

INFLUENCE OF TEMPERATURE AND CdS CONCENTRATION OF THE SHORT-WAVE PHOTOLUMINESCENCE OF (Zn, Cd) S-Cu PHOSPHORS

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The short-wave emission spectrum of (Zn, Cd) S-Cu phosphors has been investigated in the temperature range from -150°C to $+70^{\circ}\text{C}$. The composition of the phosphors varied from 100% ZnS to 100% CdS.

Considerable influence of temperature on the position of the short-wave band of a given luminophor has been found, this position shifting towards greater wavelengths with increasing temperature. The shift is practically the same for all CdS concentrations and amounts on the average to about $7.9 \times 10^{-2} \text{ nm}/^{\circ}\text{C}$. If expressed in $\text{eV}/^{\circ}\text{C}$ its value is of the same order as the values of the thermal coefficients of the width of the forbidden zone for the investigated luminophors. This fact indicates that there exists a close relation between the temperature decrease in the energy E which corresponds to the maximum of the band and the temperature decrease in the energy E_g which corresponds to the width of the forbidden zone of the luminophor.

It was found that luminophors containing CdS in the range 3–10% mol. exhibit a minimum in the intensity of the investigated emission band at all temperature values considered. This is probably connected with the deformation of the matrix lattice due to the introduction of Cd into zinc sulphide.

It is also shown that the curves of the short-wave emission distribution for (Zn, Cd) S-Cu are Gaussian and that half-widths change with increasing temperature from about 0.28 eV at -150°C to about 0.32 eV at $+20^{\circ}\text{C}$.

Introduction

The build-in of copper ions into (Zn, Cd)S may result in the formation of two different luminescent centres which are responsible for two principal emission bands — a short-wave and the other a long-wave band — (van Gool 1961, D. Curie 1965, Shionoya 1966). For ZnS (wurtzite) these bands lie in the blue part of the spectrum about 445 nm and in the green roughly at 523 nm. If the percentage of CdS added to Zn is increased

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these bands shift. For pure CdS the short-wave band is shifted at 820 nm and the other band to 1020 nm (D. Curie 1965).

The problem of the long-wave emission of (Zn, Cd)S-Cu phosphors has been studied by the author in a paper devoted to the influence of temperature and CdS concentration on the intensity and position of the maximum of this emission (Łukaszewicz 1972). The results obtained in this paper stimulated the author to make similar measurements for short-wave emission; moreover the studies made so far were in the majority of cases restricted to one or two temperatures, *i. e.*, room temperature or room temperature and liquid air temperature, only (*cf.* Grosnier and G. Curie 1962, Lehmann 1963, Ortmann and Treptow 1960, Albers 1960 and others). Besides, as it follows from literature, the (Zn, Cd)S-Cu phosphors characterized by short-wave emission have so far not been investigated in that extent as the long-wave emission phosphors, probably owing to the much more difficult technology of the former.

The purpose of the present paper is the investigation of the short-wave photoluminescence of (Zn, Cd)S-Cu phosphors at several temperatures greater and smaller than room temperature. The particular problems were:

- a) influence of temperature and CdS concentration on the position of the maximum of the band,
- b) influence of temperature and CdS concentration on the intensity of this band.

1. Preparation of the luminophors and experimental procedure

It is well known (Riehl and Ortmann 1959, Ortmann and Treptow 1960, Blinks *et al.* 1961) that by applying suitable technology it is possible to obtain ZnS-Cu and (Zn, Cd)S-Cu luminophors which at a given temperature and CdS concentration have identical intensities of both emission bands. However, when the emission process is studied at different temperatures the ratio of the intensities of both bands changes.

Thus for greater intensity differences between the bands it is not possible to determine the position of the weaker maximum precisely since it is affected by the tail of the stronger band. In order to eliminate this source of error it was necessary to produce (Zn, Cd)S-Cu luminophors with only one band, *i. e.*, the short-wave band. This has been done by using a technology similar to that applied by Riehl and Ortmann (1959) in case of ZnS-Cu emitting in the blue part of the spectrum.

Samples of ten grams of ZnS-CdS with 10^{-4} g of Cu per 1 g of the mixture and 2% NaCl as fluxing agent were sintered for 20 minutes at $(900 \pm 10)^{\circ}\text{C}$ using the method elaborated by Ostaszewicz (1963), also described in the previous paper (Łukaszewicz 1972). The (Zn, Cd)S-Cu phosphors obtained in this way were normal luminophors characterized by long-wave emission. These samples were washed in boiling water and the substance was additionally mixed with 2×10^{-4} g Cu per 1 g of luminophor and then annealed for 30 minutes at 450°C . After such treatment the luminophors emitted in the short-wave band. This method was used to obtain a number of samples with constant concentration of Cu (3×10^{-4} g Cu/1 g of luminophor). Their compositions are listed in Table I.

