

THERMOLUMINESCENCE, STIMULATION AND QUENCHING BY
INFRARED OF THE LUMINESCENCE OF THE ZnS-Cu, Pb PHOS-
PHORS WITH VARYING Pb CONTENTS

BY W. HERCHOLD

Technical University, Poznań*

AND

A. WRZESIŃSKA

Technical University, Łódź**

(Received May 20, 1968)

Thermoluminescence and stimulation as well as quenching by infrared radiation ($\lambda = 700\text{nm}$) of the luminescence of phosphors ZnS-Cu, Pb are studied for varying Pb concentration and constant concentration of Cu.

The thermoluminescence curves of a series of ZnS-Cu, Pb phosphors samples indicate a decrease in the height of the low-temperature thermoluminescence peak with increasing Pb concentration.

Investigations of quenching and stimulation with a weak beam of infrared radiation ($\lambda = 700\text{ nm}$) indicate a systematically increasing stimulation and decreasing quenching with increasing Pb concentration.

These results can be interpreted (in accordance with the suggestion of Kalmann) in terms of the influence of infrared radiation on the release of holes from excited Cu-centres and the existence in the ZnS-Cu, Pb phosphors of centres with greater cross-section for radiative transitions than the cross-section for such transitions in Cu-centres which absorb the excitation energy.

The paper gives a concept of the structure of centres with large cross-section for radiative transitions in ZnS-Cu, Pb and ZnS-Cu. However the results of the study of stimulation by an intense IR beam (laser) with $\lambda = 700\text{ nm}$ could not be interpreted in terms of the previous model. They suggest in the case of the ZnS-Cu, Pb phosphors a participation of electrons which are held in local levels for a long time (several minutes) even at room temperatures.

* Address: Politechnika Poznańska, Poznań, pl. M. Curie-Skłodowskiej 5, Polska.

** Address: Politechnika Łódzka, Łódź, ul. Gdańska 155, Polska.

The phenomena occurring during the illumination with *IR* radiation of the phosphors ZnS-Cu and ZnS-Cu, Pb were the subject of studies of many authors [1, 2, 3, 4, 9]. Two stimulation and quenching bands are well known: a long wavelength band at about 1300 nm and a second one ranging from 600 to 800 nm with a maximum at about 700 nm.

In spite of numerous investigations there are considerable discrepancies between the particular results and in the opinion on the mechanism elucidating the experimental results.

In addition to the above-mentioned phosphors a number of others *IR*-sensitive is known, all characterized by a stimulation-flash under the influence of *IR* radiation with suitable wavelength when used during the luminescence of a previously excited phosphor. Such substances are some of the doubly-activated phosphors; the best known are SrS-Eu, Sm and SrS-Ce, Sm. In case of these phosphors the luminescence spectrum is characteristic for the first activator — the main activator (Eu or Ce) while the stimulating properties and the stimulation spectrum are characteristic for the second activator which sensitizes the phosphor to *IR* light (more generally to long -wavelength radiation).

All investigations indicate that in this type of *IR*-sensitive phosphors the second activator gives rise to the production of deep traps in the phosphor and the action of *IR* radiation consists in freeing electrons out of these traps. According to this picture the stimulation spectrum is characteristic for the sensitizing activator.

The luminescence of phosphors of this last type can be also quenched by *IR*-radiation, however, with wavelength other than that of the stimulating *IR*-radiation.

The simple mechanism of the influence of infrared radiation (*trap release*) given above cannot be applied, however, to phosphors like ZnS-Cu and ZnS-Cu, Pb because:

- a) in case of ZnS-Cu there is only one activator,
- b) addition of lead to the ZnS-Cu phosphor considerably improves the stimulating properties of the phosphor, however the *IR*-bands inducing stimulation in ZnS-Cu, Pb are identical with those giving this phenomenon in ZnS-Cu [4],
- c) the *IR*-bands (1300 nm and 600–800 nm) inducing largest stimulation of the above-mentioned phosphors are at the same time the bands of strongest quenching of luminescence of these phosphors.

According to Kallmann the action of *IR* on excited phosphors ZnS-Cu, and ZnS-Cu, Pb consists in the release of holes from excited Cu-centres, which are wither subject to non-radiative recombination with free electrons (*IR*-quenching) or are captured by other luminescence centres which have a greater cross-section for radiative recombination (Fig. 1).

In ZnS-Cu, Pb phosphors these centres would be produced when adding Pb. However, the nature of centres of large cross-section for radiative transitions in ZnS-Cu, Pb phosphors is still not quite clear. There is still less information about the centres with large cross-section for radiative transition in the ZnS-Cu phosphors (without Pb).

The present paper concerns the study of the spectrum of stationary luminescence, thermoluminescence, stimulation and quenching by *IR*-radiation from 600–800 nm band for a series of phosphors with constant concentration of copper amounting to $9.2 \cdot 10^{-6}$ g Cu/g

ZnS and varying (between $2.4 \cdot 10^{-5}$ and $2.3 \cdot 10^{-3}$ g/g) concentration of lead built — in the crystal lattice. In addition the ZnS—Pb phosphor has also been investigated.

The aim of the study of a whole series of phosphor samples with varying lead contents was to obtain some information on the sensitizing role of lead, and the influence of lead on the distribution of traps in the phosphor *etc.*

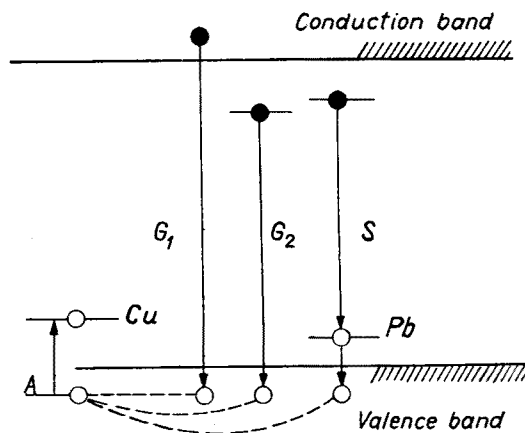


Fig. 1. Suggested transition scheme for action of infrared radiation on excited ZnS-Cu, Pb: transition *A* — Cu; release of a hole from excited Cu centre; non radiative electron — hole recombinations: G_1 = band-band (according to Kallmann); G_2 = trap-valence band (D. Curie); *S* = radiative recombination trap-stimulating acceptor level

I. Thermoluminescence curves

The first part of investigations of the series of phosphor samples, *i.e.*, the method of preparation, the study of the amount of Pb built in, ZnS the spectra of stationary luminescence (shift of the maximum of this spectrum towards shorter wavelength with increasing Pb-con-

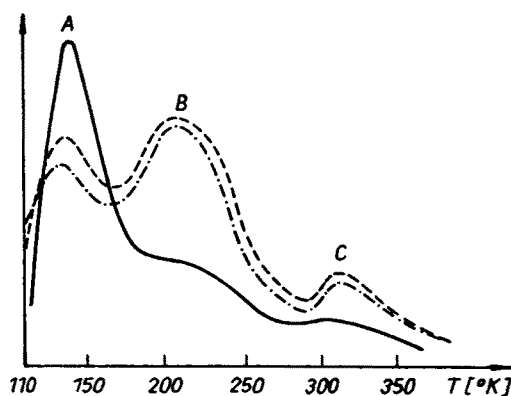


Fig. 2. Thermoluminescence curves for ZnS-Cu, Pb phosphor fired at $1100^\circ\text{C} + 2\%$ NaCl. — 0% Pb, --- 3% Pb, -.-.- 4% Pb

centration from 525 nm for ZnS-Cu to 500 nm for ZnS-Pb) and the thermoluminescence curves have already been published [5].

