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ELECTRO- AND PHOTOLUMINESCENCE PROPERTIES OF Mn^{2+} IN ZnS AND ZnCdS

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Some aspects of the nature of the Mn center in ZnS and ZnCdS and of the influence of electric fields on the luminescence mechanism are reviewed. The photoluminescence properties of isolated Mn ions on the four main sites of polymorphic crystals are considered. The influence of more distant stacking faults and the combined action of several stacking faults on the Mn excitation and emission are discussed tentatively. A survey is given on the effects of an increasing amount of Mn: (1) The shift of the zero-phonon lines which is due to inhomogeneous line broadening; (2) the appearance of additional zero-phonon lines both in emission and excitation due to Mn–Mn pairs; (3) the observation of additional low-energy emission bands for highly doped ZnS : Mn crystals. The a.c. EL of ZnS : Cu, Mn, *X* powders where *X* stands for Fe, Ni, Co is discussed with respect to an energy transfer between deep centers during the low-field period of the EL cycle. It turns out that a strong energy transfer exists between these centers due to thermally controlled hole liberation. The influence of Auger quenching on the Mn emission is considered. It turns out that some effects already reported earlier in a.c. EL can be explained in that way. Finally the field enhancement of the Mn emission ("out-of-phase enhancement") is considered as due to the control of the Auger quenching by electric a.c. field and/or additional red or infrared irradiation control of the density of electrons in the conduction band, where any reduction of this density involves a reduction of the Auger quenching.

1. Introduction

Mn plays a predominant role in the high-field electroluminescence (EL) of II–VI compounds [1]. A lot of work has been done during the last few decades in order to bring about a better understanding of both the luminescence centers due to manganese and the photo- and electroluminescence mechanisms in II–VI compounds doped by manganese. Most of the work has probably been done on ZnS : Mn, because this material is the most efficient system in high-field EL [2]. By now there is a great deal of safe insight into the luminescence of ZnS : Mn. However, some points are still more or less controversial and some other problems are far from being solved.

Among the safer insights there is the more or less general model of the luminescence center in ZnS : Mn as Mn^{2+} at a Zn^{2+} site. The emission can be excited either by band-to-band absorption within the ZnS lattice or by direct absorption of visible light within the 3d shell giving rise to five broad excitation bands at room temperature or to sharp zero-phonon lines and to corresponding phonon satellites at low temperatures. The fluorescent transition has the assignments $^4T_1 \to {}^6A_1$, the three low-energy excitation bands are assigned to the transitions $^6A_1 \to {}^4T_1$, $^6A_1 \to {}^4T_2$, $^6A_1 \to {}^4E$, $^4A_1$ in terms of simple crystal field approximation.

Other details of the model are still controversial or simply unknown. First there is the obstinate problem of the situation of the ground state $^6A_1(^6S)$ of the 3d system with respect to the valence band of the ZnS, which is an important problem in the discussion of the possibility of direct excitation by electric fields. Some of the confusion may come from lack of a precise definition. As far as we discuss here the relation between both systems, the effective mass system of the ZnS lattice and the many-electron system of the Mn^{2+} impurity, we understand by ground state energy the charge transfer energy of the transition $Mn^{2+} \to Mn^{3+}$ with the transfer of one electron to the conduction band of the ZnS lattice. The main question of the discussion is: Does the ground state $^6A_1$ of Mn^{2+} lie below or above the top of the valence band? In an early rough estimation [3] we calculated a ground state energy of about 10 eV below the bottom of the conduction band. Langer et al. [4] found the 3d shell of Mn^{2+} to lie about 3 eV below the top of the valence band. However the considerations of Allen [5] give rise to a ground state 0.1 eV above the top of the valence band and recent calculations of Vogl [6] predict a place above the valence band. Following Allen's calculation one should predict two experimental results: First, one should observe a level due to Mn^{2+} by photocapacitance measurements as reported by Grimmeiss for some other materials [7]. Second, one should observe a decreasing EPR signal of Mn^{2+}, whenever visible light gives rise to the transition $Mn^{2+} \to Mn^{3+}$. The result of Watkins [8], who claims to have seen such an effect, have still to be confirmed.

The second question waiting for definite answer is concerned with the transition $^6A_1 \to {}^4A_1$. In the simple crystal field approximation the degeneracy of the levels ^4E and $^4A_1$ is not lifted by the crystal field. However, the influence of covalency should lift the degeneracy. Using the covalency parameters of Koide and Pryce [10] Neumann [9] estimated an energetic difference of about 200 cm^{-1} in ZnS. Parrot [11] estimated about 1000 cm^{-1} for the line separation. He pointed out the possible weakness of the line, because the transition $^6A_1 \to {}^4A_1$ is strongly forbidden. Even by time-resolved spectroscopy we were not able to discover the corresponding zero-phonon line.

The next in our list of unsettled questions is concerned with the assignments of the high-energy absorption bands at 23000 cm^{-1} and 25000 cm^{-1} [9]. The tentatively given assignments $^2T_2$ (I), $^4T_2$ (D) and ^4E (D) [9,12] should be revised and/or confirmed.

The problem of the influence of the environments of the Mn^{2+} upon the luminescence excitation and emission is by now on the way to being solved, but still far from being settled. There are two main points to be considered. First: How do slight disturbances of the crystal environment such as stacking faults act on the zero-phonon lines of Mn and how can this be connected to the oscillator strength and decay time of luminescence? Second: What happens when two Mn^{2+} ions are on nearest-neighbour sites and interacting? The first question is mainly concerned with the influence of the crystal structure and stacking faults on the luminescence properties; the second question deals with the Mn–pair lines, the influence of concentration of Mn on the excitation spectra and the appearance of low-energy emission bands with increasing amounts of Mn. The unsolved problems of radiationless transitions within the Mn^{2+} center in ZnS possibly get an interesting solution by considering the Auger effect as suggested by Gordon and Allen [13] and Langer [14]. Some consequences of this proposal on the EL and electrophotoluminescence will be discussed in this paper.

One of the important points of the current controversial discussion is the question whether the Mn center is excited directly by hot or ballistic electrons accelerated in the electric field or indirectly involving levels within the forbidden gap. Having in mind the possibility of exciting the Mn^{2+} directly by hot or ballistic electrons as discussed by Dean [1], Langer [14], Allen [15], Williams [16] and Howard [17] we would like to draw attention in this paper to the points where energy transfer obviously takes place after the excitation processes.

The most confusing problem seems to come from the different types of memory effects [16]. These memory effects should be seen in the context of different types of enhancing and diminishing effects which are observed under the action of electric field and/or infrared radiation and should be discussed with respect to the levels in the forbidden gap, which are involved. The main question deals with the influence of levels in the forbidden gap on the luminescence of Mn. This point is an important one in the discussion of (i) the energy transfer during the a.c. cycle of the EL, (ii) the memory effects and (iii) the radiationless transitions in EL. These levels are introduced by doping with Fe, Ni and Co. On the other hand when we know how these levels in the forbidden gap act during the luminescence cycle we can compare these effects with the phenomena which appear with increasing amounts of Mn.

In order to have a detailed model some photoluminescence properties due to isolated Mn ions on different lattice sites are reviewed in sect. 2. Sect. 3 deals with three effects of increasing amounts of Mn: first with the shift of zero-phonon (zp) lines (inhomogeneous line broadening); second with the appearance of additional zp lines due to Mn–Mn pairs both in excitation and emission; third with the observation of additional low-energy bands in emission. In sect. 4 the influence of deep centers due to iron group elements on the Destriau type EL is reviewed, and finally in sect. 5 some new aspects of the influence of electric fields on the photoluminescence of non-electroluminescent ZnS-type powders containing Mn are discussed.

2. Photoluminescence studies on isolated Mn in ZnS

The classical method used for describing the luminescence center due to isolated Mn in ZnS is the crystal field approach. Starting from wave functions of the free Mn^{2+} ions, the observed zp lines both in absorption and emission are explained by the influence of the central field upon the tetrahedrally coordinated Mn^{2+} ion. This implies that additional interactions between the surroundings of the emitting Mn should be reflected by the luminescence properties, differing sites of isolated Mn^{2+} ions should deliver differing zp lines both in emission and excitation.