Measurements of the spectral intensity distribution of photoluminescence have been

TABLE I

Specification of luminophors used

Luminophor No	Content of mixture in mol % (each mixture had an addition 3×10^{-4} g per gram mixture)
0a	100.0 ZnS+ 0.0 CdS
1a	97.5 ZnS+ 2.5 CdS
2a	95.0 ZnS+ 5.0 CdS
3a	92.5 ZnS+ 7.5 CdS
4a	90.0 ZnS+ 10.0 CdS
5a	85.0 ZnS+ 15.0 CdS
6a	80.0 ZnS+ 20.0 CdS
7a	70.0 ZnS+ 30.0 CdS
8a	60.0 ZnS+ 40.0 CdS
9a	50.0 ZnS+ 50.0 CdS
10a	40.0 ZnS+ 60.0 CdS
11a	30.0 ZnS+ 70.0 CdS
12a	20.0 ZnS+ 80.0 CdS
13a	10.0 ZnS+ 90.0 CdS
14a	0.0 ZnS+100.0 CdS

made by means of the method described in a previous paper. The apparatus was also the same as previously, except the photomultiplier which was used in the short-wave part of the spectrum. The photomultiplier applied in the present work was a Zeiss M12FS52A with spectral sensitivity 300–600 nm and was used for measurements of the short-wave band of photoluminescence of (Zn, Cd)S-Cu phosphors up to 40% mol. concentration of CdS. Measurements above this concentration were made with a FEU-22 photomultiplier (USSR). All samples were excited by the 365 nm Hg line from a Wood lamp which was supplied from a voltage regulator. Luminophors containing more than 40% mol. CdS were irradiated through filters composed of aqueous solution of CuSO_4 . The basic measurements were made at the following temperatures -150°C , -90°C , -40°C , $+20^\circ\text{C}$ and $+70^\circ\text{C}$. In addition for ZnS-Cu and some other luminophors with small CdS concentration they were made at $+120^\circ\text{C}$ and $+180^\circ\text{C}$.

2. Experimental results

(Zn, Cd)S-Cu phosphors investigated by the authors in the previous work (Łukasiewicz 1972) at low temperatures and for small CdS concentration, have in addition to the strong long-wave band a weak short-wave band. The maximum of the short-wave (blue) band of ZnS-Cu at -150°C is at 452 nm and that of the long-wave one (green) at about 537 nm. These positions of the maxima of emission bands indicate the sphalerite structure of this luminophor (D. Curie 1965). This structure corresponds to the sintering temperature (about 900°C) in which ZnS crystallizes in Cubic (sphalerite) system.

Another type of crystal structure (probably wurtzite) is characteristic for the short-wave band emitting ZnS-Cu luminophor. As it can be seen from Fig. 1 this luminophor

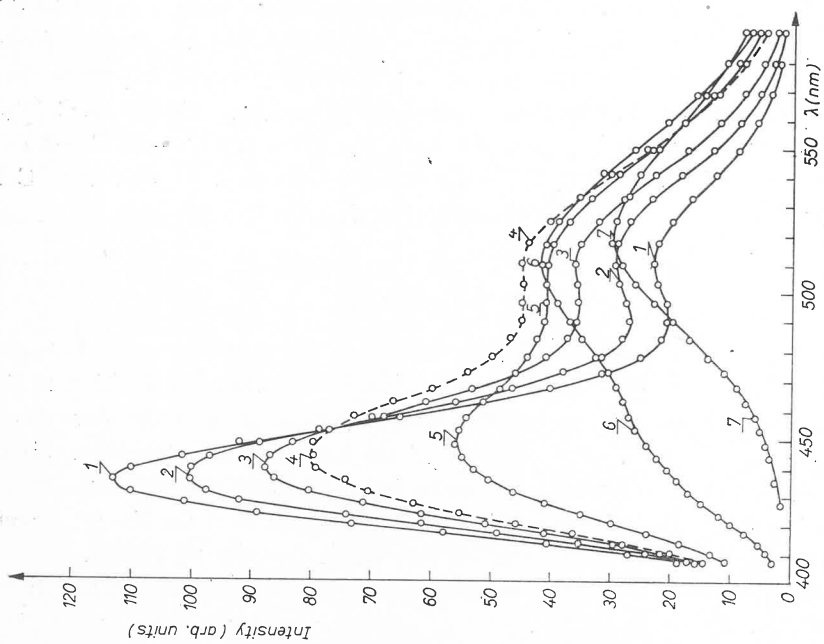


Fig. 1

Fig. 1. Spectral distributions of intensity versus wavelength for sample No Oa (ZnS-Cu) at the temperatures: 1) -40°C , 2) -90°C , 3) -40°C , 4) $+20^{\circ}\text{C}$, 5) $+70^{\circ}\text{C}$, 6) $+120^{\circ}\text{C}$, 7) $+180^{\circ}\text{C}$