However, some of these results will be referred to in the present paper for the purpose of interpretation and comparison with the results of further studies. Fig. 2 shows the thermoluminescence curves of the ZnS-Cu, Pb phosphor (fired at 1100° C with the addition of NaCl) for several concentrations of lead.

Table I shows the lead contents built-in the crystal for concentration of lead added to ZnS-Cu ranging from 0 to 5%. The built-in lead concentrations were determined by means of the polarographic method.

TABLE I

Phosphor	ZnS-Cu, Pb		Cu — 9.2 10 ⁻⁴ %		
	1	2	3	4	5
Amount of Pb-added to ZnS in %					
Amount of Pb after annealing in %	2.4 × 10 ⁻³	2.1 × 10 ⁻²	4.6 × 10 ⁻²	7.6 × 10 ⁻²	3.3 × 10 ⁻¹

Three thermoluminescence peaks occur on all curves, however, as the concentration of lead increases, the height of the low-temperature peak becomes smaller whereas that of the peak occurring at higher temperature grows. According to our calculations the low-temperature peak occurring in these phosphors corresponds to traps of the depth of about 0.3 eV. The thermoluminescence curves in Fig. 2 indicate that the addition of Pb does not

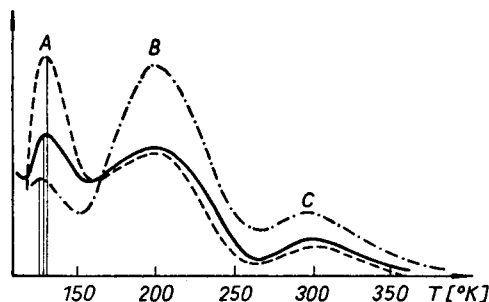


Fig. 3. Thermoluminescence curves of ZnS-Cu phosphor fired at 1100°C + 5% NaCl (from Ref. [6]). — — — 10⁻⁶, — — — 10⁻⁵, — — — 10⁻⁴ g(Cu)/g ZnS. Note: The thermoluminescence curves in Figs 2 and 3 have been obtained by continuous recording by means of modified apparatus from Ref. [11]

introduce new traps¹ but for increased Pb concentration the contribution to thermoluminescence of electrons from shallow traps decreases while there is an increased contribution of electrons freed from deeper traps.

¹ Strictly speaking no traps are introduced which would correspond to the thermoluminescence peaks lying in the temperature range below temperature quenching.

A certain small broadening of the curve toward higher temperatures may be the result of decreased temperature quenching, due to the contribution of centres with larger cross-section for radiative recombination in phosphors with greater concentration of lead.

A similar effect of lowering of the height of the low temperature thermoluminescence peak of ZnS-Cu phosphor with increasing concentration of copper has been observed and interpreted by Wrzesińska [6], p.81.

The thermoluminescence curves from Ref. [6] p. 81 for the ZnS-Cu phosphor fired at 1100° C are shown in Fig. 3. The observed thermoluminescence changes occurring when changing the concentration of Cu have been interpreted in favour of the hypothesis of Riehl and Ortmann [12] which suggest that the „green” copper centres are formed by Cu⁺-ions in interstitial positions in the vicinity of sulphur vacancies. As it is well known a „non-associated” sulphur vacancy forms traps of the depth of 0.28 eV which correspond to the peak *A* in Fig. 2 and 3.

Considerations of the results of the present paper cause the authors to assume that electrons from traps corresponding to sulphur vacancies may directly recombine on excited copper centres so that optical transitions of the type donor-acceptor associated may occur [13]. It is well known from the theory the optical transitions corresponding to such mechanism are characterized by large cross-section [7].

Another argument favouring association of excited copper centres with electrons in traps is the lack of paramagnetic resonance after excitation of ZnS—Cu [14].

Such resonance should be expected both from electrons in traps and localized holes, if they were not associated.

In our opinion only in some fraction of Cu-centres in ZnS—Cu phosphor occur transitions of the type donor-acceptor associated.

As concerns green luminescence in ZnS—Cu with the emission maximum at 525 nm which is characteristic for Cu, there were numerous investigations which have shown that it is rather of the recombination type; that the electrons from traps go through the conduction band before recombination with ionized centres. However, some investigations of Grillot [10] and Wrzesińska (unpublished) indicate the complex character of green luminescence in ZnS-Cu. It seems that it consists of two bands of different character. This is also proved by the results of phosphorescence decay for ZnS-Cu after exciting by *UV* radiation ($\lambda = 365$ nm). The decay curve obtained without using a filter before detector is shown in Fig. 4*a* and that obtained with a 500 nm interference filter is shown in Fig. 4*b*.

Using on analogous interpretations as in Ref. [6] to thermoluminescence changes of the ZnS—Cu, Pb phosphor with changing Pb-concentration, one may state that the lead green centre is formed by Pb ion in interstitial position associated with structure defect to which shallow levels correspond (peak *A* in Fig. 2). These would be also donor-acceptor associated centres.

Studying the luminescence growth of ZnS—Pb, when excited in the absorption band of Pb ($\lambda = 436$ nm) and the dependence of photoconduction on temperature, Shionoya *et al.* [9] have come to the conclusion that Pb “green centres” (emission maximum at 500 nm) are localized. According to Ref. [9] the excited level of the Pb centres is 0.36 eV above the bottom of the conduction band. The depth of the levels corresponding to the