As has been known for many decades ZnS can be grown with polytypes corresponding to the sequence of double layers ABCA.... This is zincblende with the site symmetry T_d [18]. The other important sequence of the double layers is ABA.... This is wurtzite with the site symmetry C_{3v}. Last not least there are varying stacking sequences along the $[111]_w$ axis. This sequence of stacking faults can be regular, e.g. with the polytypes 4H, 6H, 9R, or irregular. In both cases we have inequivalent sites with trigonal symmetry C_{3v} [19]. Of course the number of possible inequivalent sites depends on the number of double layers, which are included in the consideration.

Basically there are four main sites to be expected for Mn in polymorphic ZnS: pure cubic, pure hexagonal sites and two sites with axial distortions depending on whether there are prismatic or antiprismatic surroundings and whether there is a third nearest neighbour or not (AX1 $\cong$ AS and AX2 $\cong$ PN). A lot of work has been done on absorption and EPR measurements in order to identify the four main sites [20–29]. The identification of corresponding lines in excitation and emission is only possible by applying laser spectroscopy. By that method we can find out which zp lines in excitation ${}^6A_1 \rightarrow {}^4E$, ${}^6A_1 \rightarrow {}^4T_2$ and in emission ${}^4T_1 \rightarrow {}^6A_1$ are associated with each other in crystals with different crystal sites for the Mn [30]. By registering only small spectral ranges of the emitted light ($\Delta\tilde{\nu} \leqslant 3\ cm^{-1}$) we were able to discriminate between the four main groups of zp lines due to Mn^{2+} at cubic, hexagonal and axially distorted sites. An example of an emission spectrum with four zp lines due to the sites AN, PN, AS and PS is given in fig. 1.

However, there are more than four lines connected with each crystal field level in the spectrum. For clarifying these structures we used site selecting spectroscopy [18]: We registered only a small part $\Delta\tilde{\nu}_{em}$ of the emission line when varying the wavenumber $\tilde{\nu}_{ex}$ of the dye laser beam within the corresponding excitation line. The results are combined in a set of curves $I_{em} = f(\tilde{\nu}_{ex}, \tilde{\nu}_{em})$ in a three-dimensional relief and in contour lines. An example is given in fig. 2.

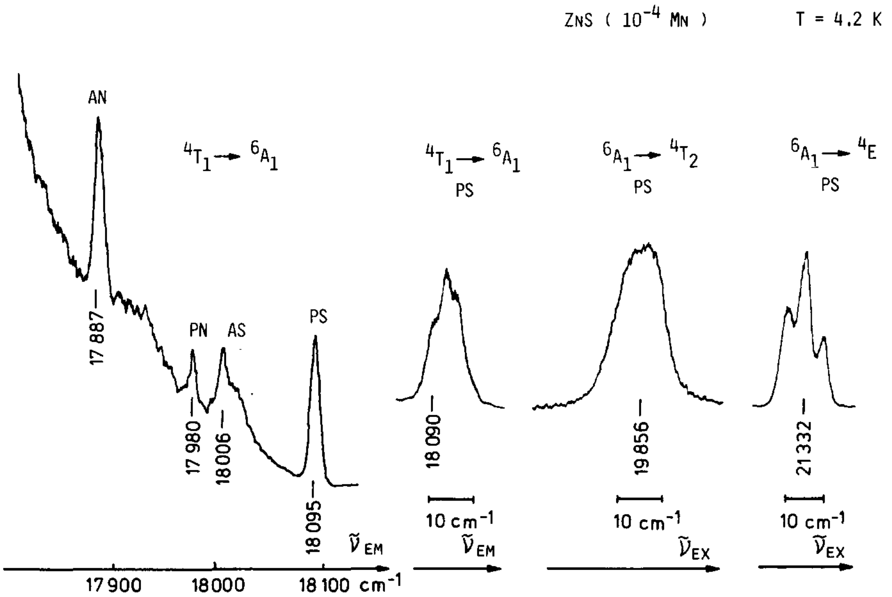

Fig. 1. Left-hand side? Emission spectrum excited within the line $\tilde{\nu}=21\,332$ cm^{-1} ($^6A_1 \rightarrow {}^4E$; PS: hexagonal). AN: cubic; AS, PN: stacking faults. Right-hand side: Corresponding excitation lines [18].

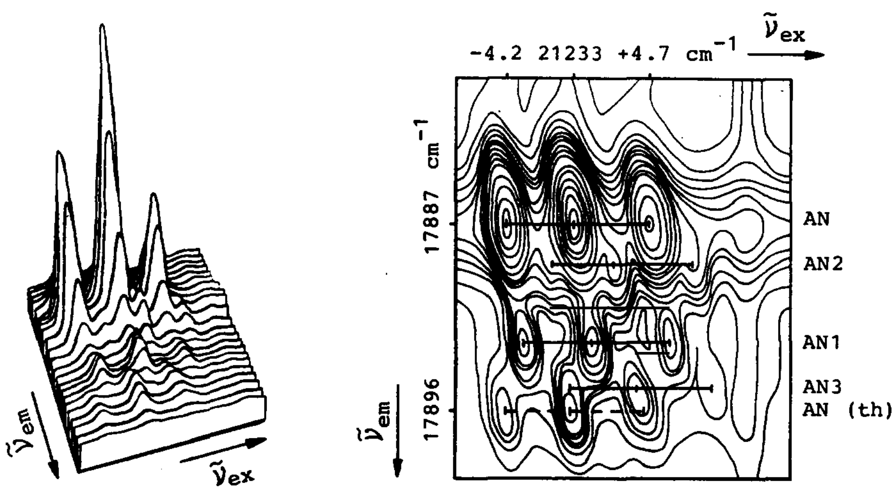

Fig. 2. Combined emission ($^4T_1 \rightarrow {}^6A_1$; AN) and excitation ($^6A_1 \rightarrow {}^4E$; AN) spectra of ZnS: 10^{-4} Mn; T=4.2 K. (a) Emission intensity I_{em} as a function of both excitation and emission wave number (relief). (b) Corresponding contour lines [18].

In the range of the main group ($\Gamma_7, \Gamma_8, \Gamma_6$ of the ^4E level) more groups of the three-fold lines are observed. Obviously this reflects the situation in the crystal well. We do not have only the direct action of the four main stacking faults on the atomic levels of the Mn; but we have also to take into account the action of more distant stacking faults and the combined action of more than one stacking fault on the manganese. We tried to give the assignments tentatively by considering the possible configuration of stacking faults within the range of six double layers of ZnS [18]. In this analysis it turned out that we observe nine out of sixteen possible sites by only considering six double layers in ZnS as grown in the direction $[111]_w$ for the distorted cubic crystals. The last part of this analysis has only a tentative character, whereas the analysis of Mn on four main sites is on safe ground by now. Parrot et al. [19] used the results of site selection spectroscopy and uniaxial stress experiments. They take into account the fact that the structures of the ^4E states are identical for the cubic and axial sites, and conclude that the observed structures for the orbital triplet states associated to the cubic and axial sites can be analyzed in terms of a Jahn–Teller coupling to degenerate or almost degenerate E vibrational modes. The authors determine the strength of the Jahn–Teller coupling and the Jahn–Teller shift with respect to the electronic states for each level in the cubic and axial centers and analyze the shifts of the electronic states ^4E, $^4T_2$ and $^4T_1$ for Mn^{2+} in axial symmetry with respect to the electronic states in cubic symmetry. In that analysis local strains and interaction of distant neighbours are taken into account. As for the ^4E states of the Mn, only the ligand field of first neighbours should act on these levels. Therefore the authors interpret the shift of the ^4E electronic states in terms of local strains of A_1 symmetry, which act on MnS_4 clusters. It follows from this consideration that the local A_1 strains presumably correspond to dilations of the MnS_4 clusters for axial centers. The interpretation of the shift of the $^4T_2$ and $^4T_1$ electronic states given by Parrot et al. [19] differs from the interpretation of the ^4E level. In that case the shift of the levels are explained partly by local strains A_1, and partly by the variation of the ligand field of A_1 symmetry in stacking faults. Fig. 3 summarizes the level scheme of the levels due to ^4E, $^4T_1$, $^4T_2$ of Mn on cubic, hexagonal and axial distorted sites following the calculations of Parrot et al. [19]. As for the experimental results, the observed lines and their assignments are summarized in table 1 [18].

