Vol. XXXV (1969) ACTA PHYSICA POLONICA Fasc. 6

ACTA PHYSICA POLONICA Vol. XXXV (1969) Fasc. 6

THE DEPENDENCE OF ELECTROLUMINESCENCE ON TEMPERATURE

By A. Wrzesińska and W. Arsoba

Department of Technical Physics, Technical University, Łódź*

(Received September 11, 1968)

The temperature dependence of the brightness of electroluminescence $B = f(T)$ is studied for the Zn–S–Cu phosphor (2.10^{-2} gCu/gZnS) in insulating mounting without dielectric.

The parameters were the voltage applied across the cell or the frequency.

Both global electroluminescence and luminescence separated from both emission bands of this phosphor trough interference filters $\lambda_1 = 450$ nm and $\lambda_2 = 525$ nm were investigated. The difference in the curves for λ_1 and λ_2 consists mainly in the fact that sudden electroluminescence decay (temperature quenching) occurs in the case of blue emission at lover temperature than that in the case of green emission.

The influence of voltage on the $B = f(T)$ curves in the range up to about 450 V (for cell thickness 10^{-2} cm) is the following:

a) the peaks shift towards lower temperatures with increasing voltage,

b) the low-temperature peak broadens with increasing voltage from the low-temperature side,

c) and a faster increase in the height of the low temperature peak with increasing voltage.

For higher voltages ($U > 450$ V) the increase in voltage results in a much faster growth of the high temperature peak than the growth of the low-temperature peak.

The influence of previous illumination of the phosphor by Wood's light on $B = f(T)$ has also been investigated as well as the influence of ageing of the phosphor on the intensity ratio of the low — and hightemperature peaks of the $B = f(T)$ curve.

Introduction

In the collision mechanism of intrinsic electroluminescence excitation suggested by Destriau, developed by Curie [1] and Williams and Piper [2, 3], and supplemented by other autors one can distinguish three stages:

1. Freeing of electrons from donor traps (Williams, Piper) or conducting precipitates (*e.g.* Cu_2S in Zn-S-Cu, see Zalm [4], Maeda [5], Fischer [6]).

2. Acceleration of these electrons to optical energies in strong field regions — potential barriers.

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* Address: Katedra Fizyki Technicznej Politechniki Łódzkiej, Łódź ul. Gdańska 155, Polska.

3. Exciting collisions.

The emission occurs during the recombination of free electrons with excited centres in the second half of the a.c. voltage period.

The probability of the energy gain by an electron not smaller than the ionization energy of the luminescence centre is a most rapidly (exponential) growing function of field strength. In the papers [1], [2] and [3] several formulas for the dependence of electroluminescence brightness B on field strength have been obtained, under the assumption that the influence of the field on the first and third stage of electroluminescence excitation is negligible. These formulas are in fair agreement with the experiment.

Although the colision mechanism proposed by Destriau has been accepted by the majority of authors, there are many problems concerning the mechanism of electroluminescence which are still not quite clear. This concerns, in particular, the role of traps and thermal energy.

It seems that some information on this problem may be obtained from the study of the dependence of the brightness of electroluminescence on the temperature $B = f(T)$. This dependence has been studied already by many authors. The parameters most frequently used in the investigation of the $B = f(T)$ dependence were the frequency of the sinusoidal or rectangular field strength and the measurements were made for global emission. All this results show that an increase in frequency gives rise to a shift of the maximum of B *vs* T curve towards higher temperatures, whereas the results of investigation of the influence of voltage on the position of the maximum of $B = f(T)$ are inconsistent with one another [11, 12, 13, 15, 16].

The present paper deals mainly with the influence of external voltage on the $B = f(T)$ dependence and the measurements have been made separately for radiation separated by interference filter from two emission bands of the ZnS-Cu (2.10^{-2} g Cu/g ZnS) — phosphor. It is namely known, from the studies on photoluminescence that the temperature dependences of the intensity of the varius emission bands of the ZnS-Cu phosphor are different, and, in addition, in electroluminescence, the intensity ratio of both bands is frequency-dependent and may also depend on voltage.

Experimental conditions and results

The present paper gives the results of $B = f(T)$ measurements for sinusoidal voltage in the case of the ZnS-Cu phosphor in insulating mounting, both for global emission and luminescence separated from the blue and green electroluminescence bands by interference filters $\lambda_1 = 450$ nm and $\lambda_2 = 525$ nm[1]. The measurements were made in an EL-cell with a polycrystalline phosphor layer without dielectric in order to avoid the disturbing influence of temperature changes on the dielectric constant of the latter.

