ON THE ELECTROLUMINESCENT BRIGHTNESS-WAVES OF ZnS SINGLE CRYSTALS

By J. Schanda

Research Institute for Technical Physics of the Hungarian Academy of Sciences, Hungary

ZnS:Cu single crystals were excited alternatively by positive and negative pulses. Brightness-waves of single lighting spots were examined. With the help of probing pulses some characteristics of delayed recombination were established. The voltage dependence of the single light flashes showed special characteristics in the green and blue band. On the basis of the alternation of the lighting colour in the different light-pulses a comparison with sine wave excitation is possible. The brightness-wave of the red ZnS:Cu band shows the characteristics of a discrete centrum lighting calling for an association centrum interpretation.

1. Introduction

In the study of electroluminescent phenomena the main problem is how the luminescent centres gain the energy responsible for the emission. In this connection the study of brightness-waves, the kinetics relating variations of the electric field and light emission is of great importance.

In our latest report on this subject [1] we were able to show that if primary luminescent spots are considered, some definite conclusions can be derived as to the mechanism of electroluminescence acting in different crystals under various field conditions. In the present paper, it is our aim to solve the question of the relation between the primary and secondary maxima in the case of pulse excitation. Recent papers by Kubátová and Pátek [2], Harper [3] and Thornton [4] have shown that the terms "primary" and "secondary maxima" should not be used as denoting only the higher and smaller light-pulse, respectively, but should be employed to designate light-pulses acting during the appropriate time intervals predicted by an electroluminescent theory. In the following we shall attempt to analyze the brightness-waves produced during pulse-excitation and shall try to find terms equivalent to those used with sine-wave excitation.

ACTA PHYSICA POLONICA Vol. XXVI (1964) Fasc. 3–4

2. *Experimental material*

We used ZnS single crystals produced in our laboratory by Kovács [5]. These were in their original form non-electroluminescent and showed either green or blue and in some cames orange photoluminescence.

The crystals were activated with copper by Lendvay; the procedure of which is described in another paper prepared for this Conference [6].

The activated crystals showed mainly blue electroluminescence, in some cases combined with a red band.

3. *Experimental arrangement*

The experimental apparatus was a somewhat simplified version of our pulse-counting spectrometer [7] used for spectral energy-distribution measurements of brightness-waves (Fig. 1). The exciting unit consisted essentially of three

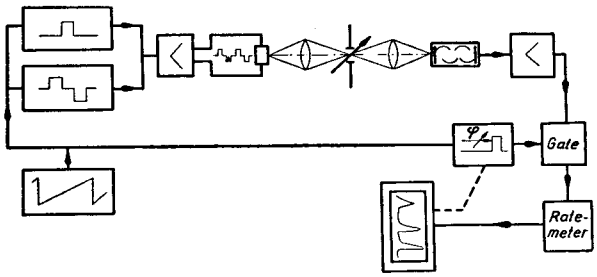

Fig. 1. Block diagram of experimental arrangement

pulse-generators, the output of which could be combined to produce a positive and negative double pulse approximately one-one msec long with an off period between the pulses of approximately one msec. One every second pulse train of this kind it was possible to superpose a special short (50–100 μsec long) probing pulse of either polarity.

The crystals mounted on microscopic baseplates were contacted with a special indium-gallium alloy producing non-blocking contacts (for the kind delivery of the formule of this contacting alloy the author is highly obliged to Dr Gutsche of the PTI of DAW, Berlin) and placed on a microscope cross-table. An adjustable diaphragm was placed in the input pupil of the projecting eye-piece. Behind the image-plate a photomultiplier was arranged, the output pulses of which were amplified. A gate, with continuously variable phase-position, let pass only pulses of appropriate phase-angle. These pulses were discriminated and counted by a pulse counting rate-meter, the output current of which energised a potentiometric recorder. The variable gating-pulse was

produced by means of a linear saw-tooth voltage and a comparator. The reference voltage of the latter was varied synchronically with the paper feeding.