It is interesting to compare the decay times of the luminescence transition $^4T_1 \rightarrow {}^6A_1$ of Mn on different sites. The decay times are measured by exciting within the zp lines of absorption and by recording only the luminescence of the corresponding zp lines in emission due to Mn on the same sites. The results are compiled in table 1 [18]. As it turns out, the slowest decay is due to Mn^{2+} on a cubic site, the fastest corresponds to Mn^{2+} on a hexagonal site. The luminescence decay times of Mn connected to the stacking faults AX 1 and AX 2 lie in between. However, within the limits of our present measurements there is only

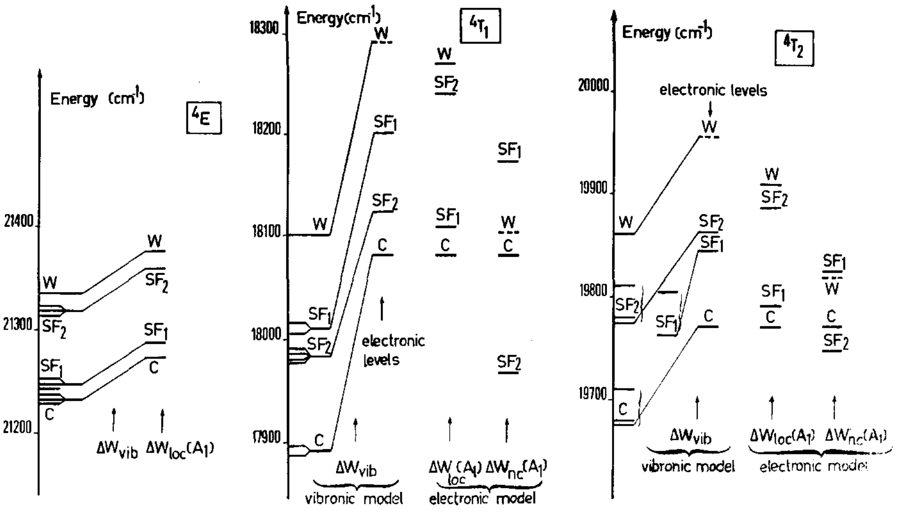

Fig. 3. Shift of the levels of the lines due to the cubic (c), hexagonal (w) and stacking fault sites (SF_1,SF_2) originating from ^4E, $^4T_2$ and $^4T_1$ levels according to the calculation of Parrot et al. [19].

one decay time for all subsystems of one main system. So far time-resolved spectroscopy does not seem to be helpful for discriminating between small differences in environmental distortion.

3. Concentration effects of photoluminescence

With increasing activator concentration some peculiar phenomena are observed which are discussed in the following subsections.

3.1. Shift of the zero-phonon lines

The observation of the line structure as the amount of Mn increases gave rise to some speculation. Neumann [9] observed a shift of the zp lines due to the levels $^4T_1$, $^4T_2$ and ^4E towards higher energies with increasing Mn concentration. Fig. 4 gives a shift of 23 cm^{-1}/wt%. The reason for this shift is obviously not, as one might expect, some magnetic interaction of the Mn ions, but inhomogeneous line broadening [18,31,32]. Using site selecting spectroscopy as described earlier we obtained the following results. Whenever the emission is registered within small spectral ranges of the zp lines, one observes small zp lines in excitation, even if the amount of Mn is as high as 1%. These excitation lines shift to higher energies, when the spectral window of emission is shifted to higher energies. It turns out that the line broadening is inhomoge-

Table 1
Zero-phonon lines in excitation and emission of Mn^{2+} on different lattice sites in polymorphic ZnS and corresponding decay times of luminescence emission

	$\tilde{\nu}(^4E)(cm^{-1})$				$\tilde{\nu}(^4T_2)(cm^{-1})$				$\tilde{\nu}(^4T_1)(cm^{-1})$			τ (ms)
cub												
AN	0	21233	−4.2	+4.7	0	19676	+3.9	+34	0	17887	+9.3	1.77
AN1	+1.2	21234	−4.3	+4.9	–	–	–	–	+5.6	17893	+94	
AN2	+2.6	21236	−4.1	+5.0	–	–	–	–	+1.9	17889	+9.5	
AN3	+3.9	21237	–	+4.9	–	–	–	–	+7.8	17895	–	
ax1												
AS	+15.1	21248	−4.3	+4.7	+86.4	19763	0	+42	+118.7	18006	+9.4	1.30
AS2	+17.5	21251	−4.2	+4.7	–	–	–	–	+120.5	18008	+9.5	
ax2												
PN	+85.6	21319	−4.3	+5.1	+97.7	19774	+6.0	+37	+90.4	17977	+2.6/8.8/12.4	1.62
PN1	+87.5	21321	−4.2	+5.1	–	–	–	–	+99.1	17986	+2.1/9.1/13.2	
hex												
PS	+99.3	21332	−4.1	+5.0	+180	19856	–	–	+203	18090	+4/7/13/17/22	1.15

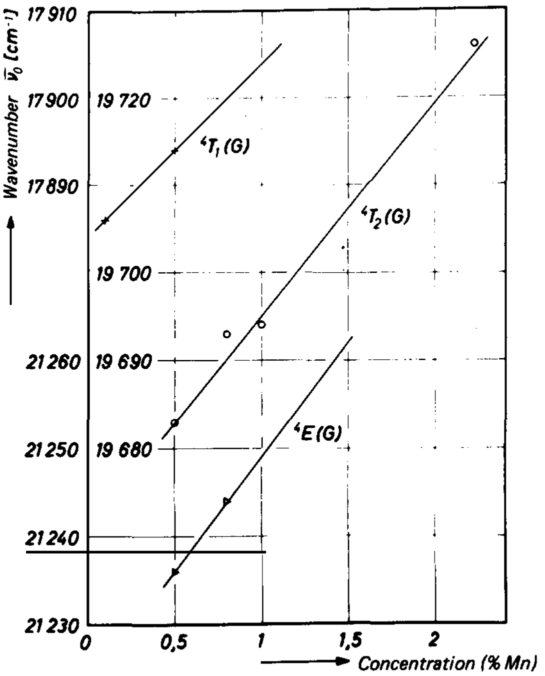

Fig. 4. Shift of the zero-phonon lines of emission ($^4T_1 \to {}^6A_1$) and excitation ($^6A_1 \to {}^4E, {}^6A_1 \to {}^4T_2$) as a function of activator concentration; $T = 6$ K [9].

neous and increases with increasing manganese concentration. In conclusion there is no real shift of the zp lines, but preferentially on the high-energy side of the original zp line a quasi-continuum of additional zp lines appears, when the amount of Mn increases. This inhomogeneous line broadening will be discussed on the basis of fluctuations of the lattice constant in a forthcoming paper [32], taking into account the different radii of the Zn and Mn ions and therefore the disturbance of the ZnS lattice.

3.2. Mn–Mn pairs

Earlier, McClure explained some fine structure in absorption of ZnS : Mn in terms of transitions in exchange coupled Mn–Mn pairs [33]. Röhrig gave a level scheme of Mn–Mn pairs in ZnS obtained by EPR measurements [34]. Behringer [35] calculated the probability of formation of Mn–Mn pairs as a function of Mn concentration. According to these ideas the excitation and emission lines due to Mn pairs should show the following behaviour: (i) The additional zp lines both in absorption and emission should increase with increasing amounts of manganese. (ii) Some of the additional zp lines in excitation should only be observed at temperatures $T > 10$ K because of thermalization effects within the ground states split by the Mn–Mn interaction. (iii) The oscillator strength of Mn pairs in both absorption and emission should be increased compared to the oscillator strength of single ions. This implies a shortening of the mean lifetime of the luminescence level $^4T_1$ (G). Point (iii) has been used for identifying the zp lines due to Mn pairs by time-resolved spectroscopy [36]. In contrast to the decay time of the luminescence of a Mn ion on a cubic site ($\tau = 1.77 \times 10^{-3}$ s) [18], we found for Mn–Mn pairs a decay time varying between $\tau = 10^{-4}$ and 2×10^{-4} s [36]. The time-resolved spectroscopy, by which only the short component ($\tau < 10^{-4}$ s) or the long persisting component ($\tau > 3 \times 10^{-3}$ s) was registered, was a good tool for discriminating between zp lines due to single ions and Mn–Mn pairs. It turned out that the zp lines at $\tilde{\nu} = 21410$ cm^{-1} and $\tilde{\nu} = 21448$ cm^{-1} in excitation are due to transitions within Mn–Mn pairs. The zp line $\tilde{\nu} = 17769$ cm^{-1} is the most prominent zp line in emission due to an internal transition $^4T_1$ (G) → $^6A_1$ (S) in Mn–Mn pairs (fig. 5). The concentration dependence and the temperature dependence of the pair lines follow at least quantitatively the three "rules for Mn pairs" mentioned earlier. Therefore, the existence of Mn–Mn pair emission and absorption zp lines is supposed to be certain.

