# The Decay Laws of the Afterglow of Zinc Sulfide Phosphors in the Temperature Extinction Region

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Results are presented of an investigation of the effect of temperature and intensity as well as the length of excitation on the decay law of the afterglow of some zinc sulfide phosphors near and in the extinction region.

## 1. PRESENTATION OF THE PROBLEM

THE laws of the afterglow of zinc-sulfide phosphors in the low temperature region, where the length of the afterglow is considerable, have been studied sufficiently fully. In spite of this, there is no uniform point of view on the fundamental decay law of the afterglow. Three laws: the exponential[1], the square law[2] and Adirovich's law[3] figure in the literature as fundamental decay laws. This state of the question is explained by the absence of experimental data which confirms beyond dispute the use of any one of these laws.

The ability to explain the behavior with temperature may be taken as a criterion of the correctness of a theory. Investigations of the laws of the afterglow in the temperature extinction region can serve as a test of the theory. It is worth noting that these investigations have value not only as control experiments, but have an independent interest, inasmuch as the decay laws in the extinction region have been comparatively little studied.

The present work contains a description of some investigations carried out by us on the afterglow of some zinc sulfide phosphors in the extinction region.

## 2. LAWS OF THE AFTERGLOW OF ZnS-Cu PHOSPHORS

Two ZnS-Cu phosphors with a copper concentration of $10^{-4}$ gm/gm were studied. In the process of preparation, one was heated to 900 °C, the other to 1100 °C. For both samples, qualitatively identical laws were obtained. The curves given below are for only one sample, namely the one heated to 1100 °C.

The sample was studied in the form of a thin (3 mg/cm$^2$) layer of powder. The phosphor was heated and cooled in vacuum. It was excited with light from a mercury lamp (the 365 mμ triplet). Decay curves were taken visually with the aid of a Pulfrich photometer. Measurements in all cases were begun within 0.7 second after turning off the exciting light.

Temperature extinction of the green zone of the ZnS-Cu phosphor began at 444 °K. The afterglow, however, was studied in the interval 398-506 °K, i.e., near and in the extinction region. The investigations were carried out with both continuous (strong and weak) and instantaneous excitation. Sample and arrangement remained unchanged throughout the measurements. For all conditions of excitation, the temperature behavior of the total light was determined.

Three series of measurements were made in all. The first series was from strong excitation to equilibrium (excitation time 30 sec). The second series was from weak excitation to equilibrium ( excitation time 1 min ), with the intensity of the exciting light 10 times less than in the first series. The third series was with instantaneous excitation. The intensity of the exciting light was the same as in the first series, but the time of excitation was 0.01 sec.

The decay curves corresponding with strong continuous excitation are presented in log-log and semi-log coordinates in Fig. 1, *a* and *b*. It can be seen that near extinction (397-431 °K) they approximate to a 1.72 power law, with the exponent independent of the temperature. In the extinction region, the exponent increases. At the temperatures 476 and 488 °K, the initial part of the curve approximates an exponential while the remainder of the curve is a power law. The exponentials in Fig. 1*b* are continued dotted. At temperatures 499 °K and higher the curves are exponentials from beginning to end.

[1] G. F. Garlik and A. F. Gibson, Nature **158**, 704 (1946); Proc. Phys. Soc.(London) **60**, 574 (1948); G. F. Garlik and M. H. Wilkins, Proc. Roy. Soc. (London) **184A**, 408 (1945); J. T. Randall, Proc. Roy. Soc. (London) **184**, 365,374 (1945); J. T. Randall and M. H.F.Wilkins, Proc. Roy. Soc. (London) **184**, 390(1945)

[2] V. V. Antonov-Romanovskii, Trudy Fiz. Inst. Akad. Nauk SSSR 1, 35 (1937): **2**, 157 (1942)

[3] E. I. Adirovich, *Some Questions on the Theory of the Luminescence of Crystals*, Gostekhizdat, (1951)

