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ELECTROLUMINESCENCE OF ZnS-Cu, ZnS-Cu-Pb and ZnCdS-Cu

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Basing on results of author and on the concept of electroluminescence mechanism deriving from a Mott-Schottky type potential barrier and electron traps, an explanation is proposed of the effect of the exciting field's frequency on the electroluminescence intensity distribution in all three groups of luminophors investigated *i. e.* on the change in colour from green to blue in ZnS-Cu, the slight shift of the green band towards shorter wavelengths in ZnS-Cu-Pb, and the hardly perceptible change from green to blue in ZnCdS-Cu.

The phenomenon of ageing of luminophors in the process of light emission is investigated and discussed in detail.

A discussion is given of the electroluminescence mechanism and the experimentally measured low energy yield related thereto.

Introduction

According to Piper and Williams' definition (1958), electroluminescence is light emission resulting from the effect of a potential difference applied to the luminophor. Electroluminescence of ZnS-Cu under the effect of an *AC* electric field was first observed by Destriau (1936), who applied *AC* voltage to the electrodes of a plane condenser after filling the space to the them with a suspension of the luminophor in a liquid dielectric (castor oil). Since then, electroluminescence has become the domain of increasingly numerous research workers. Just as other newly detected phenomena, it had to be investigated from the foundations. The work carried out by Destriau (1953), Gumlich (1953), Gobrecht, Hahn and Gumlich (1954) and other has shown convincingly that electroluminescence is a primary effect, in that light emission by the luminophor is a direct result of the *AC* voltage applied to it. Simultaneously, technological processes were worked out for obtaining luminophors yielding electroluminescence emission. In this field, besides the authors already mentioned, considerable progress is due to Zalm, Diemer and Klasesns (1954), Diemer (1955), Homer, Rulon and Butler (1953), Froelich (1953) and many others. An obstacle arose owing to the fact that luminophors with good photoluminescence properties failed to exhibit electroluminescence. Indeed, it was not known that the effect hinged on an appropriately high activator concentration, as the latter has to form a very thin layer of a distinct Cu_2S

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phase around the elementary crystals of ZnS-Cu. Such luminophors, exhibiting gray colouring owing to the presence of Cu_2S, are in some cases able to produce electroluminescence. Electroluminescence was investigated in its dependence on the voltage applied (Destriau 1947), (Lehmann 1955), on the frequency of the exciting field (Jerome and Gungle 1953), (Waymauth 1953) and on the temperature (Gumlich 1953), (Haake 1955), (Mattler 1954) *et al.*

Particular stress was laid on the shape of the curve representing the dependence of the emitted luminescence on the changes of voltage with time — the so-called brightness wave (Destriau 1955), (Georgobiani and Fok 1960). As a matter of fact, the light of luminescence excited with an AC field is pulse-form. Brightness waves excited with a sine field or with rectangular pulses are not regular but present perturabtions; they reproduce neither the sine nor the rectangular pulse.

We have a problem that is of the highest importance from the point of view of the mechanism of electroluminescence.

As the experimental results became more and more numerous, various authors proceeded to the elaboration of a light emission mechanism basing on solid state theory and on that of semiconductors. In this respect one should cite Destriau and Ivey (1955), D. Curie (1952, 1953), Piper and Williams (1952, 1955, 1958), Fok (1960, 1961), Bonch-Bruyevich (1962), and others.

The aim of this paper consists in:

1. An investigation of electroluminescence in the luminophors produced by this author in this dependence on the voltage and on the frequency of the exciting field, taking into consideration aspects not discussed hitherto;
2. An investiation of the ageing effect taking place in the luminophor in the process of light emission;
3. An attempt to provide a theoretical interpretation of the experimental results obtained, basing on the concept of a potential barrier and electron trap mechanism.

All three kinds of luminophor were produced by the method already described (Ostaszewicz 1963). ZnS-Cu and ZnS-Cu-Pb luminophors were sintered at a temperature of (980 ± 10)°C, whereas ZnCdS-Culuminophors — with regard to the higher volatility of CdS — at (900 ± 10)°C. Also, the reader is referred to that paper for the method of preparing the electroluminescence cell, the method of investigating the intensity distribution, and the spectral dependence of ZnS-Cu electroluminescence on the copper content of the luminophor.

1. Dependence of electroluminescence on the voltage

We investigated the dependence of the electroluminescence on the voltage in the following luminophors:

11 — $ZnS+7.8\cdot10^{-4}$ g Cu per 1 g ZnS,
11 — 1 — $ZnS+12.2\cdot10^{-4}$ g Cu per 1 g ZnS,
I — 3 $ZnS+8\cdot10^{-4}$ $Cu+6\cdot10^{-3}$ g Pb per 1 g ZnS,
II — 2 — 90% ZnS+10% $CdS+7.8\cdot10^{-4}$ g Cu per 1 g of the basic substance, in the

form of a suspension in castor oil[1] at the appropriate optimal weight ratio (the suspension resembled dense cream).

The electroluminescence cell had the shape of a disk of radius 1.8 cm and total thickness 0.05 mm with a 0.02 mm protective mica layer.

Two kinds of dependence had to be investigated here, namely:

a. that of the spectral intensity distribution on the voltage,

b. that of the luminance on the voltage.

a) In order to establish the dependence of the spectral intensity distribution on the voltage, we employed an *ИСП*-51 glass three-prism spectrograph with *M*-12-*S* photomultiplier and amplifying device[2]. Investigation dealt with luminophors 11, I-3 and I-2. The intensity distributions as obtained *versus* the wavelength are shown in Figs 1*a*, 1*b* and 1*c*. All three types luminophors are seen to present similar and dissimilar properties with respect to the voltage-dependence of their electroluminescence intensity distribution.

The similarities are these:

1. With increasing voltage, the over-all (total) intensity of electroluminescence increased more strongly than linearly up to a voltage of 900 V. This ceased to be the case in luminophor II-2 at the higher voltage of 1100 V.
2. The maxima of the intensity distribution curves do not shift with increasing voltage.

The dissimilarities reside in the shape of the intensity distribution curves, beginning with curve *2* in all three diagrams. Luminophor 11 yielded two emission bands: a weak blue band with maximum at 4545Å, and an intense green band with maximum about 5270 Å. Luminiophor I-3 yielded only the green band with maximum abount 5270 Å. Luminophor II-2 gave a wide band with two maxima at 5050 Å and 5200 Å whose width at half-height was much greater than that of the remaining luminophors.

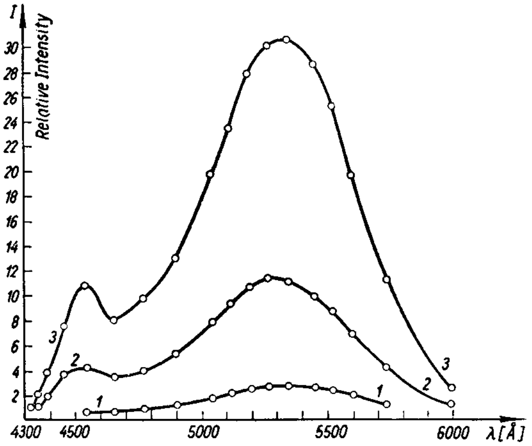

Fig. 1*a*

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[1] All quantitative results presented in this paper have been obtained with luminophors suspended in castor oil.

[2] All spectral investigations were carried out with the same apparatus.

