar vessel; 10. Level of liquid nitrogen.

excitation, liquid nitrogen was poured into the Dewar. The measurement of the temperature controlled luminescence was begun 15 seconds after the end of the excitation. The temperature of the phosphor was increasing at a steady rate of 0.25 degree/sec. The curve of variation of temperature with time is shown in Fig. 2.

The described construction of the equipment permitted us (1) to change samples without changing the fixed position of the phosphor being investigated; (2) to excite the phosphor at any temperature in the range of $-190°$ C to $+100°$ C and maintain the temperature constant with an accuracy of $\pm2°$ during a 10-15 min interval, and (3) to insure a strictly constant rate of heating during the experiment.

Excitation of the phosphor was made using lamp PRK-4 with a filter which transmits a section of the mercury spectrum from $\lambda_{max} = 436\,m\mu$ to $\lambda_{max} = 366\,m\mu$. Duration of the excitation was 10 minutes. The radiation of the phosphor was measured visually by means of the luminescence photometer GOI.

3. THE ROLE OF ACTIVATORS Cu, Zn AND OXYGEN IN THE FORMATION OF ELECTRON LOCALIZATION LEVELS

As pointed out above, it had not been clearly established until recently, which of the bands of local levels, and to what extent, are formed by copper. We have therefore prepared a series of samples whose copper concentration varied from 3×10^{-6} to 10^{-3} gm/gm and measured their curves of temperature luminescence (Fig. 3).

The curves obtained had three basic maxima, the mean positions of which correspond to the temperatures $-120°$, $-60°$ and $+20°$ C. It should be noted that the maxima in curves I ($T = -120°\,C$) and II ($T = -50°\,C$) exhibit a nonsymmetrical form, indicating that these bands of local levels represent a superposition of several narrower
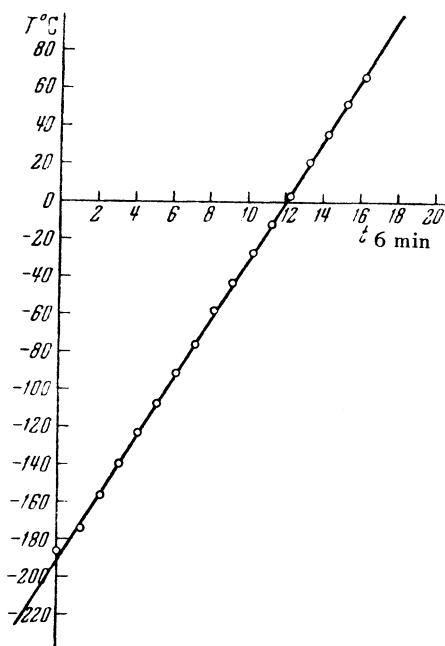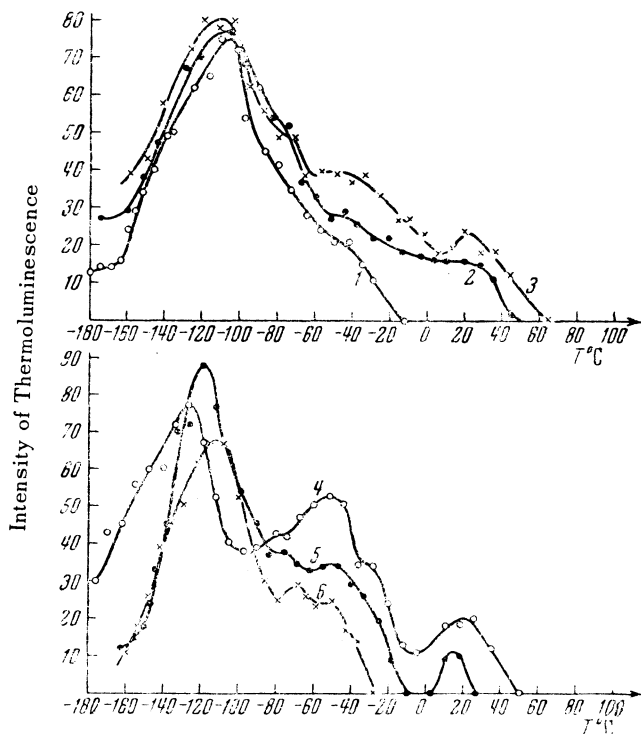
FIG. 2. Variation of the phosphor temperature in time.

FIG. 3. Thermoluminescence curves of samples of ZnS-Cu phosphor with copper concentration in gm/gm: *1.* 3×10^{-6}; *2.* 3×10^{-5}; *3.* 10^{-4}; *4.* 3×10^{-4}; *5.* 6×10^{-4}; *6.* 10^{-3}.

bands. In further experiments, it was found that concentrations of oxygen as well as iron, nickel and cobalt produce different effects in the various regions of the II maximum. This enabled us to divide the region of maximum II into three sections bounded by the temperatures from −90° to −60°, from −60° to −40° and from −40° to 0° C.