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[1] For average frequency $\nu = 1$ kHz and at temperatures below temperature quenching, the intensity of luminescence for $\lambda = 450$ nm was in the case of the investigated phosphor about 2 times greater than for $\lambda = 525$ nm.

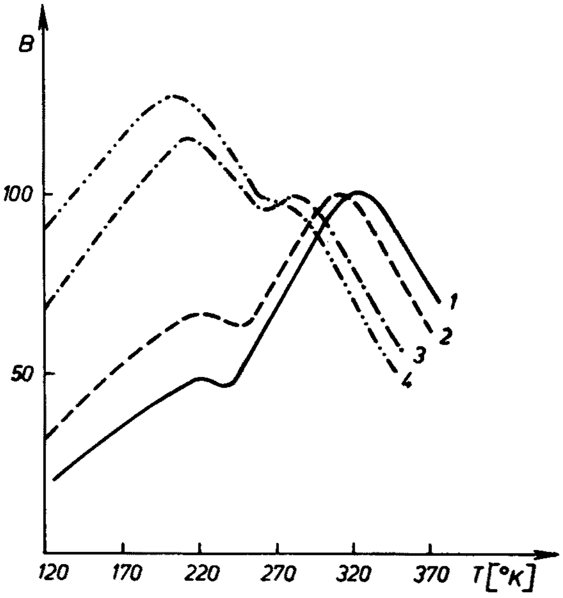

Fig. 1. $B=f(T)$ for global emission of the ZnS-Cu (2.10^{-2} g Cu/g ZnS) phosphor at the frequency of 3 kHz. Voltages: *1* – 100 V, *2* – 200 V, *3* – 300 V, *4* – 400 V

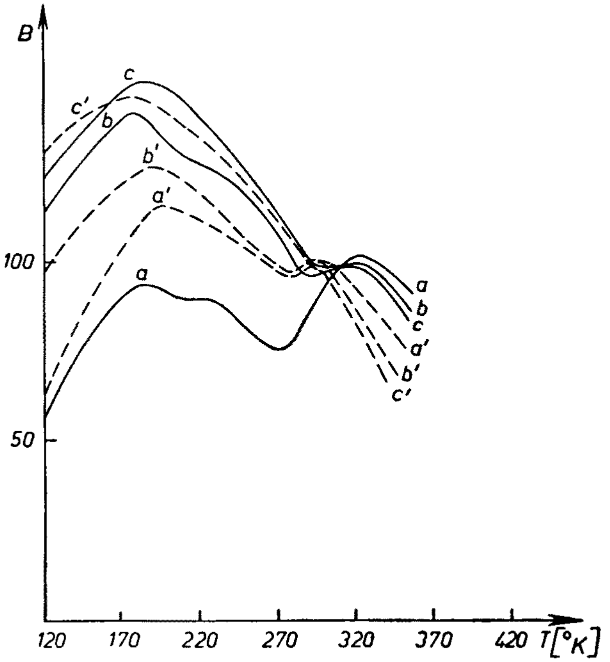

Fig. 2. $B=f(T)$ at 3 kHz. ——— $\lambda = 525$ nm; *a* – 200 V, *b* – 300 V, *c* – 500 V, – – – $\lambda = 450$ nm; *a'* – 260 V, *b'* – 300 V, *c'* – 500 V

1. The dependences of electroluminescence brightness on temperature $B = f(T)$ given in Figs 1 to 4 show[2] that:

a) the $B = f(T)$ function has at least two maxima both in the case when B denotes global emission (Fig. 1) and when B denotes the brightness of luminescence separated from the particular emission bands through interference filters $\lambda_1 = 450$ nm and $\lambda_2 = 525$ nm (Figs 2, 3 and 4),

b) the sudden decrease in brightness (temperature quenching) of the $B = f(T)$ curves occurs for blue band at lower temperatures than for the green band, similarly as in photoluminescence and the high-temperature maximum for blue luminescence appears at a slightly lower temperature than that for green luminescence.

2. The influence of voltage applied across the cell on the $B = f(T)$ dependence is rather complicated:

a) in the low voltage range (100–500 V for cell thickness of 10^{-2} cm) the electroluminescence intensity increases with increasing voltage more rapidly at low temperatures than at the higher ones, (in agreement with the data from literature) (Figs 1–6), and in addition for green luminescence faster than the blue one.