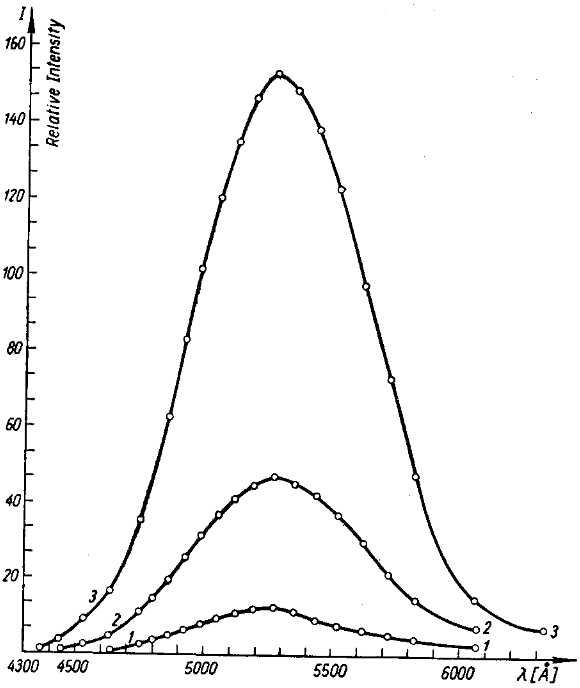

Fig. 1*b*

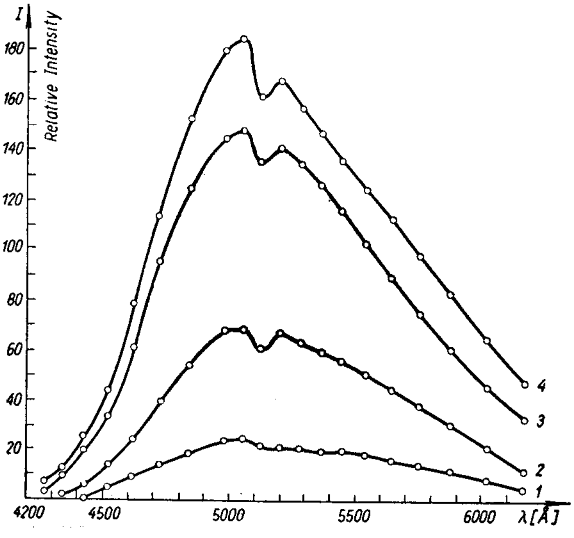

Fig. 1*c*

Figs 1*a*, 1*b* and 1*c*. Electroluminescence intensity distribution *versus* the voltage
1*a* — luminophor 11 ν= 200 Hz, 1 — 350 V, 2 — 500 V. 3 — 700 V
1*b* — luminophor I — 3 ν= 500 Hz, 1 — 400 V, 2 — 600 V, 3 — 800 V
1c — luminophor II-2, ν = 300 Hz, 1 — 500 V, 2 — 700 V, 3 — 900 V, 4 — 1100 V

b) To investigate the depencence of the luminance of the electroluminescence cell on the voltage, we used a photoelectric cell whose window in the form of a spherical sement can be considered as a directionally reflecting surface and which was placed ar a distance of some 10 to 20 mm from the electroluminescence cell. We measured the illumination intensity on the surface of the photoelectric cell's window, a quantity related to the luminance of the surface by the formula (Oleszyński 1957)

$$L = \frac{E\varrho}{\pi} \tag{1.1}$$

(L — the luminance of the surface of the window, E — its intensity of illumination, ϱ — its reflection coefficient). On the other hand, the luminance L of a directionnally reflecting surface — in our case the window of the photoelectric cell — is related to that of the light source illuminating the surface, L', *i.e.* the luminance of the electroluminescence cell, as follows:

$$L = L'\varrho. \tag{1.2}$$

Eqs (I, 1) and (I, 2) yield

$$L' = \frac{E}{\pi}. \tag{1.3}$$

Thus, measurement of the illumination intensity of the photoelectric cell's window yields the luminance of the electroluminescence cell. The latter quantity will be henceforth denoted by B.

The apparatus for comparative luminance measurements was in accordance with diagram of Fig. 2. The light receiver consisted of an *MKGS* type photocell (factory number 29031) of sensitivity 191 $\frac{A}{lm}$ for white light with a galvanometer of type *GES* 2—*C* 2 of sensitivity $C = 3 \cdot 10^{-8}$ A per scale unit.

Investigation covered the voltage range 400—1200 V for luminophor 11—1, 500—1500 V for I—3, and 500—1100 V for II—2.

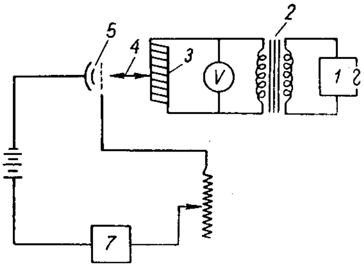

Fig. 2. Arrangement for investigation of electroluminescence luminance. 1 — *RC* acoustic generator, 2 — high voltage transformer, 3 — electroluminescence cell, 4 — distance between electroluminescence cell and photocell, 5 — photocell, 6 — 80 V supply, 7 — light spot galvanometer, V — valve voltmeter

The dependence of $\log B$ (the luminance) on $\frac{10}{V}$ (with V denoting the applied voltage) is shown in Figs 3*a*, 3*b* and 3*c*, whence the theoretical formula proposed by Zalm and co-workes (1955) and by Taylor and Alfrey (1955) for voltages up to 1000 V,

$$B = A \exp\left(-\frac{b}{\sqrt{V}}\right) \tag{1.4}$$

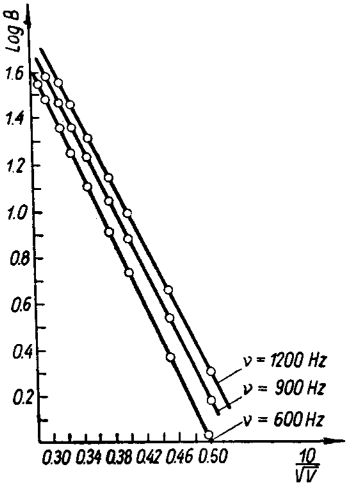

Fig. 3*a*

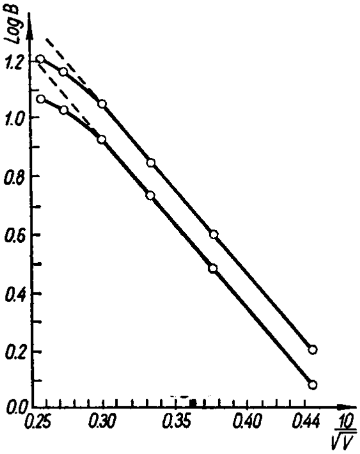

Fig. 3*b*

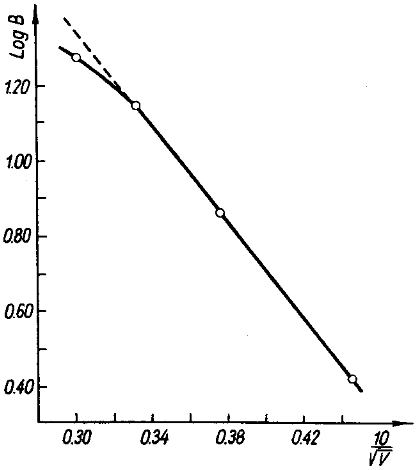

Fig. 3*c*

Figs 3*a*, 3*b* and 3*c*. Luminance log *B* of electroluminescence cell *versus* the voltage
3*a* — luminophor 11-1,
3*b* — luminophor I-3, I — 300 Hz, II — 600 Hz,
3*c* — luminophor II-2, ν= 300 Hz

is seen to be confirmed very satisfactorily by the experimental results (B — luminance, A and b — constants, V — applied voltage). Indeed, Eq. (1.1) is fulfilled for luminophor 11—1 up to 1200 V, for luminophor I—3 up to 1100 V, the two last points corresponding to 1300 and 1500 V revealing some divergence from linearity, while for luminophor II—2 the last point, which corresponds to 1100 V, deviates from the straight line.

2. *Dependence of electroluminescence on the frequency of the exciting field*

Even from a merely empirical point of view the problem of the dependence of electroluminescence on the frequency of the exciting field has not been hitherto dealt with adequately in the literature. Consequently, we destined as many as eight luminophors for this investigation, so as to avoid leaving some important detail unnoticed:

11 — $ZnS+7.8\cdot10^{-4}$ g Cu per 1 g ZnS[3]
11—1 — $ZnS+12.2\cdot10^{-4}$ g Cu per 1 g ZnS
12 — $ZnS+15\cdot10^{-4}$ g Cu per 1 g ZnS
I—1 — $ZnS+8\cdot10^{-4}$ g $Cu+2\cdot10^{-3}$ g Pb per 1 g ZnS
I—2 — $ZnS+8\cdot10^{-4}$ g $Cu+4\cdot10^{-3}$ g Pb per 1 g ZnS
I—3 — $ZnS+8\cdot10^{-4}$ g $Cu+6\cdot10^{-3}$ g Pb per 1 g ZnS
I — 4 — $ZnS+6.2\cdot10^{-4}$ g $Cu+4\cdot10^{-3}$ g Pb per 1 g ZnS
II—2 — $90\%\,ZnS+10\%\,CdS+7.8\cdot10^{-4}$ g Cu per 1 g of the basic substance.