In most measurements the length of the gate-pulse was 100 μsec. With a measuring time constant of 20 sec and a total measuring time of 30 minutes it was possible to measure the brightness waves of objects smaller than 10 μ in diameter, with approximate spectral resolution and relatively low exciting voltage.

ACTA PHYSICA POLONICA Vol. XXVI (1964) Fasc. 3–4

4. Experimental results

Our measurements mainly concerned the properties of the blue and green components of electroluminescent emission. A typical emission curve taken with a blue filter is seen in Fig. 2. The applied voltage is plotted on the upper curve; the photocurrent is shown in the lower one. The following features

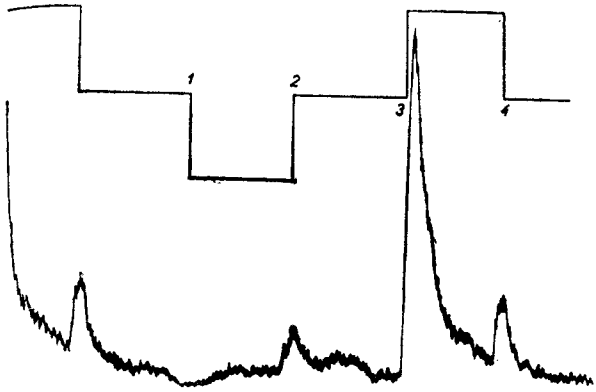

Fig. 2. Registered brightness-wave of a single emitting spot taken with a blue filter. Upper curve: voltage wave; lower curve: brightness-wave. (Numbers 1 to 4 denote positions on the voltage wave referred to in the text)

seem to be characteristic in our measurements: On applying negative voltage to one end of the crystal, the light falls to zero intensity. On removing this voltage a characteristic light flash can be seen. The voltage pulse — now with positive polarity — produces a large light burst. Switching off this voltage produces a third flash, not reported by other investigators using the same excitation method.

The first question investigated dealt with the problem of energy storage between voltage excitation and recombination radiation. For this purpose a small probing pulse was superposed on the exciting voltage during the different parts of the voltage cycle.

1. If the probing pulse was set between the time marks 3 and 4 the following possibilities could be distinguished:

a. If the amplitude of the probing pulse was higher or as high as the main pulse, but of reverse polarity, an independent light pulse was observed at the moment of the probing pulse, and the amplitude of the flash at 4 was not affected.

b. If the amplitude of the probing pulse was smaller than the main pulse, and of reverse polarity, a small light flash in phase with the probing pulse was sometimes observed. This is mainly the case in the blue spectral band, In the green band it is more usual to find some slight quenching at the beginning of pulse and a small flash at the end of it (see Fig. 3a and 3b).

