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Thermoluminescence of ZnS

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A number of zinc sulphide phosphors containing cobalt was prepared with various concentrations of additional impurities. Co^{++}-ions in both copper and silver activated phosphors produce a characteristic glowcurve, showing three distinct peaks above liquid nitrogen temperature. It was established that the first and probably the second glowpeak is connected with distinct traps, while the third peak is caused by a continuous distribution of traps. Measurements of thermoluminescence spectra as well as investigations of energy storage capacity and temperature dependence of electron capture in traps pointed to a local association of traps and luminescence centres in the case of the first two glowpeaks, whereas electron transfer via the conduction band from traps to separated luminescence centers was assumed for the third peak. An already existing model was used for discussing the experimental results obtained.

1. Introduction

Regardless of the many various publications in this field so far, it is rather uncleared what physical processes actually take place in the luminescence of zinc sulphide phosphors. A series of different models was proposed which in most cases could only partially be fulfilled by the various experiments [1–4]. Even the uniform luminescence model for zinc sulphide phosphors suggested in 1966 [5], which makes a particularly easy understanding cannot be considered final.

The aim here was to acquire some more knowledge of the various luminescence centres and mechanisms in ZnS. It was of special interest whether an explanation for the thermoluminescence could be found within the framework of existing models.

2. Experimental

For the thermoluminescence measurements an apparatus developed by ROTHERMEL [6] was used with slight modifications. The arrangement allowed a simultaneous recording of the total luminescence and the thermoluminescence spectra. Glowcurves could also be registered in place of the spectra at various wavelengths. All the measurements were taken at the same photomultiplier voltage, so that given intensities (photocurrents) of the spectrally undistributed (EMI 6256 S) as well as those of the spectrally distributed glowcurves (EMI 9558 QB, S 20 cathode) are approximately comparable. The phosphors were excited with the UV-part of the spectrum of a high pressure mercury lamp (Schott-filter UG 11) usually to saturation. Fluorescence spectra at different temperatures could also be measured after some simple alterations to the device. For measurements of the electron paramagnetic resonance (EPR) an AEG 20-X-spectrometer was used.

Pure ZnS was used in preparing the various phosphors. These were accordingly doped with nitrates and chlorides, which were added in the form of highly diluted solutions. In addition 2 mole percent NaCl were added in the same way [7].

After drying at 120 °C the substance was fired at 1000 °C for an hour in a nitrogen atmosphere. As shown later by ESR measurements (Mn^{++}-signals), the result was an almost pure cubic structure [8]. All doping concentrations are given in mole per mole ZnS.

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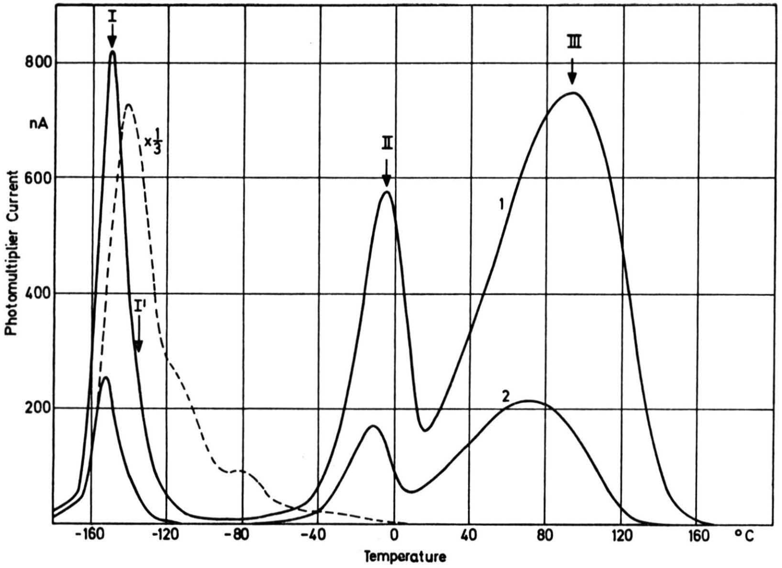