As in the preceding Section, we investigated two kinds dependence:

1. The intensity distribution *versus* the excitation frequency.
2. The luminance *versus* the excitation frequency.

1.a) ZnS—Cu luminophors *i.e.* 11, 11—1 and 12.

The experimental results are given in Figs 4*a*, 4*b* and 4*c*, whence the electroluminescence intensity distribution is seen to vary differently in each luminophor according to the excitation frequency. Luminophors 11 and 11—1 show two distinct emission maxima: the one blue and weaker at 4555 Å, the other stronger and green at 5270 Å. In luminophor 11—1 the intensity almost achieves saturation at a frequency of 2000 Hz, whereas in luminophor 11 there is no sign of this even at 2500 Hz. This is probably due to the fact that luminophor 11—1 was sintered twice.

The intensity distribution of luminophor 12 exhibits the outline of a weak blue maximum at about 4700 Å and at much higher frequencies upward of 6000 Hz there is a well-defined shift of the maximum of the principal green band towards shorter wavelengths to 5050 Å. Also, electroluminescence intensity almost achieves saturation.

Quite generally, in the case of all luminophors of the present section, a rise in excitation frequency is accompanied by an increase in intensity in the short wavelength region causing electroluminescence to change from green to blue.

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[3] The coper concentration in all luminophors is the real value as measured polarographically by the method already described (Ostaszewicz 1963).

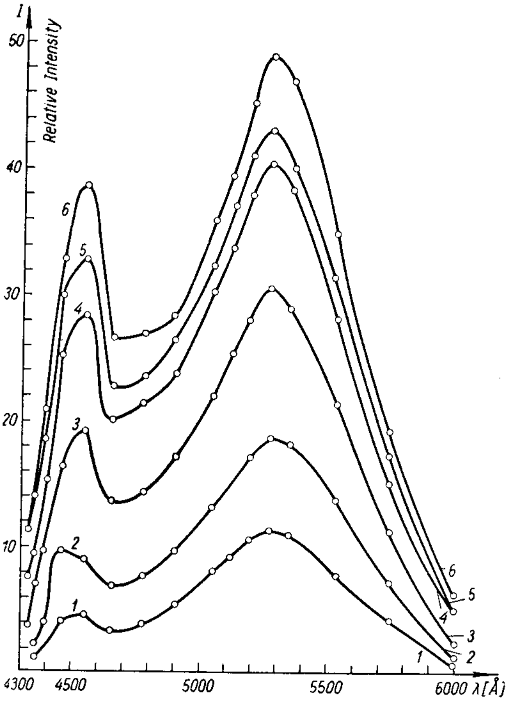

Fig. 4*a*

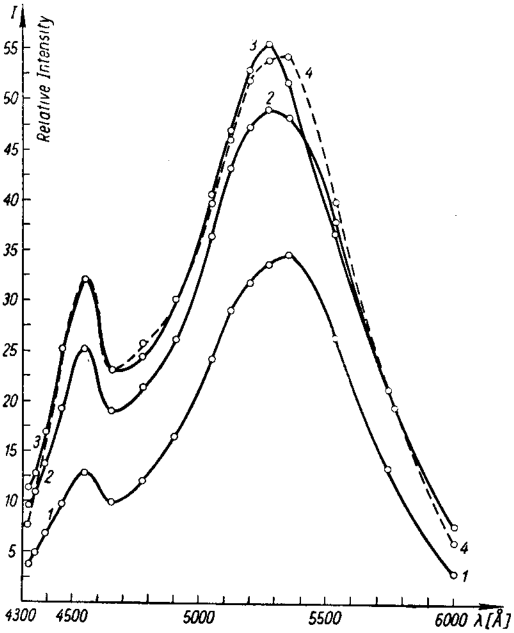

Fig. 4*b*

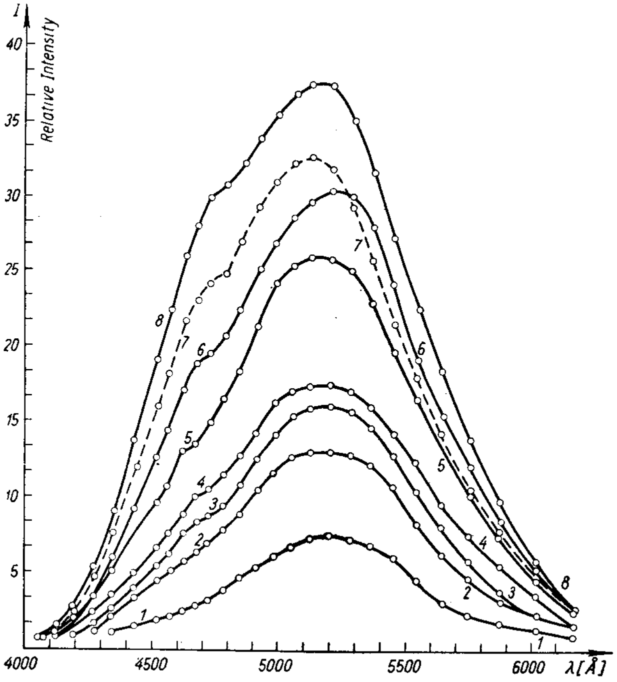

Fig. 4*c*

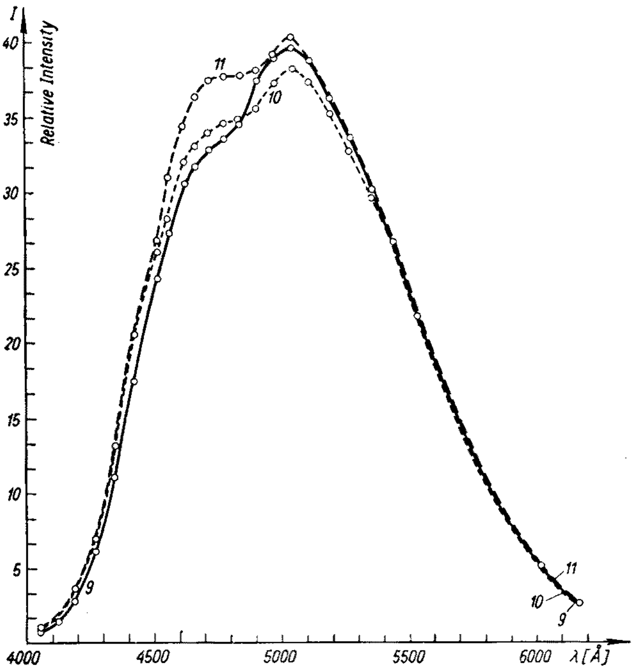

Fig. 4*d*

Figs 4*a* and 4*b*. Electroluminescence intensity distribution *versus* the exciting frequency
4*a* — luminophor 11, $U = 500$ V, 1 — 200 Hz, 2 — 500 Hz, 3 — 1000 Hz, 4 — 1500 Hz, 5 — 2000 Hz, 6 — 2500 Hz
4*b* — luminophor 11-1, $U = 550$ V, 1 — 500 Hz, 2 — 1000 Hz, 3 — 1500 Hz, 4 — 2000 Hz
Figs 4*c* and 4*d*. (continued) luminophor 12 U = 300 V, 1 — 250 Hz, 2 — 500 Hz, 3 — 750 Hz, 4 — 1000 Hz, 5 — 1500 Hz, 6 — 2000 Hz, 7 — 3000 Hz, 8 — 4000 Hz, 9 — 6000 Hz, 10 — 8000 Hz, 11 — 10000 Hz

According to the results of *X*-ray investigations[4], these luminophors have the wurtzite structure and consequently contain two kinds of copper luminescence centres, blue and green (Zhyrov 1940). Thus, two bands appeared here, a blue band with maximum at 4545 Å and a green band with maximum at 5270 Å.

As seen from the graphs obtaines for luminophors 11 and 11—1, with increasing excitation frequency the height of the blue band's maximum increases by a larger amount than of the green band. Electroluminescence changes accordingly from green to blue. In order to achieve better understanding of the phenomenon, it is worth while to give some thought to the blue and green luminescence centres.