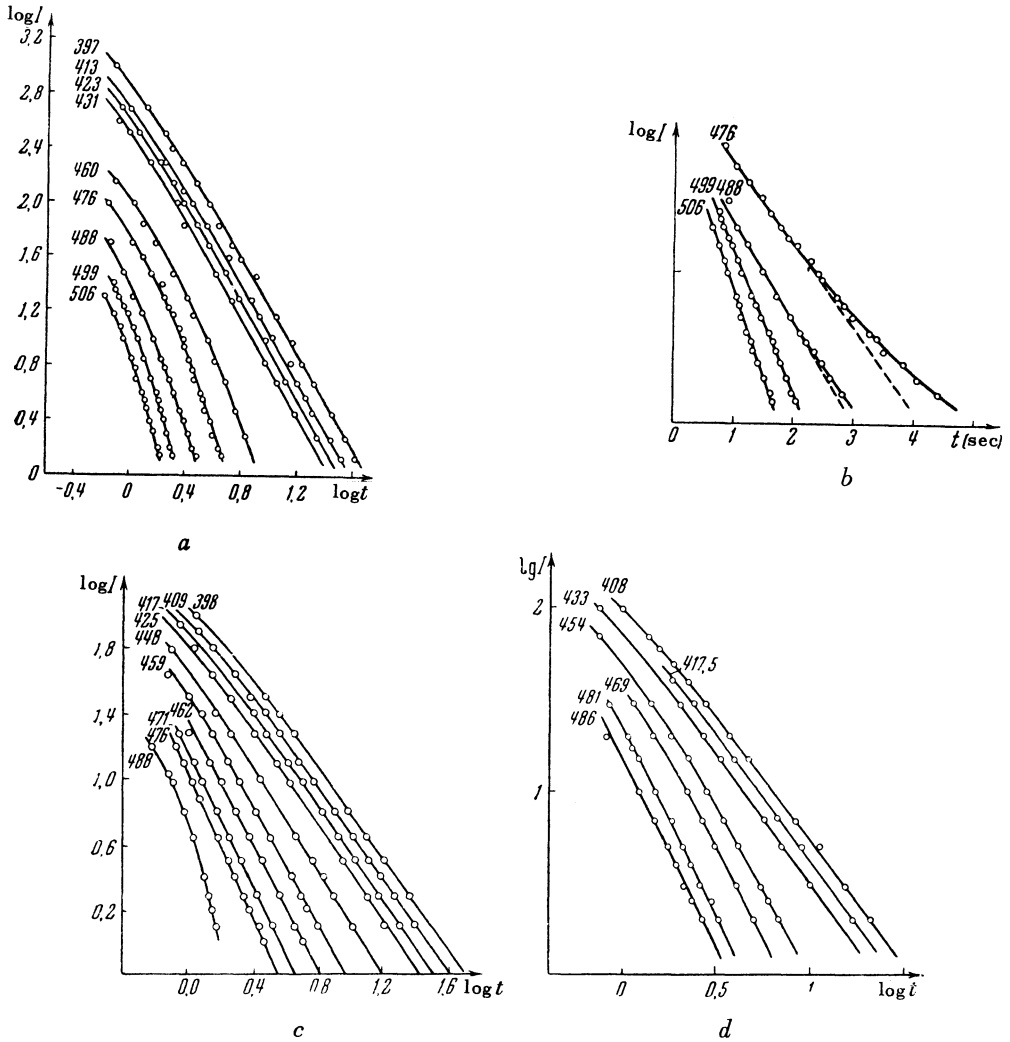


Fig. 1. Decay curves of the afterglow of a ZnS-Cu phosphor. *a* and *b* - Continuous strong excitation; *c*-continuous weak excitation; *d*-instantaneous exitation.

From the slopes of the exponentials the time constants $p$ were determined. They varied with temperature according to the law $p = p_0 e^{-\epsilon/KT}$

With weak continuous excitation, the decay curves, both in and near the extinction region were power law (Fig. 1*c*). Near the extinction (398-425 °K), the exponent $a$ did not change with temperature, and was equal to 1.44. In the extinction region (448-476 °), it increased with temperature. An analogous behavior of $a$ for ZnS-Cu phosphors was found in reference 4. The last curve ($T = 488$°K) in Fig. 1*c* was an exponential.