Figure 3 shows that the introduction of copper and the increase of its concentration changes the intensity of maxima II (T = −60° C) and III (T = +20° C) and has almost no influence on the intensity of the maximum I (T = −120° C).

Figure 4 shows the change in the intensity of maxima II and III in relation to the intensity of maximum I as a function of copper concentration.
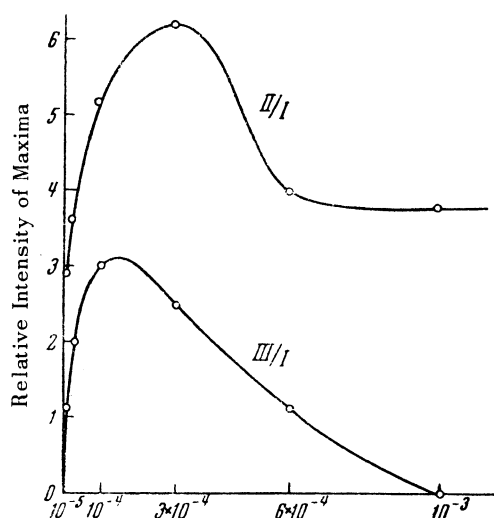

FIG. 4. Concentration of Cu in gm/gm.

The appearance of maximum III with the increase of copper concentration, the fact that this maximum reaches a peak at the concentration of about 1.5 × 10⁻⁴ gm/gm and then completely disappears at the concentration of 10^{-3} gm/gm , leads to the conclusion that the presence of copper is necessary for the formation of maximum III. This confirms the similar qualitative conclusions made by previous investigators [1,2]. It is possible that, besides copper, oxygen also has an influence on the formation of maximum III, as recent experiments of Hoogenstraten[4] have shown. However, it is not clear from these experiments whether the presence of oxygen is a necessary condition for the formation of band III or only intensifies this band. Further experiments are necessary to clarify this point.

The change in the maximum III with the increased concentration of copper is qualitatively and quantitatively analogous to the corresponding change in intensity of the green emission band (λ_{max} = 530 $m\mu$) and the complementary absorption of the copper centers[2,5]. As shown in reference 5, the introduction of copper into zinc sulphide leads to the complementary absorption in the region 350-450 $m\mu$ which increases with the increased concentration of copper. This is accompanied by a simultaneous increase in intensity of the green emission band. At copper concentration of $\sim 10^{-4}$ gm/gm, the growth of the complementary absorption stops and its abrupt decrease begins. Simultaneously, the green band decreases in intensity and at concentrations of $\sim 10^{-3}$ completely disappears.

The above analogy indicates that the III band of electron localization levels is directly connected with the copper luminescent centers and that its disappearance at concentrations $\sim 10^{-3} gm/gm$ as well as the disappearance of the green emission band and of the complementary absorption of copper, is explained by the transition of a portion of the copper into a nonluminescent state. It follows from this that if copper ceases to be the source of luminescent centers, it does no longer provide any centers of electron localization.

It is seen from Figs. 3 and 4 that not only maximum III but also maximum II increases with the increase of copper concentration. Beginning with the concentration of 3 × 10⁻⁴ gm/gm, the intensity of II maximum as well as that of the III maximum decreases but only up to a certain definite value. Further increase in the copper concentration has practically no effect on the intensity of the II maximum. Considerable change in intensity of the II maximum with change in copper concentration indicates that the II maximum is connected with the penetration of copper into the ZnS lattice. The general increase in intensity of the II maximum takes place mainly at the expense of the intensity growth in the temperature regions of −60° to −40° and from −40° to 0° C. It follows, therefore, that these very sections of the II maximum are connected with the presence of copper in the ZnS lattice. The intensity in the −90° to −60° region of temperature changes only slightly with the increase of copper concentration.

The difference in the shapes of the two curves

[5] M. N. Alentsev and A. A. Cherepnev, J. Exper. Theoret. Phys. USSR **26**, 473 (1954).

of Fig. 4 indicates that besides copper, some other components of the nonactivated ZnS influence the formation of the II maximum. In order to study the nature of this maximum more fully, we have prepared three samples of the ZnS phosphor without addition of the copper activator but with different degrees of admission of air during the heat treatment. The curves of the temperature controlled luminescence for these samples are shown in Fig. 5. Increase of air admission corresponds to an increase in the labeling number on the curves of Fig. 5.
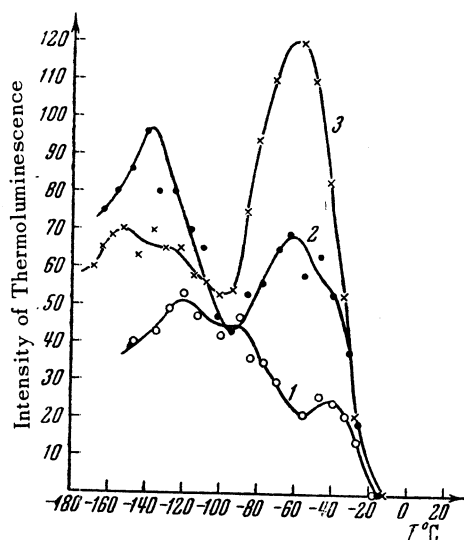

FIG. 5.