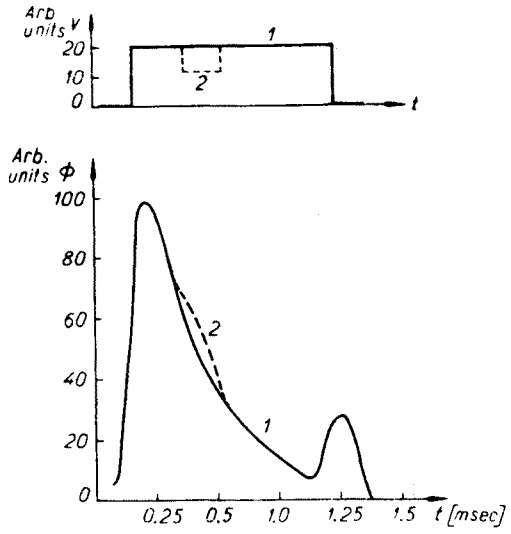

Fig. 3a

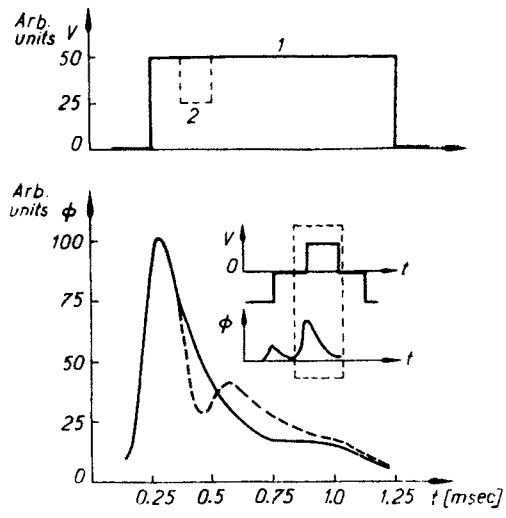

Fig. 3b

Fig. 3a. Brightness-wave section of the blue luminescent band. 3b. Brightness-wave section of the green luminescent band. The upper curves represent the voltage wave, the lower ones the brightness-wave. Curves *1* are for the unperturbed cases; curves *2* for the case of probing pulses

2. If the probing pulse was applied after position 4 and its polarity was equal to that of the preceeding main pulse, at the beginning of the pulse some surplus and at the end of it some deficiency of light as compared with normal afterglow was observed.

3. If the probing pulse was applied between positions 2 and 3 with a polarity opposite to that of the preceeding main pulse it always had a quenching action on the pulse at 3. The afterglow of the light-flash at position 2 was also affected by this pulse (see Fig. 4): at the beginning of the probing pulse a light flash was observed; at the end of it the light fell to nearly zero intensity. If the polarity of the probing pulse was equal to the preceeding main pulse, its action on the brightness-wave was much less pronounced.

ACTA PHYSICA POLONICA Vol. XXVI (1964) Fasc. 3–4

4. Pulses applied during the period between positions 1 and 2 were of a rather small effect on the brightness-wave.

The second question we dealt with was the voltage dependence of the single brightness peaks. In this case rather the peak value than the light sum was measured, because some observations showed that during the on period of the voltage cycle there is superpostion of two phenomena: the pulse-like brightness-wave produced at the moment of switching, and a steady state *D.C.* electroluminescence.

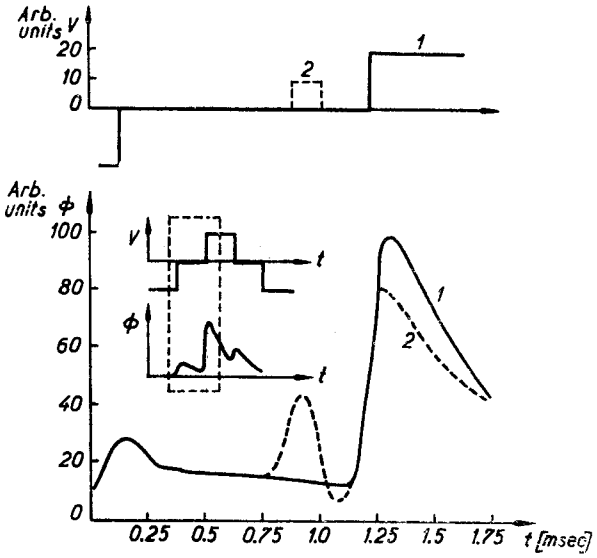

Fig. 4. Brightness-wave section of the blue band without (curve *1*) and with (curve *2*) application of a probing pulse

In our measurements we were primarily interested in the behaviour of the light flashes. Some results of this investigation are represented by the curves reproduced in Fig. 5 and 6. Fig. 5 shows the voltage dependence of the blue band at position 3. As can be seen, this brightness peak shows the usual voltage dependence

$$\Phi = B\exp(-b/\sqrt{V})\,. \tag{1}$$

Fig. 6 shows some interesting phenomena: curve B_3 represents the same measurement as Fig. 5. Curves G_3, and G_2, however, show the voltage dependence of the green band at the same position and position 2 of the brightness-wave. It can be seen that this curve is rather linear than exponential. At position 4 the brightness values are relatively low; thus measurement of the voltage dependence was much more inaccurate. However, it is estimated that at this position neither the green nor the blue band shows the usual voltage dependence of Eq. (1). As voltage was reduced a further interesting phenomenon oc-