Of course there are still quite a number of open questions. Besides the appearance of the first nn pairs we should expect in cubic ZnS two kinds of second nn pairs, the "stretched" pairs (P_{2A}) and the "bent" pairs (P_{2B}) [31]. As can be demonstrated by simple calculation [31] the type P_{2B} is more frequent at any Mn concentration than the type P_{2A}. The results of Knaak [31] give some hints in the direction of the discrimination of both types of pair lines, but this has to be confirmed, because there are obviously different methods of energy transfer between single ions, first nn pairs (P_1), second nn (P_{2A}) and second nn (P_{2B}) centers.

3.3. High concentration emission bands

Comparing both efficient thin film devices and a.c. EL devices of the Destriau type, the ZnS:Mn emission spectra of the thin films often have a second peak shifted to lower energies. Also in photoluminescence there are emission bands in the low-energy range, which appear at concentrations higher than 4% Mn. These emission bands have a peculiar temperature dependence as pointed out by Neumann [9]. Fig. 6 shows as an example the spectral distribution of emission of a crystal with about 8 wt.% Mn at different temperatures. The yellow emission band ($\tilde{\nu} = 17000$ cm^{-1}) is to be seen within the range 4–300 K. However, there are additional emission bands peaking at 15800 and 13106 cm^{-1}. With increasing Mn different emission bands are prevailing at different temperatures, as Neumann reported [9]. This quite striking dependence on temperature is demonstrated in fig. 7 in a more explicit way. In this

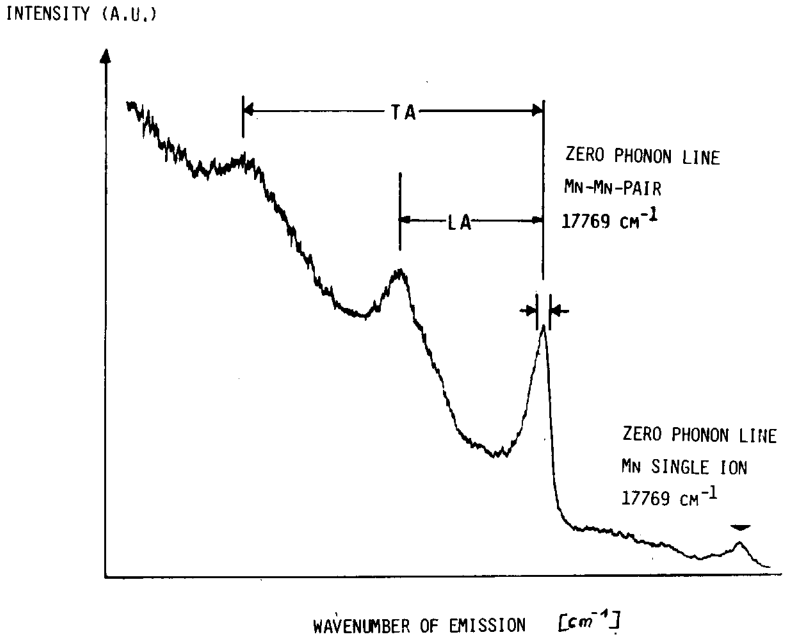

Fig. 5. Emission spectrum of ZnS: 10^{-2} Mn excited in the Mn–Mn pair line of $^6A_1 \rightarrow {^4E}$; $T=4.2$ K. Only the fast part of the emission was registered ($\tau < 10^{-4}$ s) [67].

figure the emission intensity is given as a function of reciprocal temperature and shows maxima as a function of temperature: the red band between 110 and 140 K, the yellow–orange band between 70 and 90 K. The yellow emission

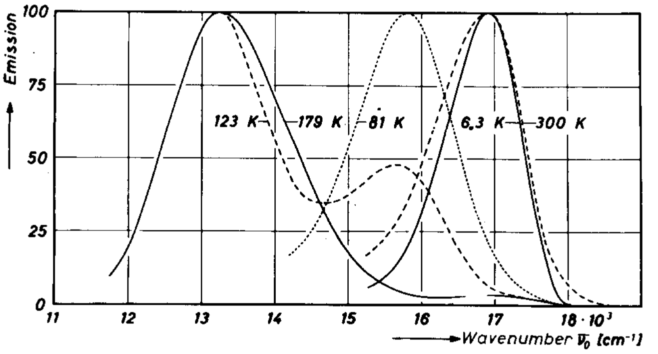

Fig. 6. Emission spectra of a ZnS crystal doped with 8.4% Mn. The spectra are normalized and registered at the temperatures when each emission band shows the highest intensity. These temperatures are indicated [9].

band consists of two parts in the temperature range near 100 K, which correspond to the emission bands having maxima at 20 and 300 K respectively. As Neumann pointed out [9], there is always an exponential part of $I = f(T^{-1})$ in the curves. These exponential parts have been used for determining the thermal activation energy for the transition from one band to the other.

As we succeeded in correlating zp lines in emission and excitation for both single ions and Mn–Mn pairs we should analyze high concentration excitation bands. The spectra taken by Neumann [9] are shown in fig. 8. It turns out that all three emission bands have about the same five excitation bands as already known from the luminescence of low concentrations of Mn. The only difference consists in the fine structure. At 4% Mn and at low temperature ($T = 5$ K) there is still some fine structure to be observed in the excitation band at 21500 cm^{-1}. However at higher temperatures and higher concentrations of Mn the fine structure disappears. We therefore conclude that the excitation of the high concentration emission bands of Mn ($x > 1\%$ Mn) takes place within the 3d shell of manganese, and that there is possibly an energy transfer between different Mn centers.

Finally the decay times of the high concentration emission bands (13100 cm^{-1}, 15800 cm^{-1}, 17000 cm^{-1}) are to be considered. It is worthwhile noting that the low-energy emission bands, which appear at higher concentrations of Mn, have longer decay times than the Mn "single" emission band and longer than the Mn–Mn pair emission [9]. As an example, fig. 9 gives the decay time of a crystal activated with 8.4% Mn as a function of temperature. It is interesting to note that the quenching temperatures of all Mn emission bands are very similar.

Summarizing, we should say that the mechanism of the high concentration emission bands is not yet clear. We think that there is some interaction of Mn, because all emission bands have superlinear increasing intensity with increas-

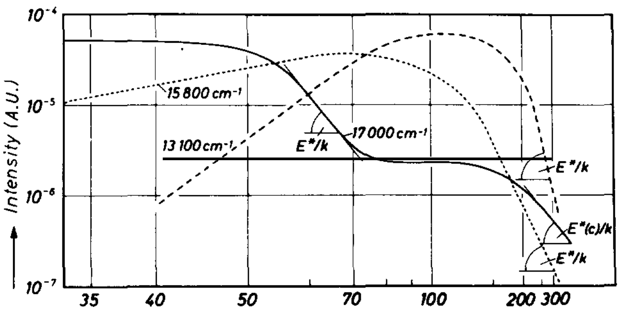

Fig. 7. Temperature dependence of the intensity of the high concentration emission bands of ZnS: 8.4×10^{-2} Mn [9].