In all cases, the curves exhibited only maxima I and II. The absence of maximum III confirms the conclusion reached above concerning the connection of this maximum with the presence of copper in the ZnS lattice. These samples had only traces of copper. At room temperature, these samples exhibited a blue phosphorescence of very low persistence. It is characteristic that the high temperature portion (from –40° C to 0° C) of the II maximum is completely absent in the curves under consideration. This indicates that the origin of the latter is also connected with the presence of copper in the ZnS lattice.

As seen from Fig. 5, the intensity of the maximum II changes considerably depending on the conditions of heat treatment. High rate of air admission during the heat treatment (curve 3) increases the intensity of maximum II almost fivefold compared with the intensity corresponding to the heat treatment at the low rate of air admission (curve 1). Increased intensity of the II maximum is at the expense of growth of intensity in the

temperature regions from –90° to –60° and from –60° to –40° C due to the increase of the amount of oxygen in the ZnS lattice. The conclusion concerning the possibility of the influence of oxygen on the formation of levels of electron localization is in agreement with references 3 and 4.

It was shown above that the origin of the central portion of the II maximum (from –60 to –40° C) is connected with the presence of copper. Its existence in the curve 1, Fig. 5, is apparently due to traces of copper in the ZnS lattice. Its considerable growth in intensity with the increase of oxygen in the ZnS lattice indicates that the origin of this portion of the II maximum is apparently due to the combination of oxygen and copper. Considerable growth in intensity of the low temperature portion of the II maximum (from –90° to –60° C) with the increase of the oxygen content and the fact that an increase of copper concentration has almost no effect on the intensity (see Fig. 3), lead to the conclusion that the origin of this portion of the II maximum is due to the presence of oxygen in the ZnS lattice.

We now turn to the discussion of the origin of the I maximum. From Figs. 3 and 5, it can be seen that neither oxygen nor copper cause the formation of the I maximum. The conclusion that the nature of maximum I is entirely different from that of maxima II and III is very clearly confirmed from the study of influence of the melting processes on the formation of the levels of electron localization[6]. On the other hand, it is clear that the excess zinc which is the second activator in all activated zinc sulphide phosphors, can produce levels of electron localization. The presence of excess zinc in ZnS phosphors and its role as an activator was established by experiments of Bundel and Rusanova[7] and others. Inasmuch as neither the II nor III maximum is connected with the presence of zinc, it is natural to suppose, by the process of exclusion, that the only remaining maximum(I) is connected with the excess zinc.

Confirmation of this assumption follows from the comparison of the spectra of instantaneous illumination of ZnS-Cu phosphor samples with the curves of the temperature controlled luminescence. Fig. 6 contains curves for two samples; the first was prepared without alloying; the second with the introduction of 25% NaCl. Figure 7 shows the luminescence spectra of these samples. These figures show that almost complete destruction of

[6] N. V. Zhukova, Dokl. Akad. Nauk SSSR 85, 981 (1952)