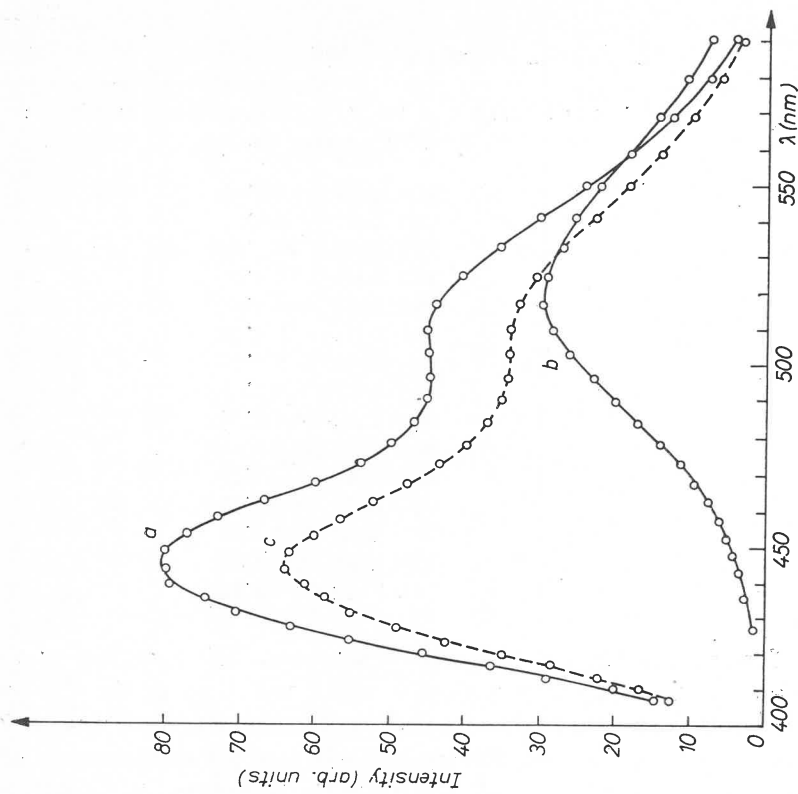


Fig. 2

Fig. 2. Reversibility of the transition blue \leftrightarrow green for ZnS-Cu. The particular curves correspond to the temperatures: a) $+20^{\circ}\text{C}$, b) $+180^{\circ}\text{C}$, c) $+20^{\circ}\text{C}$

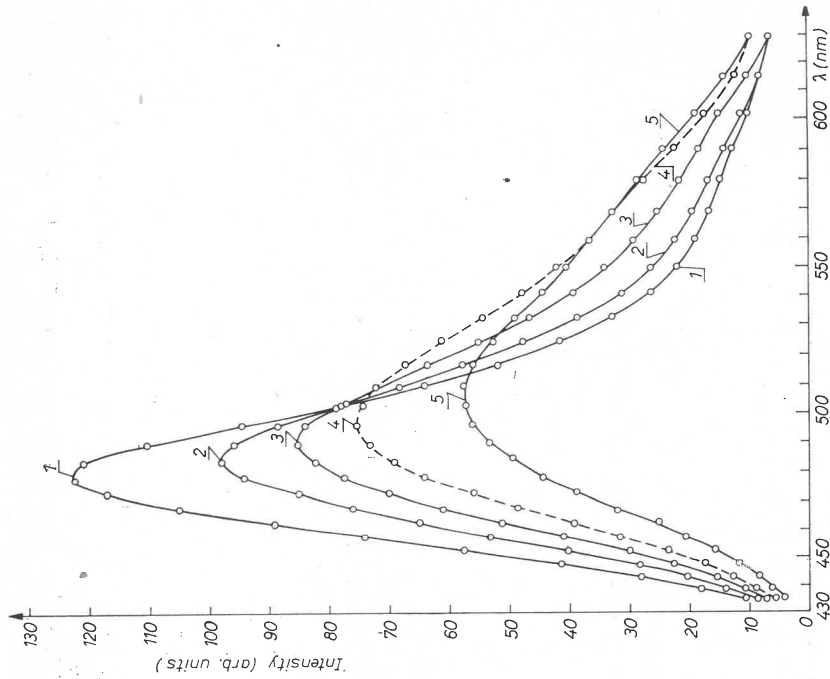


Fig. 3

Fig. 3. Spectral distributions of intensity versus wavelength for sample No 2a (95ZnS+5CdS)-Cu at the temperatures: 1) -150°C, 2) -90°C, 3) -40°C, 4) +20°C, 5) +70°C, 6) +120°C, 7) +180°C

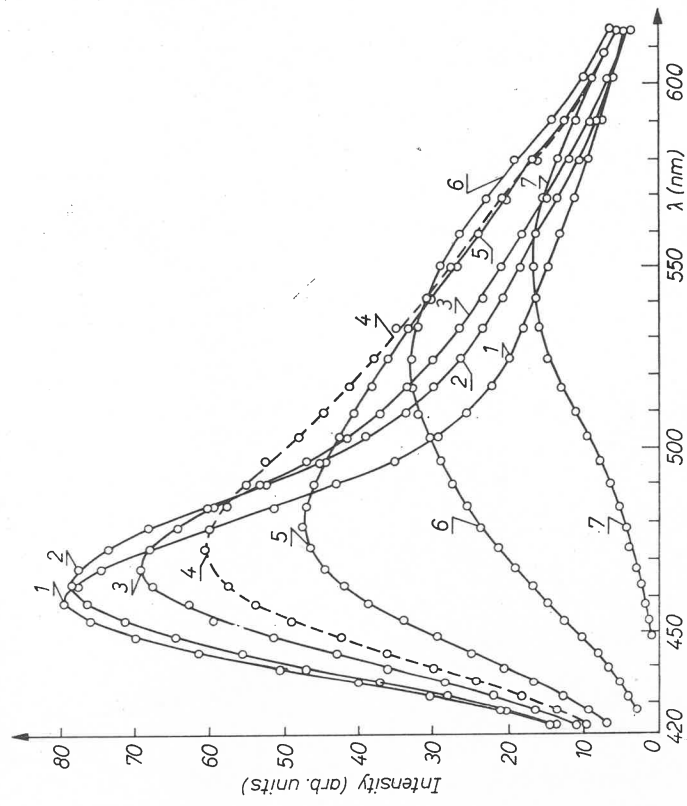


Fig. 4

Fig. 4. Spectral distributions of intensity versus wavelength for sample No 4a (90ZnS+10 CdS)-Cu at the temperatures: 1) -40°C, 2) +20°C, 3) -40°C, 4) +20°C, 5) +70°C