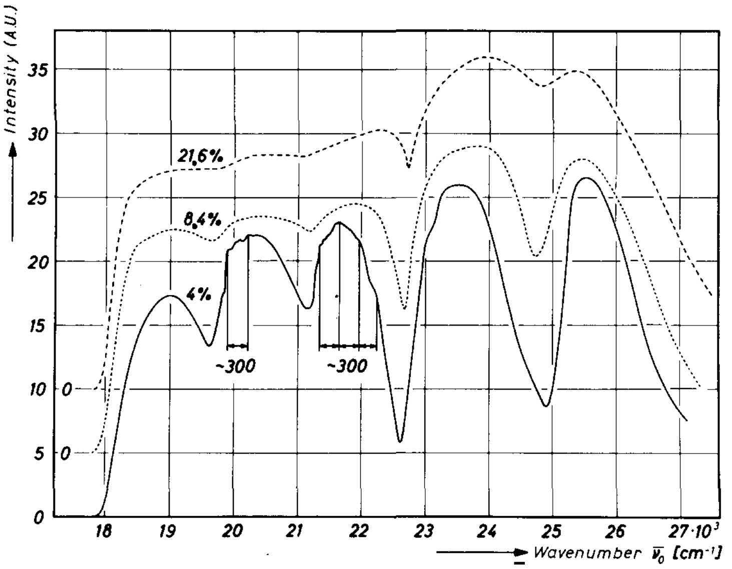

Fig. 8. Excitation spectra of the emission band peaking at 17000 cm^{-1}; $T = 5$ K [9]. Content of Mn $x = 4$; 8.4; 21.6%. Some phonon structure is indicated.

ing Mn concentration [9]. However, the slow decay time of these bands contradicts a model assuming a simple interaction of Mn–Mn pairs as was proposed by Neumann [9]. On the other hand, the excitation of all Mn emission bands within the same five excitation bands proves that the 3d shell of the Mn^{2+} is involved in the luminescence process.

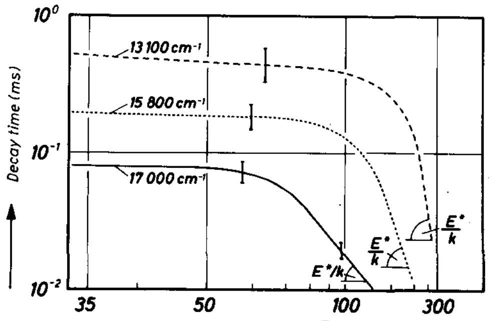

Fig. 9. Decay time of the high concentration emission bands peaking at 17000 cm^{-1}, 15800 cm^{-1} and 13100 cm^{-1} as a function of temperature of the crystal ZnS : 8 × 10^{-2} Mn [9].

4. Energy transfer in the a.c. EL (Destriau effect)

According to some results obtained with single crystals and thin films [1,13–17] we also assume for ZnS : Cu, Mn powders the possibility of exciting the Mn^{2+} emission by direct electron-center collision. However, there are obviously a number of phenomena which can only be explained by energy transfer between excited and emitting centers having levels of different depths within the forbidden gap of ZnS. Most prominent is the energy transfer by hole migration during the a.c. period of the electric field. Less prominent are phenomena which are observed by registering the time dependence of the EL.

Based on microscopic measurements [37] we can assume that a three-step model can be used for explaining the phenomena of the Destriau effect. (i) Injection of electrons from a Cu or Cu_2S precipitation into the conduction band of ZnS. In the high-field range near the Cu or Cu_2S the free electrons are accelerated and therefore able to ionize or excite deep centers and to excite electrons of the valence band to the conduction band. (ii) Electrons and ionized impurity states are separated by electron migration. During this period the recombination does not take place, but the holes having only a weak effective mobility are able to be thermally released at room temperature and to reach, during one half period of the field, a quasi-Fermi distribution over the levels above the valence band provided the time of carrier separation is sufficient. (iii) At the reversal of the external field the electrons flow back into the range of ionized centers and recombine according to the distribution of holes over these centers. Therefore, the spectral distribution of the luminescence as a function of voltage, frequency and temperature reflects the energy transfer by hole migration during the carrier separation. Based on this simple model we are able to compare the behaviour of the Mn emission with the copper emission under the influence of competing iron group elements Fe, Ni, Co which create deep levels in the forbidden gap and which are introduced additionally into the ZnS : Cu, Mn. There are three groups of experiments giving some insight into the action of deep levels in EL: the voltage dependence, the dependence on field frequency and temperature, and the time dependence. Some of the characteristic results of these experiments will be reviewed.

4.1. Voltage dependence

To investigate the EL on powders excited by a.c. fields two methods are used: (1) the light of a great number of grains with numerous light spots is registered (macroscopic measurements); (2) the emission of single light spots is observed in a microscope (microscopic measurements). One of the most important microscopic observations supporting the three-step model is that the light spots generally emit in one half period of the field only, whereas other spots emit whenever the field has the opposite direction [37]. The intensity of the time integrated light emission I of a single spot (microscopic measurements) depending on the applied voltage U follows approximately the relation $I \sim \exp(-B/U)$, whereas the intensity I of many dissimilar lines observed simultaneously (macroscopic measurements) obeys a law $I \sim \exp(-B/U^{1/2})$. The slope B should reflect the ionization or excitation energy of the centers excited or ionized by hot or ballistic electrons. As an example of the voltage dependence of the EL of ZnS: Cu, Mn, x, Co, fig. 10 shows the influence of Ni on both the blue Cu emission and the yellow Mn emission [38]. From this kind of plot we draw the following conclusions.

(i) The killer elements Fe, Ni, Co do not change the slope B of the voltage dependence of the brightness. Obviously the great majority of deep levels due to these elements are not ionized directly by impact collisions, but act as recombination channels predominantly during the low-field period.

(ii) The slope B of the yellow emission due to manganese changes at relatively low voltages. This change of slope, which has already been observed by Mattler and Ceva [39], does not depend on the presence of killers. We are tempted to explain this effect by Auger quenching as was recently suggested by Gordon and Allen [13].

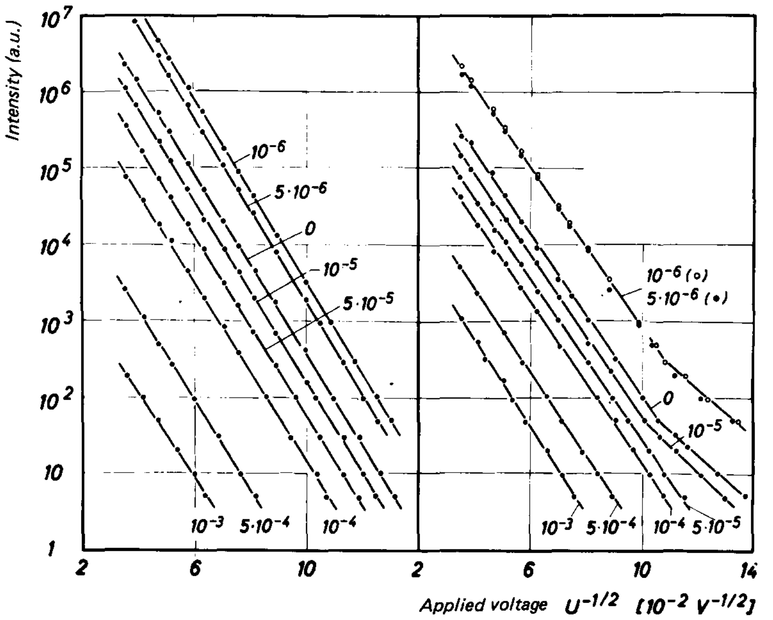

Fig. 10. Voltage dependence of the blue copper (left) and the yellow manganese (right) EL emission band of the phosphors ZnS:Cu,Mn,x,Ni. Content of Ni $x = 0 - 10^{-3}$ g Ni/g ZnS. Frequency $f = 750$ Hz, temperature $T = 293$ K. The curves with $x = 10^{-6}$ and 5×10^{-6} g Ni/g ZnS are shifted for one order of magnitude for reasons of clarity [38].

(iii) The blue and the green emission due to copper have the same slope B, but the slope of the yellow Mn emission differs from the B values of the copper emission of all phosphors. Therefore, the ratio of recombinations of different Cu-centers and Fe, Ni, Co centers does not depend on the voltage and on the number of free carriers, and this ratio is not constant in the relation between Mn and Cu centers and Mn and Fe centers. Therefore the voltage dependence of the EL does not provide arguments in favour of the direct excitation of centers by hot electrons nor do the results support any model of hole liberation of electric fields. The survey of the slopes B tends to indicate rather that the field strength in the luminescence region is small compared to the field strength of the carrier generation region. This conclusion is supported by the temperature and frequency dependence of the EL of ZnS:Cu, Mn, X with $X =$ Fe, Ni, Co.