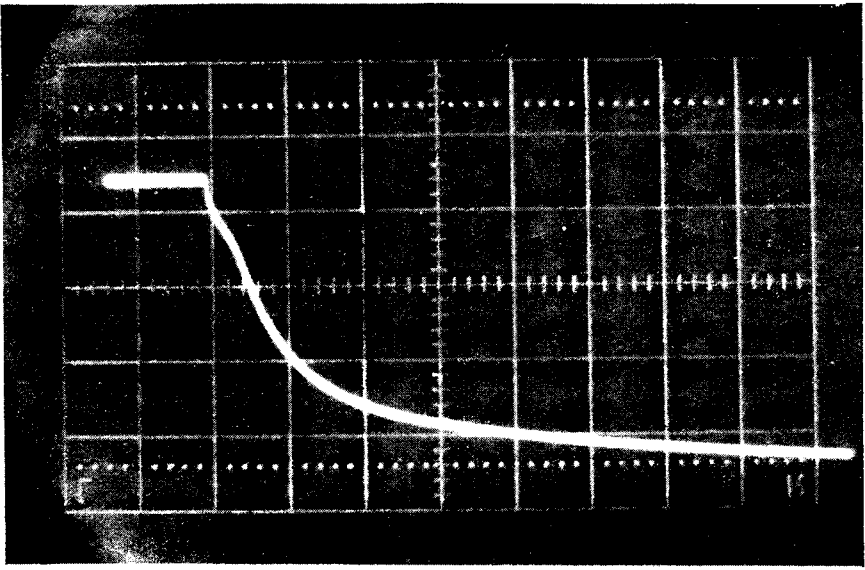


Fig. 4a

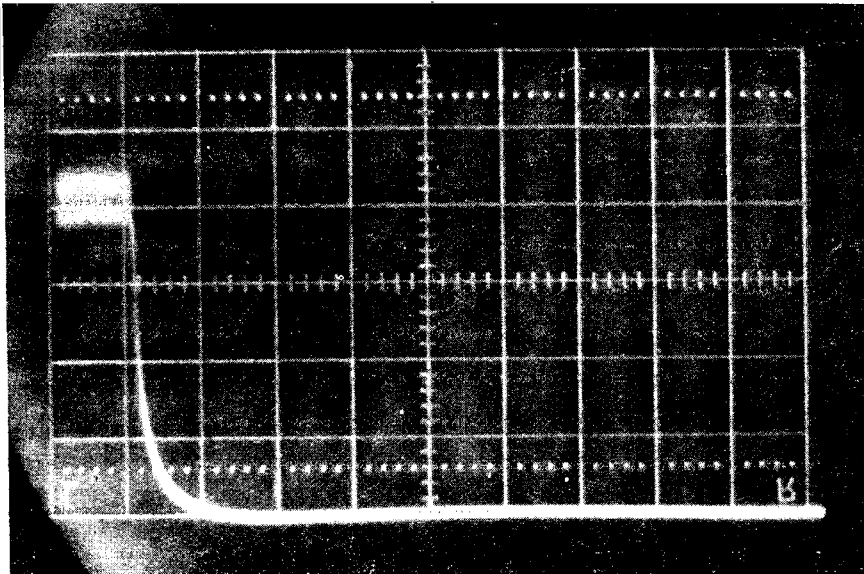


Fig. 4b

Fig. 4. Luminescence decay of the ZnS-Cu phosphor excited by UV ($\lambda = 365$ nm): a) global luminescence (amplification 1 V/cm, time 2 s/cm); b) $\lambda = 500$ nm luminescence, (amplification 0.5 V/cm, time 2 s/cm)

peak *A* in Fig. 2 is only about 0.30 eV. In thermoluminescence we deal with levels of non-associated defects. During the association of a donor defect with an acceptor defect the distance of the donor level should increase with respect to the bottom of the conduction band because of additional binding force of the electron from the donor defect with the positive local charge of the acceptor defect.

II. Stimulation and quenching by infrared radiation ($\lambda = 700$ nm) of the series of ZnS-Cu, Pb phosphor samples

The present paper gives the results of investigations on the influence of IR-radiation from the short wavelength stimulation band ($\lambda = 700$ nm) of ZnS-Cu, Pb phosphors with the use of weak IR-source and also a strong IR beam from a ruby laser.

A. In the first case the IR-beam was obtained by transmitting the radiation from a 100 W, 12 V incandescent lamp (Narva) through a Zeiss interference filter ($\lambda = 700$ nm). The apparatus is shown in Fig. 5. The results concerning luminescence quenching by IR-radiation with simultaneous excitation by 365 nm radiation are summarized in Table II.

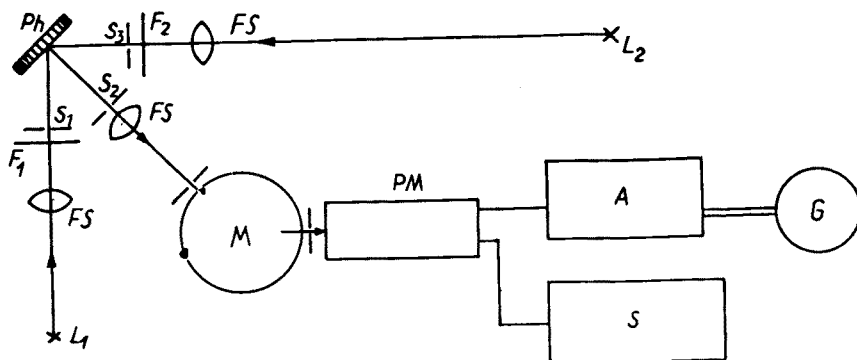


Fig. 5. Block diagram of the apparatus for the study of the spectrum as well as IR stimulation and quenching: L_1 = Wood's lamp, L_2 = Narva lamp, F_1 = interference filter ($\lambda = 365$ nm), F_2 = filter ($\lambda = 700$ nm), Ph = phosphor sample, M = monochromator, PM = photomultiplier (Zeiss M12 FS 35), S = supplier, A = amplifier, G = galvanometer, FS = focussing lens, S_1, S_2, S_3 = slits

TABLE II

No	Phosphor	G	Max. for UV emission	Max. for UV+IR
1	ZnS-Cu	1.6	522 nm	520 nm
2	ZnS-Cu, Pb 1%	1.24	527	524
3	Pb 2%	0.64	525	520
4	Pb 3%	0.41	524	495
5	Pb 4%	0.35	523	500
6	Pb 5%	0.25	515	500
7	Cu, Pb 4%	0.25	500	495

As a measure of quenching by *IR*-radiation we have accepted $G = \Delta I/I_2$, where $\Delta I = I_0 - I_2$, I_0 is the intensity of stationary luminescence during excitation with 365 nm wavelength and I_2 is the intensity for simultaneous excitation with this wavelength and illumination with *IR*-radiation ($\lambda = 700$ nm) after the establishment of equilibrium (Fig. 6).

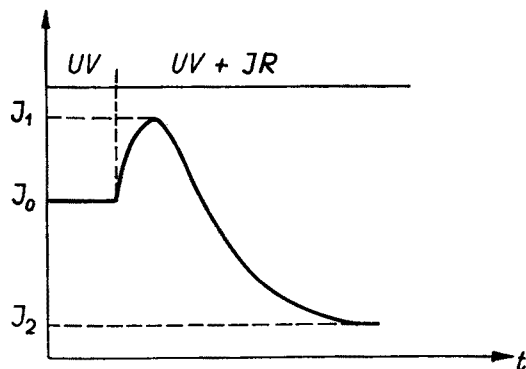


Fig. 6. Influence of *IR*-radiation on the luminescence of ZnS-Cu, Pb

Quenching is the greatest for the ZnS-Cu phosphors (without Pb) and the smallest for the ZnS-Cu, Pb phosphor with greatest concentration of Pb (in this series of phosphor samples) and for the ZnS-Pb phosphor (not containing Cu). Table II gives also wavelengths corresponding to maxima of stationary emission for *UV* and *IR*-radiation. Illumination with *IR*-radiation always shifts the maximum towards shorter wavelength (even in the case of ZnS-Cu without Pb).

Illumination with *IR*-radiation with the same wavelengths as before always gives rise to a short flash (stimulation) of previously excited phosphor. The stimulation was studied in two stages:

- 1) Using *IR*-illumination during the excitation with *UV*-radiation (Table III).
- 2) Using *IR*-illumination five minutes after stopping *UV* excitation (Table IV).

The measure of absolute stimulation was accepted as ΔI and of the relative stimulation as $S = \Delta I/I_0$, where ΔI is the maximum increase of the intensity, induced by *IR*-illumination.

