

THE EFFECT OF TEMPERATURE AND CdS CONCENTRATION ON THE LONG-WAVE PHOTOLUMINESCENCE OF (Zn, Cd) S—Cu PHOSPHORS

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A study has been made of the long-wave emission spectrum of (Zn, Cd) S—Cu phosphors as a function of changes in composition from 100% ZnS to 100% CdS in the temperature range from -150°C to $+200^{\circ}\text{C}$. Apart from the well-known shift of the emission band towards the long wavelengths with increased CdS concentration, two other phenomena were discovered:

- a) high-temperature luminescence at a CdS concentration of about 4–8 mol %, and
- b) a simultaneous effect of temperature and CdS concentration on the energy of emitted photons.

It is also shown that the spectral curve of luminous emission of (Zn, Cd) S—Cu in the long wavelength region is Gaussian in shape, and that the half-width of such a curve at a given temperature is constant and independent of the ZnS to CdS content ratio. On the other hand, the band half-width changes with a change in temperature, from about 0.29 eV at -150°C to about 0.40 eV at $+200^{\circ}\text{C}$.

1. Introduction

Among the large class of sulphide phosphors, those with a mixed basic substance, namely, (Zn, Cd)S, constitute a quite important group. These may be unactivated phosphors or ones activated with such elements as Ag, Cu or Au. Activation with copper or silver yields phosphors which emit light in almost the entire visible range — from blue to red. Therefore, they are extensively used in the production of X-ray and colour-television screens. Despite such important technical applications, much less scientific research has been carried out on (Zn, Cd)S phosphors than with ZnS and CdS themselves.

The mixed crystals of (Zn, Cd)S phosphors were discovered by Guntz in 1926. Since then many researchers have engaged in work on revealing their properties: Levshin

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and Fridman (1935), Rothschild (1938, 1946, 1963), Kröger (1939), van Gool (1958), Albers (1960), Ortmann and Treptow (1960), Lehmann (1963, 1966), Ostaszewicz (1965) and others.

One outcome of these researches is important, namely, a gradual replacement of ZnS by CdS causes a smooth displacement of the maxima in the emission bands towards the long waves. According to Grosnier and Curie (1961), the maximum of the long-wave band in (Zn, Cd)S—Cu phosphors changes its position in the spectral region from 535 nm for ZnS—Cu (blende) to 1020 nm for CdS—Cu, whereas the maximum of the short-wave band from 460 nm to 820 nm, respectively. Ortmann and Treptow (1960) found that the energy spacing between the maxima of the two bands is independent of the ZnS to CdS ratio and equals 0.36 eV at room temperature. Also, as demonstrated by Lehmann (1963), the half-width of these bands at room temperature equals 0.36 eV and is independent of the CdS concentration in the phosphor. Moreover, this authors also showed that single emission bands of (Zn, Cd)S phosphors may be exactly described by Gaussian curves. On the other hand, Albers (1960) found that the curves of the shifts of the maxima of the long- and short-wave emission bands against CdS content and the absorption edge all run parallelly to each other. Whence it follows that the energy terms of these bands are at equal distances from the valence or conduction band, irrespectively of the ZnS to CdS ratio. According to Albers (1960) temperature, which enormously affects the intensity of emission bands, bears no effect at all on the position of the maxima.

The experiments of all of the mentioned authors, including Albers, had been conducted only at room temperature or sometimes at liquid air temperature. Because there is a lack of experiments carried out at several different temperatures, and especially at high temperatures, no adequate data is available in the accessible literature on the simultaneous effect of temperature and CdS concentration on the photoluminescence of (Zn, Cd)S—Cu phosphors.

The aim of this study was to investigate the long-wave photoluminescence of (Zn, Cd)S—Cu phosphors at several temperatures lower and higher than room temperature. On the basis of the obtained experimental data we hoped to establish a) the effect of temperature and CdS concentration on the position of the peak in the spectral region, and b) the effect of temperature and CdS concentration on the intensity of the band under study.

2. Preparation of the luminophors

The (Zn, Cd)S—Cu luminophors were prepared from ZnS and CdS manufactured by the Fabryka Odczynników Chemicznych (Chemical Agents Plant) in Gliwice, Poland, specified to be of "special purity for luminophors".

The mixture of basic substances, Cu activator in the form of an aqueous solution of $\text{Cu}(\text{NO}_3)_2$, and 5% of NaCl flux was dried at about 120°C and then sintered according to the method given by Ostaszewicz (1963). Sintering was accomplished in covered quartz test tubes arranged standing up in a resistance furnace heat up earlier to the required temperature. Ten-gram samples were sintered 20 minutes at a temperature of $(900 \pm 10)^\circ\text{C}$.

The sintering atmosphere consisted of the gases liberated from the samples, namely, S, SO₂, NO₂, Cl₂, HCl, Zn and Cd. The ready luminophors were cooled in the same test tubes at room temperature.

Several tens of luminophors had been prepared in this manner. The Cu concentration in all of them was constant and equal to 10⁻⁴ g per gram of basic substance, while the CdS concentration was variable. The nineteen samples specified in Table I were used in the experiments. The molar concentrations of ZnS and CdS and the activator and flux concentration given in Table I are values for the mixture before sintering. According to Drozd and Levshin (1961) and Rothschild (1963), the loss of CdS due to sublimation at temperatures below 980°C is relatively small and does not exceed 1% of the initial quantity. The obtained luminophors were of a mixed sphalerite-wurtzite structure because of the relatively low sintering temperature, at which ZnS crystallizes in the sphalerite form and CdS in the wurtzite form (Curie 1964, 1965, Lehmann 1965, Zhirov 1940).

3. Experimental procedure

For carrying out the study of the photoluminescence of the (Zn, Cd)S–Cu luminophors, thin films of them were glued with organic glass onto aluminium disks 20 mm in diameter. The samples of various CdS concentrations prepared thus were placed in a special device devised and constructed by Kulaszewicz (1969) which allowed high and low temperatures to be achieved during the experiments. The low temperatures were acquired by means of cooling by liquid air, whereas the high ones by means of an additional electric heater.

The spectral distributions of the intensity of photoluminescence for the individual phosphors were examined at five different temperatures: –150°C, –90°C, +20°C, +120°C and +200°C. Temperature determinations were made with the use of a calibrated iron-constantan thermocouple and a GES2–C2 mirror galvanometer of a sensitivity of 3 × 10⁻⁸ A/division. The accuracy of temperature determinations was ±2 degrees.

The luminophors were excited by the 365 nm wave emitted by a Philips HPW-125W mercury lamp with a Wood filter. The red radiation of the lamp was absorbed by a filter in the form of a 20 mm layer of aqueous solution of CuSO₄ of concentration 57 g/liter. The spectrum of the emitted light was acquired by means of a Zeiss SPM-1 prism monochromator, and it was recorded by using a Zeiss M12S or Soviet-made FEU-22 photomultiplier with a d. c. amplifier and GES2-A2 mirror galvanometer of a sensitivity of 4 × 10⁻⁹ A/division. The block diagram of the arrangement is shown in Fig. 1.

The distance between the mercury lamp and luminophor was 25 cm, whereas that between the luminophor and the monochromator's entrance slit was 26 cm. The width of the entrance and exit slits of the monochromator was 0.1 mm in measurements with luminophors Nos 0 to 9 and 0.5 mm in measurements with luminophors Nos 10 to 18. The emission spectra of the latter group of luminophors were recorded with the FEU-22 photomultiplier and, as its sensitivity is lower than that of the M12S device, the slits were wider.