4.2. Temperature and frequency dependence

Using the three-step model and assuming the creation of an equal number of free carriers during each period of the a.c. field at constant applied voltage and assuming only one type of (radiative) recombination center, we would expect a linear frequency dependence of the EL intensity. However when different types of recombination centers exist in the phosphors there are different non-linear frequency dependencies to be expected since the frequency of the a.c. field controls the time of separation of holes and electrons and therefore the migration of holes, which are thermally released. Whenever the phosphors of the type ZnS:Cu (without Mn, Fe, Ni or Co) emit only in one band (e.g. the blue band), then the emission intensity increases linearly with frequency ($I \sim f^n, n = 1$) up to 2 kHz and tends towards a saturation at higher frequencies. However, when the phosphors emit in different bands, e.g. ZnS : Cu, Mn in the Cu bands at 455 and 515 nm and the Mn band at 580 nm, even n is a function of the field frequency at room temperature. When ZnS:Cu is emitting in two bands, the blue emission band increases sublinearly. Important in our discussion of the Mn center is the change of spectral distribution of ZnS : Cu, Mn with increasing frequency. The blue and green copper band show the same behaviour as in the case discussed before, however the sublinearity of the yellow Mn band is even more pronounced than the sublinearity of the green Cu emission. Generally speaking the spectral distribution of multiband EL ZnS is always shifted at room temperature in favour of the high-energy emission band, when the frequency increases. Observations of the frequency dependence of ZnS : Cu, Mn phosphorus with additional deep levels due to Fe, Ni or Co support the hole migration model. The emission intensity of the phosphors with Co increases faster than the intensity of phosphors without Co. This rule is valid for all of the three emission bands, including the Mn emission band. Fig. 11 gives as an example the ratio of blue Cu to yellow Mn emission intensity. It should be mentioned that the Q–log f curves with intermediate Co-doping (10^{-5} and 3×10^{-5} g Co/g ZnS) have an inflexion point, which is shifted to higher frequencies with increasing Co. Besides the lack of an inflexion point, which could only be observed for Co in the frequency range below 10^5 Hz, Fe and Ni behave like Co. Consequently we conclude that the killer action of iron group elements changes with increasing time of the period of the a.c. field. This quenching action is especially strong at low frequencies: this means for long separation times of electrons and holes. At the liquid nitrogen temperature the non-linearities of the frequency dependence of the ratio of different emission bands disappears. This gave us the possibility of doing simple kinetics [40] and comparing the results with the experimental observations.

Summarizing the main points of our discussion on the EL emission due to Mn we conclude from the frequency and temperature dependence of ZnS containing Mn and other recombination centers that the Mn emission behaves as if there were one or more levels involved which were within the forbidden gap. Several possibilities should be kept in mind: (i) The ground state $^6A_1(^6S)$ of Mn^{2+} lies in the forbidden gap and Mn can be ionized by electric fields. Until now this seems to be unlikely, as discussed before. (ii) The isoelectronic Mn^{2+} creates an effective mass-like state in ZnS, which if at all, probably would be very shallow. A very shallow trap would not fit into the temperature dependence, whenever one admits that these traps would first capture electrons or holes and then the opposite electronic particle, and thus would transfer the recombination energy to the 3d shell of Mn. (iii) Filling and emptying of traps in the neighbourhood of the Mn center control the Auger effect, which

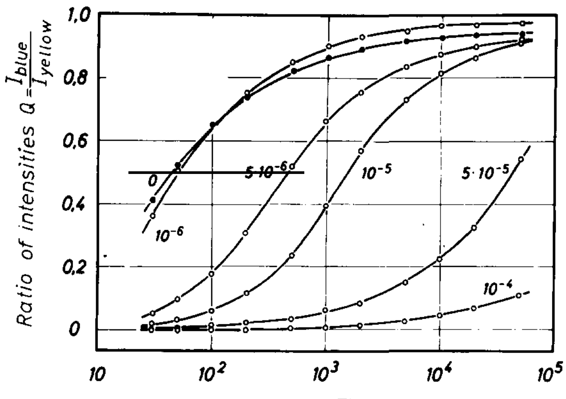

Fig. 11. Frequency dependence of the rate of emission $Q=I_{blue}/I_{yellow}$ due to copper and manganese of ZnS : Cu,Mn,x,Co phosphors doped by different amount of Co ($x=0$–10^{-4} g Co/g ZnS); $U=300$ V,$T=293$ K [38].

quenches the Mn emission. This effect [13], which needs only the filling and emptying of traps, would explain the behaviour of the Mn emission.

4.3. Time dependence

Even from the time dependence of EL we get some hints on the existence of levels in the forbidden gap, which are connected with the emission of Mn^{2+}. Generally speaking there are three phenomena in the time dependence of a.c. EL which can be related to the existence of levels in the forbidden gap.

(i) The "overshooting effect". The EL emission does not reach its stationary intensity immediately but only a few periods after the exciting field is applied. Obviously this build-up phenomenon during the first cycles is controlled by the generation of free carriers, the occupation of electron and hole traps and the change of the space-charge region [41,42]. This build-up phenomenon depends upon the numbers of a.c. cycles after the start of the a.c. field, but not significantly upon time. In special cases the EL intensity passes a maximum after about 3 or 4 cycles and decreases to its steady-state value ("overshooting"). This overshooting effect depends clearly on the presence of deep levels (e.g. Co), on the temperature and on the field frequency. A quite complete analysis of the overshooting effect has been given by Neumann [9].

(ii) "Secondary peaks". The EL of powders is always modulated by the double frequency of the electric field ("brightness wave") whenever the light is emitted from numerous different ranges ("comets"). The maxima of emission belonging to one half cycle of the field originate from the recombination of electrons returning into the luminescence zone when the field has changed polarity, as has already been discussed. Additional maxima arising at characteristic frequencies and temperatures are assumed to be due to electrons bound temporarily to traps. They appear when the carriers return with delay to the holes trapped in the luminescence centers ("secondary maxima"). This model was suported by the behaviour of the secondary maxima as a function of Co-doping, field frequency and temperature [9,42].

(iii) "Phosphorescence effect". When the decay of the Mn emission is longer than the intrinsic decay time of Mn on a cubic site ($\tau = 1.77$ ms), the additional energy is supposed to come from electrons captured temporarily in traps like Cl or Co. This effect can be monitored in the brightness waves of EL by watching the degree of modulation of luminescence in the a.c. field [9].

All three effects are observed simultaneously in the Mn emission at characteristic temperatures, which are correlated to thermal emptying of traps. One very special feature is the dependence of the build-up curve of the Mn^{2+} EL emission upon the previous stimulation by visible or IR radiation [9]. Whenever no previous IR irradiation is applied the overshooting effects is observed in different ranges of temperatures, e.g. at about 100 K and 250 K [9]. However if the phosphors are stimulated by infrared light before applying the electric field, the overshooting at 100 K and 250 K disappears but the overshooting effects is now to be observed at 4 K and 90 K. As Neumann [9] pointed out the equilibrium between levels in the forbidden gap can be reached sometimes only after hours of waiting after visible and IR irradiations are applied. The action of both visible and IR irradiatons is related to different ranges of temperatures in each of which overshooting appears. Fig. 12 gives as an example the build-up curve of the Mn emission intensity as a function of the numbers of a.c. cycles after the a.c. field is switched on. These observations should also be discussed with respect to a possible Auger quenching mechanism: The filling state of traps near the Mn^{2+} controls the Auger quenching. This filling state is supposed to be changed by stimulating irradiation before the a.c. field is switched on. This changes the build-up curve of EL. This mechanism could explain the behaviour of the overshooting effect even if we assume that the Mn is excited directly by ballistic or hot electrons.