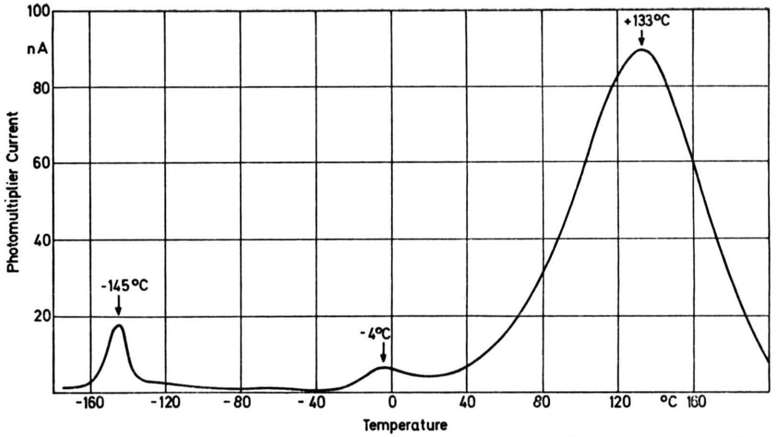

Fig. 2. Thermoluminescence glow curve of ZnS/10^{-4} Ag, $5\cdot10^{-5}$ Co after UV-excitation (saturation) at −183 °C. Heating rate: 36 deg./min.

← Fig. 1. Thermoluminescence glow curves of ZnS/10^{-3} Cu, 10^{-5} Co (———) [heating rates 56 deg./min (1) and 13 deg./min (2)] and of ZnS/10^{-3} Cu (– – –) (36 deg./min) after UV-excitation (saturation).

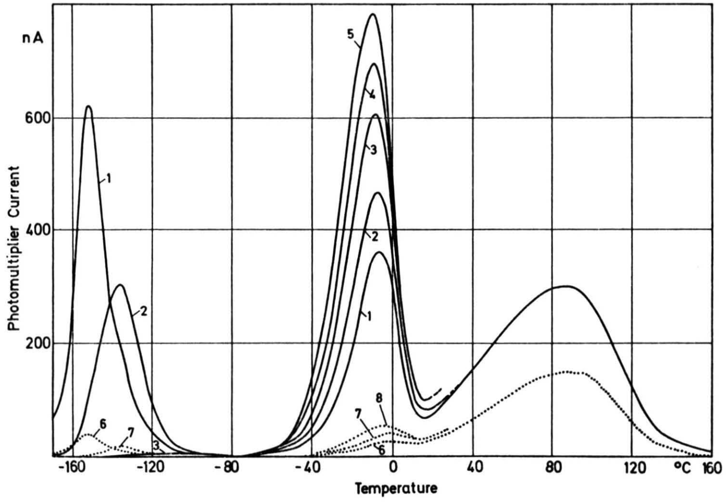

Fig. 3. Thermoluminescence glow curves of ZnS/10^{-3} Cu, 10^{-5} Co after UV-excitation (———) to saturation at different temperatures: −183 °C (1), −152 °C (2), −122 °C (3), −95 °C (4) and −70 °C (5). — Dotted curves: Excitation with unfiltered mercury light (saturation) at −183 °C (6), −152 °C (7) and −70 °C (8). Heating rate: 36 deg./min.

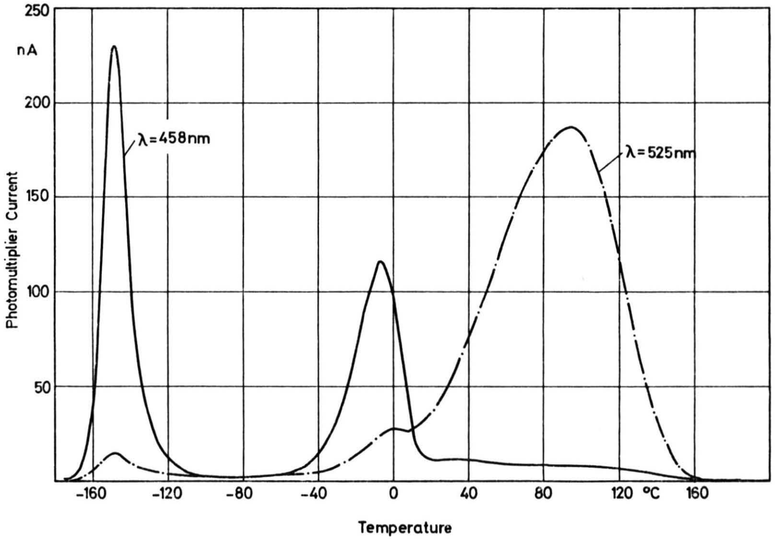

Fig. 5. Thermoluminescence glow curves of the blue and the green emission bands of ZnS/10^{-3} Cu, 10^{-5} Co after UV-excitation (saturation) at −183 °C. Heating rate: 36 deg./min.