TABLE III

	ZnS(Cu) 0% Pb	ZnS(Cu, Pb)		Cu = 0.2 · 10 ⁻⁴ %			ZnS(Pb)
		1% Pb	2% Pb	3% Pb	4% Pb	5% Pb	
I_0	247	83.5	86	67	193	69.5	40
I_1	260	95.0	27.0	310	600	600	110
ΔI	13	11.5	184	243	407	530	70
$S = \frac{\Delta I}{I_0}$	0.05	0.138	2.14	3.63	2.11	7.63	1.71

TABLE IV

	ZnS(Cu)	ZnS(Cu, Pb)		Cu = 9.2 10 ⁻⁴ %			ZnS(Pb)
		1% Pb	2% Pb	3% Pb	4% Pb	5% Pb	
I_0	3	1	2.0	1.5	4	1	0.5
I_1	15	11	80.0	150.0	255	260	40.0
ΔI	12	10	78.0	148.5	251	259	39.5
$S = \frac{\Delta I}{I_0}$	4.00	10.0	39.0	99.0	62.7	259	79.0

nation, $\Delta I = I_1 - I_0$, I_0 is the intensity of luminescence at the instant preceding the infrared illumination and I_1 the intensity at the maximum of stimulation (Fig. 6).

In both cases, *i.e.* $\Delta t = 0$ and $\Delta t = 5$ minutes (Tables III and IV) the smallest absolute stimulation was obtained for the phosphors ZnS-Cu and ZnS-Cu, Pb 1% and the maximum stimulation for ZnS-Cu,Pb with maximum lead concentration.

Figs 7 and 8 show the time dependences of luminescence intensity (obtained by means of the OSA 611-oscilloscope) for ZnS-Cu and ZnS-Cu,Pb with maximum lead contents during illumination with *IR*-radiation ($\lambda = 700$ nm) and after stopping the illumination. *IR*-illumination was used after a two-minute of luminescence decay of the phosphor at room temperature. The *IR*-illumination times were 1 and 3 sec. Some of these curves were obtained using an interference filter (500 nm or 525 nm) before the detector (photomultiplier). It can be seen from Fig. 8 that the short-wavelength component of the phosphor (500 nm) rapidly decays already during the *IR*-illumination, whereas the intensity of radiation of longer wavelength (525 nm) decreases slowly during the *IR*-illumination.

The time of growth of the intensity after starting the *IR*-illumination to its maximum value is much longer in case of ZnS-Cu than for ZnS-Cu,Pb. This difference is still more distinct when using a laser as *IR*-source and an OSA-611 oscilloscope with shorter sweep time (of the order of milliseconds).

Figs 9a and 9b show curves of luminescence intensity *vs* time obtained for continuous *IR*-illumination starting two minutes of luminescence decay.

B. Influence of radiation from a ruby laser on the luminescence of a series of ZnSCu,Pb phosphors samples. The radiation of a ruby laser ($\lambda = 694.3$ nm) is also in the region of the short wavelength band of stimulation and quenching of the investigated phosphors. In the investigations two beams were used: a stronger one (0.12 J per pulse after passing through interference filters used before the phosphor) and a six times weaker beam. Interference filters were also used before the detector of luminescence; 525 nm in the case of ZnS-Cu and 500 nm in the case of ZnS-Cu,Pb (Fig. 10).

The influence of the strong and short (0.4 msec) pulse of laser beam on the investigated series of phosphor samples was studied during excitation with *UV*-light as well as after different times Δt from stopping excitation. The luminescence intensity *vs.* time curves obtained by means of the OSA-611 oscilloscope are shown in Figs 11-15.

Fig. 11 shows the changes in luminescence intensity produced by laser pulses during

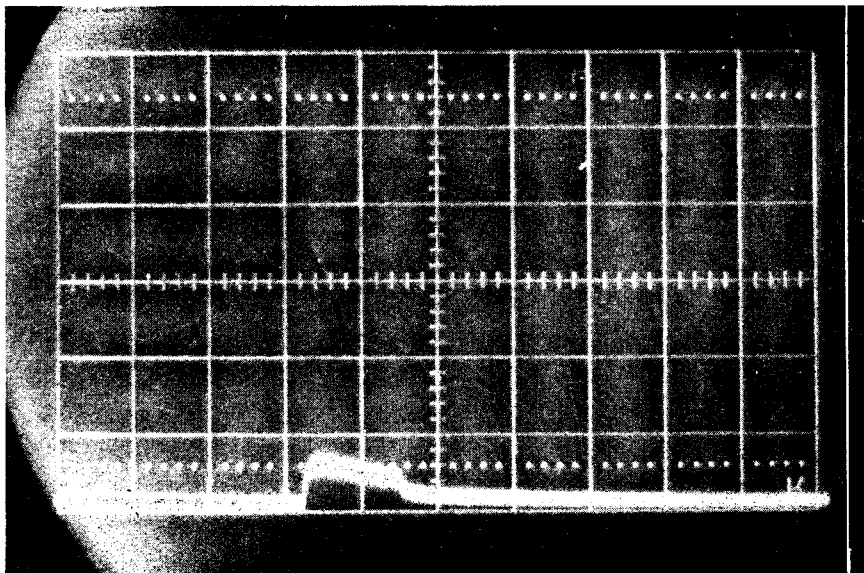


Fig. 7a

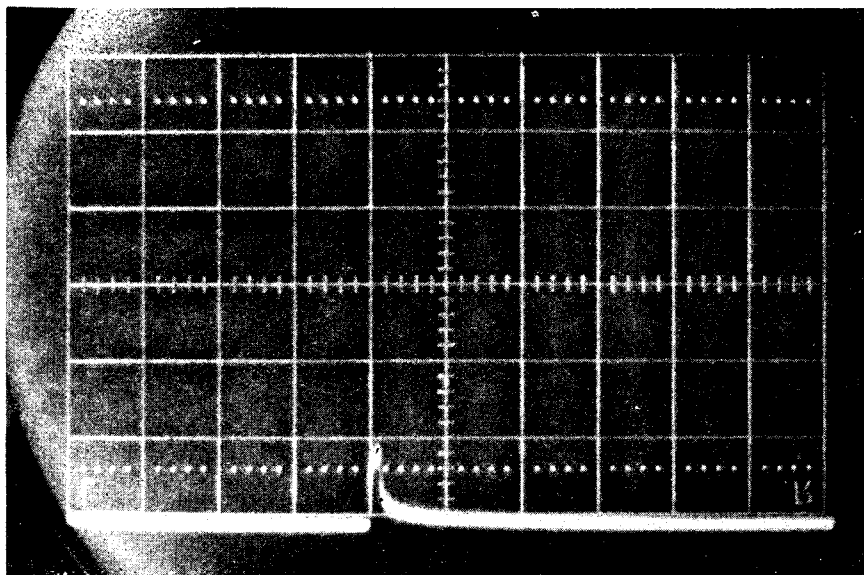


Fig. 7b

Fig. 7. Oscillograms of the time dependence of luminescence of ZnS-Cu, under the influence of IR-radiation: a) 3 s of IR; $\lambda = 525$ nm luminescence (amplification 0.05 V/cm, time 2 s/cm), b) 1 s of IR; $\lambda = 500$ nm luminescence (the same amplification and time)