[7] A. A. Bundel and A. I. Rusanova, Izv. Akad. Nauk SSSR, Ser. Fiz. 13, 173 (1949).
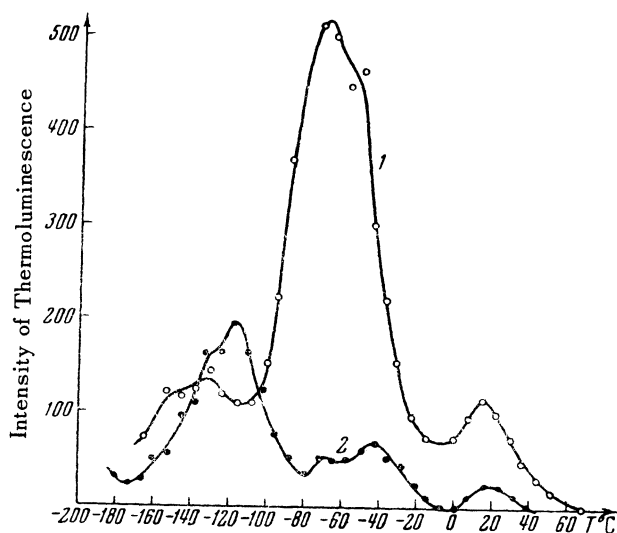
FIG. 6. Thermoluminescence curves of phosphor samples
ZnS-Cu 3×10^{-4} gm/gm. Curve 1--without the melt; Curve 2--
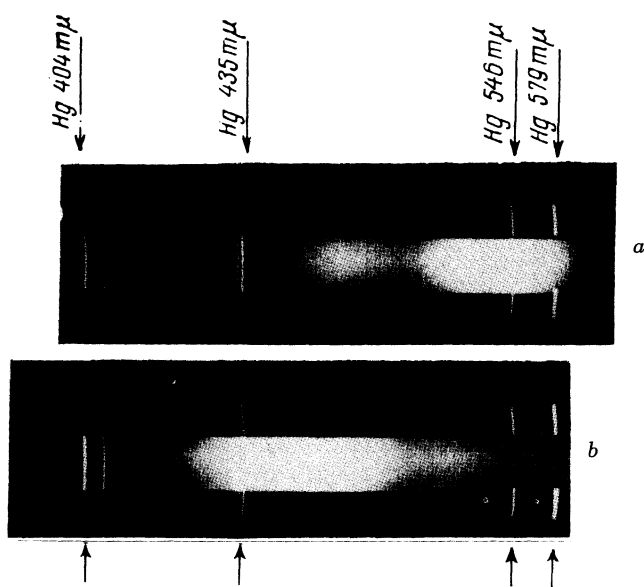with 25% NaCl.

FIG. 7. Luminescent spectra of samples ZnS-Cu 3×10^{-4} gm/gm.
a. Without melt; b. With 25% NaCl.

maxima II and III carries with it the destruction of
the green band with $\lambda_{max} = 530$ $m\mu$. This is under-
stood since the green band is associated with
copper, and the maxima II and III, as shown
above, are connected with the presence of copper
in the ZnS lattice.

As a result of the sharp decrease in intensity
of the green band, there appeared a bright light
blue band with $\lambda_{max} = 460$ $m\mu$. The work of
Alentsev and Cherepneva[5] has definitely es-
tablished that this luminescent band belongs only
to the excess of zinc. The accompanying pre-
servation and even increase in the area of the
first maximum (Curve 2, Fig. 6) indicates that the

first band of levels of electron localization as well as the blue luminescent band with λ_{max} = 460 $m\mu$, in all probability, belongs to the same centers, i.e., excess zinc.

4. THE INFLUENCE OF IRON, NICKEL AND COBALT ON THE THERMOLUMINESCENCE OF ZnS-Cu PHOSPHOR

In the course of preparation of ZnS-Cu phosphor samples, we have encountered the strong influence of iron, nickel and cobalt on the thermoluminescence of the samples being investigated, which presented a considerable difficulty. Although the quenching action of these elements on the luminescence of zinc sulphide phosphors has long been known, their quenching of thermoluminescence has been very little investigated. Neither has the question been cleared up whether the quenching action of iron, nickel and cobalt is

explained by the decrease (up to complete destruction) of the possibility of electron localization or by the increase in the number of radiationless transitions associated with the freeing of levels.

In this connection, it was of interest to investigate how the quenching of the different maxima of thermoluminescence take place. For this purpose, we have prepared three series of ZnS-Cu phosphor samples with different concentrations of Fe, Ni and Co. The curves of thermoluminescence of these samples are shown in Figs. 8, 9 and 10. They show a considerable reduction in the maxima of the curves of thermoluminescence with the increase in the concentration of iron, nickel and cobalt. It is seen from Fig. 10 that, in addition to the usual quenching action, cobalt at concentrations of 10^{-6} gm/gm forms new local levels which are deeper than all previously existing
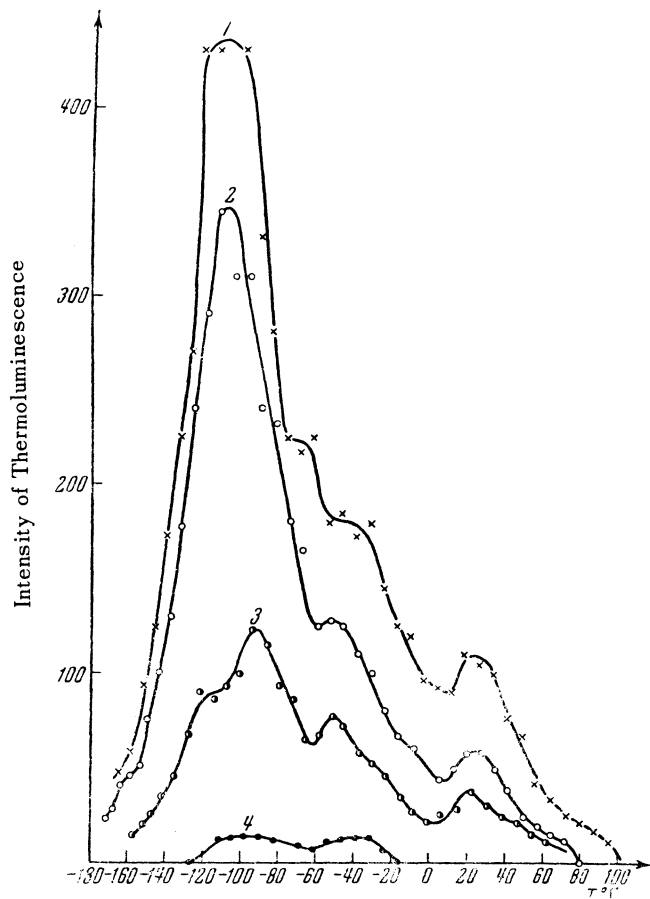