3. Experimental Results

A number of cobalt containing phosphors was prepared. Thereby it appeared that the incorporation of spurious amounts of cobalt causes a complete quenching of fluorescence and thermoluminescence. A much different behaviour results, if copper (as Cu^+) is also incorporated. In this case the presence of Co decreases the fluorescence completely, but on the other hand an intensive thermoluminescence is observed. The glowcurve here, with three isolated glowpeaks, takes a form unusual for ZnS. Maximum intensities are obtained with 10^{-3} gram atoms of Cu^+ and 10^{-5} gram atoms of Co^{++} per mole ZnS. The glowcurves for two different heating rates are given in Figure 1. A comparison between the curves and the glowcurve of a phosphor prepared in the same series without cobalt (dotted line) shows the considerable influence of small amounts of cobalt. The observed glowpeaks will be denoted by I, II, and III, whereby a weak glowpeak I′ can be seen hung to peak I. The temperatures at the glowpeaks are −150 °C (I), −133 °C (I′), −8 °C (II), and +95 °C (III) at a heating rate of 36 deg./min. A change in the Cu and Co contents alters the position of the glowpeaks I and II very little, whereas the temperature of peak III cannot be reproduced. A similar glowcurve form is obtained when Ag^+ is substituted for Cu^+ (Figure 2).

Investigations of trap level spectra of ZnS phosphors have so far always revealed a quasicontinuous trap level distribution [9, 10]. But the form of the glowmaxima I and II probably indicates discrete trap levels. To examine this, we used a technique given by HOOGENSTRAATEN [11]. This technique proved more satisfactory for our phosphors than the usually applied initial rise methode [6]. In case of ZnS /10^{-3} Cu, 10^{-5} Co we find that the peaks I and I′ correspond each to a discrete trap level, while peak III results from a continuous or quasicontinuous trap level distribution. For glowpeak II we can only state that there are at least two different trap levels, without excluding the possibility of the existence of further trap levels of course.

The possible filling to saturation of specific traps depends considerably on the temperature during excitation. For the measurements, shown in Fig. 3, the sample was always irradiated to saturation at the given temperatures. The phosphor was than fastly cooled down to 77 K. It is obvious that the intensities of the maxima I′ and II increase with the excitation temperature. The third glowpeak which has different shapes for different measurements, shows no correlation with the excitation temperature. It is not possible to make a corresponding observation for peak I, because the available temperature is not sufficiently low. It must be mentioned here that the degree of trap filling obtained at saturation is due to an equilibrium, which results from the excitation and stimulation effects of irradiating light. The shape of curve 1 is also obtained when after excitation to saturation at −70 °C, and still before taking the glowcurve, the excitation of the specimen is repeated shortly with UV light at liquid nitrogen temperature. If the stimulation effect is increased by removing the UV-filter and thus allowing for the participation of the visible part of the Hg-spectrum, the glow intensity decreases sharply (Fig. 3, curves 6 to 8).

The emitted thermoluminescence consists of three different bands, one in the blue, one in the green, and the other in the red spectral region. The thermoluminescence spectra, which vary highly with the temperature are shown in Figure 4. We have thereby taken into consideration the spectral sensitivity curve of the photomultiplier and the band width of the monochromator which, because of the dispersion of the prisma, is not constant. The blue band appears in glowpeak I at 445 nm and in peak II at 458 nm. The green band too, which appears at first at about 525 nm, shifts with increasing temperature towards longer wavelengths. The position of the red band can be put approximately at 660 nm.