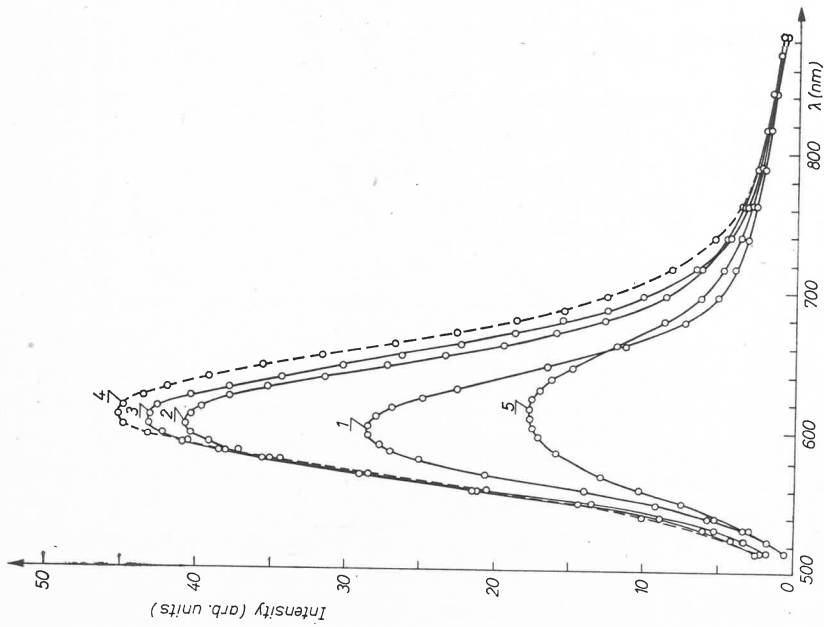


Fig. 5

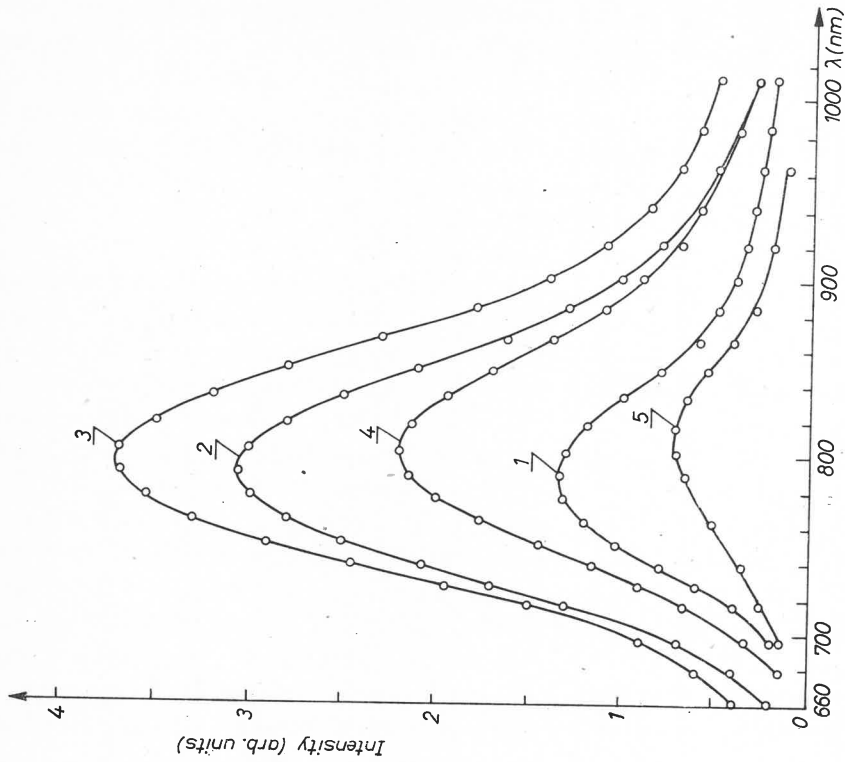


Fig. 6

Fig. 5. Spectral distributions of intensity versus wavelength for sample No 9a (50ZnS+50CdS)-Cu at the temperatures: 1) -150°C, 2) -90°C, 3) -40°C, 4) +20°C, 5) +70°C.

Fig. 6. Spectral distributions of intensity versus wavelength for sample No 14a (CdS)-Cu at the temperatures: 1) -150°C, 2) -90°C, 3) -40°C, 4) +20°C, 5) +70°C.

has also two emission bands at low temperature but the dominating one is now the short-wave (blue) band. At -150°C these bands lie at about 436 nm and at 511 nm, respectively, which is typical for the wurtzite structure of ZnS (D. Curie 1965). When the temperature increases, the short-wave band shifts towards greater wavelengths from about 436 nm at -150°C to about 449 nm at $+70^{\circ}\text{C}$. This indicates that this band is due to the blue centres of Cu rather than to the self-activated ZnS luminophor (Shionoya 1966). A change in temperature also influences the intensity of both bands. The intensity of the blue band decreases with increasing temperature and vanishes at $+180^{\circ}\text{C}$ as it can be seen in Fig. 1 while the intensity of the green band first increases, becoming maximum in the vicinity of $+20^{\circ}\text{C}$, and then decreases owing to temperature quenching. According to D. Curie (1965) the blue band emission of ZnS-Cu vanishes at temperatures lower by 100–150 deg than those corresponding to vanishing green emission. It follows from the spectral distribution of the intensity of photoluminescence of the ZnS-Cu phosphor shown in Fig. 1 that $+180^{\circ}\text{C}$ is the transition temperature at which the blue centres of copper become green. A similar temperature of complete transition of Cu centres, namely $+200^{\circ}\text{C}$, has been obtained by Riehl and Ortmann (1959). This transition is reversible, as it can be seen in Fig. 2. The only result of temperature increase is the decrease in the intensity of both emission bands. This indicates that some number of colour centres of Cu of both types is destroyed. According to Gurvich and Ilyina (1966) the reversibility of blue \rightleftharpoons green colour centres of Cu occurs only in case of "unquenched" luminophors. Their statement is in agreement with the results of the present paper since the investigated (Zn, Cd)S-Cu luminophors were cooled in air at room temperature both after sintering and annealing.