The results of the measurements for instantaneous excitation are given in Fig. 1*d*. Near extinction (408-433 °K) the decay curves follow a 1.37 power law. In the extinction region, beginning at 469 °K, they are square law. In the interval 433-469 °K, the exponent varies from 1.37 to 2.

Comparing Figs. 1 *a*, *b*, *c* and *d*, it is seen that under all conditions of excitation, the decay is power law near extinction, with only a change in the value of the exponent from one condition to another. In the further stages of temperature extinction, i.e., at the highest temperatures studied, the decay curves approximate exponentials for both strong and weak excitation. In the transition region the decay law is more complicated. By transition region we mean the temperature interval in which , with strong continuous excitation, the initial exponential decay goes over into a power law. This region corresponds to the initial stages of tempera-

4 V. A. Iastrebov, Trudy Fiz. Inst. Akad. Nauk SSSR 3, 123 (1946)

ture extinction. In a given region, the decay law depends upon the intensity of the excitation, and whether it is continuous or instantaneous. Thus, for example, in the temperature interval 469-481 °K with strong continuous excitation the decay curves are exponentials in the initial stages (Fig. 1b) and go over into power laws later on. With weak continuous excitation, they are power laws (Fig. 1c). With instantaneous excitation, they are square law (Fig. 1d).

Some quantitative characteristics were determined from the curves. Thus, from the temperature variation of the time constants of the exponentials (Fig. 1b), the energy $\epsilon_1$ was determined. From the displacements $\Delta$, parallel to the axis of log $t$, of the square law curves in the extinction region and the power law curves near extinction (Fig. 1d), using the method of Antonov-Romanovskii[5] the depth of the localized levels $\epsilon_1$ was determined from the formula:

$$\Delta = \frac{\epsilon_1}{4{,}6\,k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \qquad (1)$$

The values of the activation energy are given in Table 1. From the table it is obvious that the energies, determined from the displacements $\Delta$, have different values depending upon whether they are in or near the extinction region. In the extinction region greater values of the activation energy were obtained than near extinction. An analogous result was found in reference 5.

For all conditions of excitation, the total light radiation was determined planimetrically from the curves of intensity against time. We corrected the temperature variation of the total radiation to temperature extinction, although other authors do not do this[4]. In Fig. 2, to coordinates of log $L$ against $1/T$, is plotted the temperature dependence, corrected to extinction, of the total light for a series of curves, taken with continuous weak excitation. From the Figure it is obvious that this dependence is described by two intersecting straight lines, with the slope of the line in the extinction region greater than near extinction.

From the temperature variation of the total light near extinction the depth of the localized levels $\epsilon$[4] was determined from the formula:

$$L = L_0 e^{\epsilon/2kT} \qquad (2)$$

From the same formula, the activation energy in the extinction region was determined. The results are given in Table 1. Values of the activation energy obtained for other conditions of excitation are given in the same Table.

From the Table it is obvious that, independent of the condition of excitation, practically identical values are obtained for the activation energy from the temperature variation of the total light. We are the first to have noticed this result.

The values of the activation energy obtained for a ZnS-Cu phosphor heated to 900 °C are likewise given in Table 1.

In order to test whether or not the laws which we

TABLE 1

| Activation energy ev | | | Phosphors | | | |
|---|---|---|---|---|---|---|
| | | | ZnS-Cu | ZnS-Cu Heated to 1100 °C | ZnS-Cu Heated to 900 °C | ZnS-Cu,Co |
| From the temperature variation of the Time Constant of the Exponential | | | 0.23 | 0.67 | 0.17 | 1.57 |
| From the displacement $\Delta$ | Near Extinction | | | 0.62 | 0.22 | |
| | In the Extinction region | | | 1.38 | 0.63 | 2.12 |
| From the temperature variation of the total light radiation | near extinction | strong excitation | | 0.64 | | |
| | | weak excitation | | 0.63 | 0.2 | |
| | | instantaneous excitation | | 0.6 | | |
| | in the extinction region | strong excitation | | | | 2.38 |
| | | weak excitation | | 1.33 | 0.68 | |
| | | instantaneous excitation | | 1.35 | | 2.10 |