The distribution of the various bands to the different peaks is best taken from the “monochromatic glowcurves”. As Fig. 5 shows, the blue band appears only in peak I, I′, and II while the green band is confined to the third peak. The glowcurves shown in Fig. 6 are obtained when the monochromator is regulated to the red band. Because of the low intensity a red filter (Schott RG 1, 2 mm) is added between the sample and the monochromator to suppress — at least partly — the scattered green light. Obviously the peaks I, I′, and II contain red components. The glowcurve taken at the higher excitation temperature shows very clearly that the second main peak is made up of two components where the first is identified with glowpeak II in Figure 1. The second, which we still here refer to as II′, does

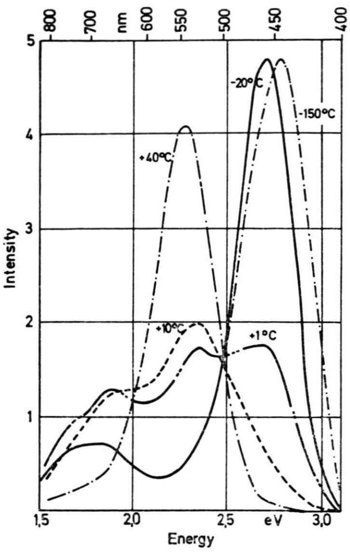

Fig. 4. Spectra of thermoluminescence of ZnS/10^{-3} Cu, 10^{-5} Co at various temperatures.

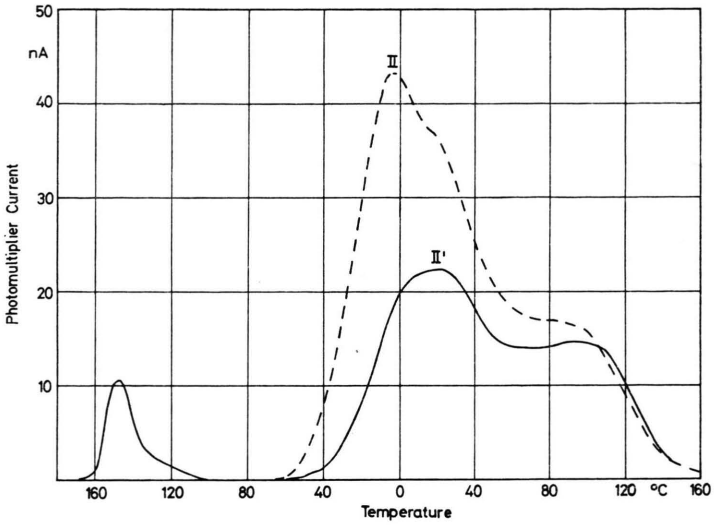

Fig. 6. Thermoluminescence glow curve of the red emission band of ZnS/10^{-3} Cu, 10^{-5} Co after UV-excitation (saturation) at −183 °C (———) and −70 °C (– – –). Heating rate: 56 deg./min.

not show any growing with increasing excitation temperature, as is the case for glowpeak II.

Figure 7 illustrates the relative fluorescence efficiency of the three bands as a function of the temperature. These curves are obtatined from fluorescence spectra, which are continuously taken with increasing temperature (heating rate: 3 degrees/min). For excitation we use 150 kV X-rays, which enables us to register only the fluorescence light which is here very weak, without the participation of the exciting source. The ordinates in Fig. 7 give the intensities of the various band maxima at corresponding temperatures. In spite of the low heating rate the results are slightly falsified by simultaneously emitted thermoluminescence (maximum of the 445 nm curve at −20 °C and rise of the 525 nm curve above 0 °C). The most important result of the fluorescence efficiency measurements is the fact that the green and the blue bands in the fluorescence spectrum, as opposed to thermoluminescence, remain in intensity approximately the same in the whole temperature interval below about 40 °C.

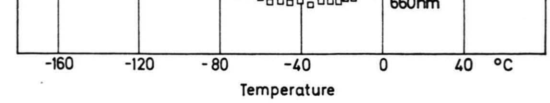

Fig. 7. Intensities of the blue, green and red components of the luminescence of ZnS/10^{-3} Cu, 10^{-5} Co during irradiation with 150 kV X-rays as a function of temperature.

The EPR-spectrum of ZnS/10^{-3} Cu, 10^{-5} Co is shown in Figure 8. In addition to the six sharp,

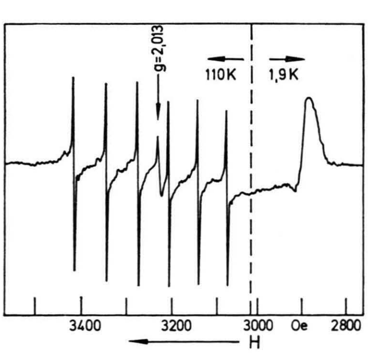

Fig. 8. EPR-spectrum of ZnS/10^{-3} Cu, 10^{-5} Co after UV-irradiation.