The spectral distribution of photoluminescence intensities of the luminophors was determined with a normal lamp of colour temperature 2854 K as reference. For this lamp Planck's formula

$$I(\lambda) = \frac{C_1}{\lambda^5} \left[\exp\left(\frac{C_2}{\lambda T}\right) - 1 \right]^{-1}, \quad (3.1)$$

may be used, where $I(\lambda)$ is the radiation intensity for the given wavelength, C_1 and C_2 are constants, and T is temperature in degrees Kelvin. In comparative measurements C_1 is eliminated, whereas C_2 is a universal constant equal to 1.438 cm deg.

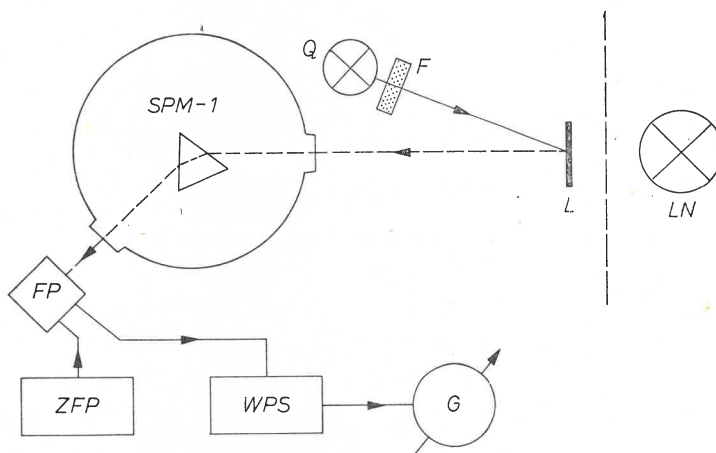


Fig. 1. Block diagram of measuring arrangement. *SPM-1* — monochromator, *Q* — mercury lamp, *F* — $\text{CuSO}_4 + \text{H}_2\text{O}$ filter, *L* — luminophor, *FP* — photomultiplier, *ZFP* — photomultiplier supply, *WPS* — d.c. amplifier, *G* — galvanometer, *LN* — normal lamp

The same normal lamp was used for determining the spectral sensitivity of the two photomultipliers, which is not identical throughout their total measuring range.

If we denote the photoelectric current of the normal lamp by $i_n(\lambda)$, and the relative radiation intensity by $I_n(\lambda)$, then

$$i_n(\lambda) = \gamma(\lambda) \cdot I_n(\lambda), \quad (3.2)$$

where the coefficient of proportionality $\gamma(\lambda)$ is the spectral sensitivity of the photomultiplier. From Eq. (3.2) we have

$$\gamma(\lambda) = \frac{i_n(\lambda)}{I_n(\lambda)}. \quad (3.2a)$$

When determining the spectral sensitivity of the photomultiplier the luminophor *L* and mercury lamp *Q* in Fig. 1 were removed, and the monochromator slit was illuminated

by the normal lamp LN from a distance of one meter. The wavelength responses of the photomultiplier spectral sensitivities are presented in Fig. 2.

The relative distributions of photoluminescence intensities of the examined luminophors were also determined from Eq. (3.2) which is valid when the monochromator slit

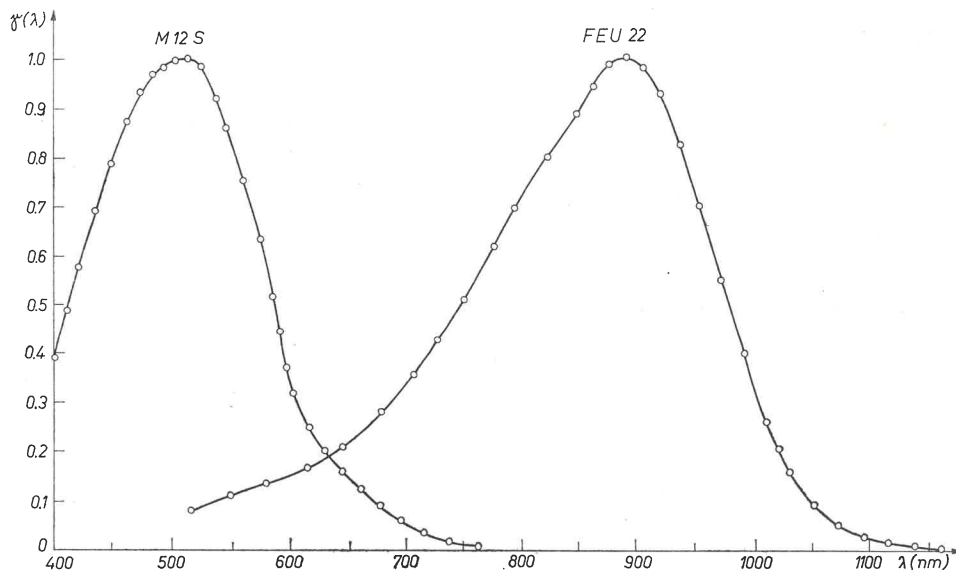


Fig. 2. Spectral sensitivity of M12S and FEU-22 photomultipliers versus wavelength

is illuminated by the light from the luminophor as well as when the normal lamp is used. Therefore, we can write

$$i_L(\lambda) = \gamma(\lambda) \cdot I_L(\lambda)$$

or

$$I_L(\lambda) = \frac{i_L(\lambda)}{\gamma(\lambda)}. \quad (3.3)$$

Here, $i_L(\lambda)$ is the intensity of the photoelectric current obtained when the monochromator slit is illuminated by the examined luminophor, and $I_L(\lambda)$ is the intensity of the falling on the photomultiplier.

This method is valid only when the electric and geometric parameters are strictly identical in measurements of both $i_n(\lambda)$ and $i_L(\lambda)$.

4. Results of measurements

Measurements of the spectral distribution of intensities were performed for all of the luminophors listed in Table I. Closer details are given here for some of them (Nos 0, 4, 10, 15 and 18), as the spectral distributions of the other luminophors are intermediate ones of those just mentioned.

A multitude of earlier studies (Kröger 1949, Riehl and Ortmann 1959, van Gool 1961, Wrzesińska 1962, Curie 1965, Ostaszewicz 1965, and others) have shown that the ZnS-Cu luminophor has two principal emission bands — a blue one in the shorter wavelengths and a green one in the longer wavelengths. They are seen in Fig. 3, which presents the spectral distributions of intensities of the luminophor No 0 (ZnS-Cu) at various temperatures. The short-wave band occurs distinctly only at temperatures lower than room temperature, and its peak shifts with a rise in temperature towards the longer waves (from about 452 nm at -150°C to about 458 nm at -90°C). This is proof that its origin is blue copper centers and not the self-activated ZnS luminophor (Shionoya 1966). At room and higher

TABLE I

Specification of luminophors used

Luminophor No	Content of mixture components in mol % (each mixture had an addition of 10^{-4} g Cu per gram mixture)
0	100.0 ZnS + 0.0 CdS
1	98.7 ZnS + 1.3 CdS
2	97.3 ZnS + 2.7 CdS
3	96.2 ZnS + 3.8 CdS
4	93.7 ZnS + 6.3 CdS
5	90.8 ZnS + 9.2 CdS
6	88.2 ZnS + 11.8 CdS
7	85.6 ZnS + 14.4 CdS
8	83.1 ZnS + 16.9 CdS
9	78.7 ZnS + 21.3 CdS
10	71.2 ZnS + 28.8 CdS
11	64.9 ZnS + 35.1 CdS
12	59.7 ZnS + 40.3 CdS
13	54.3 ZnS + 45.7 CdS
14	47.1 ZnS + 52.9 CdS
15	37.2 ZnS + 62.8 CdS
16	22.9 ZnS + 77.1 CdS
17	12.9 ZnS + 87.1 CdS
18	0.0 ZnS + 100.0 CdS

temperature the short-wave band does not appear; according to Levshin (1951) and Curie (1965) this is due to temperature quenching. The low intensity of the short-wave band is explainable by the fact that in this luminophor, sintered at a low temperature and containing little activator, there are a great many less blue luminous centers of copper linked with the wurtzite structure of ZnS than green ones associated with the sphalerite structure. This is in agreement with the results of Riehl and Ortmann (1955), Shrader and Larach (1958), Ostaszewicz (1965) and others.