According to Riehl and Ortmann (1959), both kinds consist of copper ions, albeit differently built into the crystal lattice. They consider that the blue centre is rendered by the model of a Cu^+ ion at an interstitial site beside Cu^+ at a node. Electrically, the two

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[4] The author is indebted to Professor W. Trzebiatowski at whose Institute the *X*-ray investigations were effected.

copper ions together are equivalent to one Zn^{++} ion. The model of a green centre is given by a Cu^{+} ion at a node replacing Zn^{++} (Fig. 5). To conserve equilibrium of the electrical charges, a Cl^{-} ion builds in together with the Cu^{+} ion in place of S^{--}. Riehl and Ortmann were able to determine the energy of transition of one kind of centres into the other, which amounted to 03.8 eV.

Blicks *et al.* (1961) considered the transition of blue into green centres and inversely on the basis of Riehl and Ortmann's model, obtaining a dissociation (association) energy of 0.38 eV.

The above values for the transition energy were derived along lines having nothing to do with electroluminescence. In the present investigation, from our experimental results, we obtained a values of 0.375 eV for the separation of the levels of the blue and green centres.

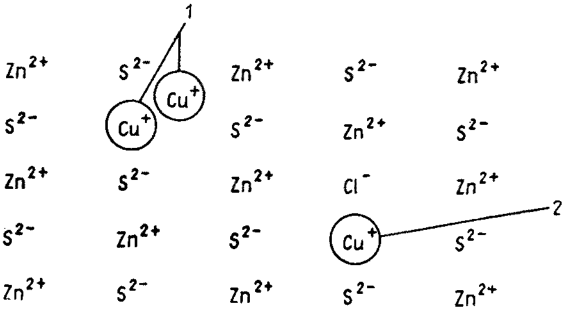


Fig. 5. Diagram of blue and green luminescense centres in ZnS-Cu (according to Riehl and Ortmann 1955); 1 — blue centre (Cu^{+} at interstitial site beside Cu^{+} at node), 2 — green centre (Cu^{+} at node)

From theoretical considerations (G. Curie and D. Curie 1960), the levels of the blue and green luminescence centres can be represented by means of band diagrams as done in Figs 6*a* and 6*b*. That of Fig. 6*a* gives a direct transition of electrons from the conduction band to the levels of the blue or green luminescence centres, whereas Fig. 6*b* shows direct

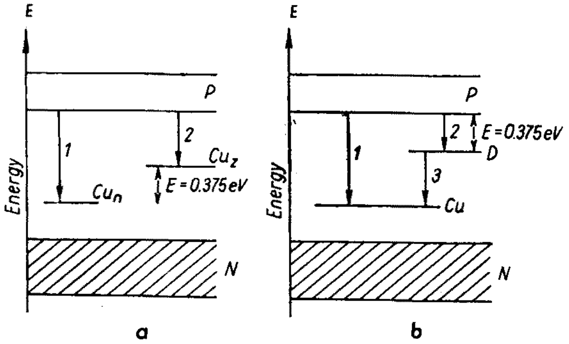


Fig. 6*a* and 6*b*. Band diagrams applied to ZnS-Cu luminophors *N* — valence band, *P* — conduction band Cu_n — level of blue centres of copper, Cu_z — level of green centres of copper, Cu — level of copper and at the, same time acceptor level, *D* — donor level

transition for the blue band and indirect transition over the donor level — which is simultaneously the level of electron traps — to the green band.

With regard to electroluminescence phenomena, the experimental results favour the diagram of Fig. 6*b*. Indeed, with increasing excitation frequency, the direct transitions prevail (indirect transitions are unable to follow the high rate of switching of the electrical field) and electroluminescence changes from green to blue.

1.b) ZnS—Cu—Pb green luminophors *i.e.* I—1, I—2, I—3 and I—4.

Luminophors of this kind are well-known in the domain of electroluminescence (Orlov 1960; Tanaka 1959). Nevertheless, it is felt that the present results may contribute towards better insight into the relationships.

To take note of various insignificant and not immediately graspable details, we carried out analogous investigations with all luminophors. The results are shown in Figs 7*a*, 7*b*, 7*c* and 7*d*. A rise in excitation frequency is seen to cause a slight shift of the entire electroluminescence spectrum towards shorter wavelengths, the amount by which it is shifted increasing with higher lead concentration in the luminophor. This effect is due to two reasons:

1. The increase in excitation frequency gives rise to electron jumps from higher energy levels of the excited state.

2. The rise in Pb concentration in the luminophor causes an increase in the internuclear distance in the excited state. A similar effect occurs in the fluorescence spectra of ZnS-Cu at higher copper concentration, as discussed in our previous paper (Ostaszewicz 1963). Neither of these two factors have been hitherto discussed in the field of electroluminescence.

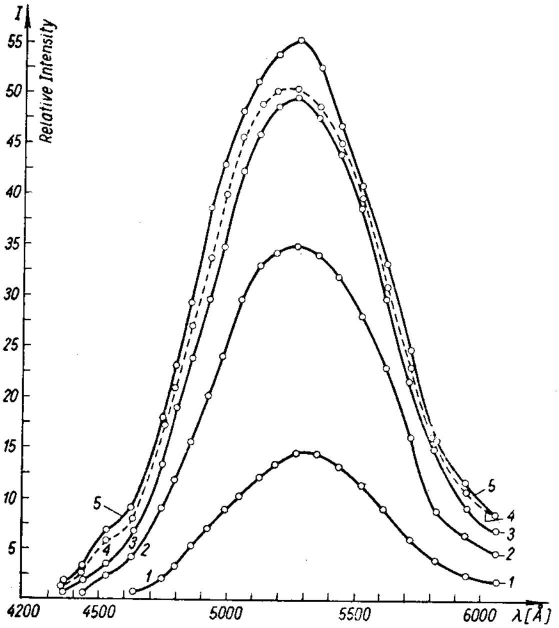
Moreover, from Fig. 7*d*, the brightness of emission from luminophor I—4 is much smaller than that of the other luminophors. This is due to the too low copper content in the one in question ($6.2 \cdot 10^{-4}$ g per 1 g ZnS). Hence, for obtaining satisfactory electroluminescence, a high content of copper in the luminophor is essential (about 10^{-3} g Cu per 1 g ZnS) even if another activator is present.

1.c) Luminophor II—2 of composition: 90% ZnS+10% CdS+$7.8 \cdot 10^{-4}$ g Cu per 1 g basic substance.

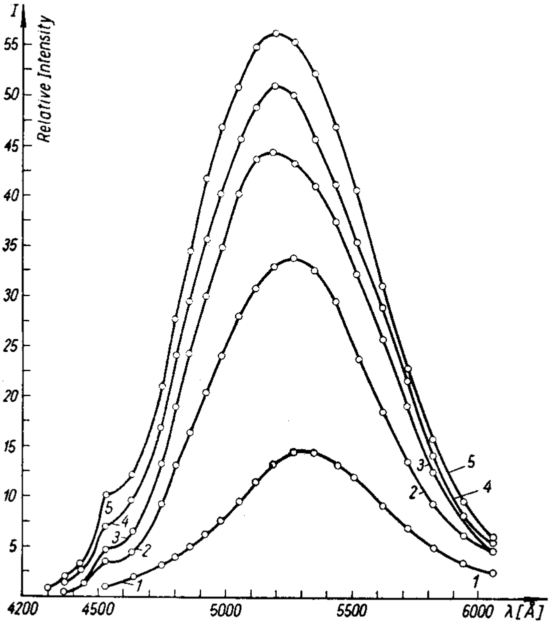
Electroluminescence of ZnCdS—Cu in an *AC* electric field is mentioned by Lehmann (1957), who states that ZnCdS—Cu yields no electroluminescence. Albeit, on mixing that luminophor with metallic copper powder of appropriate grain size, he obtained weak green electroluminescence. On illumination with light of wavelength 2537 and 3650 Å, the luminophor yielded yellow fluorescence.

Luminophor II—2 was prepared by the sintering method described in Section 1, at 900° C *i.e.* at a temperature somewhat lower than the remaining luminophors because of the greater volutility of CdS as compared with ZnS (Zhyrov 1940).