The main effect of gradual exchange of Zn^{2+} ions in the matrix lattice of zinc sulphide by Cd^{2+} ions is, as it can be seen from Figs 3–6, a shift of the short-wave emission band towards greater wavelengths, *e. g.* at $+20^{\circ}\text{C}$ from about 445 nm for ZnS-Cu to 801 nm for CdS-Cu. This is a well-known effect, and it is in this case in good qualitative agreement with many previous papers (Albers 1960, Ortmann and Treptow 1960, Lehmann 1966 and other authors). The increase in the Cd to Zn ratio in the (Zn, Cd)S-Cu luminophor gives also rise to a change in the intensity of the short-wave emission. Similarly as in the case of long-wave emission the intensity at a given temperature first rapidly decreases becoming minimum at the concentration of CdS of about 5% mol. (Fig. 3) and then increases again becoming maximum at about 10% mol. CdS (Fig. 4). After this maximum the intensity of the short-wave band gradually decreases until in case of CdS-Cu (Fig. 6) it becomes a value some dozen times smaller than that corresponding to ZnS-Cu (Fig. 1). A similar behaviour of the intensity of short-wave emission of (Zn, Cd)S-Cu phosphors as a function of CdS concentration at constant temperature has been observed among others by Gurvich and Ilyina (1967).

The temperature change in the intensity of the band, which is described above, occurs at each of the temperatures under consideration.

Another characteristic property of the investigated luminophors is the change in the relation between the intensity maxima of the band which correspond to the particular temperatures. This change occurs with changing concentration of CdS. For ZnS-Cu,

the maximum intensity of the short-wave emission is at the lowest of the investigated temperatures, *i. e.*, at -150°C (Fig. 1). When the concentration of CdS increases this maximum appears at higher temperatures. After exceeding 30% mol. CdS the luminescence is the greatest at $+20^{\circ}\text{C}$. This is seen in Fig. 5 which shows the spectral distribution of the photoluminescence intensity for (Zn, Cd)S-Cu luminophor with CdS concentration of 50% mol. Such situation persists up to CdS concentration of about 60% mol. After ex-

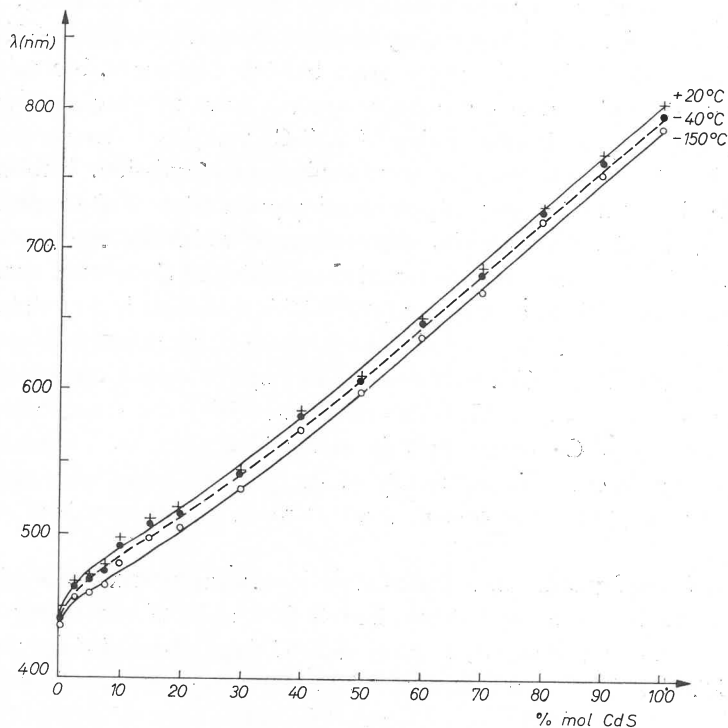


Fig. 7. Dependence of the position of the short-wave band maximum for (Zn, Cd)S-Cu on the CdS concentration at various temperatures

ceeding this concentration the maximum intensity goes over to temperatures somewhat less than room temperature. This is seen in Fig. 6 for the CdS-Cu phosphor whose emission is strongest at -40°C .

The temperature also influence the position of the maximum of the short-wave band of the luminophor in the spectrum, namely a temperature increase results in a shift of the band towards greater wavelengths (Figs 1-6). This effect occurs for all the investigated (Zn, Cd)S-Cu luminophors and is approximately the same for all of them.

The long-wave emission has been effectively damped by the technology used in the preparation of the (Zn, Cd)S-Cu luminophors. Only in case of small concentrations of CdS and at temperatures above $+70^{\circ}\text{C}$ (Fig. 1, 3, and 4) this emission being dominant prevents the separation of the short-wave band. At CdS concentration of 50% mol. (Fig. 5) and greater, the long-wave band practically does not exist. In such

a situation the problem of this emission will not be discussed further, in accordance with the assumption of the present paper.