Both maxima shift towards lower temperatures when the voltage increases. This is particularly apparent for the high-temperature peak while in the case of the low-temperature

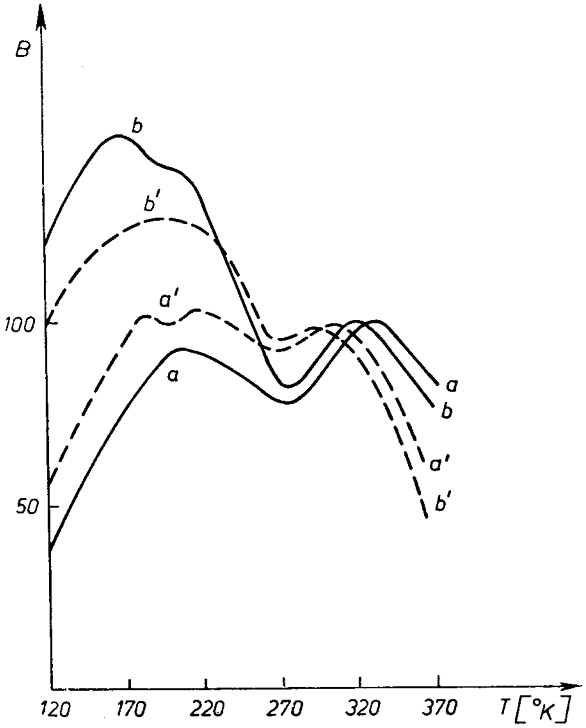

Fig. 3. $B = f(T)$ at 1 kHz. ——— $\lambda = 525$ nm, a – 260 V, b – 500 V, - - - $\lambda = 450$ nm, a' – 260 V, b' – 500 V

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[2] The curves in this figures are normalized to the height of the high-temperature maximum.

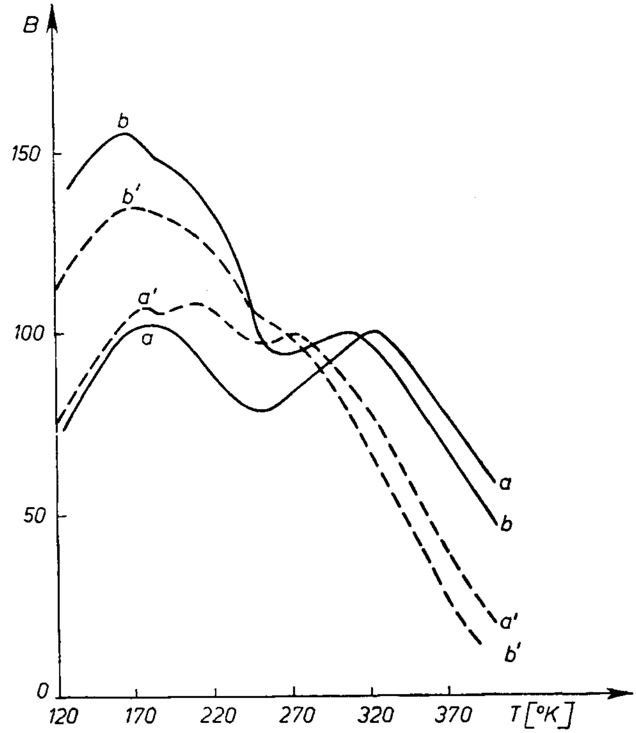

Fig. 4. $B = f(T)$ at 0.3 kHz. ——— $\lambda = 525$ nm; a – 260 V, b – 500 V, - - - $\lambda = 450$ nm; a' – 260 V, $b' = 500$ V

Note: All curves in Figs 1–4 are normalized to the high-temperature maximum.