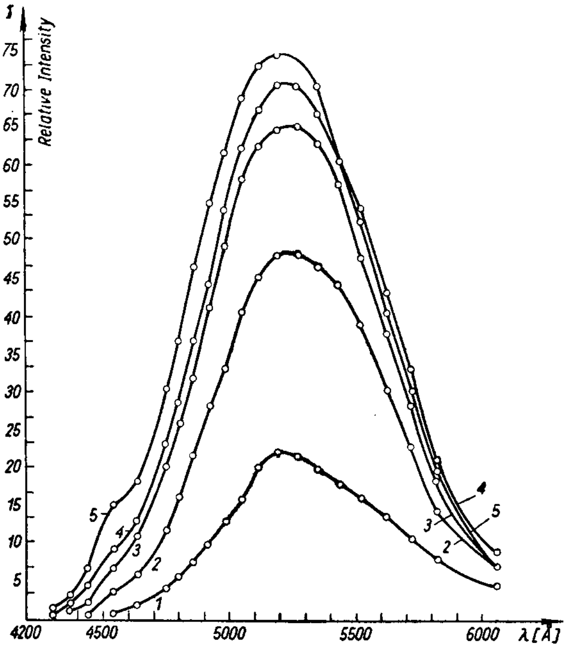
The intensity distribution was investigated with an *AC* field of the same order of frequency as used in the case of ZnS—Cu. Sufficiently intense electroluminescence was obtained, comparable with the green emission of ZnS—Cu. The intensity distribution *versus* the excitation frequency is given in Fig. 8, where the shape of the curves is seen to vary, an increase in the frequency causing an increase in the intensity maximum situated at 4980 Å which falls steeply towards shorter wavelengths at all frequencies considered whereas towards



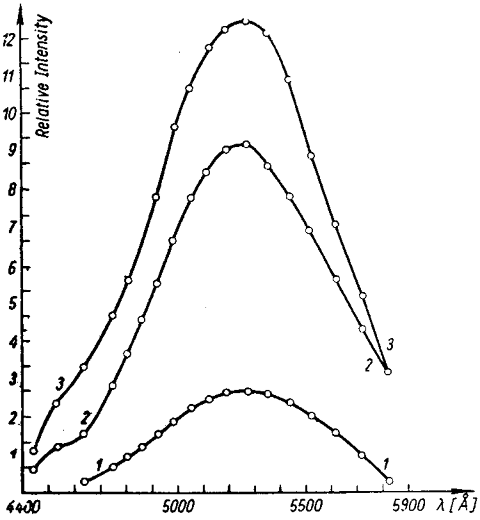
Figs 7*a*, 7*b*, 7*c* and 7*d*. Electroluminescence intensity distribution *versus* the exciting frequency
7*a* — luminophor I-1 $U = 420$ V, 1 — 200 Hz, 2 — 500 Hz, 3 — 1000 Hz, 4 — 1500 Hz, 5 — 2000 Hz



7*b* — luminophor I-2 $U = 320$ V 1 — 200 Hz, 2 — 500 Hz, 3 — 1000 Hz, 4 — 1500 Hz, 5 — 2000 Hz



7c — luminophor I-3 $U = 400$ V 1 — 200 Hz, 2 — 500 Hz, 3 — 1000 Hz, 4 — 1500 Hz, 5 — 2000 Hz



7d — luminophor I-4 $U = 670$ V 1 — 200 Hz, 2 — 500 Hz, 3 — 1000 Hz longer wavelengths at lower frequencies the steepness is small and at higher frequencies much greater. Owing to this, electroluminescence turns blue towards higher frequensies.

In contradistinction to luminophors of the other groups, there is no displacement of the electroluminescence intensity maximum towards shorter wavelengths with increasing frequencies of excitation. It is noteworthy that in luminophor II—2 the shape of the curves of the intensity distribution *versus* the frequency at constant voltage (Fig. 8) and *versus* the voltage at constant frequency (Fig. 1*c*) varies differently. In the first case it is the maximum at 4980 Å that increases more, whereas in the second case the two maxima at 5050 Å and 5200 Å increase uniformly.

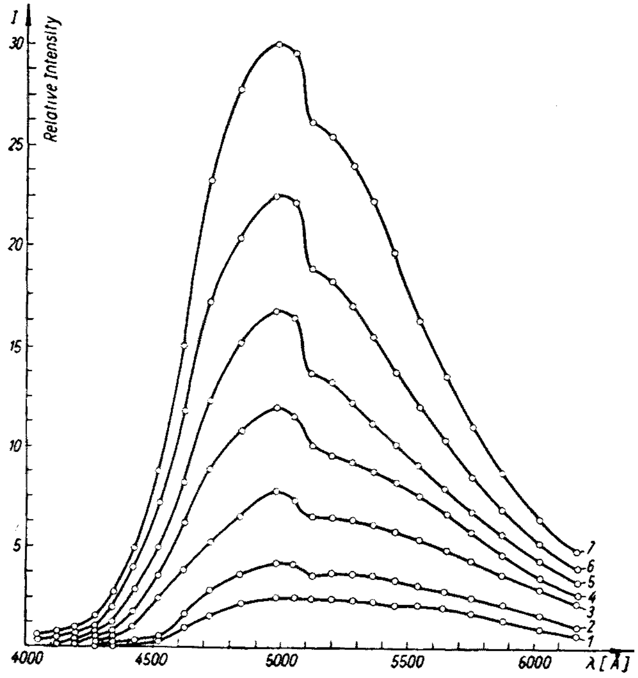


Fig. 8. Electroluminescence intensity distribution *versus* the excitation frequency
Luminophor II-2 $U = 500$ V 1 — 250 Hz, 2 — 500 Hz, 3 — 1000 Hz, 4 — 2000 Hz, 5 — 3000 Hz, 6 — 4000 Hz, 7 — 5000 Hz

2. The dependence of the luminance on the frequency of the exciting field was investigated by Diemer (1955), Zalm and co-workers (1955), and many other, using fields of relatively low frequencies up to 2 or 3 kHz. Let us consider this problem more closely.

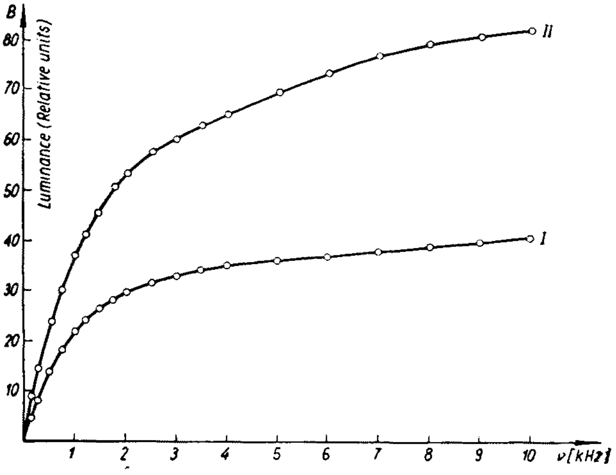
D. Curie (1953) derived a theoretical formula for the dependence of the luminance on the excitation frequency, on the assumption that electrons recombine with luminescence centres according to bimolecular law as appropriate for ZnS. His formula was of the form

$$B = \frac{Kn_0^2a}{1 + \frac{n_0a}{2f}} \tag{2.1}$$

with B denoting the luminance, K — a coefficient, n_0 — the initial electron concentration in the conduction band, a — the recombination coefficient defined by the equation $dn/dt = -an^2$, and f — the frequency of excitation. In accordance with Eq. (II, 1), a being large with regard to f, the luminance should be proportional to f, as is usually the case. If the excitation frequency is sufficiently high, $n_0a/2f \ll 1$ and a state of saturation results, again in agreement with experiment. D. Curie based the above results on elementary considerations and specifically stated that n_0 could not be independent of the frequency of excitation.

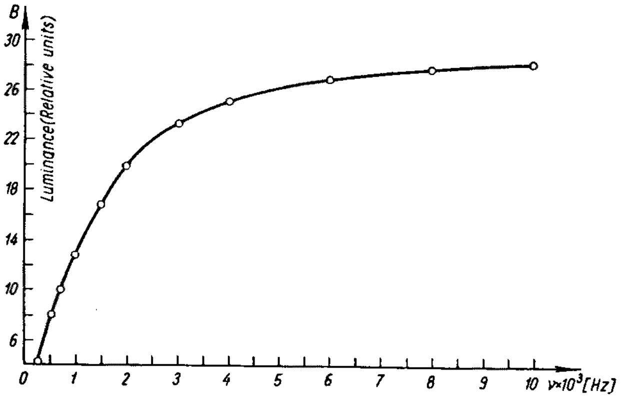
We investigated the dependence of the luminance on the exciting field frequency for three luminophors, namely 12, I—3 and II—2. Two methods were applied.