The long-wave band which appears at each of the considered temperatures (Fig. 3) possesses a maximum lying more or less in the same spectral region (about 537 nm) for temperatures from -150°C to $+120^{\circ}\text{C}$. On the other hand, at $+200^{\circ}\text{C}$ it is shifted towards

the longer waves by 8 nm lies at about 545 nm. The intensity of the long-wave band of ZnS-Cu increases with temperature, reaching maximum value at +20°C, after which it decreases monotonically right down to the highest temperature of +200°C achieved in this experiment. This is in agreement with earlier studies by Ostaszewicz (1969) and Kulaszewicz (1970).

Introducing increasingly greater quantities of cadmium sulphide into zinc sulphide causes Zn^{2+} ions in the lattice to be gradually substituted by Cd^{2+} ions. As shown by nu-

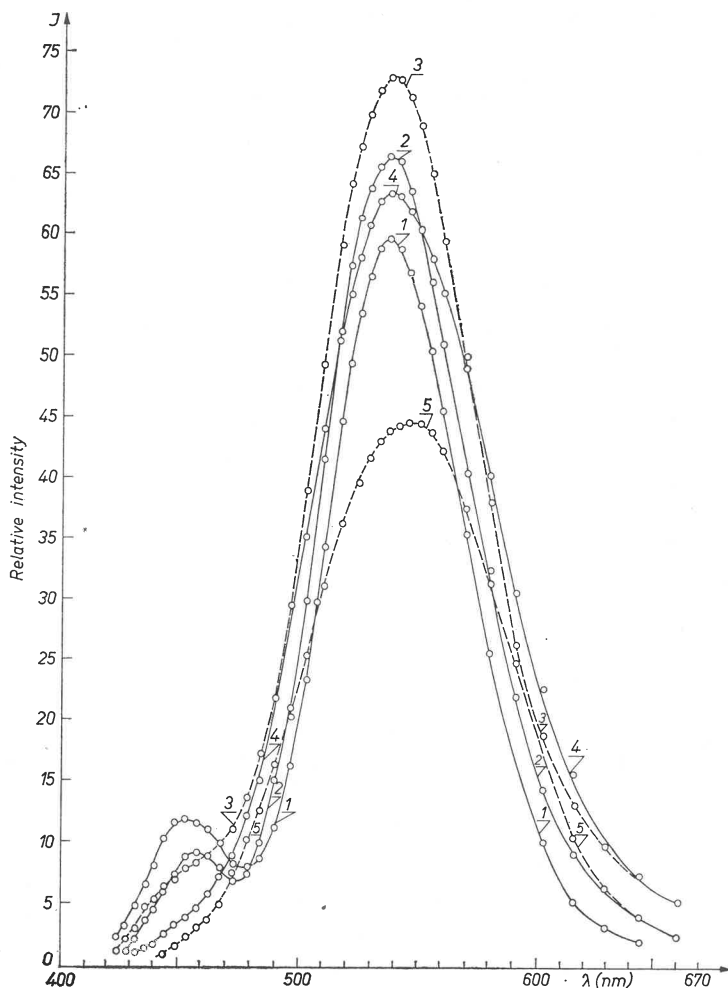


Fig. 3. Luminophor No 0 — ZnS-Cu. Spectral characteristic at various temperatures. 1. -150°C, 2. -90°C, 3. +20°C, 4. +120°C, 5. +200°C

merous authors (Levshin 1951, Albers 1960, Ortmann and Treptow 1960, Grosnier and Curie 1962, and others), this causes a smooth shift of the peaks of both the short- and long-wave bands towards the red and infrared regions. The results of the present work are in

conformity with this well-known-experimental fact and such shifting is observed, as may be seen from Figs 4 to 7 depicting the spectral distributions of photoluminescence intensities of (Zn, Cd) S—Cu luminophors of successively higher CdS concentrations. The technology of the luminophors was chosen such, as to have the short-wave band vanish when CdS was added to the ZnS, since it interferes in the measurement. This goal was achieved, for beginning with a CdS concentration of about 29 mol % (Fig. 5), the short-wave band ceases to appear.

The gradual substitution of ZnS by CdS gives rise to yet another phenomenon. Namely, the intensity maximum of the long-wave band of (Zn, Cd) S—Cu luminophors at first becomes shifted with increasing CdS concentration towards the temperatures higher

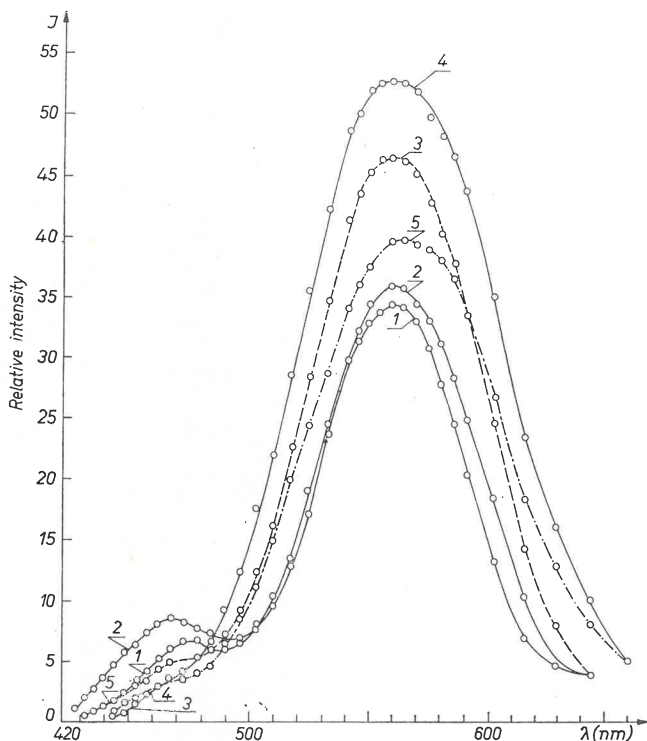


Fig. 4. Luminophor No 4 — (93.7 ZnS + 6.3 CdS)-Cu. Spectral characteristic at various temperatures. 1. -150°C , 2. -90°C , 3. $+20^{\circ}\text{C}$, 4. $+120^{\circ}\text{C}$, 5. $+200^{\circ}\text{C}$

than room temperature (Fig. 4). Then, after exceeding a certain value of concentration it tends to go back to room temperature, passes it and heads towards the lowest temperatures (Figs 5–7).