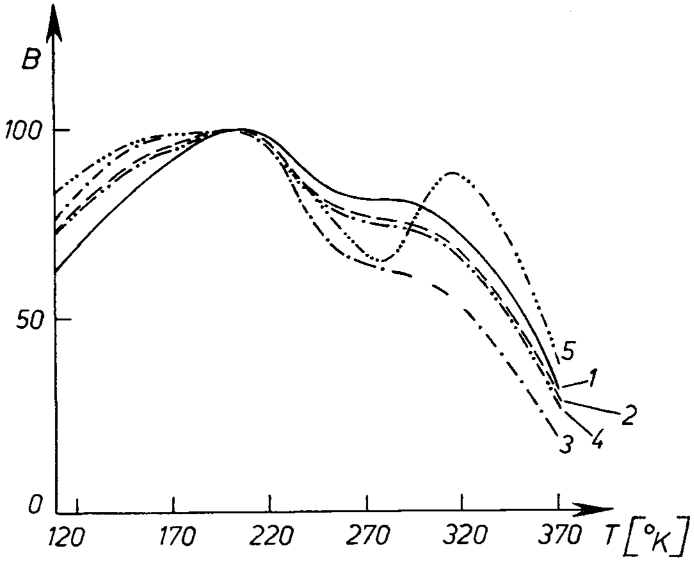

Fig. 5. $B = f(T)$ at 1 kHz; $\lambda = 450$ nm. 1 – 200 V, 2 – 300 V, 3 – 400 V, 4 – 500 V, 5 – 600 V

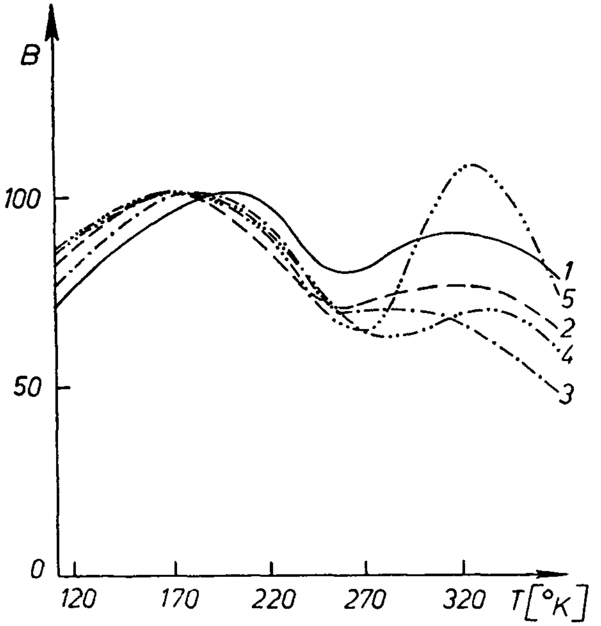

Fig. 6. $B=f(T)$ at 1 kHz; $\lambda = 525$ nm (designations of the curves as in Fig. 5)

Note: The curves in Figs 5, 6 and 8, 9 are normalized to the low temperature maximum.

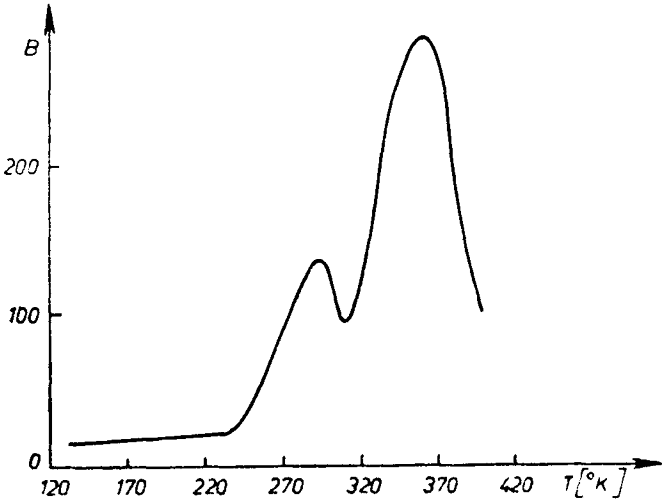

Fig. 7. $B=f(T)$ for $U > 600$ V and for $\lambda = 525$ nm

peak the influence of voltage increase consists mainly in a broadening of the peak from the low-temperature side.

b) From about 500 V on (Figs 5 and 6) the high-temperature peak starts to increase faster with increasing voltage than the low-temperature one and the sudden fall on the high-temperature side shifts towards higher-temperatures.