5. The action of electric field on non-electroluminescent phosphors containing manganese

Some of the features of the Mn emission described in sect. 4 are possibly influenced by the high amount of copper necessarily added to the ZnS powders in order to obtain significant EL. It is therefore worthwhile to recall the action

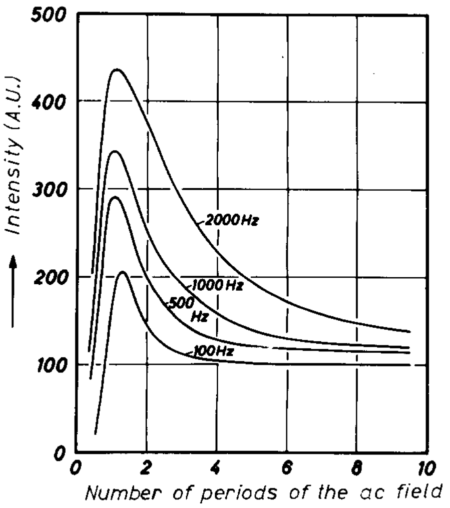

Fig. 12. Envelope of the build-up curve ("overshooting") of the yellow Mn emission band of ZnS:Cu,Mn as a function of the number of field periods after the beginning of excitation for different field frequencies; $T = 290$ K [9].

of the electric a.c. field on ZnS-type phosphors containing manganese but no or only weak amounts of copper and therefore showing no Destriau effect. The well-known field effects to be observed in such phosphors are:

(1) The Gudden–Pohl effect [43]. The electric field empties traps giving rise to short light pulses during the first cycles of the applied a.c. field.

(2) The Déchêne effect [44]. The electric field reduces the emission of photoluminescence intensity during its application.

(3) "Out-of-phase" field enhancement: Electric fields acting before or during the excitation of phosphors containing Mn by radiation (electrons, X-rays, UV) enhance some characteristic luminescence bands [45].

(4) "In-phase" field enhancement: incident radiation controls the carrier generation and by that the electroluminescence [46].

In this section we concentrate on the "out-of-phase" enhancement effect, because this effect is relevant to our discussion on the Mn center. The most important features of the enhancement effect are:

(1) The enhancement of the luminescence by electric fields is only observed in phosphors of the ZnS-type which are activated by Mn. For this effect there is an optimum manganese concentration of about 2×10^{-3} g Mn/g ZnS [47,48].

(2) Field enhancement is already observed at low fields ($E \leqslant 10^3$ V/cm), and is one order of magnitude less than necessary for exciting EL on comparable ZnS : Cu, Mn phosphors [41].

(3) As for the enhancement effect there is an energy limit to the exciting radiation: The photons have to be able to create free holes and/or free electrons [49]. This can be done by electrons, α-rays, X-rays and by UV light. No enhancement effect is observed when the radiation is absorbed directly within the five absorption bands due to the 3d shell of Mn^{2+}.

(4) After the end of the action of the electric fields, some phosphors "remember" that action. Even after the end of the action of the electric fields the Mn emission shows a transitory enhancement, when the phosphor is excited again by radiation after a time of rest [50].

A number of different mechanisms have been proposed for explaining the enhancement effect. Most of them have as a common feature the assumption that the electric field does not change the total number of recombinations per unit time, but it does change the recombination distribution per unit time in differing centers. Destriau [50] suggested a change of the valence state of Mn^{2+} by the radiation and shift of the liberated electrons by the electric fields. Gobrecht et al. proposed a model, which includes the action of hot electrons on donors and acceptors within the forbidden gap [51]. Ivey [52] and Curie [53] suggested a model admitting field-induced fluctuations of the density of carriers.

None of these models really fits all experimental observations. It is therefore worthwhile including the Auger quenching in the discussion of the field enhancement effect, as has been done before in the discussion of a.c. EL. The model proposed for the enhancement effect should include some elements of the proposals of Gobrecht et al. [51], Ivey [52] and Curie [53]. Gordon and Allen found that the non-radiative transition rate in ZnS:Mn varies linearly with electron concentration when this concentration is varied by thermal ionization of shallow donors [13]. Based on this observation, we assume that electric fields are able to control the density of electrons and therefore the rate of Auger processes. The same should be true for the enhancement of the Mn emission by the action of additional infrared or red irradiation as observed by Melamed [54] and Jaszczyn [55] who were able to show that additional IR stimulation enhances the luminescence of Mn^{2+}, but reduces the emission of Cu in ZnS. Both effects have the same spectral distribution of the stimulating IR light ($\lambda = 800$ and 1200 nm) and are connected with the hole liberation from Cu levels [56]. The spectral distribution of unstimulated and stimulated Mn emission is the same, therefore the emission should come from the same type of Mn^{2+} center. Based on these observations it seems reasonable to assume that hole liberation and migration can also induce an enhancement effect of the Mn^{2+} emission, as was already discussed for the enhancement of the Mn emission excited by α particles by Henck [57]. From the idea of Auger quenching this would imply that hole liberation from deep Cu levels can induce a lower concentration of free electrons. This reduction in the number of free electrons can be the reason for a diminished Auger quenching. Using this model the whole recombination kinetics including all kinds of levels in the forbidden gap can be involved in the enhancement of the Mn luminescence, even if it turns out that the Mn is excited directly within the 3d shell. This can also explain the influences of the presence of dopants in addition to Mn and of the amount of Cd in ZnCds:Mn phosphors on the enhancement effect. To support this idea we remember the fact that the simple presence of Mn in ZnS is not sufficient for obtaining field enhancement, but the concentration of Mn is important. As for other dopants the most drastic influence is due to Cd. Following the results of Destriau [58] and Treptow [59] the increasing amount of Cd in ZnCdS:Mn reduces the photoluminescence (Treptow), but gives rise to an increased field enhancement effect (Destriau). It looks as though there are strong local stoichiometric fluctuations in ZnCdS:Mn: some regions may have a higher concentration of Cd than others. This is obviously reflected in the dependence of the enhancement effect upon the field frequency, which depends strongly on the excitation wavelength. Excitation wavelengths corresponding to a band-to-band transition yield very different frequency dependence of the enhancement effect [60]. It is interesting to check the influence of other impurities on the field enhancement effect: Small amounts of Au(10^{-6} to 10^{-5} g Au/g ZnCdS) give rise to an increasing enhancement effect [58]. The same is true for In, which creates a trap about 0.5 eV below the conduction band of ZnS [61] and gives rise to a pronounced field enhancement effect.

Much research has been done on the influence of Co, which also creates a trap 0.5 eV below the conduction band [62]. The main points of the action of Co on the field enhancement of the Mn emission are [41]:

(1) Small amounts of Co ($x = 10^{-5}$ g Co/g ZnCdS) give an increased, but higher amounts a decreased, field enhancement effect compared to ZnCdS : Mn without Co.

(2) The characteristic curves of the field enhancement (fig. 13) as a function of field frequency, which show a decreasing field effect with increasing frequency, show only a scaling factor with changing amounts of Co, but no general change of the behaviour. In particular, the inflection point at about 10^3 Hz does not depend upon the amount of Co within the phosphors.

(3) The voltage dependence of the field enhancement shows exponential, sublinear, and saturation (or decreasing) behaviour (fig. 14). The action of Co can be described by a scaling factor. However no qualitative change is to be observed.

As for the temperature dependence of the enhancement effect there are a lot of data available which are reviewed in [41]. Some relevant observations are:

(1) At room temperature the cathodoluminescence of ZnS : Mn due to self-activation is reduced but the emission due to Mn is enhanced. However the field effect can change sign, that is at liquid nitrogen temperature the Mn emission is quenched and the blue emission is enhanced by electric fields.

(2) The field enhancement effect of the Mn^{2+} emission is clearly connected to the filling of electron traps as pointed out by Sahm [63].

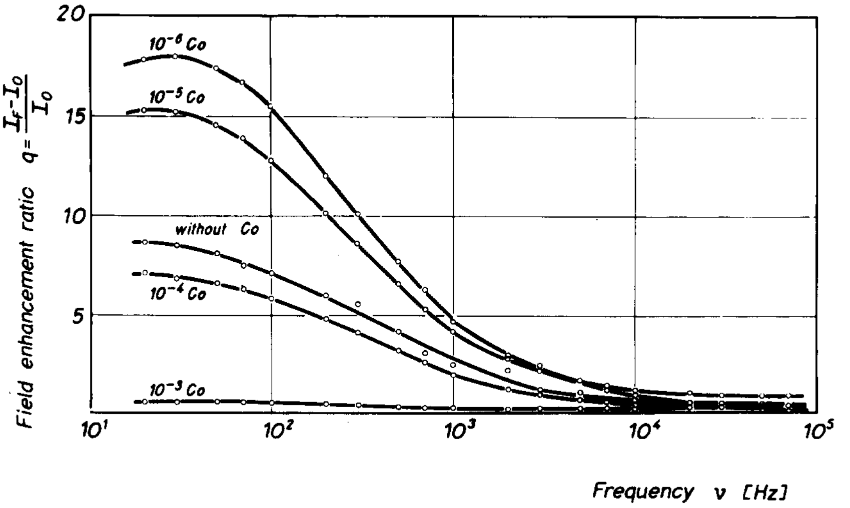

Fig. 13. Frequency dependence of the field enhancement effect $Q = (I_{\text{field}} - I_0)/I_0$ of the yellow emission of ZnCdS : Mn,Co with different amounts of Co under excitation by X-rays [41].