In ZnS—Cu (Fig. 3) maximum intensity occurs at a temperature of approximately $+20^{\circ}\text{C}$. With gradual additions of CdS the intensity maximum shifts towards the higher temperatures and at a CdS concentration of 6.3 mol % it is at a temperature of about $+120^{\circ}\text{C}$ (Fig. 4). As is seen in Fig. 4, at this concentration the band intensity even at

+200°C is higher than that at the low temperatures (−150°C and −90°C). As the CdS concentration increases further the maximum of long-wave emission intensity turns back towards the temperature +20°C and then, as follows from Figs 5, 6 and 7, to the region of lowest temperatures. In connection with this, luminophors of the highest CdS concentration

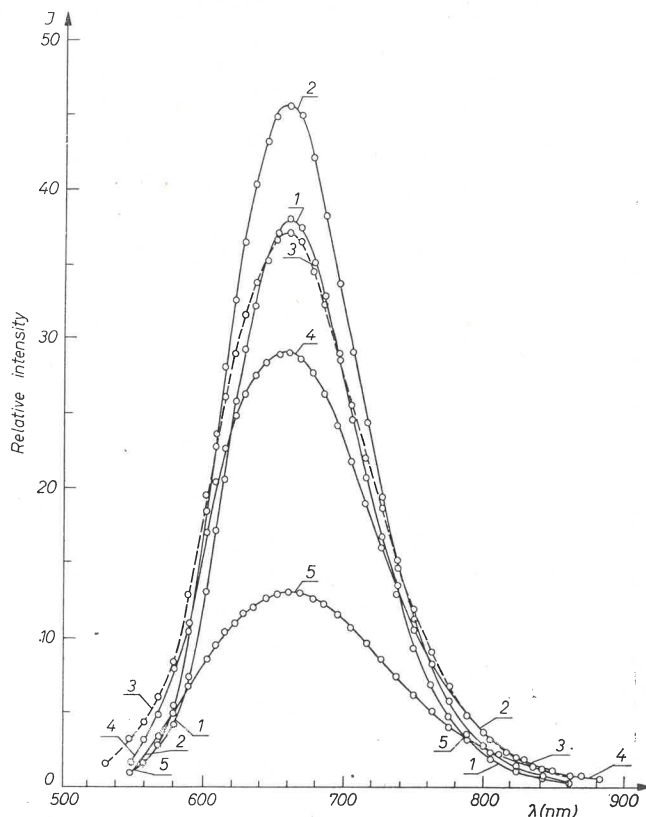


Fig. 5. Luminophor No 10 — (71.2 ZnS + 28.8 CdS)-Cu. Spectral characteristic at various temperatures.
1. −150°C, 2. −90°C, 3. +20°C, 4. +120°C, 5. +200°C

(somewhere above 70 mol %) “glow” best at the lowest temperatures — in this case at −150°C.

Temperature also affects the position of the long-wave band’s maximum of a given luminophor in the spectral region.

The band maximum of ZnS-Cu is shifted at a temperature of +200°C towards the long waves by 8 nm (Fig. 3) as compared with the position at the lower temperatures. However, as CdS is added to ZnS the magnitude of this shifting becomes smaller and smaller, and at a CdS concentration of about 29 mol % (Fig. 5) the peak of the long-wave band lies at all of the considered temperatures in the same spectral region of about 661 nm. The lack of any definite effect of temperature on the position of the band maximum, appearing at the above CdS concentration, is maintained up to CdS concentrations of something

like 60 mol %. On the other hand, once this value is passed there is observed a distinct shift of the maximum of the band under consideration towards the short waves as the temperature increases. For example, in the case of luminophor No 15 (62.8 mol % CdS, Fig. 6) the peak of the long-wave band at -150°C and -90°C lies at about 830 nm, at $+20^{\circ}\text{C}$ near 822 nm and at 120°C near 817 nm. Hence, there is a shift towards the shorter waves by about 8 nm and 13 nm, respectively.

The greatest effect of temperature on the position of the long-wave maximum appears in the case of the last luminophor of any given series, *i. e.*, CdS–Cu. As seen from Fig. 7 (luminophor No 18, 100 mol % CdS), the maximum of this band at -150°C lies at about

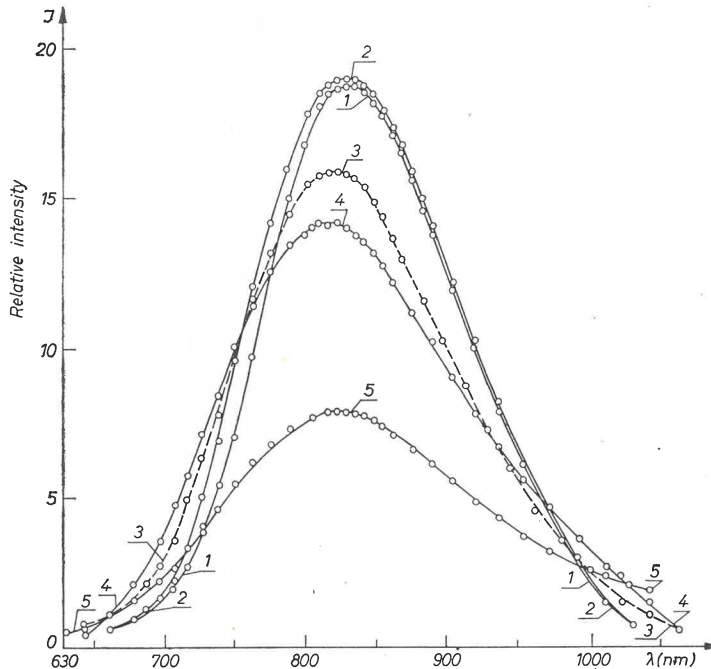


Fig. 6. Luminophor No 15 — (37.2 ZnS + 62.8 CdS)–Cu. Spectral characteristic at various temperatures.
1. -150°C , 2. -90°C , 3. $+20^{\circ}\text{C}$, 4. $+120^{\circ}\text{C}$, 5. $+200^{\circ}\text{C}$

1024 nm, whereas at -90°C in the vicinity of 1018 nm, and at $+20^{\circ}\text{C}$ and $+120^{\circ}\text{C}$ at about 1001 and 985 nm, respectively. Hence, the shift of the band maximum is greatest for the luminophor CdS–Cu and is about 6 nm, 23 nm and 39 nm, respectively.

Due to temperature quenching the intensity of the band under study at $+200^{\circ}\text{C}$ is low and its maximum is broad, so determining the wavelength corresponding to it is rendered difficult. Moreover, it should be emphasized that the positions of the peaks of the long-wave band of CdS–Cu were determined with rather poor accuracy because of the low sensitivity of the photomultiplier in the spectral region of the radiation of this luminophor. Despite this, the shifting of the band towards the short waves at rising temperature is sufficiently distinct.

Apart from the phenomena described above, in the case of (Zn, Cd) S—Cu luminophors attention is attracted by the non-uniform run of emission intensity with increasing CdS concentration.

The intensity of luminous glow, as seen from Fig. 8, at first drops quickly to reach a minimum at about 6 to 8 mol % CdS, and then slowly increases until reaching maximum

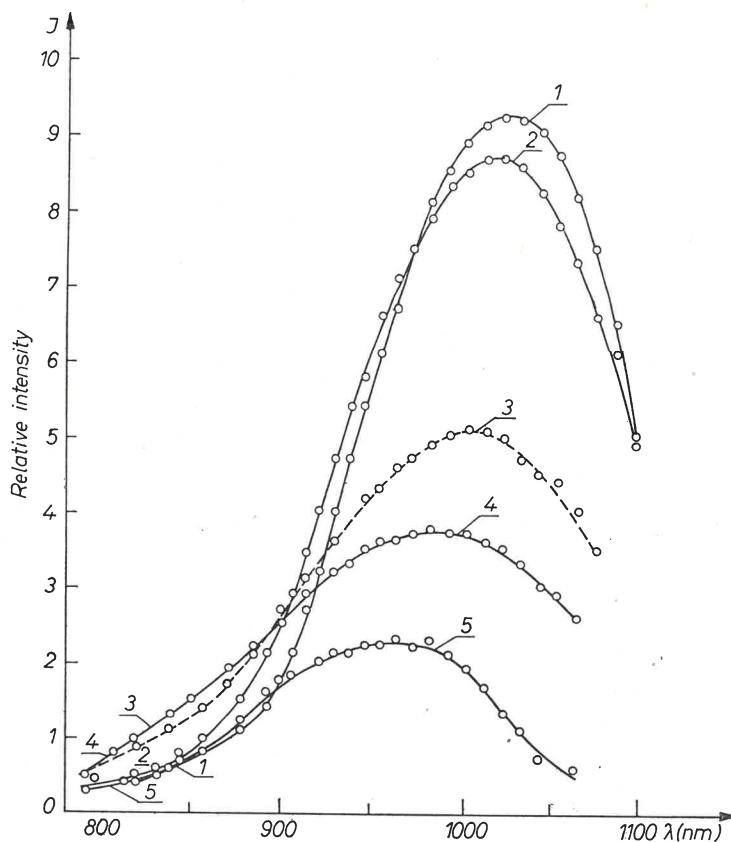


Fig. 7. Luminophor No 18—CdS-Cu. Spectral characteristic at various temperatures. 1. — 150°C, 2. — 90°C, 3. +20°C, 4. +120°C, 5. +200°C

value and drops again. A similar run of intensity of long-wave emission *versus* concentration had been observed for (Zn, Cd) S luminophors activated with Cu or self-activated (Levshin *et al.* 1961, 1970, Gurvich and Ilyina 1967, and others).