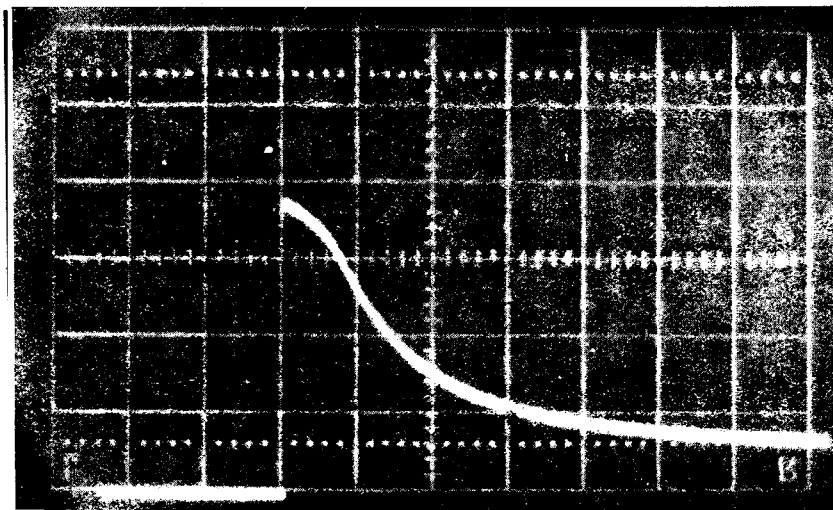


Fig. 8a

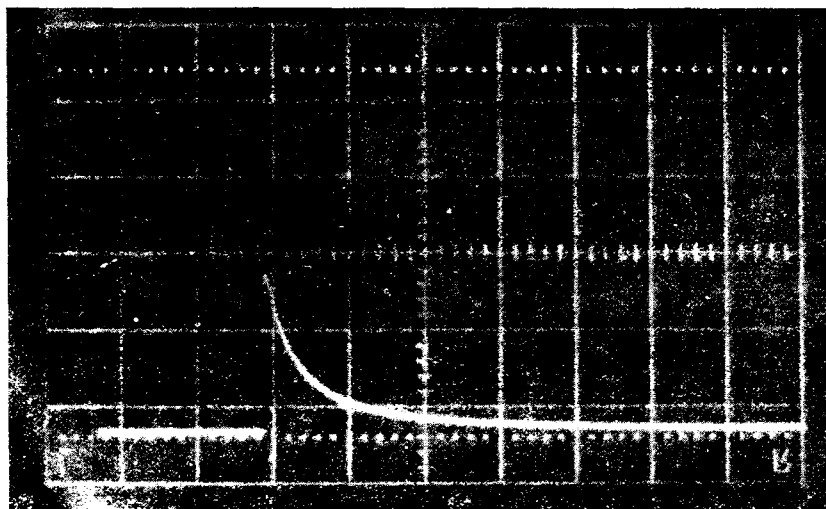


Fig. 8b

Fig. 8. Oscillograms of the time dependence of luminescence of ZnS-Cu, Pb (5%) for continuous action of $\lambda = 700$ nm IR-radiation: a) without filter before the detector (amplification 1 V/cm, time 2 s/cm), b) with a $\lambda = 500$ nm filter (amplification 0.5 V/cm, time 2 s/cm)

simultaneous illumination with exciting *UV*-light; luminescence decay after the end of the laser pulse (from 0.5 msec). Greatest stimulation is obtained for the phosphor with maximum lead contents (ZnS-Pb), and the smallest one for Zn-Cu (0% of Pb), whereas in the case of phosphors with intermediate lead contents the curves are almost identical.

The graphs in Fig. 12 obtained using a laser beam two minutes after stopping the *UV*

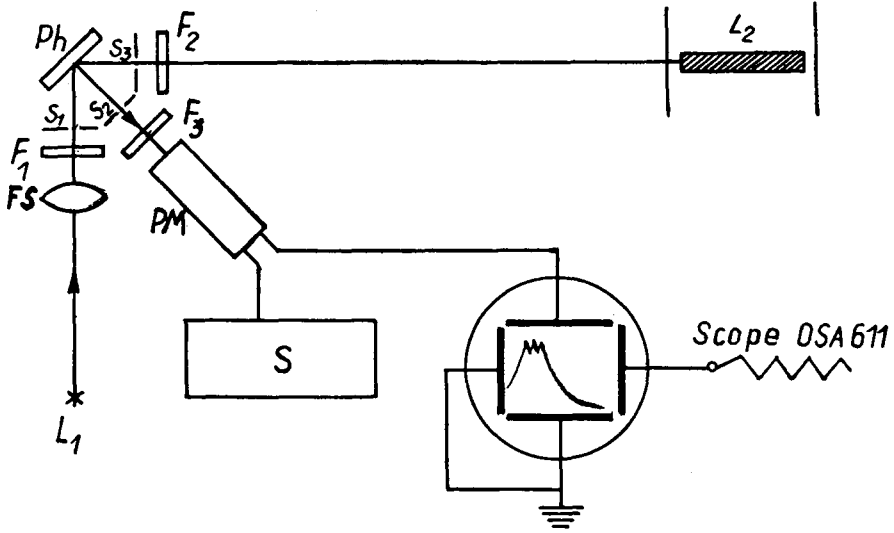


Fig. 9. Scheme of the apparatus for investigations made with a ruby laser: L_1 = mercury lamp, L_2 = ruby laser, F_1 = filter $\lambda = 365$ nm, F_2 = filter $\lambda = 700$ nm, F_3 = filter $\lambda = 500$ nm or $\lambda = 525$ nm, Ph = phosphor sample, PM = photomultiplier (Zeiss M12 FS 35), FS = focussing lens, S_1, S_2, S_3 = slits, S = supplier

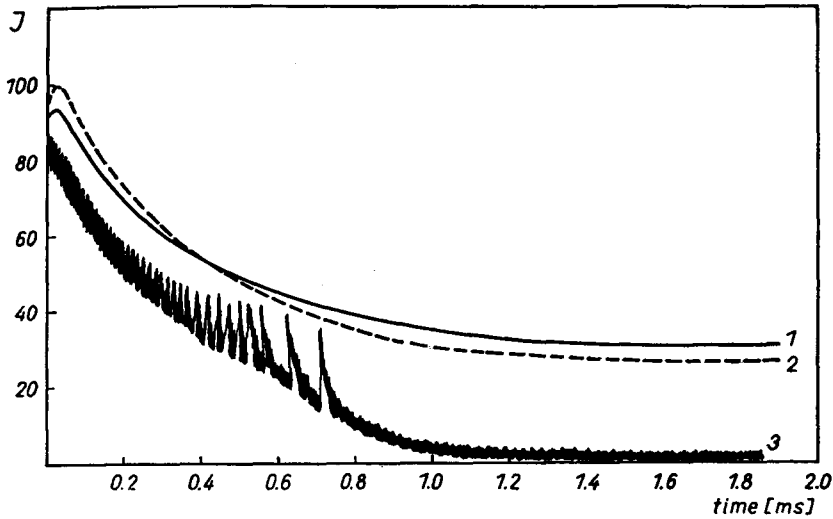


Fig. 10. Stimulation by laser beam with the energy of 0.12 J during UV-excitation: 1) ZnS-Cu, Pb; 2%, 3%, 4%, 5% of Pb, 2) ZnS-Pb, 3) ZnS-Cu

excitation show identical stimulation and decay shape after stimulation irrespective of the concentration of lead (in the concentration range from 2% to 5% of added Pb). The ZnS-Pb phosphor is characterized by faster decay during the illumination with IR-radiation and after stopping IR, while the stimulation of ZnS-Cu is much weaker, it growth slowly and