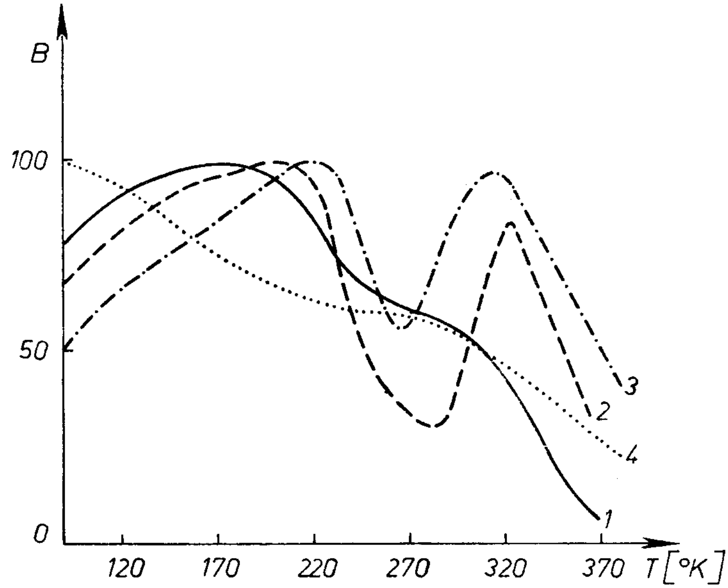

Fig.. 8. $B=f(T)$, $U=500$ V, $\lambda=450$ nm. *1* – 0.3 kHz; *2* – 1 kHz; *3* – 3 kHz; *4* – stationary photoluminescence excited by light from Wood's lamp

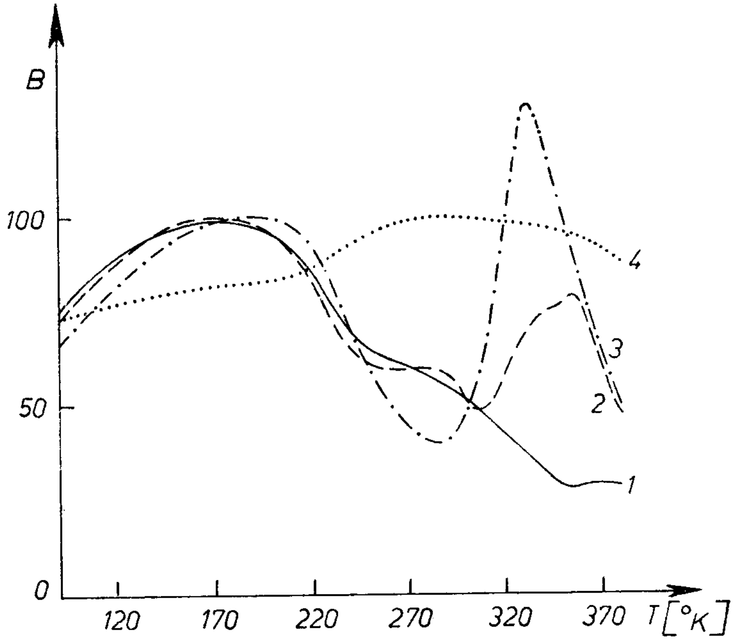

Fig. 9. $B=f(T)$, $U=500$ V, $\lambda=525$ nm (designations of the curves as in Fig. 8)

For still greater average field strengths ($U > 600$ V) and 1 kHz frequency the high temperature peak dominates the low-temperature electroluminescence, especially for $\lambda = 525$ nm (Fig. 7).

The low-temperature peak, though growing less rapidly with increasing voltage (for high voltages), becomes gradually broader on the high temperature side.

The difference in the influence of voltage and frequency as well as the shape of the low-temperature peak indicate that the latter has a complex structure.

The growth of the high-temperature peak with increasing voltage is faster for $\lambda = 525$ nm than for $\lambda = 450$ nm.

3. Figs 8 and 9 show the $B = f(T)$ — curves for different frequencies and constant voltage. These curves indicate:

a) a shift of the $B = f(T)$ — maxima with increasing frequency towards higher temperatures, particularly distinct for the low-temperature peak. This peak become narrower with increasing frequency at the low-temperature side,

b) for high voltage ($U = 500$ V see Figs. 8 and 9) the high-temperature peak grows faster with increasing frequency than the low-temperature one, especially for $\lambda = 525$ nm, in contrast for low voltages when the growth of the low-temperature peak with increasing frequency was faster, similarly as in Ref. [18].