The curves of spectral distribution of intensities of (Zn, Cd) S—Cu luminophors presented in Fig. 8 were recorded at a temperature of +20°C by means of an M12FS52A photomultiplier. Special care was taken in order to acquire luminophor layers of as nearly the same thicknesses as possible and as thin as possible for all of the examined samples. Fulfilment of these conditions made it possible to compare the emission intensities of the various luminophors under study. Moreover, repetition of measurements with another

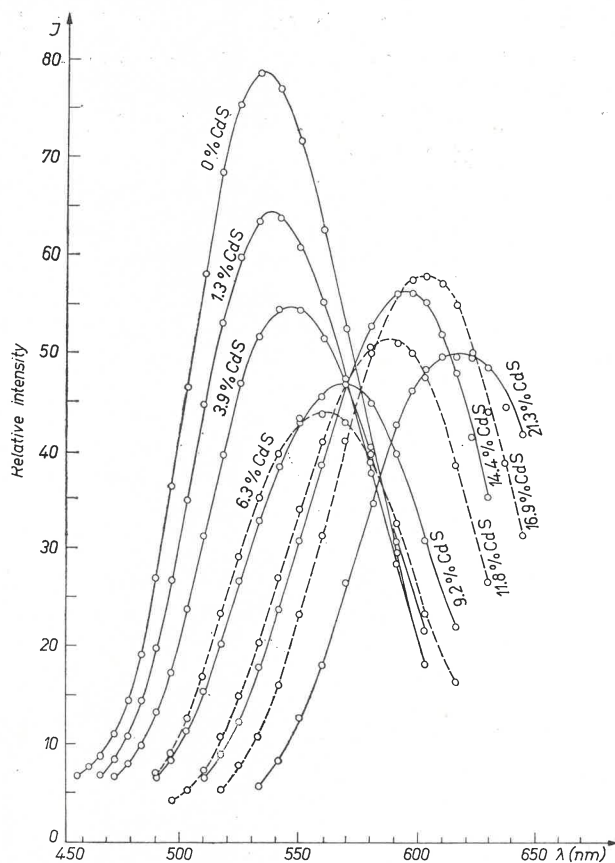


Fig. 8. Spectral characteristics of intensities of several (Zn, Cd) S-Cu luminophors *versus* wavelength at a temperature of $+20^{\circ}\text{C}$

photomultiplier demonstrated the correctness of the measuring technique, for within error limits the positions of the band maxima were identical with those found before.

In addition, on the basis of Figs 3 to 7 it can be ascertained that the drop in intensity of long-wave emission as the CdS content in the luminophors increases proceeds similarly at every temperature considered and that the intensity of the band in mention in CdS-Cu is a dozen-odd times lower than that of the analogous band in ZnS-Cu.

5. Discussion of results

The presented experimental results show that the long-wave band is the dominant one in the whole series of investigated (Zn, Cd) S-Cu luminophors. In accord with the studies of Blinks, Riehl and Sizmann (1961), van Gool (1961) and others, blue centers of copper in ZnS become formed at higher Cu concentrations relative to the co-activator concentrations, whereas the green centers at equal or almost equal concentrations.

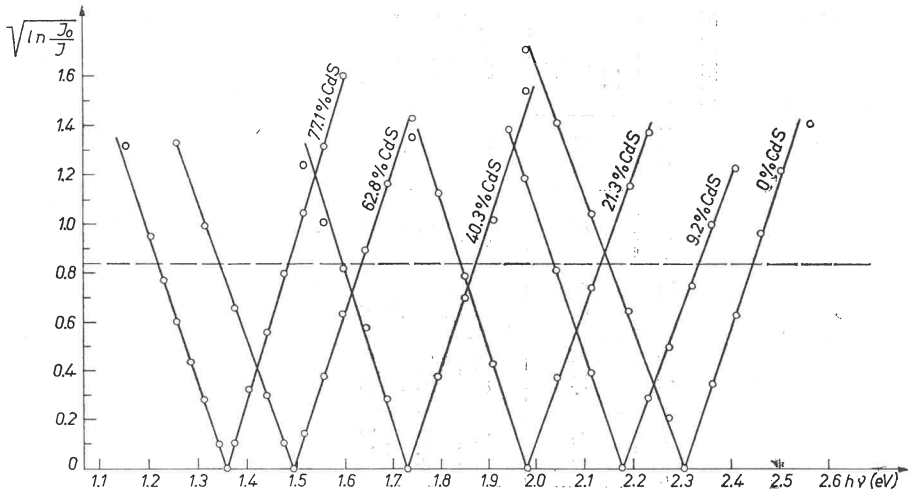


Fig. 9. $\sqrt{\ln I_0/I}$ versus energy of emitted photons for several different (Zn, Cd) S-Cu luminophors at -150°C

The results of the present investigation are in conformity with this statement, for the concentration of the coactivator Cl was higher than that of the activator Cu in the examined luminophors.

Since the intensity of the short-wave band is very low and it appears only at CdS concentrations of up to about 21 mol %, we shall henceforth disregard it. All subsequent deliberations will solely concern the long-wave band.

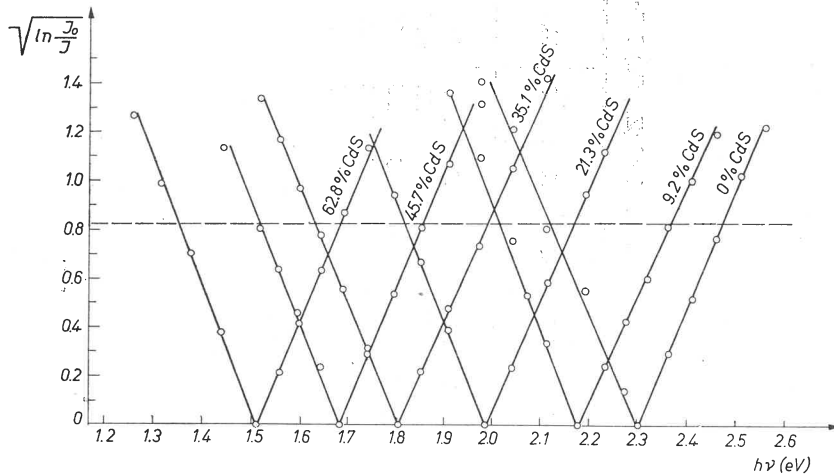


Fig. 10. $\sqrt{\ln I_0/I}$ versus energy of emitted photons for several different (Zn, Cd) S-Cu luminophors at $+20^\circ\text{C}$

The spectral characteristics of photoluminescence of (Zn, Cd) S-Cu phosphors are non-symmetric in shape if presented in the form $I = f(\lambda)$. Typical examples of such curves are shown in Figs 3 to 7. The asymmetry vanishes and all curves become quite close to Gaussian in shape when the value $(\ln I_0/I)^{\frac{1}{2}}$ is plotted against frequency ν , following the