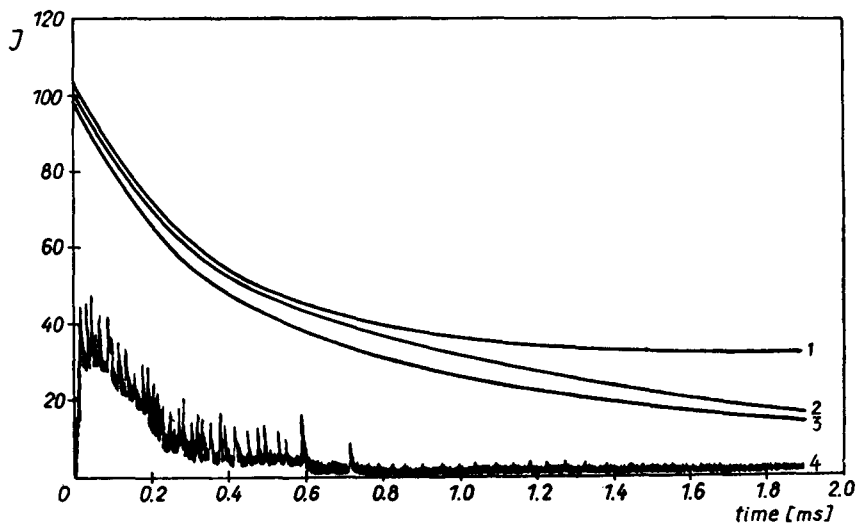


Fig. 11. Stimulation by laser beam (0.12 J), 2 minutes after stopping *UV* excitation: 1) ZnS-Cu, Pb; 2%, 3%, 4%, 5% of Pb, 2) ZnS-Cu, Pb 1% Pb, 3) ZnS-Pb, 4) ZnS-Cu

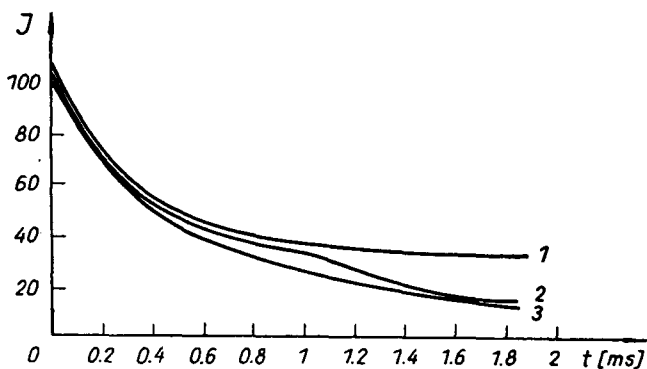


Fig. 12. Stimulation by laser beam (0.02 J), 4 minutes after stopping *UV* excitation: 1) ZnS-Cu, Pb; 2%, 3%, 4%, 5% of Pb, 2) ZnS-Cu, Pb; 1% Pb, 3) ZnS-Pb

decay rapidly. In addition very strong fluctuations of intensity occur in the latter case. The curves for the series of phosphor obtained after a four-minute interval between stopping *UV*-excitation and impact of laser beam (Fig. 13) coincide each other in the concentration range 2–5% of Pb. However, in case of the ZnS-Pb and ZnS-Cu, 1% Pb phosphors the decay after laser beam impact is faster. There is no stimulation in the case of ZnS-Cu (0% of Pb) for $\Delta t = 4$ min, whereas in the case when a weak *IR*-beam (from incandescent lamp) was used the stimulation of this phosphor was still observable after 5 minutes (Table III). Stimulation of this phosphor occurs also after five minutes when a weaker laser beam is used.

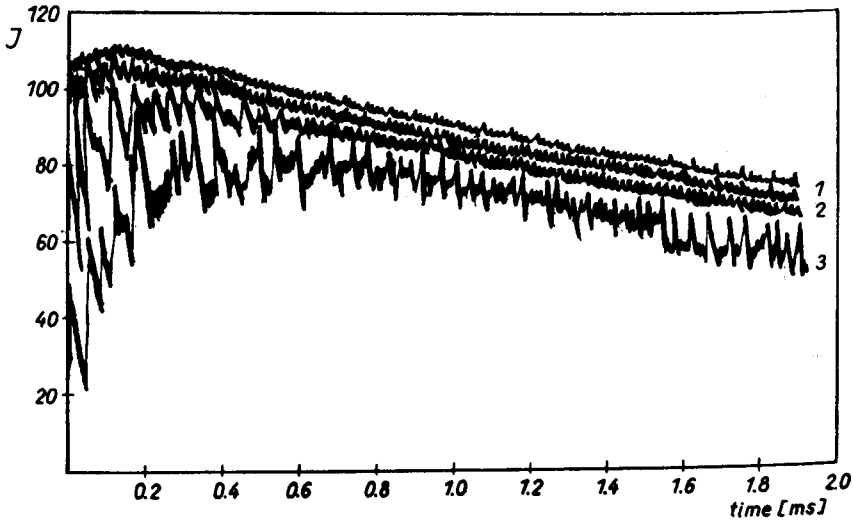


Fig. 13. Stimulation by laser beam (0.02 J), 5 minutes after stopping *UV* excitation: 1) ZnS-Cu, Pb; 1%, 2% 3%, 4%, 5% of Pb, 2) ZnS-Pb, 3) ZnS-Cu

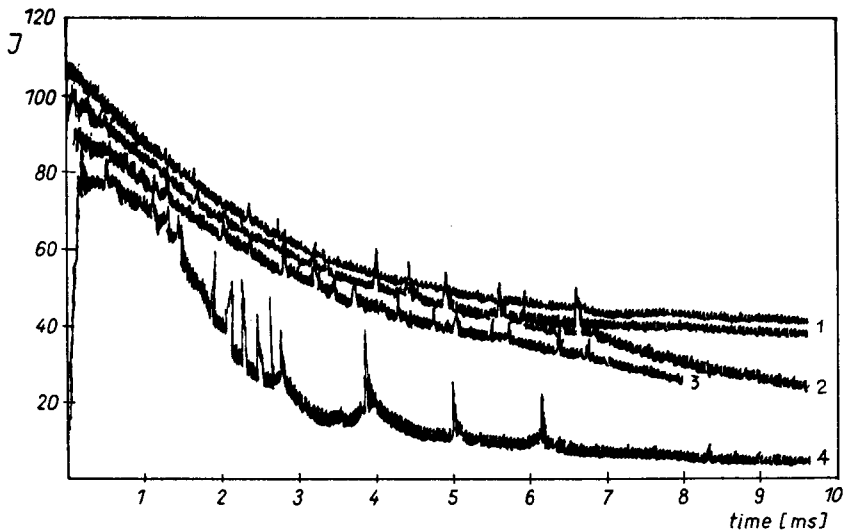


Fig. 14. Stimulation by laser beam (0.02 J), 5 minutes after stopping *UV* excitation: 1) ZnS-Cu, Pb; 2%, 3%, 4%, 5% of Pb, 2) ZnS-Cu, Pb; 1% Pb, 3) ZnS-Pb, 4) ZnS-Cu

The oscillograms of luminescence intensity *vs.* time for still greater time intervals between stopping *UV*-excitation and laser beam impact have the same character as the graphs given in Figs 12 and 13.