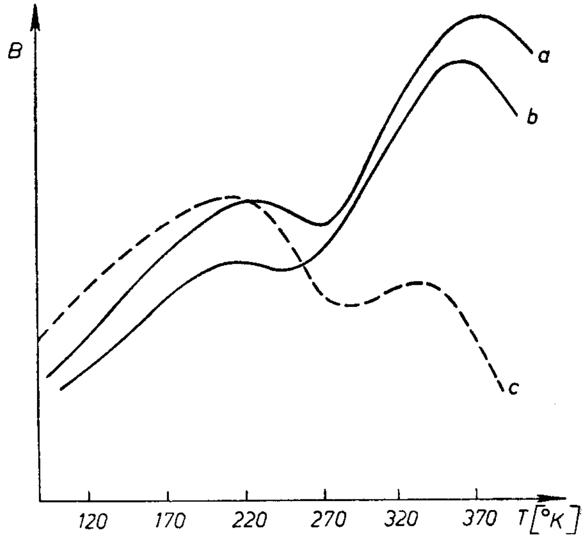

Fig. 10. Influence of ageing of the phosphor on the *B vs. T* dependence. ——— fresh prepared phosphor, *a* – 3 kHz, *b* – 1 kHz, – – – aged phosphor

4. Fig. 11 illustrates the influence of previous excitation by Wood's light on the dependence of green electroluminescence ($\lambda = 525$ nm) on temperature for sinusoidal voltage of 260 V and the frequency of 1 kHz. It can be seen that the curve obtained after previous excitation with *U V* is merely the sum of electroluminescence $B = f(T)$ without *UV* excitation and thermoluminescence. Analogous results have been obtained for blue luminescence ($\lambda = 450$ nm). In this case, however, the intensity of thermoluminescence is

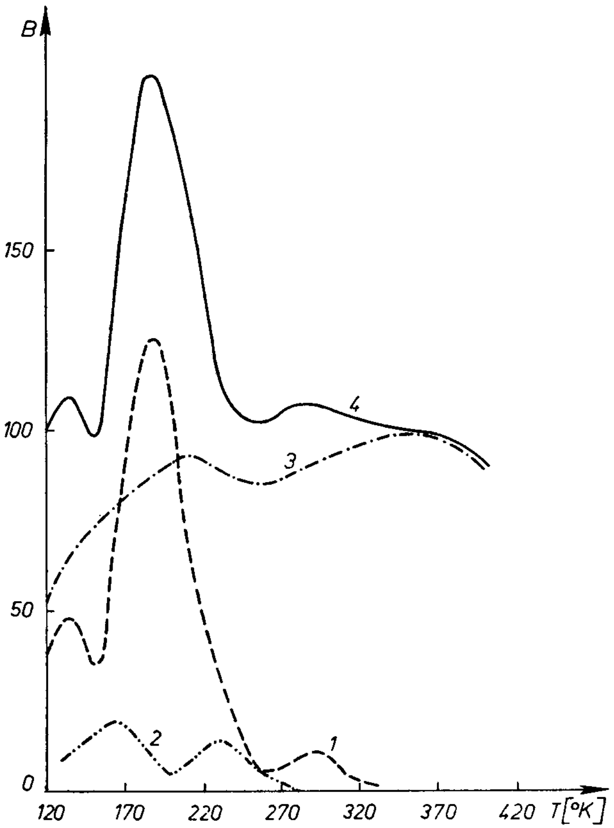

Fig. 11. *1* – Thermoluminescence ($\lambda = 525$ nm) excited by light from Wood's lamp. *2* – thermoluminescence ($\lambda = 450$ nm) excited by light from Wood's lamp. *3* – electroluminescence at the heating rate 0.14 degrees/s for $U = 260$ V and $\nu = 1$ kHz. *4* – $B = f(T)$ for electroluminescence at 260 V and = 1 kHz after prior excitation by light from Wood's lamp at 90°K

negligibly small in comparison with electroluminescence induced by $U = 260$ V and $\nu = 1$ kHz.

5. The ratio of the intensities in the maxima of the two peaks depends also whether the $B = f(T)$ was measured for freshly prepared phosphor or after some ageing time. Fig. 10 shows the influence of ageing as well as the influence of frequency on freshly prepared phosphor. The ageing process proceeds, the high-temperature peak becomes smaller and both peaks shift towards lower temperatures, which indicates an increase in the number of non-radiative transitions.

Discussion

First investigations of the dependence of electroluminescence brightness on temperature have been already made by Destriau, however, only in a small temperature range. Next systematic studies of mean brightness on temperature $B = f(T)$ as well as the influence of temperature on the shape of brightness waves have been made by Mattler [8] for the ZnS-Cu, ZnS-Ag and ZnS-Mn phosphors suspended in alordite.

For the above-mentioned phosphors Mattler obtained a single maximum on the electroluminescence dependence in the temperature interval (—150°C, +150°C).