FIG. 8. Thermoluminescence curves of samples of ZnS-Cu phosphor with different concentration of iron in gm/gm. *1.* without Fe; *2.* 10^{-5}; *3.* 6×10^{-5}; *4.* 10^{-4}.
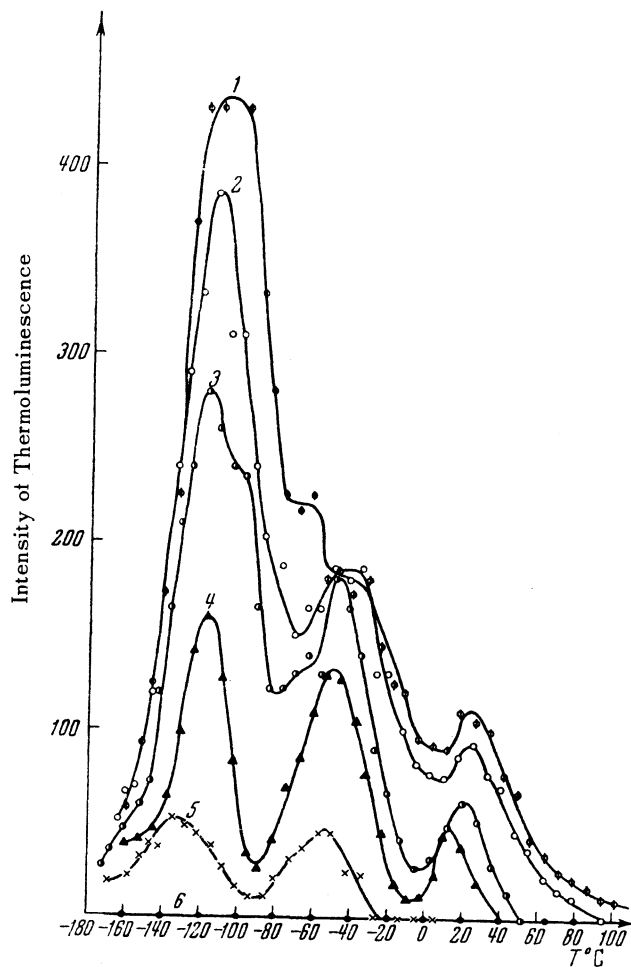
FIG. 9. Thermoluminescence curves of samples ZnS-Cu with different concentrations of nickel in gm/gm. *1.* without nickel; *2.* 10^{-7}; *3.* 10^{-6}; *4.* 3×10^{-6}; *5.* 6×10^{-6}; *6.* 10^{-5}.

levels. As the concentration of cobalt is increased to 10^{-5} gm/gm, I, II and III maxima are completely extinguished and there remains only a newly formed maximum at $T = 80°$ C. The ability of cobalt to form a new band of localization levels was noted in references 4 and 8.

Into all samples prepared for the investigation of the action of iron, nickel and cobalt, 10% molten NaCl was introduced at a copper concentration of 6×10^{-5} gm/gm. This caused a sharp increase of the I maximum and therefore maximum II is not as pronounced. Nevertheless, the nonsymmetrical form of the latter is clearly visible as before. Increased concentration of iron, nickel and cobalt

influenced unequally the regions of the II maximum contained in the temperature regions from $-90°$ to $-60°$ on one side and from $-60°$ to $-40°$ and from $-40°$ to $0°$ C on the other.

In Fig. 11 there is shown the change in intensity of the separate maxima in the curves of thermoluminescence as a function of concentration of the quenching agents. The changes in the maximum II are shown by the curves corresponding to the low temperature ($-90°$ to $-60°$ C) and the high temperature ($-60°$ to $0°$ C) regions of the maximum II.