Coming back to the transition of blue emission centres into the green ones it should be pointed out that this transition is observed only in case of ZnS-Cu and luminophors with concentrations up to 40% mol. This results from the fact that as the CdS concentration increases, the intensity of long-wave emission decreases and its temperature quenching becomes faster. Fig. 3 shows an example of the short-wave — long-wave transition of the (Zn, Cd)S-Cu luminophor with CdS concentration of 5% mol.

3. Discussion of the results

The most important property of the investigated (Zn, Cd)S-Cu phosphors is the shift of both emission bands of copper towards greater wavelength which occurs with the increase in the Cd to Zn ratio. The shift of the short-wave band of Cu observed in the

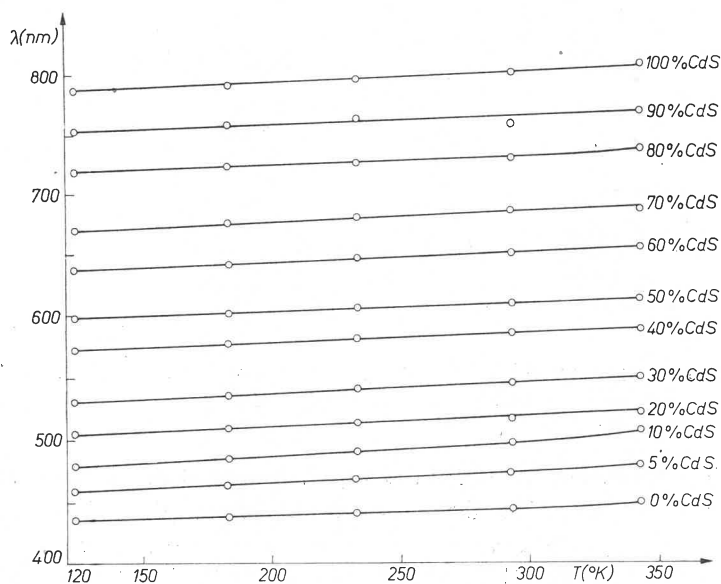


Fig. 8. Dependence of the position of the short-wave band maximum for (Zn, Cd)S—Cu on temperature for several concentrations of CdS

present work exhibits the generally known regularity and is in good agreement with the results of other authors (Albers 1960, Grosnier and G. Curie 1962 and others). This shift has been illustrated in Fig. 7 by plotting the position of the maximum of this band as a function of CdS concentration for three different temperatures, namely -150°C , -40°C and $+20^{\circ}\text{C}$. As it can be seen in this figure this dependence is almost linear within the limits of experimental errors. Slight bending of the curves seen in Fig. 7 and occurring for CdS concentrations up to about 40% has also been observed by Ortmann and Treptow (1960).

The only exception from this simple picture of band shifting (Fig. 7) is the too low position of the maximum of the short-wave band emitted by ZnS-Cu. The reason for this deviation may be the non uniform crystal structure of ZnS and (Zn, Cd)S. The elucidation of this problem can be given by structural study of these luminophors.

Another fact which can be seen directly in Fig. 7 is that the position of the maximum of the short-wave band of each of the investigated luminophors (Zn, Cd)S-Cu is highly

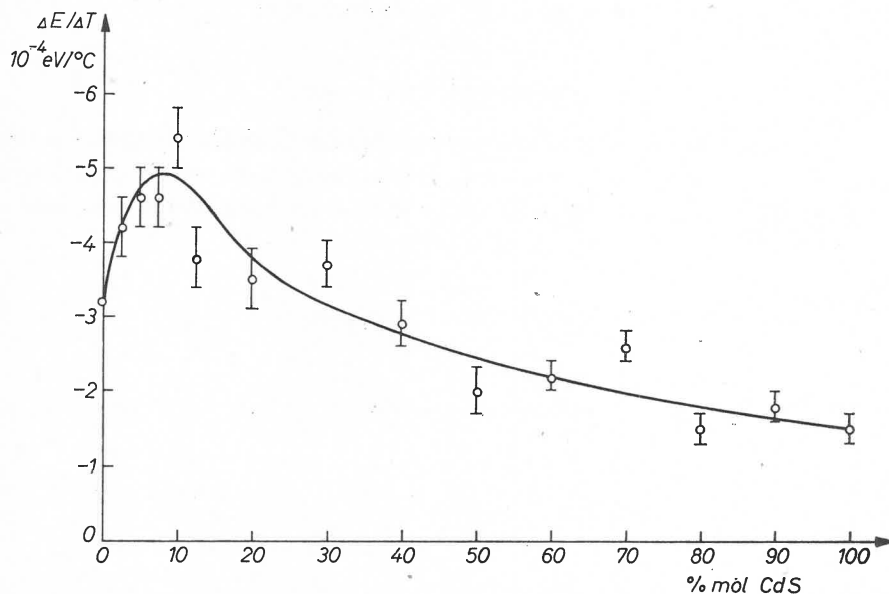


Fig. 9. Values of the temperature shift of $\Delta E/\Delta T$ of the short-wave band of (Zn, Cd)S-Cu phosphors for various concentrations of CdS

temperature-dependent. For the sake of clarity this dependence is shown in Fig. 8 for each luminophor separately. The figure displays the linear dependence of the position of the maximum on temperature. (Deviation of this regular behaviour occurs only in case of curves determined for low CdS concentration up to 10% mol. at the highest temperature. This follows from the overlap of the long-wave band and the investigated short-wave band. Namely at $+70^{\circ}\text{C}$ the ratio of the long- to short-wave emission intensities is the greatest) In addition it follows from the present results that the shifts of the band towards greater wavelengths due to increased temperature are practically the same for all the investigated luminophors. The mean value of this shift is about $7.9 \times 10^{-2} \text{ nm}/^{\circ}\text{C}$.