[5] V. V. Antonov-Romanovskii, Doklady Akad. Nauk SSSR 17, 95 (1937)

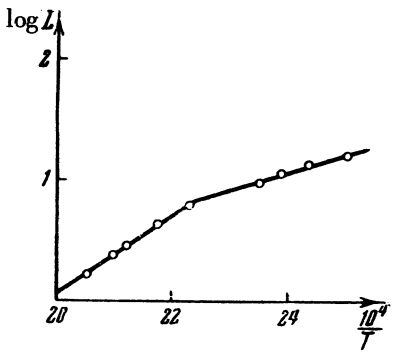


Fig. 2. Temperature variation of the light sum for a ZnS-Cu phosphor with continuous weak exitation.

observed for a ZnS-Cu phosphor are general for all zinc sulfide phosphors and likewise to study the decay law over a large interval of intensity, we investigated two more phosphors: ZnS-Cu,Co and ZnS-Zn.

### 3. THE DECAY LAWS OF THE PHOSPHOR ZnS-Cu,Co

A characteristic peculiarity of the temperature extinction curve of the green zone of this phosphor (Cu concentration $10^{-5}$ gm/gm, Co concentration $10^{-5}$ gm/gm) is that there are two temperature drop offs[6]. In the interval 170-270 °K, the first drop off is observed, then there is an increase in intensity, and beginning with 390 °K, the second drop off is observed. We studied the decay law only in the region of the second drop off. Three series of measurements were carried out. The first series: continuous strong excitation, excitation time 1 min. The second series: continuous weak excitation, excitation time 1 min , the intensity of the exciting light 20 times weaker than in the first series. Third series: instantaneous (0.2 sec) excitation, the intensity of the exciting light the same as in the first series.

The decay curves obtained with continuous strong excitation are given in log-log and semi-log coordinates in Fig. 3a,b, and c. From Fig. 3b it is obvious that at the beginning of extinction (444-470 °K) the decay curves are exponentials, going over in the further stages of decay to power laws, the transition being later, the higher the temperature. At temperatures 484-501 °K, the last points do not fit an exponential either (Fig. 3c). Beginning with 507 °K, the decay curves approximate exponentials from beginning to end of the measurement.

The results obtained for continuous weak excitation are given in Fig. 3d. It is obvious that at temperatures 473-494 °K, the decay law approximates a power law; at higher temeperatures (496-504 °K) it approximates an exponential.

Comparing Figs. 3b,c and d shows that in the case of a ZnS-Cu,Co phosphor, as well as in the case of a ZnS-Cu phosphor, the decay curves in the transition region essentially approximate exponentials with strong excitation, and approximate power laws with weak excitation.

For the temperature interval 481-508 °K, decay curves were taken for instantaneous (0.2 sec ) excitation, Fig. 3e. From the Figure it is obvious that they approximate square laws. The last curve ($T$=508 °) is an exponential.

Thus for ZnS-Cu,Co phosphor in the transition region, depending upon the intensity and the continuity of excitation, the decay curves approximate exponentials, power or square laws.

From the extinction curves of this phosphor, the activation energies were determined 1) from the temperature variation of the time constant (Fig. 3c), 2) from the displacements of the square law curves (Fig. 3e) and 3) from the temperature variation of the light sums. The results are given in Table 1.

### 4. THE DECAY LAWS OF THE BLUE ZONE OF A ZnS-Zn PHOSPHOR

Investigations of a ZnS-Zn phosphor were carried out with a blue filter. The phosphorescence was measured near 203-264 °K and in the extinction region (264-323 °K).

The decay curves, obtained with continuous strong excitation, are given in log-log and semi-log coordinates in Fig. 4, the low temperature curves in Fig. 4a, the high temperature curves in Fig. 4b. It is obvious from Fig. 4a that at low temperatures the decay curves approximate power laws, the exponent of which depends on $T$ (Fig. 5).

The curves corresponding to 283 °K are given in both log-log and semi-log coordinates (Figs. 4a and b). It is obvious that at this temperature the power law applies only to the latter part of the curve, while the initial part is described by an exponential.