The following table contains data showing the factors of intensity decrease of each maximum in the thermoluminescence of the phosphor ZnS, Cu 6×10^{-5} gm/gm, 10% NaCl by the introduction of one of the investigated quenching agents in

[8] E. S. Krylova, Dokl. Akad. Nauk SSSR **64**, 495 (1949).

TABLE

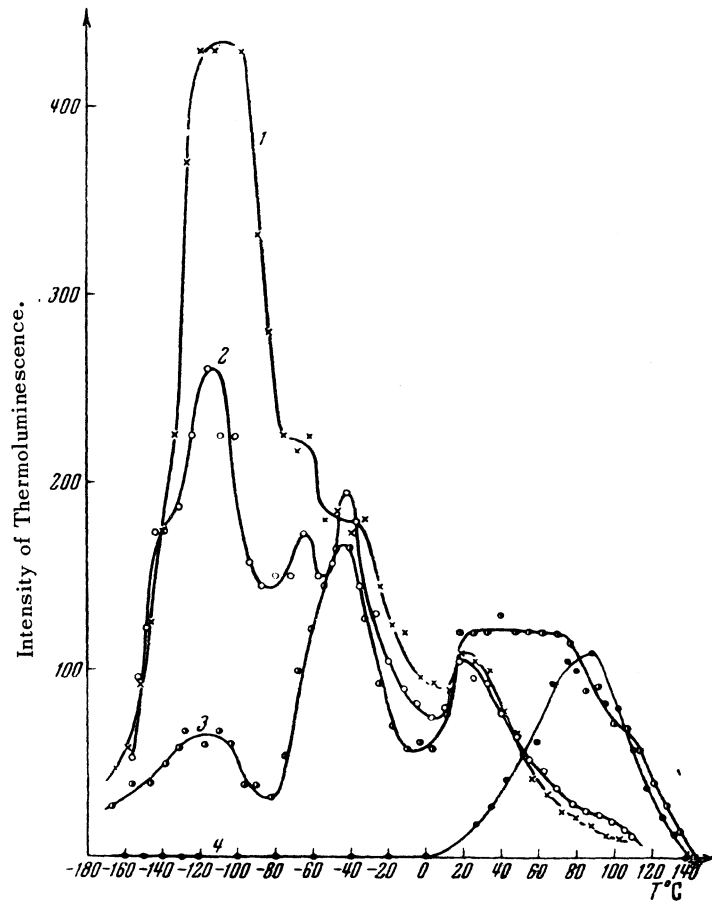| Quenching agent	I −120	II		III + 20
		Low temperature portion	High temperature portion	
Fe	1.16	1.12	1.20	1.37
Ni	8.6	11.2	4.5	Complete
Co	43	15	2.6	1.7

FIG. 10. Thermoluminescence curves of samples ZnS-Cu phosphor with different concentrations of cobalt in gm/gm. *1.* Without Co; *2.* 10^{-7}; *3.* 10^{-6}; *4.* 10^{-5}.

the quantity of 6×10^{-6} gm/gm. (In the case of cobalt, the intensity of the III maximum was taken as equal to the intensity at $T = +20°$ C.)

The comparison of the quenching of the same maximum by different elements shows that for the I maximum, as well as for the low temperature portion of the II maximum, the strongest quenching agent is cobalt, the weakest is iron. For the high temperature portion of the II maximum and basic maximum III, the strongest quenching agent is nickel, the weakest is iron. If we compare the quenching of different maxima by one and the same
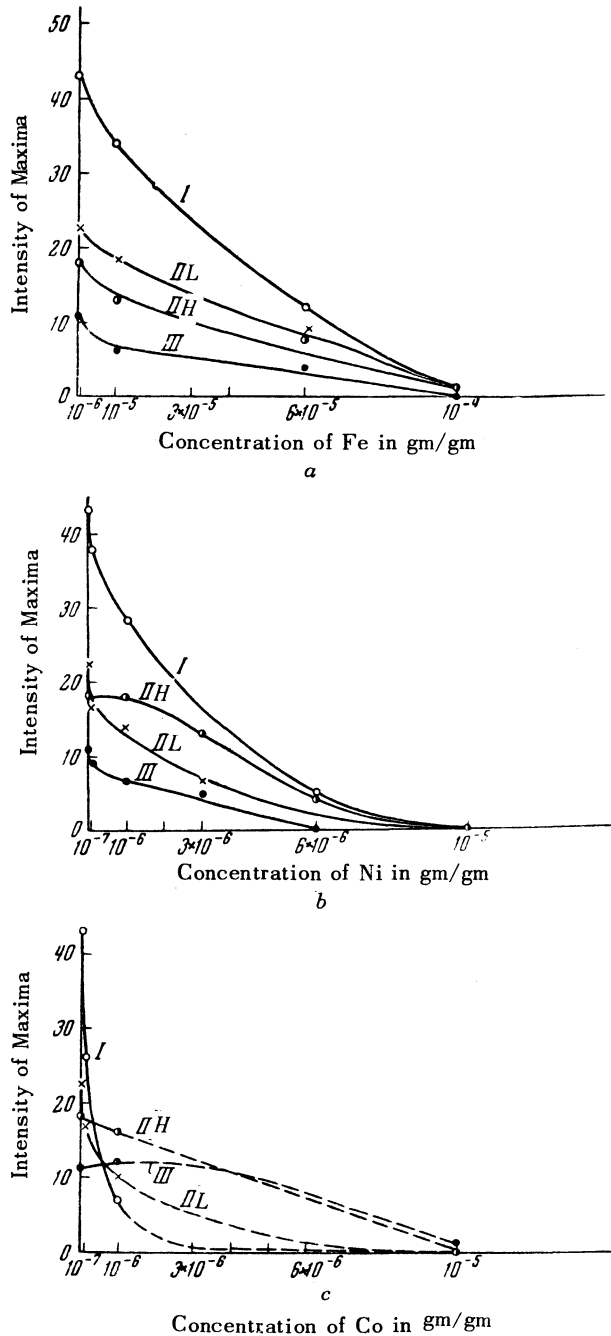
FIG. 11. Variation of intensity of the separate maxima in the thermoluminescence curves with the change of concentration of the quenching agents. O -I maximum; ×- II maximum (low temperature portion); ● - III maximum.