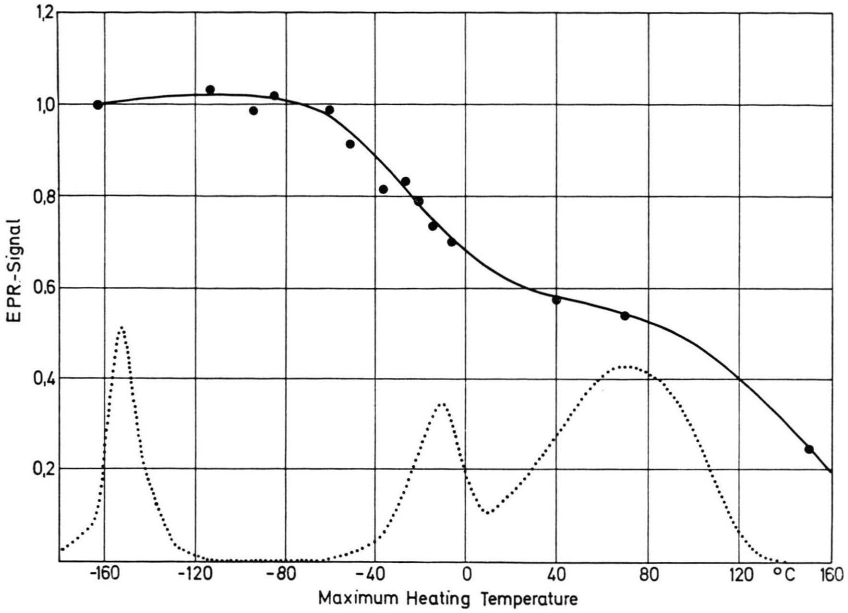

Fig. 9. EPR absorption of $ZnS/10^{-3}$ Cu, 10^{-5} Co at 110 K after UV-excitation and short time heating to various temperatures. (Dotted curve: Thermoluminescence glow curve. Heating rate: 13 deg./min.)

equidistant lines, which are always present as a result of minor Mn impurities, the spectrum shows at 110 K after UV-excitation another signal, which corresponds to a g-value of 2.013 ± 0.003. After heating the UV-excited phosphor repeatedly to different temperatures and then measuring the height of the EPR-signal, the relationship shown in Fig. 9 is obtained. We can see that there is a fast, though incomplete, decay of the EPR-centres around glowpeak II. There is still a trace of the EPR-signal even after heating up to 160 °C. At liquid helium temperature we find still another very broad signal, which is largely deformed due to the very unfavourable conditions of relaxation in this temperature interval (Fig. 8). A g-factor of 2.242 ± 0.010 is obtained.

HOOGENSTRAATEN[12] had already observed earlier that the stored thermoluminescence light sum of an excited ZnS/Cu,Co-phosphor decrease drastically with increasing waiting time between excitation and measurement. He explained this effect with tunneling processes. From measurements on ZnS $/10^{-3}$ Cu, 10^{-5} Co we find that the light of the second glowpeak (at -8 °C) decreases within a time interval of two hours by about 34%, provided the phosphor is kept at liquid air temperature after excitation. Taking a purely exponential decay, the life time of trapped electrons is calculated to be $1.84 \cdot 10^4$ s. In contrast to the second glowmaximum peak III remains stable throughout the whole period of observation.

4. Discussion

It was already established in earlier publications that the incorporation of cobalt in ZnS leads to the formation of deep trap levels with an activation energy of 0.52 eV and a quenching of the visible luminescence[13, 14]. However typical emission bands arise in the infrared spectral region, which are attributed to transitions within the 3d shell of the Co^{++} ion[15]. On the other hand KRYLOVA[16] found that cobalt does not act as a killer if copper is also present, but gives rise to a thermoluminescence glowcurve typical for cobalt. This behaviour was investigated exhaustively by HOOGENSTRAATEN and KLASENS[17]. The authors prepared phosphors with a uniform Cu^+ content of $3 \cdot 10^{-5}$ gram atoms per mole and varied the Co^{++} concentration. While the phosphor without cobalt showed a single glowpeak at about -100 °C a new maximum was formed at 110 °C with increasing cobalt content. At the same time the low temperature peak gradually disappeared. The maximum glowpeak intensity was observed with a cobalt concentration of 10^{-5}.