The comparison of oscillograms for varying Δt values shows that there are no significant differences between the time dependences of luminescence intensity when changing the time Δt from 2 min to 12 min.

Figs 14 and 15 show analogous time dependence for laser beam six times weaker than that used in measurements shown in Figs 11–13. Fig. 14 shows the oscillograms for the whole series of samples obtained after a 5 minute break between *UV* and *IR*-illumination. Also in this case the stimulation and intensity changes with time are almost identical for all ZnS-Cu, Pb phosphors in the concentration range of Pb between 1% and 5%, whereas ZnS-Cu shows a slightly weaker stimulation with a longer growth time and larger fluctuations. The decay after laser is for ZnS-Cu much faster than in the case of the remaining phosphors.

The plots in Fig. 15 give the same time dependences as those in Fig. 14 but on different time scale.

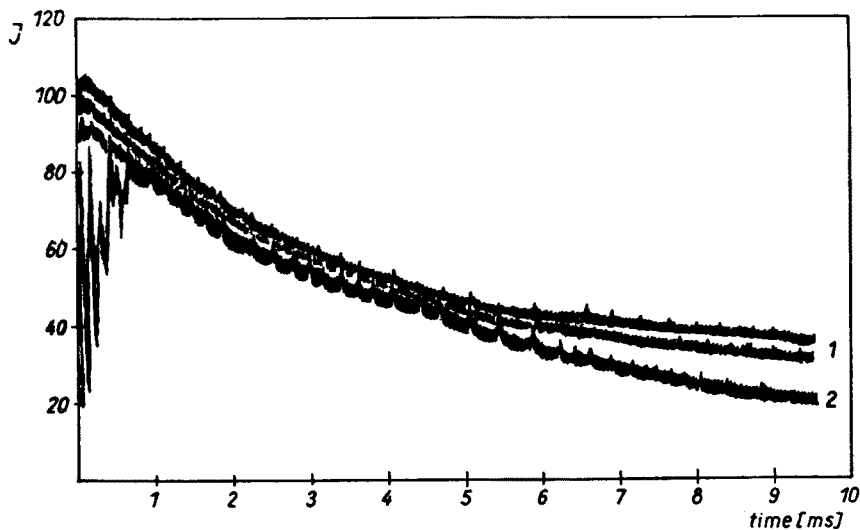


Fig. 15. Stimulation by laser beam (0.02 J) of the ZnS-Cu, Pb phosphor (3% Pb); different times Δt from stopping excitation: 1) $\Delta t = 2, 4, 5, 16$ min., 2) during the third consecutive laser beam impact

The plots in Fig. 16 concern the ZnS-Cu, Pb phosphor (3% Pb) for different time intervals Δt between stopping excitation with *UV* and impact of laser beam. Also in this case there are no differences between the curves for Δt intervals ranging from $\Delta t = 0$ to $\Delta t = 16$ min. Changes occur, however, when several consecutive laser beam impacts are used without repeating *UV*-excitation (curve *a* in Fig. 16).

The comparison of luminescence intensity changes obtained when using a stronger laser beam with those occurring when a six times weaker beam is used, shows the following characteristic features for the latter:

- the time of stimulation growth is longer for all phosphors, which is particularly distinct for the phosphors ZnS-Cu and ZnS-Pb,
- after reaching maximum the decay is slower than for the stronger laser beam,
- stimulation of ZnS-Cu is strong even after a five-minute luminescence decay of the

phosphor in the dark, whereas in the case of the strong beam there was no stimulation already after four-minute decay,

d) the curves are characterized by large fluctuations of luminescence intensity.

These fluctuations occur not only during irradiation by the laser beam but also after stopping it. They are particularly strong when the stimulation was weak, *i. e.*, for ZnS-Cu (without Pb) or for ZnS-Cu, Pb when using several consecutive laser beam pulses.

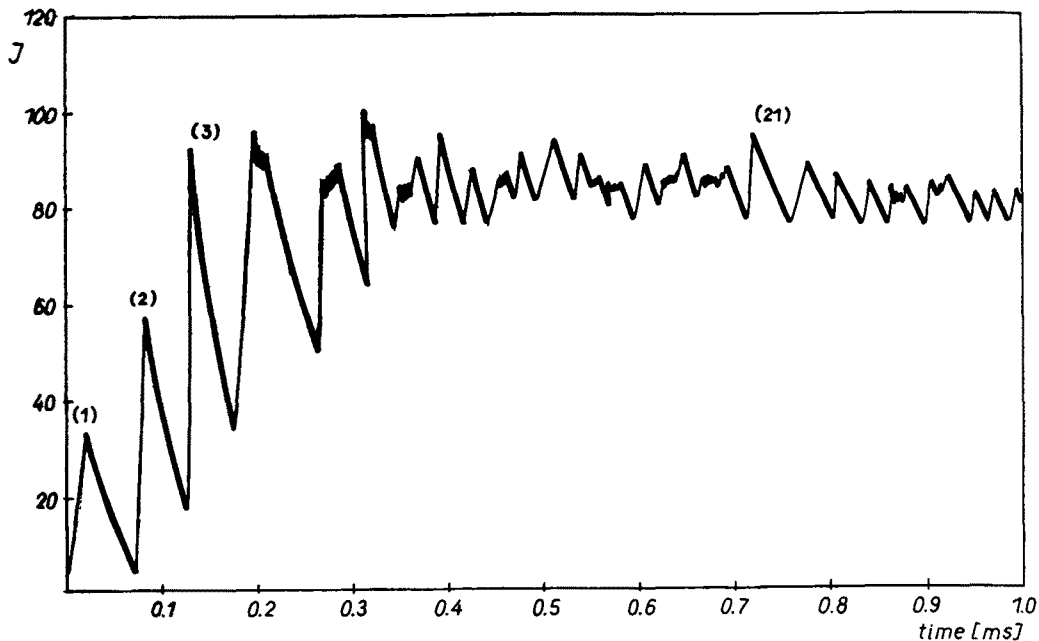


Fig. 16. Stimulation by the third consecutive laser beam impact

Investigation of the decay of such fluctuational flashes has shown that the latter are exponential in case of ZnS-Cu, Pb and the depths of the meta-stable states calculated for consecutive flashes increase from 0.201 eV for the first, 0.211 eV for the second (during the operation of the laser) *etc.* to 0.25 eV for the 21st after extinguishing the laser.

An analogous investigation of flashes made with the ZnS-Cu phosphors has shown that their nature is much more complex. It is possible to decompose them into two exponential curves; the corresponding depths amounting to 0.21 eV and 0.34 eV.