ACTA PHYSICA POLONICA Vol. XXVI (1964) Fasc. 3–4

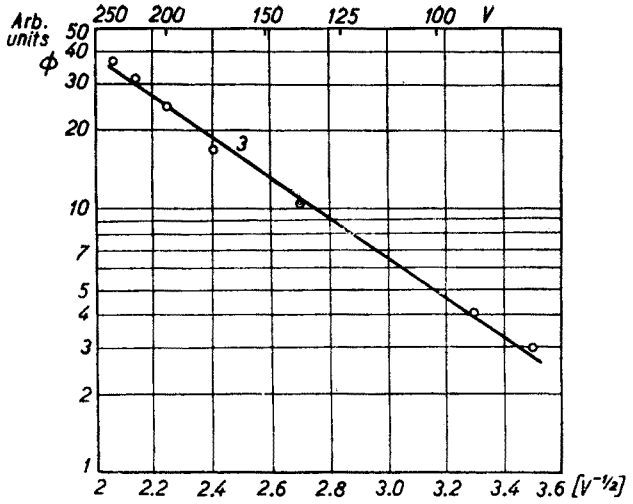

Fig. 5. Voltage dependence of the blue band at position 3

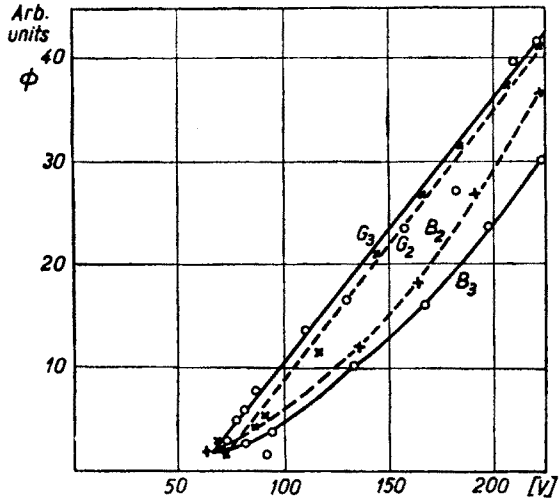

Fig. 6. Voltage dependence of the blue and green bands at positions 1 and 3

curred, *viz.* the peak intensity at position 4 was reached more and more slowly. At the lowest voltages used, a few hundred μsec-s elapsed before the light reached its highest value.

The third question taken into consideration was the spectral dependence of the brightness-waves. As already stated in connection with the two above discussed problems, the usual blue and green spectral bands show different voltage dependences. This makes the usual criterion of primary and secondary maximum somewhat problematic, as the ratio of the amplitudes of the dif-

ACTA PHYSICA POLONICA Vol. XXVI (1964) Fasc. 3-4

ferent brightness peaks vary with the voltage. Nevertheless it can be stated that the maximum at position 2 is more pronounced in blue emission. The light flash at position 3 is mainly green. The brightness peak at position 4 was slightly more blue than the peak at 3. The real light intensity of the peak at 4 could not be determined accurately, as the green band is still in strong afterglow at the position of flash 4, and at the same time the blue afterglow of the peak at 3 already fades.

For comparison the brightness wave of an orange emitting crystal was measured also. The emission of this crystal, though extremely small lighting areas were considered, showed emission during both halfcycles. The emission pattern was rather different from that of the blue and green emitting crystals. At positions 1 and 3 a rather high light flash was produced, which decreased 10 to 20%, and faded at the moment the voltage was switched off.

5. *Discussion*

It was our chief aim to try to explain the electroluminescent emission on the basis of the theory of delayed recombination. In this respect our measurements showed that this theory is indeed able to explain some of the observations. If we suppose that primary excitation takes place between the time marks 1 and 2, then at 2 a light flash is to be expected as a result of the recombination of the ionized activators with free electrons. As a potential of opposite polarity is applied, trapped electrons are field-ionized and can recombine [8]. If during the time-interval between positions 2 and 3 a probing pulse of the polarity of the next main pulse is applied, some electrons from shallow traps can already recombine, producing a light flash. At the same instant the light flash at 3 must be decreased by the number of these recombinations.