Klasens [9] obtained the $B = f(T)$ curve with two peaks for global luminescence of the phosphors ZnS-Cu, Al and ZnS-Cu, Cl. The main reason for the appearance of the two peaks (occurence of a minimum at a certain temperature) according to Klasens, is the difference in the temperatures at which thermal release of holes from excited green and blue centres occur (temperature quenching according to the model of Riehl, Schön and Klasens).

Such an explanation, however, cannot be correct since our results indicate the presence of two maxima of the $B = f(T)$ curve not only in the case of global luminescence but also for light separated from the blue and green bands ($\lambda = 450$ nm and $\lambda = 525$ nm). Two maxima in the B. *vs.* T dependence have been also obtained by Haake [16] for a phosphor with one emission band.

Among the authors examining the temperature dependence of electroluminescence who obtained one or several peaks on the $B = f(T)$ curve [11, 12, 13, 14, 15, 16, 17], especially the shift of the peaks to higher temperatures with increasing frequency there are two tendencies of explaining the experimental results. One group of authors, in particular Johnson *et al.* [3] and Zalm [10], as a decisive factor regard the influence of temperature, frequency and voltage on the release of electrons from local (donor) levels in the strong field region (potential barriers) as well as on the strength and configuration of the field in this region, *i. e.*, on the concentration of electrons in the barrier and on the probability of acceleration these electrons to optical energies.

Detailed considerations on the influence of voltage applayed to the cell and temperature on field strength and on the electron's multiplying factor in the barrier have been made by Vereshchagin [11]. Vereshchagin obtained expressions for the temperature dependence of the first two excitation stages (see introduction). By making assumption that the temperature dependence of the probability for recombination of the electron with excited centre is the same as in the stationary photoluminescence he has obtained an expression for the dependence of electroluminescence brightness on the temperature — $B = f(T)$.

The results of his theoretical considerations are in disagreement with our experimental results, since:

a) according to Ref. [11] an increase in voltage (U) should result in a shift of the $B = f(T)$ maxima towards higher temperatures, whereas in our experiment just the opposite effect occurs, at least for not very high voltages (see Figs 6 and 7).

b) according to Vereshchagin the $B = f(T)$ curves obtained for different voltages should have the same low-temperature limit, *i. e.*, B should fall to zero at the same (low) temperature, while the high temperature limit (sudden fall) should shift towards higher temperatures with increasing voltage, Fig. 12. Our $B = f(T)$ curves do not exhibit a tendency of having a common low-temperature "threshold"; their low-temperature part gradually increases with increasing voltage (Figs 5, 6).

The high-temperature $B = f(T)$ limit (quenching) for not very high voltages (100–500 V for cell thickness of 10^{-2} cm) shifts towards lower temperatures with increasing voltage

(Figs 1–4). Only after getting above 500 V this limit shifts towards higher temperatures with increasing voltage.

Another group of authors [13, 14, 15, 16] draws attention to the influence of temperature of the concentration of free electrons in thermal equilibrium with electrons in traps in weak field regions. This concentration determines the number of radiative recombinations in the second half of the a. c. voltage period, *i. e.* emission intensity.

Assuming that the influence of temperature on the concentration of excited centres and on the configuration of the field is rather small, one can regard that the amount of light emission per each voltage period depends on T approximately in the same manner as the concentration of the above-mentioned free electrons in weak field regions[3]. So the dependence of mean electroluminescence brightness on temperature $B = f(T)$ should be similar in a wide frequency interval, since all free electrons return to the region containing excited centres in the second half of the voltage period.

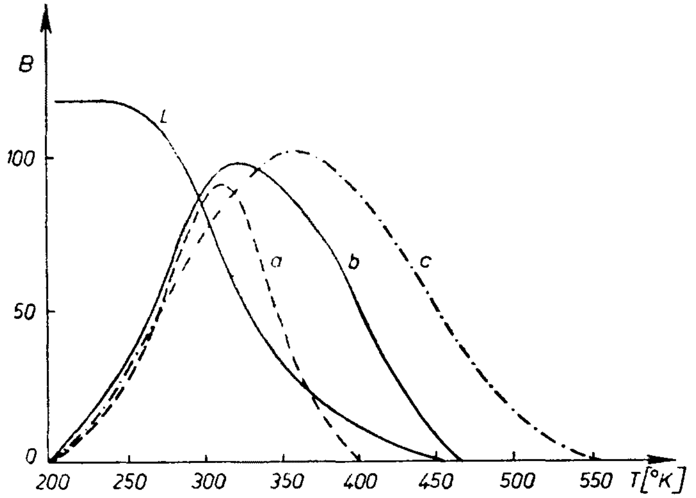

Fig. 12. L-stationary luminescenc eexcited by light from Wood's lamp. The curves *a*, *b* and *c* correspond to $B = f(T)$ for three increasing voltages (from the paper of Vereshchagin)

This condition will be not satisfied only for very high frequences.