quenching agent, it appears that iron (in concentrations of up to 10^{-5} gm/gm) lowers the intensity of III and of the high temperature portion of II maxima to a greater degree than it lowers the intensity of the I maximum and of the low temperature portion of the II maximum. In the cases of cobalt and nickel, I and the low temperature portion of II maximum are quenched to a greater extent than III and the high temperature portion of II maximum.

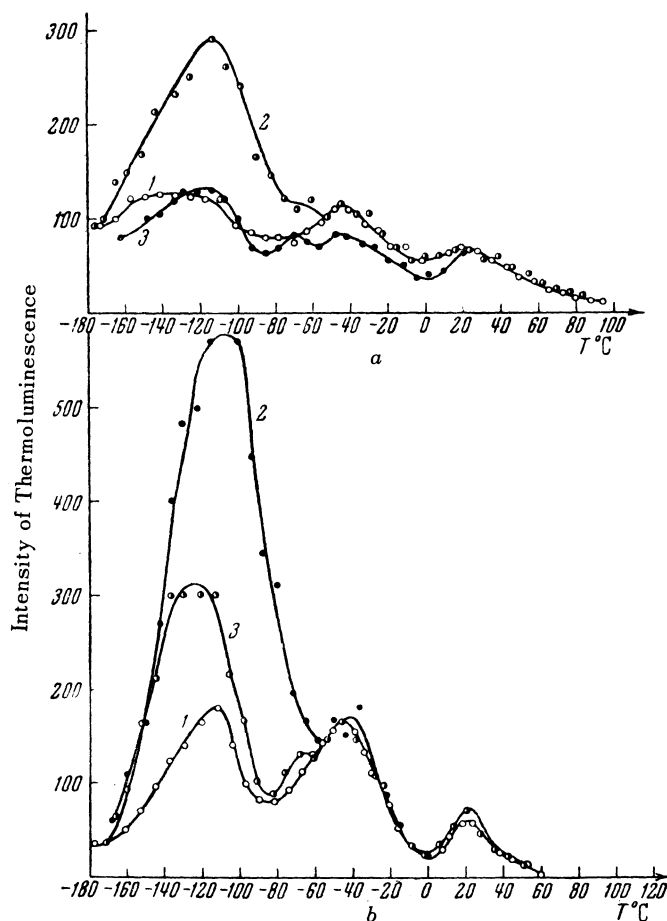We have discovered an intersesting phenomenon

FIG. 12. Thermoluminescence curves of samples ZnS-Cu phosphor with 10% NaCl, with iron and nickel. a. Cu 10^{-5} gm/gm, 1-without Fe and Ni, 2-10^{-6} Fe, 3-10^{-7} Ni. b. Cu 3×10^{-4} gm/gm, 1-without Fe and Ni, 2-10^{-6} Fe, 3-10^{-7} Ni.

in 4 samples of ZnS-Cu phosphor when small quantities (10^{-7}, 10^{-6} gm/gm) of quenching elements were introduced (Fig. 12). Introduction of 10^{-6} gm/gm of Fe into a sample of phosphor ZnS, Cu 3×10^{-4} gm/gm caused a sharp increase (approximately threefold) in intensity of maximum I ($T = -120°$ C) and had no effect on the intensity of maxima II and III. By the introduction into a sample of the same composition of 10^{-7} gm/gm Ni instead of Fe, the intensity of maximum I increased 1.7 times. The effect was repeated, but was less pronounced, when the same quantities of Fe and Ni were introduced into two other samples of ZnS-Cu phosphors of concentration 10^{-5} gm/gm.