TABLE II
Half-widths (in eV) of the long-wave band of (Zn, Cd) S-Cu luminophors of various CdS concentration at different temperatures

Temp. (°C)	mol % CdS											Mean values (eV)						
	0	1.3	2.7	3.9	6.3	9.2	11.8	14.4	16.9	21.3	28.8		35.1	40.3	45.7	52.9	62.8	77.1
-150	0.29	0.31	0.29	0.29	0.28	0.30	0.29	0.30	0.28	0.30	0.31	0.31	0.28	0.29	0.30	0.29	0.26	0.29
-90	0.31	0.31	0.31	0.31	0.31	0.31	0.32	0.33	0.31	0.32	0.31	0.33	0.30	0.32	0.33	0.31	0.28	0.31
+20	0.34	0.34	0.35	0.35	0.34	0.35	0.35	0.35	0.33	0.36	0.36	0.37	0.35	0.35	0.37	0.34	0.31	0.35
+120	0.37	0.38	0.39	0.38	0.38	0.37	0.36	0.38	0.39	0.39	0.38	0.40	0.39	0.38	0.40	0.38	0.38	0.38
+200	0.40	0.39	0.40	0.41	0.37	0.38	0.37	0.39	0.41	0.42	0.44	0.41	0.36	0.40	0.43	0.40	—	0.40

Half-widths

method proposed by Patterson and Klick (Lehmann 1963). Then, each side of the Gaussian curve becomes a straight line. Curves prepared in this way for the emission under study from several arbitrarily chosen luminophors are given in Figs 9 and 10.

All of the curves in Fig. 9 corresponding to the curves of spectral distribution of intensities of the long-wave band at a temperature of -150°C have an identical half-width, which can be defined as the distance between the two points of the curve for which $I = I_0/2$. This width is within an accuracy of ± 0.01 eV equal to 0.29 eV and independent of the ratio of ZnS to CdS concentrations.

As follows from Fig. 10 and Table II, the half-width of the long-wave band increases as the temperature rises, but at each temperature it is still independent of CdS concentration. And so, at the temperatures of -90°C , $+20^{\circ}\text{C}$, $+120^{\circ}\text{C}$ and $+200^{\circ}\text{C}$ the band half-width

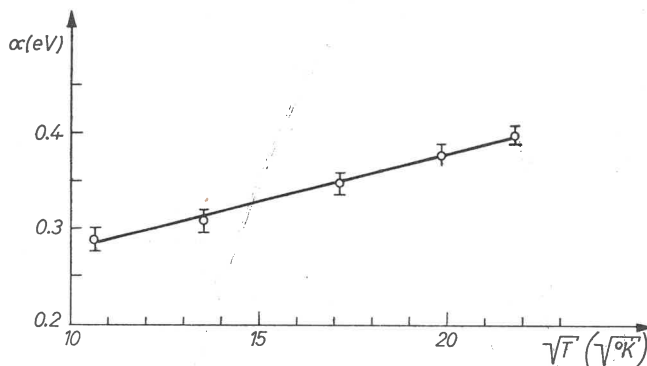


Fig. 11. Half-width of long-wave emission spectrum of (Zn, Cd)S-Cu versus \sqrt{T}

is 0.31 eV, 0.35 eV, 0.38 eV and 0.40 eV, respectively. The obtained results corroborate quite well the corresponding results of Lehmann (1963), who found the half-width of the long-wave band of (Zn, Cs)S-Cu at room temperature to be 0.36 eV, independently of the ZnS to CdS ratio. Also, Curie (1964) quotes values for ZnS-Cu, Cl which are near those obtained here, namely, 0.27 eV at -183°C and 0.33 eV at $+20^{\circ}\text{C}$.

The dependence of half-width on \sqrt{T} is within experimental error limits a straight line; this is seen in Fig. 11. This is evidence that the vibrational energy of the centers in the excited state increases parabolically as temperature rises. The significance of this fact, as pointed out by Curie (1964) and Shionoya (1966), lies in the possibility of making a choice of model for describing the luminescence centers among those proposed.

The spectral distribution curves of photoluminescence presented in the manner described above allow, apart from the convenient way of reading band half-width, a more precise determination of the wavelength corresponding to the band's maximum to be made. For finding the wavelength λ_0 at maximum intensity I_0 from spectral distribution curves plotted in the conventional manner is often rendered extremely difficult because the half-width increases as CdS concentration increases and the peak becomes increasingly more blurred, especially at the higher temperatures.

Besides the evident practical advantages, the fact that single emission bands of (Zn, Cd) S–Cu phosphors are exactly describable by Gaussian curves does not have any obvious physical meaning, according to Lehmann (1963). This author states that the Gaussian shape of the emission curves is presumably only an empirical approximation and, therefore, does not contribute any new knowledge as regards the mechanism of emission in phosphors.

In accord with the purpose of this work, special attention was paid to the behaviour of the long-wave emission of (Zn, Cd) S–Cu phosphors during variations of temperature.

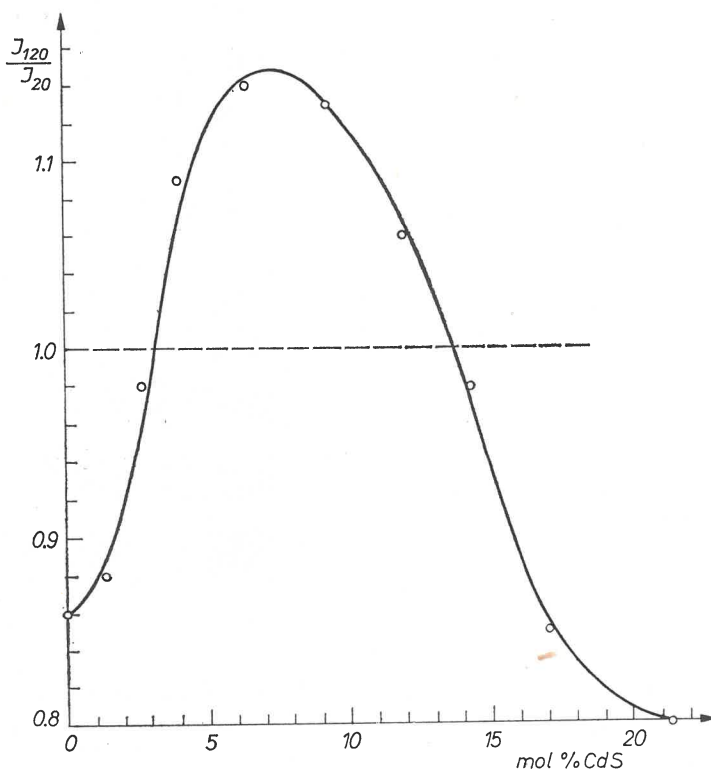


Fig. 12. Ratio of long-wave emission intensities at +120°C and +20°C of (Zn, Cd) S–Cu phosphors at various CdS concentrations

With this aspect in mind, these investigations revealed the occurrence of two, apparently unknown yet, phenomena, namely,

- 1) high-temperature luminescence, and
- 2) a simultaneous effect of temperature and CdS concentration on the energy of the emitted photons.

Both of these phenomena deserve closer examination.

1. The high-temperature luminescence of (Zn, Cd) S–Cu phosphors

It was mentioned earlier that for luminophors of CdS concentration in the 4 to 12 mol %

range the intensity of the long-wave band at $+120^{\circ}\text{C}$ is somewhat higher than that at room temperature. In order to find the CdS concentration at which the high-temperature part of the emission predominates the most, a plot was made of the ratio of emission intensity at $+120^{\circ}\text{C}$ to intensity at $+20^{\circ}\text{C}$ against molar content of CdS in the luminophors studied. This plot, shown in Fig. 12, indicates that the hottest emission is a feature of luminophors having a CdS concentration of about 7 mol %.