In the case of luminophor I—3 whose intensity distribution *versus* frequency curves hardly vary at all, we applied the arrangement shown in Fig. 2 and measured the luminance with a photoelectric cell and light spot galvanometer, at the two voltages of 200 and 250 V in the frequency range 250—10000 Hz. The results are given in Fig. 9*a*. At lower frequencies (up to 2 kHz) the luminance is seen to increase almost linearly with the frequency. As the frequency rises, the luminance curve approaches saturation, the latter being more marked at lower voltages (curve I).

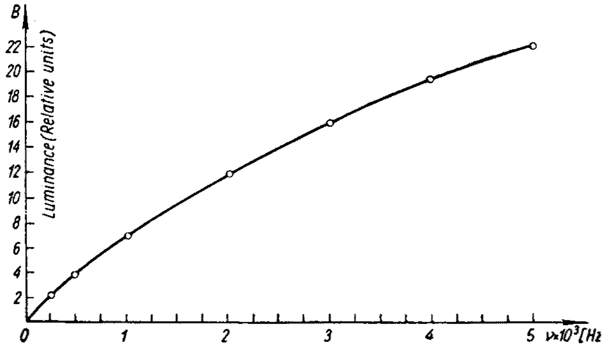


Figs 9*a*, 9*b* and 9*c*. Luminance B of electroluminescence cell *versus* the excitation frequency
9*a* — luminophor I-3 I — $U = 200$ V, II — $U = 250$ V

In the case of luminophors 12 and II—2 we were not in a position to apply this method for determining the dependence of the luminance of the excitation frequency since here the shape of the intensity distribution curves changed markedly with the frequency and the sensitivity of the photoelectric cell was not the same for different spectral regions. Thus, we determined the luminance *versus* the frequency from intensity distribution curves recorded for various frequencies as shown in Figs 4*c* and 8. The luminance is given by the area between the coordinate axes (λ, I) and the distribution curve. The areas were determined



9*b* — luminophor 12 $U = 300$ V



9*c* — luminophor II-2 $U = 500$ V

planimetrically. The results are given in Figs 9*b* and 9*c*. From Fig. 9*b*, the luminance of luminophor 12 is seen to rise almost linearly with the frequency of excitation and tends markedly to saturation above 5000 Hz.

In the case of luminophor II—2 (Fig. 9*c*), in contradistinction to the others, no steep increase in luminance is observed with growing frequencies in the initial stage; neither is there a tendency to saturation at higher exciting frequencies. (In this luminophor, with regard to investigation at higher voltages, we were unable to exceed 5000 Hz). It is noteworthy that the 10% addition of CdS to ZnS in this luminophor affected both the intensity distribution curves and the luminance *versus* exciting frequency curves. This aspect had been unknown in the literature.

3. *Investigation of luminance decay in the electroluminescence cell during operation*

Both scientifically and practically it is highly important to establish the relationship between the luminance and time of light emission by the cell. According to the results published by various authors, the luminophor exhibits ageing. The first to draw attention to this was Destriau (1947). By his results, ageing of an operating ZnS—Cu luminophor takes place only if the cell is excited at high voltages of 400—1000 V. Thornton (1957) applied cells with various dielectrics (plastic, air, vacuum) when investigating ageing, and obtained results in agreement irrespective of the dielectric used. He noticed that luminance decreased more rapidly at excitation with higher frequencies.

Roberts (1957) went far in his investigation of ageing in ZnS—Cu luminophors durimg emission of electroluminescence. He applied various solid dielectrics in thick and thin cells and excitation with higher and lower voltages of various frequencies. He was able empirically to establish the following relation between the luminance and the time of light emission:

$$B = \frac{B_0}{1 + \frac{t}{t_c}} \tag{3.1}$$

with B denoting the luminance at the moment of observation, B_0 — its initial value beginning from which descrease was slow, t_c — the time interval during which luminance decreased by a half, and t — the time of light emission by the cell.

The time of steep increase in luminance and of its rapid decrease after attaining its maximum value omited. Roberts excludes any harm to the dielectric; neither does he admit electrochemical interaction with the luminophor. He attributes the effect of ageing of the luminophor to changes occuring therein. It is his suggestion that the decrease in luminance is due to a decrease in the number of donors in the region of high electric field strength raising the ion mobility.

In dealing with this problem, we applied the device of Fig. 2, where the light was incident on a photocell connected with a light spot galvanometer. (In the luminance range and spectral distribution considered, the photocell did not exhibit fatigue.) We effected a number of measurements in different settings. In the case of several luminophors, we applied solid and liquid dielectrics in thicker or thinner cells which were excited with higher or lower voltages at various frequencies. The results are exemplified in Figs 10*a* and 10*b*.

The results are seen to vary according to the conditions of excitation — the field strength applied being essential. The thickness of the cells of Figs 10*a* and 10*b* was identical. A comparison of the voltages and frequencies apllied to the cells shows that the field strength in the cell whose luminance is given by Fig. 10*a* was considerably higher than that in the cell of Fig. 10*b*. Accordingly, the intense luminance of the former attains its maximum after 10 min[5], retaining 76.5% of its maximum value after 150 min. The latter cell, of much lesser luminance, attained its maximum after 5 hrs; after 70 hrs, luminance remained at 82% of its maximum value.

We drew the following conclusions from the experiments:

1. In the process of electroluminescence emission, the luminance of the cell decreases.
2. The rate of luminance decay is closely related with the maximum luminance of the cell: The greater the luminance, the steeper is its decay.

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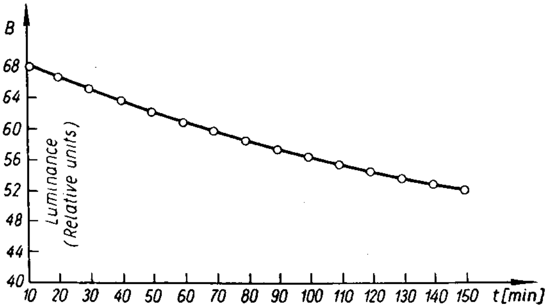
[5] Account was taken in these experiments of inertia of the galvanometer.

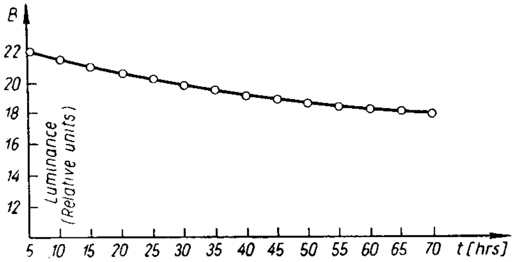
3. At higher frequencies of the field applied to the cell, the rate of luminance decay is higher.

4. The absolute value of the voltage applied has no influence on the rate of decay of luminance; albeit, the phenomenon is closely related with the electric field strength applied. It is the latter that determines the fall in luminance.

5. In a given cell, electroluminescence is an irreversible process, admitting of no regeneration. In this respect electroluminescence resembles phosporescence, which continues until all the electron traps are emptied, and the brighter the emission of a luminophor the more rapid is its decay, since the number of trapped electrons is finite.



Figs 10*a*, 10*b* and 10*c*. Luminance *B* of electroluminescence cell *versus* the time
10*a* — luminophor 11-1 $U = 400$ V, $= 1200$ Hz



10*b* — luminophor 11 $U = 400$ V, $= 400$ Hz,

It is difficult to establish the mechanism of electroluminescence decay due to the electric field, and further theoretical consideration are necessary.