The spectra of these samples have not displayed the bands characteristic of Fe and Ni luminescence. This led us to believe that Fe and Ni are capable of influencing, i.e., increasing, the possibility of localizing electrons. It is therefore considered possible that the quenching of the zinc sulphide phosphors by these elements after illumination is to be explained by the destruction of the phosphor's ability to localize electrons at the levels. The latter conclusion agrees with the data in the work of references 9 and 10, where it is shown that zinc sulphide phosphors containing nickel do not exhibit the existence of localized electrons when in a state of excitation. Note

[9] G. Garlick and A. Gibson, Proc. Phys. Soc. (London) 60, 574 (1948).

[10] C. Bull and D. Mason, J. Opt. Soc. Amer. 10, 718 (1951).

that as shown in Fig. 12, in the case of thermo-luminescence of the ZnS phosphor, the transition of electrons from shallow to deep levels is insignificant. Indeed, the sharp increase in the I maximum, and the fact that II and III maxima remain unchanged, contradict the assumption that a large number of secondary localizations of electrons takes place in the process of thermo-luminescence.

A sharp increase in the number of electrons in small local levels of the phosphor should have caused the growth of maxima II and III, which is actually not observed as Fig. 12 shows.

The expressed statement concerning the unimportance of secondary localization in the thermo-luminescence of zinc phosphors is also confirmed by the following data. We have conducted an experiment to investigate the distribution of electrons in local levels of ZnS-Cu phosphor excited at different temperatures. For this purpose, samples were first excited at the temperature of liquid nitrogen and, in subsequent experiments, at higher temperatures (up to + 20° C), after which we have plotted the curves of thermoluminescence. The number of electrons stored on the levels of any one band at a definite temperature was determined by planimetric measurement of the area of the corresponding maximum, determined by the curve of electroluminescence. It was found that the number of electrons stored at deep levels is 20-25% higher at high excitation temperatures compared with the number at low excitation temperatures. This is explained by the impossibility of binding electrons to low levels at high excitation temperatures and their secondary localization at deep levels. It is clear from this that if in the process of excitation, when the number of electrons in the low local levels is continuously being restored, only a small fraction of them (20-25%) undergoes secondary localization to deeper levels, then in the process of thermo-luminescence, when the number of electrons in low local levels is not replenished by excitation, the number of secondary localizations will be considerably less than 25%. We are referring to reference 11, in which it is shown by use of ZnS-Cu, Pb phosphor as an example, that there exists a great number of optically freed secondary electron localizations, while secondary localizations are practically absent in the process of thermo-luminescence.

It can be stated, on the basis of what has been

presented and as mentioned in the introduction, that, with certain approximation, the heights of the maxima of the thermoluminescent curves for our phosphors, under conditions of our experiments, are proportional to the number of electron filled levels.

5. CONCLUSION

I. The study of the origin of each maximum of the thermoluminescence curve for ZnS-Cu phosphor permits the following deductions:

(1) Maximum I ($T = -120°$ C) is apparently conditioned by the presence of excess zinc in the ZnS lattice.

(2) The maximum II ($T = -60°$ C) consists of three parts bound by temperatures $-90°$ to $-60°$, $-60°$ to $-40°$ and $-40°$ to $0°$ C. The origin of these parts is connected with the presence in the lattice of oxygen, combination of oxygen and copper, and copper, respectively.

(3) Maximum III ($T = +20°$ C) is formed by the luminescent centers of copper.

The existence of the Cu and Zn activators is therefore the main cause of giving rise to levels of electron localization. In addition, oxygen plays an important role in their formation.

II. The study of the quenching action of iron, nickel and cobalt on the thermoluminescence of ZnS-Cu phosphor shows that cobalt exhibits a stronger quenching action on low temperature maxima than on the high temperature maxima. It was established that as a consequence of this regular behavior, cobalt in concentrations of 10^{-6} gm/gm forms a new high temperature maximum ($T = +80°$ C). The differences in the quenching of different maxima by nickel are less pronounced. Iron, unlike cobalt, quenches high temperature maxima more effectively than the low temperature maxima. It was established that as a consequence of this regular behavior, nickel, expecially in small concentrations of $10^{-7}-10^{-6}$ gm/gm , produces a sharp increase in the intensity of the low temperature maximum ($T = -120°$ C) while the intensities of the II and III maxima remain unchanged. The latter effect indicates that there were few secondary electron localizations under the conditions of our experiments.

[11] G. F. Garlick and D. E. Mason, J. Electrochem. Soc. 96, 90 (1949).