Beginning at room temperature and higher, the decay curves are described by two intersecting exponentials. Obviously the decay laws of a ZnS-Zn phosphor are more complicated than for a ZnS-Cu phosphor, for which a single exponential was observed.

In Fig. 6 are given the exponentials obtained from analysis of complicated decay curves taken at

[6] F. I. Vergunas and Iu. M. Sainchenko, J. Exper. Theoret. Phys. USSR 14, 470 (1953)

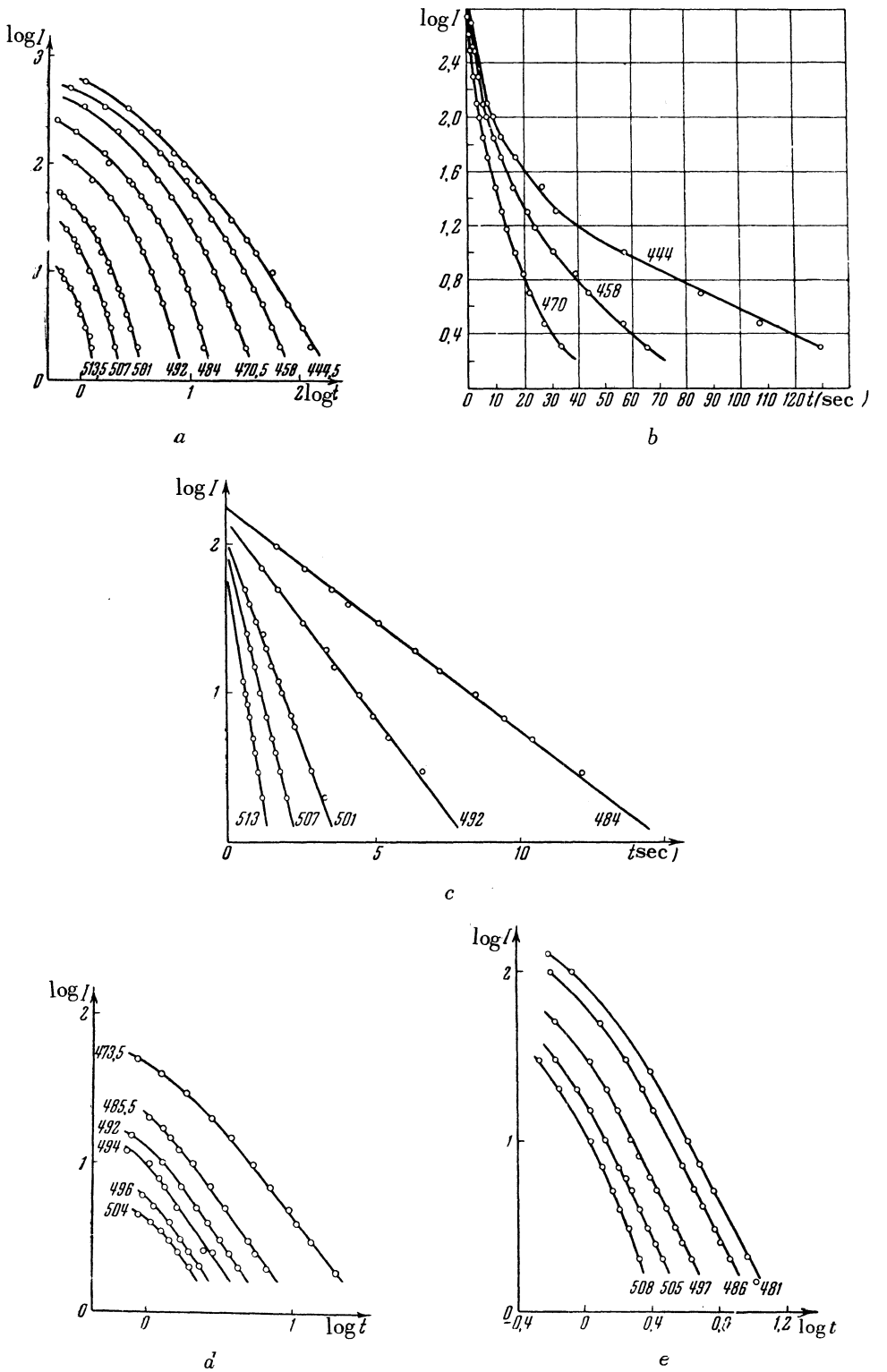


Fig. 3. Decay curves of the afterglow of a ZnS-Cu,Co phosphor. *a,b,c*,- continuous strong excitation; *d*- continuos weak excitation; *e*-instantaneous excitation.