The light-flash at 4 ought to be indentified with electrons flying back to the ionized activators, but under the action of a small internal polarizing field miss the proper centres and recombine only as the field is next switched off [9]. The lighting under the action of a small probing pulse seems to support this picture, as it might quench the pulse at 4. If the amplitude of the probing pulse is sufficiently high a second light-pulse is produced, and the main pulse is unaffected. Thus a light sum of nearly double value is produced although the voltage-swing was only half as high as in the case without probing pulse. This seems to support the idea that the recombining electrons are produced at the voltage-step at 3. The special voltage-dependence and the fact that the flash at 4 is more blue in colour than that at 3 seem to underline that the mechanism at position 4 is different from the other pulses. As the strength of this flash is higher in the neighbourhood of one of the electrodes and the light intensity falls to null at position 1, showing that there are no more electrons in traps to recombine, our opinion was that we were dealing in this case with a separate

ACTA PHYSICA POLONICA Vol. XXVI (1964) Fasc. 3–4

mode of electroluminescent excitation, perhaps like that observed by Matossi and Schmid [10].

At position 3 the observed voltage dependence in the blue spectral band could easily be understood on the basis of current electroluminescence theories. On the other hand the behaviour of the green emission showing a definite threshold voltage and in some cases even a maximum at high voltages is possibly explained on the basis of field or field and temperature ionization from traps. We have some slight indication from some of our measurements that if the temperature is raised the threshold potential lies at lower voltages.

The spectral characteristics show that primary recombination takes place at position 2 (mainly blue emission), and that the light flash at 3 shows the usual spectral composition of the secondary maximum. The special behaviour of the orange emission shows that this luminescent band produced by copper differs markedly from the green and blue copper bands. Although the appearance of this orange band has not yet been clarified in every detail, it seems to be reasonable to suppose that we are confronted with a highly associated centre. In this case every onperiod of the voltage produces light emission, and during every offperiod no emission occurs. No delayed recombination is observed.

6. Conclusions

Summing up the data observed we can state that although the theory of delayed recombination can explain some basic observations, the method of measuring the elementary emitting spots with spectral resolution can still give some further information. It was possible to find in a single crystal different emitting spots with different brightness-waves produced by different exciting mechanisms. The measurements reported in the present paper will be completed with temperature dependence measurements and more detailed spectral investigation. From these measurements we hope to obtain futher information regarding the mechanisms responsible for excitation and recombination in electroluminescence.

The author wishes to express his gratitude to the staff of the electroluminescent group of the Research Institute for Technical Physics of the Hungarian Academy of Sciences for the help in the production and activation of the single crystals as well as for their numerous discussions.

REFERENCES

1. Schanda, J., *Czech. J. Phys.*, **B13**, 147 (1963).
2. Kubátová, J., Pátek, K., *Czech. J. Phys.*, **B13**, 157 (1963).
3. Harper, W. J., *J. Electrochem. Soc.*, **109**/2, 103 (1962).

4. Thornton, W. A., *J. Electrochem. Soc.*, **110**/5, 370 (1963).
5. Kovács, P., Szabó, J., *Acta Phys. Hungar.*, **14,** 131 (1962).
6. Szigeti, G., International Conference on Luminescence, Toruń 1963.
7. Schanda, J., *Acta Phys. Hungar.*, **14,** 95 (1962).
8. Georgobiani, A. N., Fock, M. N., *Optika i Spektrosk.*, **9,** 407 (1960).
9. Pátek, K., *Czech. J. Phys.*, **9,** 460 (1959).
10. Matossi, F., Schmid, G., *Z. Phys.*, **166,** 455 (1962).

DISCUSSION

Question: G. Diemer

If the red emission in your Cu-doped samples were due to a centre, similar to the Ag-Centre described by Dr Dieleman in paper 22, the oscillograms could be an indication of a hole-injection mechanism in this case.

Answer

As the brightness-wave showed some similarities to those produced by Mn, thus it was supposed that the red centre could be an associate centre of the type of the first order. It should be further investigated wether the centre found by us is equal to that found by Dr Dieleman

ACTA PHYSICA POLONICA Vol. XXVI (1964) Fasc. 3–4