The two additional peaks I and II which we obtained in our measurements are apparently connected with the copper content, which here is greater by about two orders of magnitude. These peaks are probably characteristic of the incorporated cobalt because their positions are unaffected by the doping concentrations, not even when Ag^+ is substituted for Cu^+ (Fig. 2). It follows therefore that copper does not play an exceptional role in connection with ZnS-phosphors containing cobalt as previously assumed[17].

Various experimental results point to the fact that the thermoluminescence mechanism for peaks I, I′, and II is different from that for the third peak. The very low half width could be a result of discrete trap levels. If on the other hand we consider the temperature shift of the peaks with the heating rate shown in Fig. 1, there are temperature differences of 3 degrees (I), 7 degrees (II) and 20 degrees (III). While the ratio of the shift to the absolute temperature of the glowmaximum remains about the same for peaks I and II, a value twice as much is obtained for peak III. Finally the trap filling to saturation for maxima I, I′, and II is extremely dependent on the spectral structure of the exciting light.

An explanation of the spectral behaviour of thermoluminescence is only possible with the assumption of two different mechanisms.

For the moment we will not take the red band into consideration. Although the green band persists in the fluorescence spectrum (Fig. 7) down to liquid air temperature, in thermoluminescence measurements it is observed only in the third glowpeak. We assume that the green thermoluminescence takes place with the participation of the conduction band, and a coupling between trap levels and the "blue" luminescence centres for peak I, I′, and II. For the examination of these assumptions it was desirable to take measurements of thermally stimulated conductivity. These of course can only be carried out if single crystals accordingly doped are available. We refer here to works of different authors[10, 18] who measured thermoluminescence and thermally stimulated conductivity in ZnS crystals, both simultaneously. The result was always that the green thermoluminescence was accompanied by thermally stimulated conductivity. This kind of parallelity is so far not known for the blue thermoluminescence in ZnS. Due to our measurements on ZnS/10^{-3} Cu, 10^{-5} Co a local association of traps and luminescence centres appears probable in the case of the blue thermoluminescence. The increase in capture probability of traps observed for peak I′ and II can thus be explained in a configuration diagram of a luminescent centre with a metastable energy level. The small half width of the maxima I, I′, and II fits this assumption. In this connection the low stability of the second glowpeak, observed if after excitation the phosphor is held at liquid air temperature for some time, is of particular interest. The measured life time of the trapped electrons is by many orders of magnitude too short to explain the emptying of the traps with thermal stimulation processes. If we assume however that the trapped electron is located very close to a luminescence centre, the decay of this peak should be accelerated by tunnel recombinations.

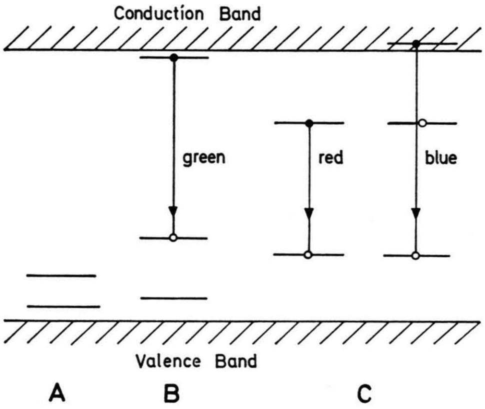

Fig. 10. Energy level diagram for the uniform luminescence centre model of ZnS.

It is difficult to apply these considerations in the case of the red band, for this band appears simultaneously with the blue as well as the green thermoluminescence. But if we base our discussion on the uniform luminescence model for ZnS phosphors[5], it is easy to interprete all spectral characteristics observed here. The basic assumption of the luminescence model is a covalently bond complex consisting of a Zn-ion and its surroundings perturbed by impurities and defects. The ground state of the complex is mainly due to Zn-eigenfunctions. There are two term groups in the forbidden zone above the valence band as shown in Fig. 10 A. An excitation of an electron leads to an increased splitting. The excited state of the centre is situated just below the conduction band, and a transition thereby to the ground state corresponds to a green band (520 nm; Fig. 10 B). A much greater splitting is obtained when an electron is excited from each of the two term groups (Fig. 10 C). In this case the excited state lies energetically within the conduction band. A blue band at 450 nm and a red band at 680 nm are attributed to this double excited centre. If it is assumed that the Zn ion is located at an interstitial and not at a lattice site the authors expect a slightly greater splitting for the two term groups. The emission bands would then lie at about 475, 580 and 620 nm respectively.