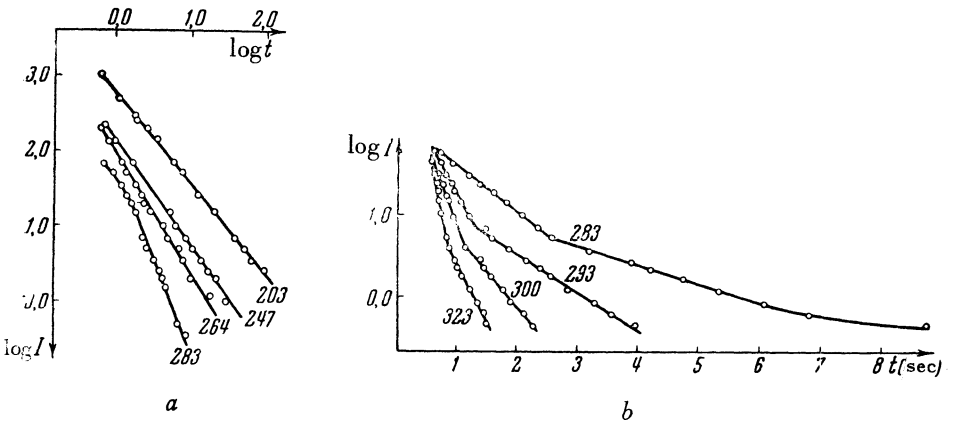


Fig. 4. Decay curves of a ZnS-Zn phosphor. *a*- at low temperatures, *b*- at high temperatures.

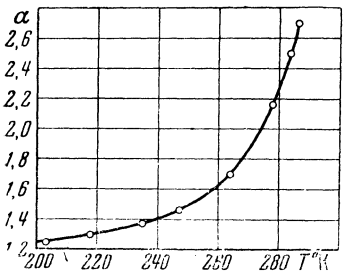


Fig 5. Dependence of the exponent $\alpha$ on temperature for a ZnS-Zn phosphor.

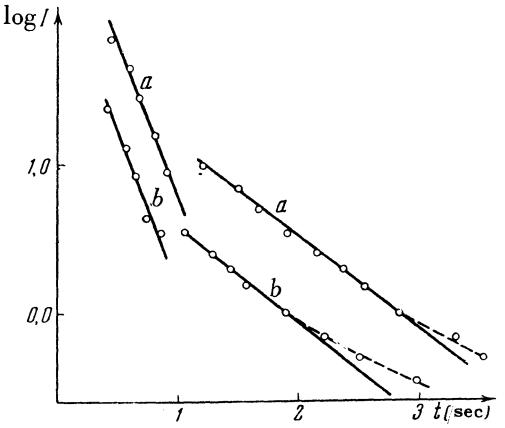


Fig. 6. Decay curves of a ZnS-Zn phosphor, obtained from the analysis of complex curves. $T = 292\,^{\circ}K$. *a*-intensity of the exciting light $E = 1$; *b*- $E = 0.14$.

292 °K with two different intensities $E$ of the exciting light. From the Figure it is clear that the slope of the straight lines does not change appreciably with a sevenfold diminution in $E$. However the last points fit a power law, shown dotted. The less the intensity of the exciting light, the earlier the transition from exponential to power law. The exponentials in the figure are continued as solid lines.

The effect of the intensity of the exciting light on the decay law in the transition region was investigated at one temperature, 283 °K. In Fig. 7, curves are given in log-log and semi-log coordinates, taken at different intensitis $E$. From the Figure it is clear that for $E = 1$ the luminescence goes exponentially at the start, then the curve goes over into a power law. For $E = 0.14$ and 0.02 the exponential part is missing; the decay goes as a power law, its slope decreasing with decreasing $E$. Accordingly, in the transition region, with decreasing intensity of the exciting light, the exponential decay law goes over into a power law. Thus in the blue zone of the ZnS-Zn phosphor the same laws were found as for the ZnS-Cu and ZnS-Cu,Co phosphors.