If the shift of the maximum of the band is expressed in $\text{eV}/^{\circ}\text{C}$ rather than in $\text{nm}/^{\circ}\text{C}$ and plotted as a function of CdS concentration than the following interesting picture is obtained (Fig. 9). As the Cd to Zn ratio increases, the value of the shift first increases becoming maximum at CdS concentration of 8% mol. and then decreases becoming smallest in case of CdS-Cu. According to Fig. 9 the value of $\Delta E/\Delta T$ for ZnS-Cu amounts to about $-3.3 \times 10^{-4} \text{ eV}/^{\circ}\text{C}$ while that for CdS-Cu is about $-1.6 \times 10^{-4} \text{ eV}/^{\circ}\text{C}$. These

values are of the same order of magnitude as the values of the thermal coefficients of the width of the forbidden energy zone for ZnS and CdS. According to Shionoya (1966) $\Delta E_g/\Delta T$ for ZnS (wurtzite) amounts to -8.5×10^{-4} eV/°C while that of CdS -5.2×10^{-4} eV/°C. This indicates a close relation between the thermal decrease in the energy E corresponding to the maximum of the band and the decrease in the energy E_g corresponding to the width of the forbidden zone of the luminophors.

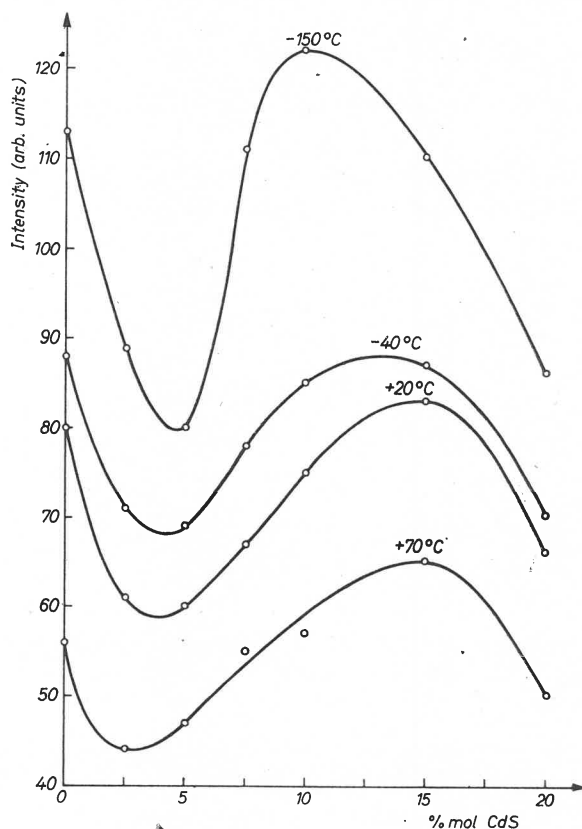


Fig. 10. Dependence of the maximum intensity values of short-wave emission of several (Zn, Cd)S-Cu luminophors on CdS concentration at various temperatures

It is also worth-while to note that the greatest value of $\Delta E/\Delta T$ is at such a concentration of CdS at which there is a minimum intensity both of the long- (Łukaszewicz 1972) and the short-wave emission (Fig. 10).

Gurvich and Ilyina (1967) have shown that the occurrence and the position of this minimum does not depend directly on the kind of activator nor on the conditions of preparing and exciting the (Zn, Cd)S-Cu luminophors. They are, however, connected with a decrease in the ratio of the number of luminescent centres to that of quenching centres. Quenching is due to electron traps formed by CdS introduced to zinc sulphide in amounts between 3 and 10% mol. According to Levshin and Senashenko (1970) the

introduction of such amount of CdS into zinc sulphide gives rise to decreased internal homogeneity of luminescent centres and thus to disturbances of the symmetry of the matrix lattice. This effect is probably the reason why for 8% mol. concentration of CdS the value of $\Delta E/\Delta T$ is the greatest. Namely in case of deformed lattice the interionic spacing grows probably faster with increasing temperature, than in case of undeformed lattice. This implies a faster change of the forbidden zone width of such a luminophor and as a result a faster change in the position of its short-wave band maximum.

As it can be seen both these facts, *i. e.*, maximum $\frac{\Delta E}{\Delta T}$ and minimum intensity of short-wave emission at CdS concentration between 3 and 10% mol. are probably closely related.

Coming back to the minimum intensity of short-wave emission presented in Fig. 10 it is seen that as the temperature increases this minimum is shifted towards lower CdS

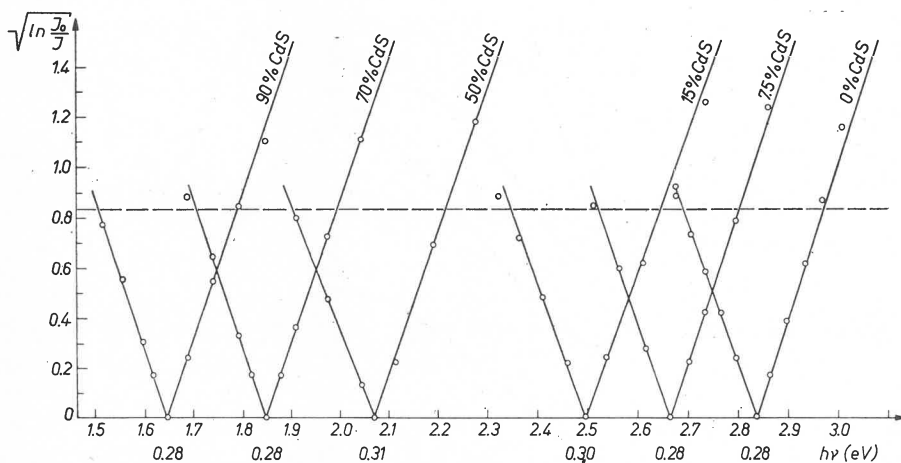


Fig. 11. Dependence of $\sqrt{\ln(I_0/I)}$ on the energy of emitted photons for several luminophors at -150°C

concentrations: from about 5% mol. at -150°C to about 3% mol. at $+70^\circ\text{C}$. This minimum widens becoming less pronounced and broader.