The results of various authors who studied the influence of electroluminescence brightness on voltage are not in agreement with one another.

Haake obtained two peaks which shifted towards lower temperatures with increasing voltage [15]. On the other hand according to Alfrey [14] there is no visible shift while Morehead [16] obtained only a very small shift towards higher temperatures.

According to Haake the shift of the $B = f(T)$ maxima with the change in voltage is due to the influence of electric field on the depth of electron traps (Thornton effect).

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[3] The assumption made here is that the time necessary for the establishment of this equilibrium free electrons-trapped electrons) is very small in comparison with the a c. period).

Our results also indicate the presence of two peaks on the $B = f(T)$ curve shifting towards low temperatures with increasing voltage (Figs. 1–7). It seems, however, that one should distinguish the difference in the influence of voltage and frequency on the low-and high-temperature part of the $B = f(T)$ curve. Besides, the low-temperature peak consists of two parts differently growing with increasing voltage and frequency, and hence the change of its shape with changing frequency and voltage.

The slower growth of the high-temperature peak with increasing voltage as well as its shift may be explained in terms of nonradiative transition whose influence becomes more important at these temperatures (about 340°K).

Microscopic studies indicate a broadening of excitation regions (elongation of the "cometary tail" with increasing voltage). Hence for definite concentration of quenching centres and sufficiently high temperature the probability of excitation energy capture by this centeres increases *i. e.* the probability of non-radiative recombination is the greater the farther the electron is moved away by the field from its "birth-place".

It follows from Fig. 11 that electrons, freed thermally from traps, do not gain, in general sufficiently high energy in the crystal (at least in our experimental conditions) from the electric field to excite centres by collisions.

On the other hand it is interesting that the hightemperature peak begins to grow very rapidly with increasing voltage for voltages exceeding 500 V (for cell thickness of 10^{-2} cm). It seems that at such voltages a certain fraction (increasing with voltage) of electrons thermally freed from deeper traps, participates in the excitation of the centres.

The depth of traps corresponding to the high-temperature peak, obtained from the formula $\omega \ldots 2\pi\ s\ \exp\,(-\varepsilon/kT)$ under the assumption of purely thermal freeing, is 0.34 eV which approximately corresponds to the most representative traps in the green thermoluminescence of the investigated phosphor. The depths of traps calculated from thermoluminescence for $\lambda = 525$ nm are given in Table I.

TABLE I

Depths of traps in ZnS-Cu $2 \cdot 10^{-5}$ g/g phosphore calculated from photo-thermoluminescence for $\lambda = 525$nm

Max. temp.	eV
−150°C	0.256
−110°C	0.339
+30C	0.610

A characteristic feature is that the peak which rapidly grows with increasing voltage corresponds to deeper traps occurring in this phosphor. In connection with the results of Neumark [19] one could think that only electrons freed from deeper traps in ZnS-Cu are "completely free" to move and may be accelerated to optical energies by the electric field.

The low-temperature peak seems to have at least two components which grow differently with increasing voltage and frequency (Figs 5–7). The growth of the highertemperature part is slower when the voltage increases but is faster when increasing the frequency, than the growth of the remaining component.

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If this component is also ascribed to electron traps, then under the assumption of purely thermal freeing of electrons we would obtain a depth of traps $\varepsilon = 0.22–0.24$ eV which together with the shift of the maximum towards lower temperatures with increasing voltage suggests a contribution of electric energy in addition to thermal energy, in the process of freeing of electrons from traps.

It is probable, however, that a small shift of the low-temperature peak with increasing voltage is also due to the increase in the number of non-radiative transitions even at such low temperatures. It follows from Fig. 10 that the ageing of the phosphor gives rise not only to a decrease in the high-temperature peak but also to a shift of both peaks towards lower temperatures.

The rapidly grows of low-temperature part of the $B = f(T)$ curve, with voltage, is probably connected with the increase in the probability of excitation of centres in the strong field region.

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