From the slopes of the exponentials corresponding with long afterglow times (Fig. 4b) the time constants were determined, and from their variation with temperature the activation energy $\epsilon_1$ was determined.

## 5. CONCLUSIONS

The character of the afetrglow of all the phosphors investigated was the same; the decay law changed with temperature, and with the intensity of the exciting light. The effect of temperature was as follows: near extinction the decay curves

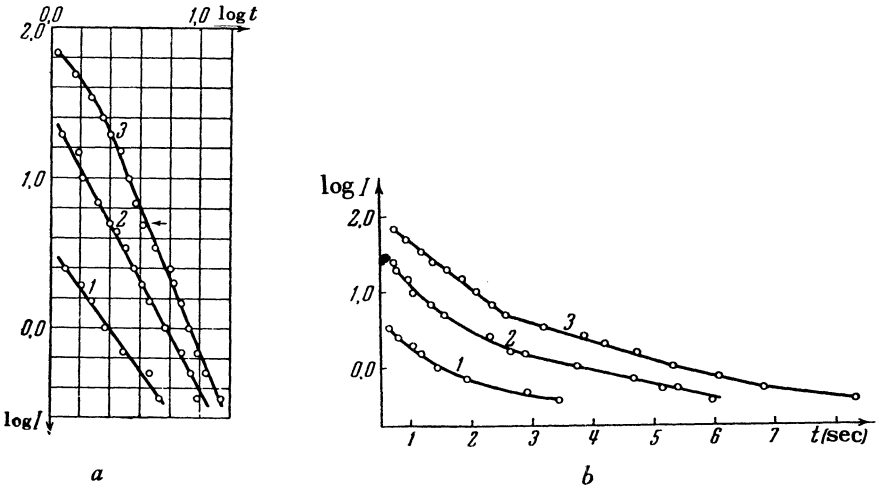


Fig. 7. Decay curves of a ZnS-Zn phosphor taken for different values of intensity of the exciting light $E$. $a$-log-log plot; $b$- semi-log plot. $1$- $E = 0.02$, $\alpha = 1.36$; $2$- $E = 0.14$ $\alpha = 1.83$; $3$- $E = 1$, $\alpha = 2.5$.

were approximate power laws, the exponent of which did not depend appreciably on the temperature. In the extinction region the exponent increased with temperature, then the initial part of the curve went over into an exponential, while the last part remained as before an approximate power law. The higher the temperature, the later the transition from exponential to power law. At sufficiently high temperatures, the power law part disappeared, and the curves were approximately exponential from beginning to end.

The intensity and length of excitation showed the following effects: Near extinction the exponent of the power law decreased with decreasing intensity of the exciting light, but the form of the decay law did not change. Nor did the decay law change in the later stages of temperature extinction. Even at the highest temperatures the curves remained exponentials for strong and weak excitation. However in the transition region the decay law changed with change in intensity and length of excitation. For large intensities of the exciting light the exponential in the initial stages of the decay went over into a power law in the later stages, while for small intensities the exponential part disappeared, and the curves approximated power laws. For instantaneous excitation in the transition region square laws were obeserved.

In all the zinc sulfide phosphors a transition region exists in which, for the same sample, at the same temperature, one finds, depending upon the conditions of excitation, an exponential, a power law or a square law. From this condition it follows that neither the exponential nor the square law is the fundamental decay law for these phosphors.

The long argument between the adherents of the exponential vs. the square law as the fundamental law of decay, is explained, in our opinion, by the fact that comprehensive experiments on the laws of the afterglow had never been carried out on the same samples over a wide temperature interval, and with different conditions of excitation.

Conclusions on the afterglow laws were made on the basis of limited experiments.

The explanation of the laws obtained by us, as well as our opinion on the form of the fundamental decay law will be given in a following paper.

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Translated by C. V. Larrick
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