According to the above statements the least ordered crystal structure from all the (Zn, Cd)S phosphors have those containing 3–10% mol. of CdS. At increased temperature the degree of orderly arrangement becomes smaller, however, there is reason to believe that this effect is not the same at different CdS concentration. Indeed, this may be the reason for the widening of the minimum and its small shift to lower CdS concentrations at which the above-mentioned electron traps appear.

Thus the results obtained in this work provide still another confirmation of the hypothesis of Gurvich and Ilyina (1967) and also of Levshin and Senashenko (1970) about the origin of the discussed minimum. The characteristic feature of the emission bands of sulphide phosphors is that their intensity distribution is described by Gaussian curves

(Lehmann 1963). For long-wave emission of (Zn, Cd)S-Cu phosphors this was proved by the author in an earlier paper (Łukaszewicz 1972). There is a simple method proposed by Lehmann (1963) for checking whether a given curve is Gaussian. By plotting the results according to this method one obtains in such a case a V shaped plot. The only condition for using this method is that the emission band represented by the given curve would be really single. As it can be seen from Figs 1-6 the majority of the (Zn, Cd)S-Cu luminophors investigated in the present paper has in addition to a strong short-wave band a weak band in the long-wave range. The latter is more pronounced at higher temperatures and prevents the application of the Lehmann method for checking whether the shape of the short-wave intensity curves is Gaussian. Thus it was possible to use this method successfully only at the lowest temperature considered (-150°C) at which the intensity of the

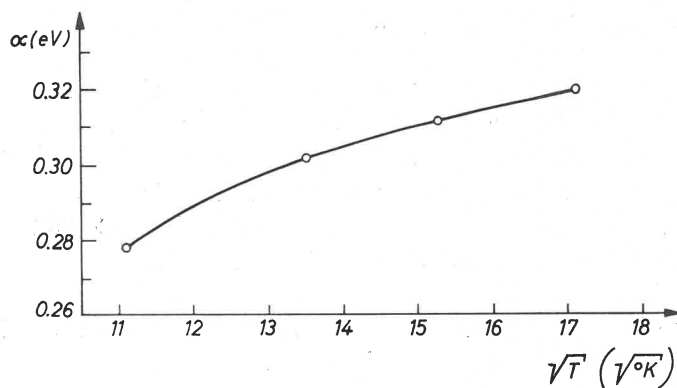


Fig. 12. Dependence of the half-width of the short wave emission spectrum on \sqrt{T} for sample No 13a (10ZnS+90CdS)-Cu

long-wave band is very small, and also for high CdS concentrations (above 50% mol.) where the long-wave band disappears. The results are shown in Fig. 11. The characteristic shapes of the plots in this figure indicate that the emission curves which characterize the short-wave band of (Zn, Cd)S-Cu phosphors are in fact Gaussian.

The half-widths of the short-wave band of the luminophors (expressed in eV) are indicated below the abscissae axis of each graph in Fig. 11. It is seen that these half-widths practically do not depend on CdS concentration in the luminophor and at -150°C equal on the average about 0.29 eV. As the temperature increases the half-width of the band becomes larger. For example, in case of sample No 13a (90% mol. CdS) the half-width increases from about 0.28 eV at -150°C to about 0.32 eV at $+20^{\circ}\text{C}$. This is shown in Fig. 12. The half-width of the long-wave band also increases similarly, namely from 0.29 eV to 0.35 eV in the same temperature range (Łukaszewicz 1972).

According to Shionoya (1966) the half-width of the short-wave band of ZnS-Cu in the investigated temperature range is slightly smaller (about a few hundredths of eV) than that of the long-wave band. This result is in agreement with that obtained in the present work, although the values given by Shionoya are somewhat smaller.

The measurements of the short-wave emission of (Zn, Cd)S-Cu phosphors made by the author confirm the features of this emission observed earlier by other authors, however, owing to the wide temperature range in which were made, they provide more information about this process.

4. Conclusions

The results which may be of some value for luminescence studies can be summarized as follows:

1) The energy of the emitted photons is influenced by both the temperature and CdS concentration.

2) The "motion" of the short-wave band towards greater wavelenths during the increase in CdS concentration is approximately the same at all the temperatures under consideration.

3) The decrease in the energy corresponding to the maximum intensity of the band which occurs with increasing temperature, is for a given luminophor of the same order of magnitude as the decrease in the energy corresponding to the width of the forbidden zone. These quantities change in the same way, which indicates their close connection.

4) The short-wave emission spectrum of each of the (Zn, Cd)S-Cu phosphors has approximately Gaussian shape. Thus the luminescent centres of this emission can be regarded as localized centres.

5) The half-width of the band at a given temperature is approximately constant and is independent of the CdS concentration in the luminophor. It increases, however, with increasing temperature and *vice versa*.

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