On the other hand, at a CdS concentration of about 6 to 8 mol % there is minimum emission intensity at all of the considered temperatures. This is depicted in Fig. 13 for

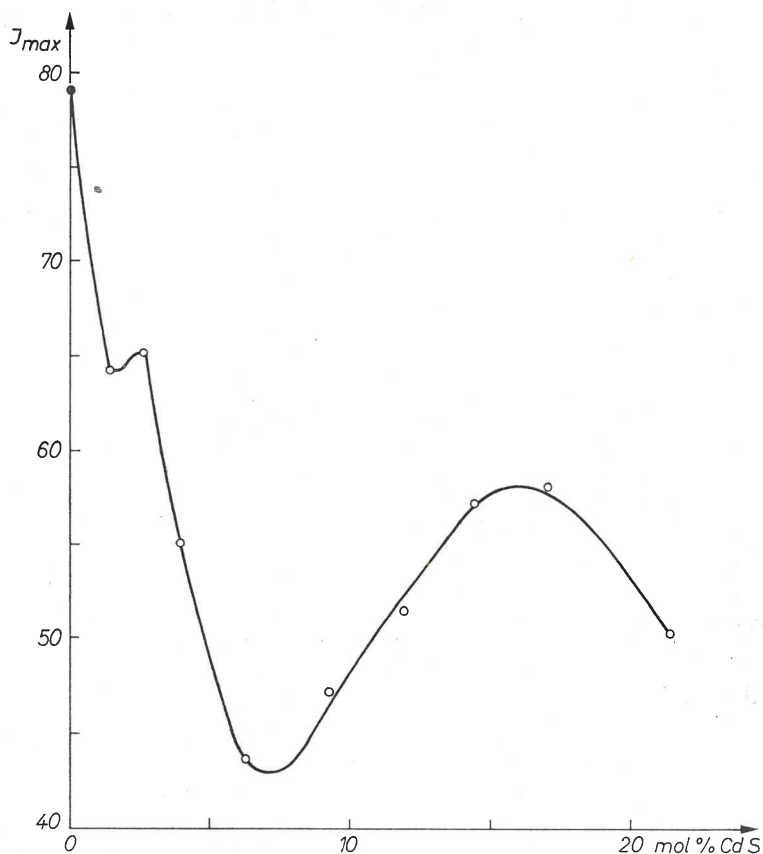


Fig. 13. Dependence of emission maxima of several (Zn, Cd) S-Cu luminophors on CdS concentration at $+20^{\circ}\text{C}$

room temperature, in which the dependence of band peak emission intensity on molar concentration of CdS is presented for several luminophors of relatively low CdS concentrations. The striking convergence of CdS concentrations at which emission is hottest and at which minimum intensity of long-wave emission of (Zn, Cd) S-Cu phosphors occurs is presumably not fortuitous.

Gurvich and Ilyina (1967) explain the occurrence of minimum photoluminescence intensity at 5 to 10 mol % CdS as due to the quenching effect of deep electron traps formed by the introduced CdS. On the other hand, Levshin and Senashenko (1970) elucidate this fact by the appearance of quenching crystal lattice defects, associated with a drop in the homogeneity of luminescence centers, which they say consist of a central Cu^+ ion and twelve Zn^{2+} and Cd^{2+} ions surrounding it.

It seems that both of these explanations are concordant, since a decrease in the internal homogeneity of a luminescence center may lead to the appearance of deep electron traps due to CdS presence. It would follow thus that the concentration of such traps at CdS concentrations of 5 to 10 mol % is the highest. However, the authors of the two papers in

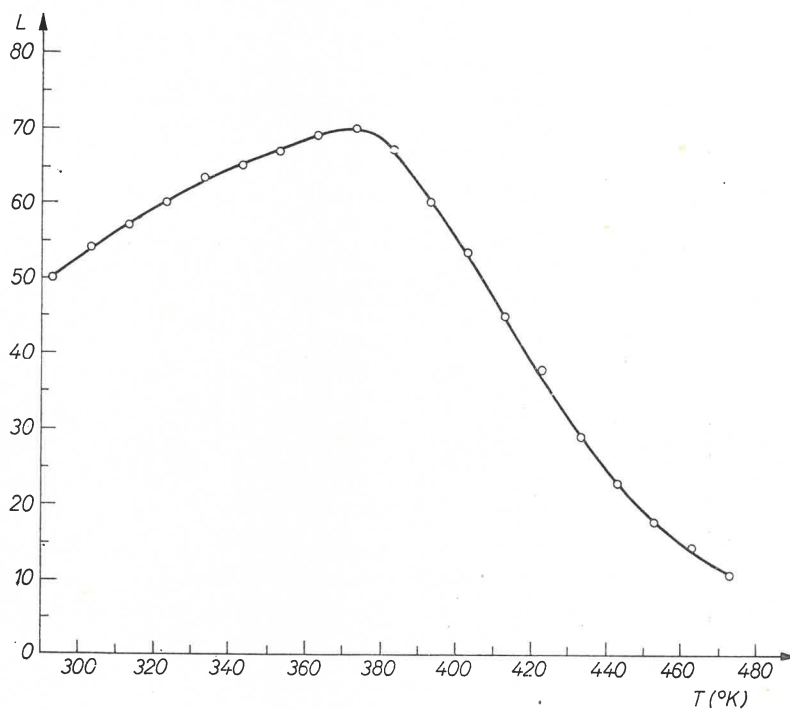


Fig. 14. Luminophor No 4 — (93.7 ZnS + 6.3 CdS)-Cu. Dependence of luminance L on temperature T

mention, not having any results of research carried out at temperatures higher than room temperature, did not give any substantial experimental proof regarding the existence of electron traps and their depth.

The high-temperature emission of (Zn, Cd) S-Cu phosphors revealed in the present study confirms the assumption of Gurvich and Ilyina regarding the formation of deep electron traps at CdS concentrations 5 to 10 mol %, the quenching action of which decreases the intensity of the considered band. For some of the electrons become caught in the traps and are unable to recombine with the ionized luminescence centers at room and lower temperatures. According to Gurvich and Ilyina (1967), the depth of these traps

is of the same order as the depth of traps formed when an addition of cobalt is introduced into ZnS.

To estimate the depth of the electron traps under consideration the following reasoning was used.

The intensity of photoluminescence drops when temperature rises, because the emission of quanta of thermal vibrations begins to compete with photon emission. Therefore, the slight increase in luminescence intensity observed in this work is the outcome of an increase in thermoluminescence intensity which in the process of luminous glow begins then to play a decisive role. The maximum of thermoluminescence of luminophors having a CdS concentration of about 6 to 8 mol % corresponds approximately to a temperature of 373 K. This value was obtained by analyzing the temperature-dependence of the luminance of the luminophor containing 6.2 mol % of CdS (Fig. 14). If this temperature is treated as the approximate temperature of thermoluminescence T^* , then the depth of electron traps corresponding to it can be calculated on the basis of the numerical formula of Urbach (Curie 1965),

$$E = \frac{T^*[\text{K}]}{500} \text{ in eV.} \quad (5.1)$$

The depth computed in this way is 0.746 eV. Since the temperature of thermoluminescence for traps introduced by cobalt in ZnS–Cu equals 380 K (Curie and Sutton 1964), their depth as found from Eq. (5.1) is 0.76 eV. As is seen, these values of trap depth do not differ much. This is yet another confirmation of the correctness of the assumption of Gurvich and Ilyina.

The existence of such traps elucidates the occurrence of high-temperature emission. Indeed, in luminophors with a CdS concentration of about 4 to 8 mol % heated to higher temperatures there is a summing of two luminescent processes — photoluminescence and thermoluminescence. Electrons freed from traps return to the conduction band and become capable of recombining with the ionized luminescence centers.