Contrary to suggested models, which attribute luminescence to band-term-transitions and which thus postulate a hyperbolic decay law, the uniform luminescence centre model suggests an exponential decay for the fluorescence. Recent measurements[19] have again led to the result that the visible luminescence of ZnS as a matter of fact does obey first order decay kinetics. Furthermore the fact that in both doped and undoped ZnS single crystals six various bands were found, whereby at least five bands were observed in one and the same undoped crystal under favourable conditions of excitation[20] supports this luminescence model. The energy diagram for the green emission, shown in Fig. 10 B, was recently confirmed by BURGETT and LIN[21], who measured the quenching of luminescence by infrared irradiation.

The uniform luminescence centre model also allows the interpretation of the spectral thermoluminescence behaviour of ZnS/10^{-3} Cu, 10^{-5} Co, including the red band. Since the excited level for the blue luminescence is supposed energetically to lie within the conduction band, it follows that the transfer of electrons via this band from traps to ionized luminescence centres should not cause blue thermoluminescence. The blue thermoluminescence should only be possible in this model when a trap and a luminescence centre are located close to one another or, when the metastable electronic level is itself part of the luminescence centre. The model attributes the blue as well as the red band to the two possible electron transitions within a doubly ionized luminescence centre. It should then be expected that with a specific probability it is always possible to get the red instead of the blue transition. A comparison between Figs. 3 and 6 shows this correlation between the two transitions. Figure 3 shows primarily the rise of the blue band in peak II with increasing excitation temperature, because of weak intensity and low sensitivity of the photomuliplier make the red component negligible. From Fig. 6 it will be seen that after excitation at $-70\ ^{\circ}\mathrm{C}$ the red component of peak II increases in the same proportion as the blue component. Since according to this model the red thermoluminescence could also result from electron transfer via the conduction band, it follows that it should also appear simultaneously with the green thermoluminescence, as long as there are still doubly ionized luminescence centres. It is therefore understandable that the red emission can still be observed also above peak II. As expected, this peak (II′), like the green peak (III), shows no dependence on the excitation temperature, both being attributed to the same traps or rather the same transfer mechanism by our model. The earlier drop in peak II′ can be explained by the filling process of the doubly ionized luminescence centres.

Unfortunately only very little can be said about the nature of the traps required here. The fact that the positions of peaks I, I′ and II are fixed by the Co^{++} while on the other hand a surplus of Cu^{+} or Ag^{+} is necessary if we are to obtain thermoluminescence at all, points to Co^{++}-Cu^{+}- or Co^{++}-Ag^{+}-associates as "thermoluminescence centres". The exchangeability of copper and silver also fits very well into the uniform luminescence centre model. In accordance with this model we can assume that the monovalent activators produce lattice defects, which are responsible for a high concentration of luminescence centres. The higher the Cu^{+}- or Ag^{+}-concentration, the greater the probability, that the Co^{++}-ions, which are responsible for the creation of the trap levels are located very close to the luminescence centres. The luminescence centres with discrete metastable states, responsible for the maxima I, I′, and II, then possibly emerge, while separately incorporated Co^{++}-ions – isolated from the luminescence centres – are responsible for the trap distribution of the third glowpeak.

As expected, the EPR-measurements presented here cannot offer a satisfactory answer to the question about the structure of the thermoluminescence centres, since, as we know, EPR spectra of powders generally give only insufficient informations. The very broad signal (Fig. 8), which was found at liquid helium temperature, has been attributed by many authors[22–24] to a Co^{++}-ion. Above all, we find paramagnetic centres, the thermal destruction of which is correlated with the thermoluminescence glowcurve, of particular interest. A similar effect had already been found in self-activated ZnS single crystals[25]. The authors found paramagnetic centres with a g-factor of 2.0182, which were destroyed within 100 to 150 K, this being accompanied by an emission of glowlight. At the same time a sharp relative decrease of the red band was observed. The

EPR-centres, which in our case were destroyed accompanied by the glowpeaks II and III, show also a g-value higher than that of the free electron. This points to hole centres. These paramagnetic centres may involve doubly ionized luminescence centres in accordance with the uniform model.

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