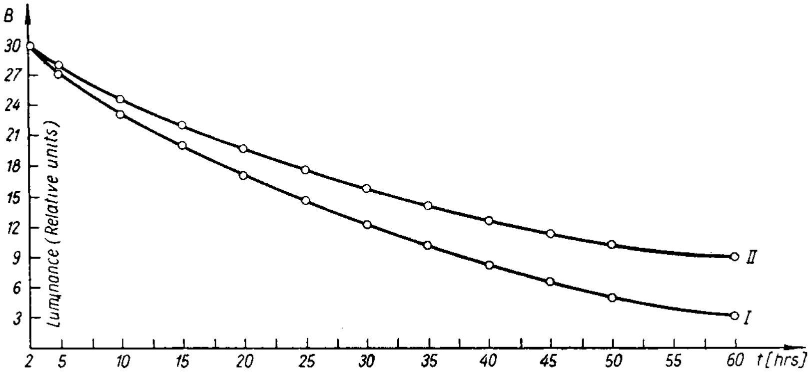
With the aim of finding out whether the electric field applied to the cell destroys the luminescence centres, we carried out the following experiment: We illuminated the electroluminescence cell with a Wood lamp during 10 min to obtain stationary luminance of fluorescence. (The needle of the galvanometer connected with the photocell which acted as receptor of the light from the electroluminescence cell assumed a position of contant deviation.) On switching off the Wood lamp, an electric field of 1200 V and 1200 Hz frequency was applied to the cell. After several hours, the luminance of the cell fell to 50% of its maximal value. On switching the field off, we again illuminated the cell with Wood's lamp. Fluorescence luminance attained its former value after exactly the same time as previously. This proves that the electric field applied to the cell had not destroyed the luminescence centres. On the other hand, we found experimentally that the emission spectra of fluorescence and electroluminescence were almost identical for a given luminophor (Ostaszewicz 1963). Differences appear only in the intensity of particular bands, according to the temperature and excitation frequency. Hence it should be assumed that the activator centres responsible for emission in either case are the same, but that the mechanism of excitation is different.

At a first glance it would seem that breakdown of the *n-p* layer contributes to the ageing effect in the luminophor. Accelerated electrons then collide with holes and are thus unable to recombine with ionized luminescence centres. This suggestion, however, should be rejected, since breakdown of the *n-p* layer requires a well-defined limit voltage (Vul 1956), whereas the luminophor exhibits ageing at whatever voltage it operates. Most probably the essential factor in ageing of the luminophor resides in its light emission under the influence of the *AC* electric field. Thus, we have to consider the mechanism of electroluminescence excitation. The generally accepted mechanism is the one proposed by Piper and Williams (1955) consisting in non-elastic collision of accelerated electrons in the conduction band with luminescence centres. The cathode is usually the souce of the electrons. However, in the case of ZnS-Cu, another Cu_2S phase is present between the cathode and luminophor, enclosing the elementary ZnS-Cu crystals. According to the literature (Fok 1962) and our results, Cu_2S is the source of primary electrons transfered to the conduction band. Indeed, we found experimentally that electroluminescence can be exhibited only by luminophors having a gray coloration *i. e.* containing a second Cu_2S phase. On applying an *AC* electric field to the luminophor, electrons from Cu_2S pass through the potential barrier to the conduction band in numbers proportional to the field strength. Such electrons are lost for the Cu_2S phase.

In this manner, during light emission by the electroluminescence cell the number of electrons in the Cu_2S phase gradually decreases. When the Cu_2S phase has been stripped of its electrons — the applied electric field is sufficiently strong to provide the energy necessary for this — the luminophor is no longer able to exhibit electroluminescence.

This indeed is the essential reason of ageing. To complete the investigation of this section, we carried out yet another experiment: Two identical electroluminescence cells were prepared with luminophor 11-1, of capacity 820 pF each, the one with non-washed and the other washed luminophor. We investigated they decay of luminance of the first cell at voltage of 800 V and an exciting frequency of 400 Hz during 60 hrs on six consecutive days, for 10 hrs on each day. Then the experiment was repeated with the second cell. The results are shown in Fig. 10*c*. The maximum luminance of the two cells is seen to have been equal, but the rate of decay very different. After 60 hrs the luminance of the first cell decreased to 10% whereas that of the second cell to 30% of this maximum value. This shows that ageing of the wasned luminophor proceeded much more (slowly) than in the one that had not been subjected to washing. Besiedes, in either case, on applying the field on the next consecutive day the luminance of the cell attained its last lowest value of the previous day. This proves that no regeneration took place in the luminophor while it rested for 10—20 hrs. Moreover, in either case, in the initial stage of light emission (up to 10 hrs) the luminance decreased much more rapidly than in subsequent stages. Hence, washing the luminophor lowers its rate of ageing, but does not eliminate ageing entirely. According to Piper and Williams (1958), the reason of ageing of a luminophor in the process of light emission resides in a displacement of donors to sites neighbouring with acceptors.

Fok (1962) suggests that ageing during light emission is due to motion of ions caused by the electric field.



10c — luminophor 11-1 $U = 800$ V, = 400 Hz
Curve I — non-washed luminophor, curve II — washed luminophor

It would seem that the above arguments are less convicing than the one put forward by us, for the following reasons:

1. Electroluminescence is produced by an electric field of a sufficiently high rate of time-variability. Such a field is hardly liable to shift heavy ions.

2. Ageing of the luminophors occurred also in weak fields whose energy was insufficient for displacing the ions.

3. Shifting of ions in a „spoilt" luminophor would have to be accompanied by hanges in its fluorescence emission spectrum; no such effect was observed in the experiments.

From the above results, the electric field not only excites electroluminescence, but also causes its decay (quenches it). Bonch-Bruyevich and Marenkov (1960) as well as Rebane (1962) basing on theoretical considerations put forward the above hypotheses somewhat earlier than the present author.

4. *Attempts at a theoretical interpretation of the results obtained*

ZnS is able to exhibit luminescence in the crystalline state only. Now, two forms of crystalline ZnS exist: sphalerite, which belongs to the regular system, and wurtzite, which is hexagonal. The temperature of total transition of the two modifications lies at 1020°C (Zhyrov 1940). At lower temperatures sphalerite prevails, at higher temperatures — wurtzite. Of the luminophors whose electroluminescent properties were investiagted by us, those with ZnS-Cu had the wurtzite structure and those with ZnS-Cu-Pb — the sphalerite structure, notwithstanding the fact that they had been sintered at the same temperature of 980°C. Both modifications form crystal lattices of the ionic-covalent type (covalent bondings prevailing up to 60%) consisting of bivalent ions of sulphur and zinc. This state of affairs exists only at absolute zero. Now, at the high temperature of sintering, owing to oscillations of the lattice; zinc and sulphur ions underge diffusion producing defects in the lattice, into foreign activator and coactivator ions can get built in (Mott and Gurney 1956). Here, in the sintering process, monovalent copper ions got built into the lattice defects as activators to replace zinc ions, and monovalent chlorine ions as coactivator to replace sulphur ions.

Additionally, in the ZnS-Cu-Pb luminophors, bivalent Pb ions built in replacing zinc ions. From our experimental results it has to be assumed that copper ions got partly built into empty nodes and partly occupied interstitial sites (Riehl and Ortmann 1955). Since cooling of the luminophors proceeded rapidly, the lattice defects with built in activator and coactivator ions became „frozen".

By semiconductor theory (Ioffe 1957), copper is an acceptor and chlorine a donor. From the results assembled in Table I (Ostaszewicz 1963), the above model of a luminophor is found to be adequate for obtaining photoluminescence only. For deriving the phenomenon of electroluminescence, it is necessary *i. a.* that a second phase (Cu_2S) essential for the light emission mechanism shall be present on the surfaces of the elementary ZnS-Cu crystals. This condition was fulfilled in luminophors 9—13 owing to which they presented grey coloration. The copper content measured in them relats to both phases: Part of the copper is bult in to the crystal lattice, and part of it envelopes the elementary ZnS-Cu crystals in the form of Cu_2S.

Let us now proceed to consider the mechanism of electroluminescence in ZnS-Cu luminophors. A comparison of their fluorescence and electroluminescence emission specta shows that the maxima of the two spectra lie in the same interval of wavelengths.

One is thus induced to assume that in either case the activator centres responsible for emission are the same, but that the mechanism of excitation is different. Activator centres can be excited or ionized according to three mechanisms (Piper and Williams 1955):

1. by the direct effect of a field of very high voltage,
2. by injection of non-intrinsic charge carriers — holes, since conduction in ZnS is electronic,
3. non-elastic collisions of conduction electrons with ions of the activator as such electrons gain sufficient kinetic energy from the applied field.