2. The effect of temperature and CdS concentration on the energy of emitted photons

It has been found (Leverenz 1950, Asano 1955, Albers 1960) that increasing CdS concentration in luminophors causes a smooth shift of the long-wave emission peak towards the longer wavelengths. The relevant results obtained in the present work are presented in Fig. 15, which gives the dependence of the band peak position (in nm) on the molar concentration of CdS. It is evident from the figure that the shift just mentioned is different at different temperatures. At lower CdS concentrations in the luminophor the curves run almost parallelly except for the curve at the temperature +200°C, whereas once the CdS concentration exceeds about 60 mol % the curves diverge. Therefore, at –150°C the long-wave band of (Zn, Cd)S–Cu shifts at the fastest rate (in terms of nm per mol % CdS) towards the infrared, whereas at +200°C this rate is the slowest. In order to have a more usable presentation of the data, the temperature-dependence of the position of the long-wave band maximum is plotted for the various luminophors in Fig. 16. As these plots show, the position of the maximum of any band is up to a CdS concentration of about

17 mol % independent of temperature, except at the temperature of +200°C. At the latter temperature the long-wave band is shifted somewhat towards the longer waves, but the magnitude of this shift decreases as the CdS concentration increases.

As had been mentioned in Section 3, this shift amounts to about 8 nm for ZnS-Cu. This corresponds to a drop in photon energy of 0.036 eV. Bearing in mind that the thermal

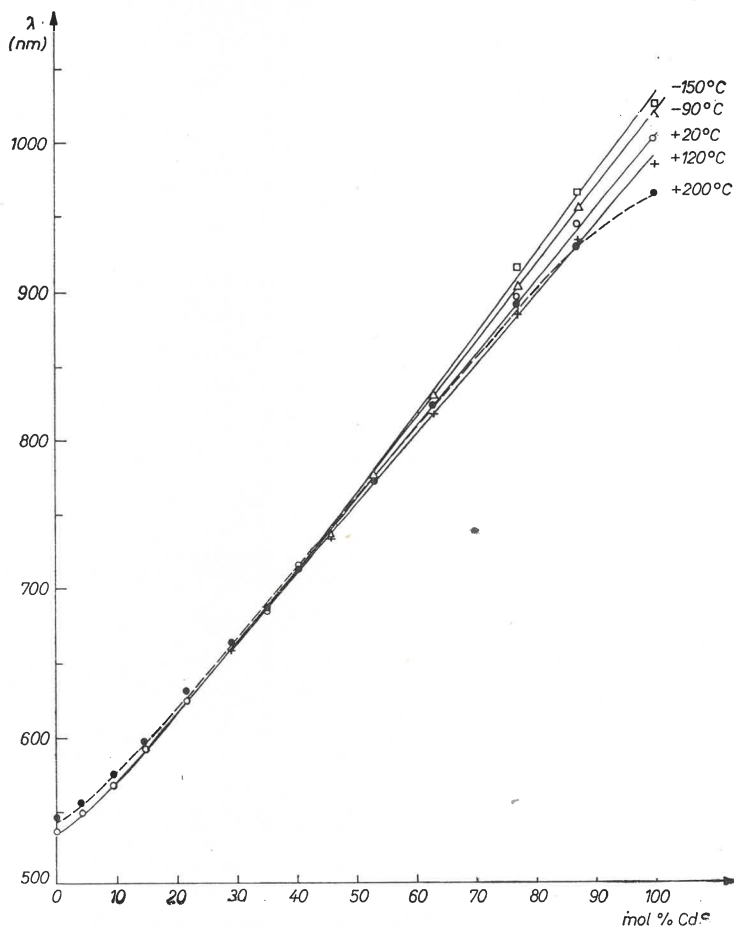


Fig. 15. Position of long-wave band peak for (Zn, Cd) S-Cu against ZnS to CdS ratio at various temperatures

coefficient of the forbidden zone width for ZnS blende is 4.6×10^{-4} eV/K (Shionoya 1966), the magnitude of the decrease in the width of this zone can be calculated for the change of temperature from -150°C to $+200^\circ\text{C}$; it is found to equal 0.161 eV. Hence, it follows that the shift of the peak of the long-wave band of ZnS-Cu towards the long waves is caused by something else besides the decrease in the width of the forbidden energy zone.

Beginning with a CdS concentration of about 17 mol % and up to about 60 mol %

(Fig. 16) the position of the long-wave band peak in (Zn, Cd) S–Cu is independent of temperature. The lack of any shift of the band towards the long waves, in face of the decrease in the width of the forbidden energy zone of (Zn, Cd) S at increased temperature, is further evidence that some other factors affect the energy of the emitted photons.

The most outstanding result of this study, however, is that after exceeding a CdS concentration of about 60 mol% the maximum of the long-wave band shifts as temper-

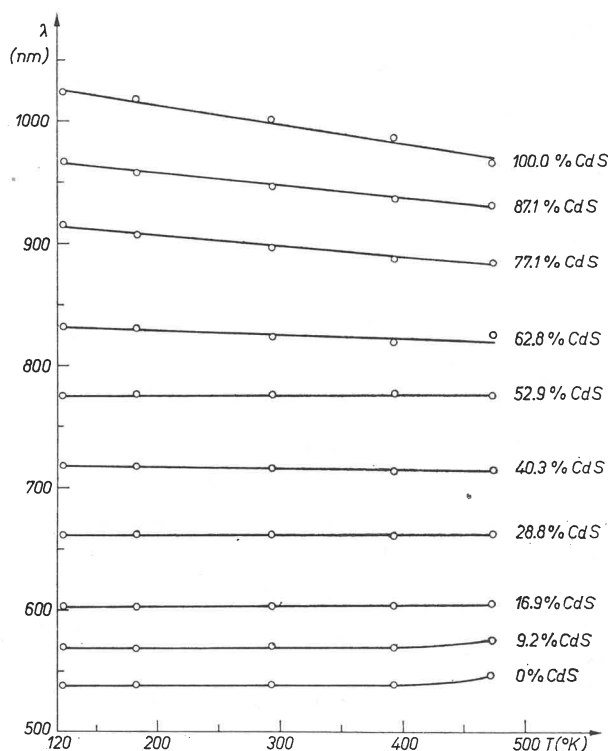


Fig. 16. Dependence of long-wave band peak position on temperature for several different (Zn, Cd) S-Cu luminophors

ature rises towards the shorter waves, this shift being bigger when the concentration of CdS in the luminophor is higher. As is seen in Fig. 16, the shift is largest for CdS–Cu. Specifically, at +120°C the long-wave band peak of this luminophor is shifted towards the shorter waves by about 39 nm relative to its position at –150°C. This corresponds to an increase of energy of the emitted electrons of 0.047 eV. Meanwhile, the width of the forbidden energy zone for CdS ($\beta = 5.2 \times 10^{-4}$ eV/K) decreases by 0.14 eV when the temperature rises from –150°C to +120°C. Hence, according to our reasoning above, in no event may the shift of the long-wave band peak in CdS-Cu be linked up with the change in width of the forbidden energy zone of cadmium sulphide.

Recapitulating, it may only be said that the presented behaviour of the long-wave emission of (Zn, Cd) S–Cu when the temperature of the studied samples was altered is

presumably the outcome of a change in position of the acceptor level in the description of the classical Riehl-Schön-Klasens model, or a change in position of the donor level if the Prener-Williams model is considered. It would be premature to draw any further conclusions at the present moment, as there is yet but little experimental data to work with. Similar studies for the short-wave band of (Zn, Cd)S-Cu are to be undertaken in the nearest future. It is expected that such subsequent data on the photoluminescence of phosphors of the type in mention will allow a better understanding of the processes taking place to be achieved.

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