III. Discussion and conclusions

The results obtained for ZnS-Cu, Pb phosphors with a weak 700 nm *IR* beam (from a Narva incandescent lamp) and listed in Tables II, III and IV, can be in principle explained in terms of the mechanism proposed by Kallmann (Fig. 1).

Introduction of Pb to the ZnS-Cu phosphor gives rise to the formation of centres with greater cross-section for radiative transitions. The greater the concentration of these centres

(increased Pb concentration) the greater fraction of holes freed under the influence of *IR*-radiation from "normal" Cu-centres becomes captured by Pb-centres (stimulation) and the smaller fraction participates in non-radiative transitions (*IR*-quenching).

The changes in thermoluminescence with changing Pb concentration observed in the present work suggest that the green Pb centres (emission maximum 500 nm) are of the associated donor-acceptor type. It seems also necessary to assume for the interpretation of the results that *IR*-radiation does not free any holes out of these centres but only out of the Cu centres.

Since there is also some stimulation in case of ZnS-Cu (without Pb) and since an increase in Cu concentration (within the interval 10^{-6} to 10^{-4} g Cu (g ZnS) gives rise to changes in thermoluminescence consisting in a height decrease of the low-temperature peak, it seems to the authors that the green Cu-centres of the type donor-acceptor associated suggested in Ref. [6] occur with a certain concentration in ZnS-Cu beside "normal" Cu-centres originating from Cu not associated with the donor.

Associated copper centres would have a larger cross-section for radiative transitions. The studies of the phosphorescence of ZnS-Cu (decay after *UV* excitation) indicate that the radiation transmitted through the 525 nm filter decays more slowly than that transmitted through the 500 nm filter (Fig. 4).

Weak stimulation and strong quenching of ZnS-Cu by *IR*-radiation indicate that the number of (associated) Cu-centres, with greater cross-section is small in comparison with the number "normal" Cu-centres.

In the stimulation flash, in addition to the rapidly decaying luminescence with $\lambda = 500$ nm, there is also some luminescence with the wavelength $\lambda = 525$ nm which decays slowly during *IR*-illumination.

In the case of ZnS-Cu the strongest *IR*-stimulation was obtained during the excitation with *UV*. This stimulation decreases rapidly with increasing break interval Δt between stopping *UV* excitation and impact of laser beam. This result is in disagreement with that obtained by Curie [8] for ZnS-Cu. The disagreement may be due to the difference in concentration of the Cu activator in both works. In the phosphors investigated in this paper the concentration of Cu is small, 10^{-5} g Cu/g ZnS, thus shallow trap prevail in the phosphorescence process. At room temperature the phosphor loses a considerable fraction of total light sum very rapidly. This loss will be slower for higher Cu-concentrations (however, only in a certain concentration interval — *cf.* Ref [6]).

The interpretation of the results obtained for ZnS-Cu, Pb with ruby laser seems to be more difficult. The fact that the luminescence intensity *vs* time-curves are independent of Pb concentration in the range between 2% and 5% of (added) Pb seems to be in disagreement with the results given in Tables III and IV obtained by using a weak *IR*-beam of the same wavelength ($\lambda = 700$ nm). In the case of laser beam use the stimulation ΔI is also independent of luminescence decay time Δt in a wide range of the latter ($t = 2-16$ min) before applying *IR*-illumination.

In order to explain these discrepancies it seems necessary to assume the existence of local levels in which electrons are trapped for a very long time, even at room temperature. These may be deep donor levels or electron traps not revealed in thermoluminescence.

The analysis of the decay curves obtained after the laser beam impact shows that it is complex, rather of bi-molecular type, and the contribution of electron from deeper traps seems to be the greater the weaker the *IR*-beam. The comparison of the decay of the same phosphor for three different *IR*-intensities (Narva lamp, weaker and stronger laser beam) leads to the same conclusion. The depths of the local levels calculated from the decay vary between 0.28 eV and 0.48 eV.

The interpretation of the occurrence of fluctuational flashes not only during, but also after the action of the laser seems to be difficult, (at least for the time being). The decay of these flashes is exponential in the case of ZnS-Cu, Pb and the depth of meta-stable levels calculated from this decay slightly increases (in the range from 0.20–0.22 eV) with increasing flash number during the illumination with *IR* beam reaching 0.25 eV for the flash after stopping the illumination.

It is well known from literature that shallow local levels occur in the ZnS-Cu phosphor. However, at room temperature the lifetime of electrons on these levels is of the order of miliseconds. These levels could not remain filled for the period $\Delta t = 2\text{--}16$ minutes after excitation with *UV* radiation. One has to assume either that these traps were filled during the action of *IR*-radiation as a result of capture of electrons freed from deep traps, or that filled shallow traps were bound (associated) with acceptor levels.

The lifetime of electrons on shallow levels, "associated" with acceptor levels, would be longer than the lifetime on non-associated levels.

The comparison of thermoluminescence curves of the investigated phosphors (after excitation with *UV*) before and after *IR* illumination shows that the result of the latter is above all a height decrease of the low-temperature luminescence peaks. This fact favours rather the second one of the above mentioned two possibilities as well as the hypothesis about the structure of centres with greater cross-section for radiative transitions, presented in this paper.

Finally one should draw attention to the fact that in order to apply the transition scheme shown in Fig. 1 to the explanation of stimulation of ZnS-Pb (without Cu) it is necessary to assume the existence of two kinds of centres in this phosphor with different cross-section of radiative transitions.

It seems that further studies, in particular repeated experiments with laser beam at low temperatures will shed more light on the mechanism of this phenomenon.

REFERENCES

- [1] G. Fouda, *J. Opt. Soc. Amer.*, **136**, 382 (1946).
- [2] H. Kallmann, B. Kramer, A. Perlmutter, *Phys. Rev.*, **99**, 391 (1955).
- [3] H. Kallmann, K. Luchner, *Phys. Rev.*, **123**, 2013 (1961).
- [4] G. Curie, *Ann. Phys. (France)*, **5**, 377, 392 (1960).
- [5] W. Herchold, *Zesz. Nauk. Politech. Poznańskiej*, **2**, 85 (1967), in Polish.
- [6] A. Wrzesińska, in *Zur Physik und Chemie der Kristallphosphore II*, Akademie Verlag, Berlin 1962.
- [7] D. Curie, *Luminescence Cristallone*, Dunod, Paris 1960.
- [8] D. Curie, *J. Phys. Rad.*, **26**, 565 (1965).

- [9] S. Shionoya, K. Era, H. Katayama, *J. Phys. Chem. Solids* (GB), **26**, 697 (1965).
- [10] M. Grillot, *CR Acad. Sci. (France)*, **E238**, 1216 (1954).
- [11] A. Wrzesińska, *Acta Phys. Polon.*, **15**, 151 (1956).
- [12] N. Riehl, H. Ortmann, *Ann. Phys. (Germany)*, **4**, 3 (1959).
- [13] J. S. Prener, F. E. Williams, *J. Phys. Rad.*, **17**, 59 (1956).
- [14] P. Jaszczyn-Kopeć, J. Gallagher, H. Kallmann, B. Kramer, *Phys. Rev.*, **140**, 1309 (1965).