The forbidden band width in ZnS-Cu amounts to 3.7 eV whereas the excitation energy for copper built into ZnS-Cu is 3 eV. Hence both Cu levels lie within the forbidden band the fundamental level above the valence band, and the excited level below the conduction band. At high voltage a system like this is unstable and breakdown takes place easily. Hence the plausible mechanism of excitation is the one stated sub 3. Here, according to D. Curie (1953), the process of electroluminescence excitation proceeds in the following three stages:

1. Transfer of electrons from the donor levels to the conduction band under the effect of the applied electric field,
2. their acceleration in the conduction band,

3. non-elastic collision of the accelerated electrons with the luminescence centres which thus undergo excitation or ionization, or with lattice ions yielding electron-hole pairs (excitons).

As sources of primary electrons available for transfer to the conduction band we have the second Cu_2S phase, donor levels of chlorine, and invested electron traps (the latter, when in a region of high field strength, act as donors of primary electrons, *cf.* Haake, 1957). Conduction electrons in the electric field are both accelerated and decelerated. However, in a sufficiently intense field,the electrons can achieve an energy that suffices for ionizing activator levels by non-elastic collision. By a formulation of Seitz (1949), in order that an electron in a field of strength $\mathcal{E}$ shall achieve an energy equal to the depth of a luminescence centre, it has to undergo acceleration along the path l. Its energy is then

$$E = e\mathcal{E}l. \tag{4.1}$$

With l_m denoting the mean free path in the direction of the field, the probability that an electron shall traverse the path l is

$$p = \exp\left(-\frac{l}{l_m}\right). \tag{4.2}$$

The probability that an electron shall gain the energy necessary for ionization is

$$p = \exp\left(-\frac{E}{l_m e\mathcal{E}}\right). \tag{4.3}$$

Such high energies cannot be achieved by a great number of electrons in fields below breakdown. Herein resides an essential cause of the low energy yield of electroluminescence. For this reason, too, electroluminescence is observed only in crystals wherein covalent bonding is prevalent. It cannot take place in ionic crystals with regard to the short free path, too short for the electrons to achieve sufficient energy for non-elastic collision with the ions of the activator (Fok 1962).

Albeit, the above mechanism presents a difficulty consisitng in the fact that breakdown occurs in fields of 10^6 V/cm, and that in fields by one order weaker the probability of accelerating electrons to very high kinetic energies is very small. On the other hand, electroluminescence is observed even in fields as low as 10^4 V/cm, emission occurring at distinct points. The above two experimential facts induce us necessarily to assume the existence within the crystal of a potential barrier wherein the local fields rise to breakdown values. Most plausible is the Mott-Schottky type exhaustion barrier involved by the difference in work function, which plays an essential part in the phenomenon of electroluminescence. This is supported by the fact that light emission in individual crystals is localized at the electrodes, whereas inside the crystal the mean field strength is small and there is no emission of light.

Let us consider more closely the Mott-Schottky type barrier (Piper and Williams 1955). The ZnS-Cu luminophor is an n-type semiconductor with high resistivity and low work function. When placed between two metal electrodes to which a potential difference is applied, the crystal is traversed by electrons which attain the anode, while the passage of electrons from the cathode into the luminophor is stopped by the potential barrier. With increasing potential difference, the field strength at the cathode increases until the barrier becomes so thin that electrons from the cathode begin to get through. At field strengths above that critical value, *DC* current will flow through the luminophor.

The field strength in a layer of space charge is given by Poisson's formula

$$\frac{dE}{dx} = \frac{4\pi Ne}{\mathcal{E}}, \tag{4.4}$$

where E is the field strength, N — the donor electron concentration, $\mathcal{E}$ — the dielectric permittivity of the semiconductor, x — the distance from the cathode, and Ne — the density of space charge in the barrier region. Integration yields

$$E(x) = \frac{4\pi Ne}{\mathcal{E}} x + C. \tag{4.5}$$

By Eq. (4.5), the field strength in the barrier varies linearly with the distance from the cathode.

For the boundary conditions $E(d) = 0$ (here d is the width of the barrier) the field strength is given by

$$E(x) = \frac{1}{2} A^2(x-d), \tag{4.6}$$

with

$$A = \left(\frac{8\pi Ne}{\mathcal{E}}\right)^{1/2}.$$

The potential of the field at the point x amounts to

$$V(x) = -\int_x^d E(x)dx = \frac{1}{4} A^2(d-x)^2, \tag{4.7}$$

From (4.6) and (4.7), we have

$$E(x) = A[V(x)]^{1/2}. \tag{4.8}$$

Let V_0 denote the potential of an electron near the cathode, with respect to the anode; in Eq. (4.6), we now have $x = 0$ and a comparison of (4.6) and (4.8) yields

$$d = \frac{2V_0^{1/2}}{A}. \tag{4.9}$$

Consequently, as the applied potential difference increases, the barrier widens and the field strength in the barrier grows as the root of the voltage applied.

If *AC* voltage is applied to the electrodes, the layers of the luminophor neighbouring on the electrodes will be emptied of an filled with electrons periodically. Electron traps if present in a region of the field with low field strength will capture electrons during their return towards the traps, whereas if in a region of high field strength will act as electron donors. If the donor levels are at various depths, below the conduction band, the field will also ionize the deeper ones. Conduction electrons set free from the deeper donor levels will now move with acceleration in the field attaining high kinetic energy. This means they will gain energy at a higher rate than they can transmit energy to the lattice for phonon emission. At energies above 3 eV, they will be able to excite the Cu luminescence centres, whereas if their energy rises above 3.7 eV they will be able to raise valence electrons to the conduction band. The holes left by the latter will ionize luminescence centres. Subsequent capture of electrons from the conduction band by luminescence centres lead to emission of light. Indeed all conduction electrons absorb energy from the electric field, but only those that the field sets free from the deepest donor levels are liable to be sufficiently highly accelerated by the field for exciting the luminescence centres by way of non-elastic collision. Hence the energy yield of electroluminescence is relatively small and we can see no conceivable way of raising it. At *AC* voltage applied to the electrodes, the width of the Mott-Schottky barrier attains its maximum for each electrode when the maximum negative voltage is applied to it. As the negative potential decreases, the barrier's width diminishes, while the barrier near the other electrode grows. The deep donor levels are emptied during that phase of the excitation cycle during which the barrier width increases maximally. As already stated, electrons or holes present in the barrier region can be accelerated up to high kinetic energies. An accelerated charge can recombine with an ionized activator centre leading to the phenomenon of electroluminescence.

5. *Results*

The experimental results of this investigations prove that in all three groups of luminophors — ZnS-Cu, ZnS-Cu-Pb, and ZnCdS-Cu — the spectral distribution of electroluminescence does not depend on the voltage at constant frequency of the exciting field. On the other hand, if the frequency is varied at constant voltage, the spectral distribution is found to change in a manner characteristic for each group.

Thus, in the group of ZnS-Cu luminophors, with increasing excitation frequency, the intensity of the blue electroluminescence band increases much more strongly than that of the green band; this is so because, as the electric field changes its direction at an increasingly high rate, direct transitions prevail since indirect transitions cannot keep pace with the field.

In the ZnS-Cu-Pb group, with increasing frequency of exitation there occurs a slight shift of the green band towards shorter wavelengths due to the increasingly great number of transitions from higher energy levels of the excited state. The fact that this displacement increases with increasing Pb content in the luminophor is related with the increasing internuclear distance in the excited state.

In the ZnCdS-Cu luminophor, with increasing frequency of excitation, the intensity maximum at 4980 Å of the band with shorter wavelength increases more strongly, whereas the intensity of the other band at 5200 Å increasses less strongly, so that electroluminescence assumes a green-blue coloration.

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On the basis of the results obtained, the effect of ageing exhibited by the luminophors in the process of light emission is discussed in detail. However, the problem still requires theoretical consideration.

A discussion is given of the phenomenon of electroluminescence, basing on the concept of the Mott-Schottky potential barrier and electron traps. From the mechanism assumed it results that, of the electrons accelerated in the conduction band, only those acquire sufficient kinetic energy for producing excitation of luminescence centres which move in the region of the barrier with highest potential (the region adjacent on the cathode). The energy of the remaining electrons is insufficient for this. The number of such electrons with maximum energy is relatively small. This explains the low energy yield of electroluminescence.

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