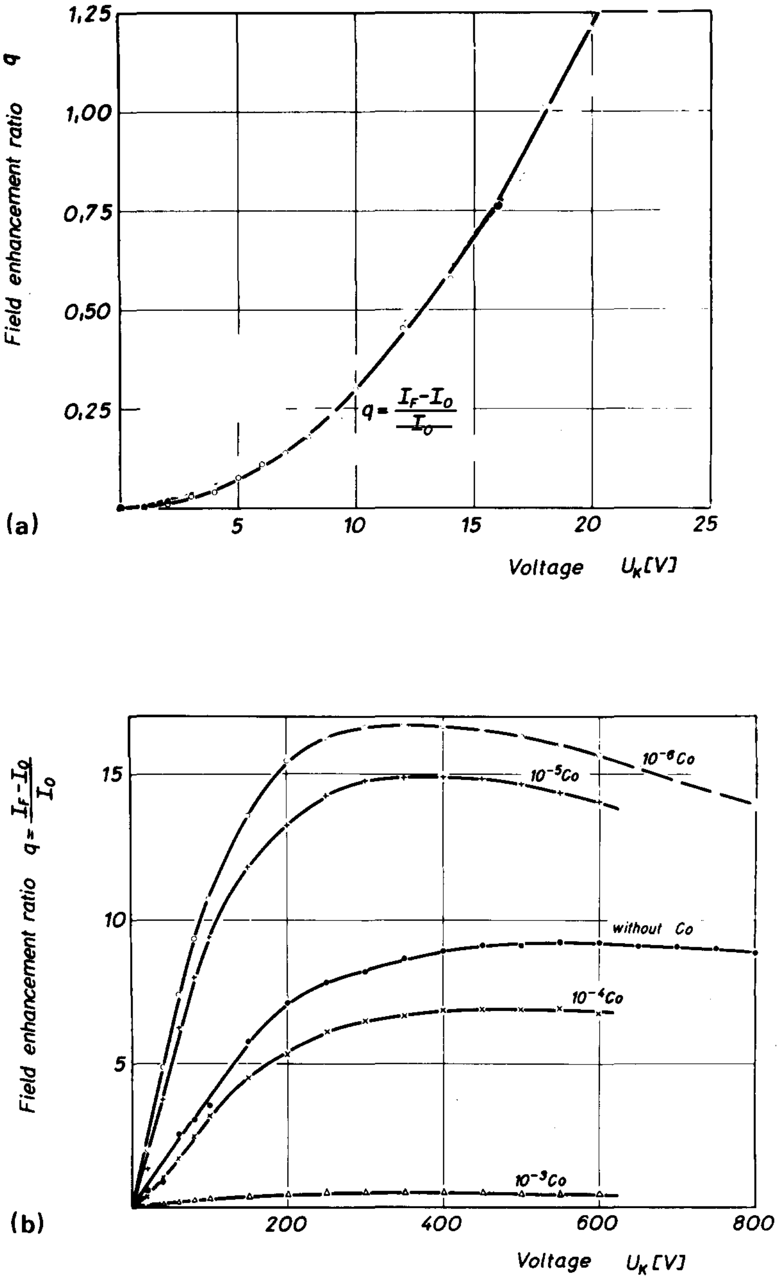

Fig. 14. Voltage dependence of the enhancement effect $Q=(I_{\text{field}}-I_0)/I_0$ of the yellow Mn emission band of ZnCdS(Mn,x,Co) under excitation by X-rays. (a) $x=10^{-5}$ g Co/g ZnS. (b) Different amounts of Co are indicated [41].

These observations are in line with the whole set of memory effects. The memory effect is not only observed when the electric field is applied simultaneously with the exciting radiation [45] but also when the field is applied (without any simultaneous irradiation) before any excitation by X-rays takes place [64]. Even temporarily elevated temperatures give rise to the memory effect [64].

Pingault [65] found that very similiar memory effects can be observed by irradiation with IR. It should be mentioned that even now it still seems to be quite difficult to make the connection to the memory effect reported by Howard [17] even if we assume that in all cases levels in the forbidden gap play the predominant role.

Finally, comparison of the simultaneous action of both IR radiation and electric field allows some conclusions on the interdependence of both enhancement effects [66]. The basic idea of this kind of experiments is demonstrated in fig. 15. The lower curve shows the enhancement of the Mn luminescence by additional red and IR irradiation with the wavelengths 700 and 1300 nm, the dashed straight line gives the degree of field enhancement by electric fields only, the upper curve demonstrates the combined action of both IR irradiation and electric fields [60]. At low intensities of additional irradiation there is a first-order linear superposition of the action. At higher IR intensities the a.c. electric field even reduces the enhancement effect of the IR. It is interesting to note that the voltage dependence delivers a field-independent transition point separating the field enhancement from the field quenching range of IR stimulated phosphors. However there is no such critical IR intensity in view of the combined action of a.c. field frequency and IR radiation. At low frequencies field enhancement can always be observed; at high frequencies, the field quenching prevails.

Fig. 15. Enhancement effect of the yellow Mn emission band $q = I/I_0$ as a function of the wavelength of additional irradiation with and without simultaneously acting electric field. Dashed line: Enhancement by the electric field only, without irradiation. $U = 100$ V, $F = 800$ Hz [66].

Summarizing, it seems to be evident that the emission due to Mn^{2+} in ZnS and ZnCdS is due to an internal transition $^4G \rightarrow {}^6S$ within the 3d shell, but that the luminescence efficiency is controlled by levels within the forbidden gap. All experimental observations on the field enhancement we know at present can be explained by assuming that an Auger effect quenches the Mn^{2+} emission in ZnS, whenever free electrons in the neighbourhood of Mn are present. This quenching can be reduced by changing the density of free electrons within the range of the Mn centers by the electric field. When hole liberation from deep acceptors by IR is followed by electron–hole recombination, the IR indirectly diminishes the density of free electrons and therefore the rate of Auger quenching processes.

6. Conclusions

The nature of the Mn luminescence center in ZnS is understood as far as the emission of tetrahedrally coordinated $Mn^{2+}(^4T_1 \rightarrow {}^6A_1)$ and two excited states $(^4T_2, {}^4E)$ are concerned. The other excited states are either not yet observed $(^4A_1)$ or their proposed assignments are to be revised or confirmed. As for the influence of the crystalline environment the four main inequivalent sites in polymorphic ZnS are identified. The assignments of some other inequivalent sites have been given tentatively. As for the high concentration effects two zp lines in excitation and one zp line in emission have been identified by time-resolved spectroscopy. The origin of some other lines, which are probably due to Mn–Mn pairs, is not yet resolved unambiguously. The additional low-energy emission bands appearing at higher concentrations, i.e. $\geqslant 1\%$ Mn, seem to be connected to transitions within the 3d shell of Mn^{2+}, but they are not simply due to the Mn–Mn interaction because their decay time is significantly longer than the decay time of Mn–Mn pairs. From the results of EL and of the "out-of-phase" enhancement effect we assume that the emission due to the internal transition $^4T_1 \rightarrow {}^6A_1$ can be influenced by an Auger effect. This Auger quenching depends on the number of free electrons in the neighbourhood of the Mn^{2+} centers. The number of free electrons can be controlled by hole liberation by thermal energy in the Destriau type EL and by a.c. electric fields or additional red or infrared irradiation in the luminescence enhancement effect. This mechanism is consistent with both the model of direct excitation of the Mn emission by impact of hot or ballistic electrons and the Mn^{2+} ion and with the model of the energy transfer from recombinations within the forbidden gap to the Mn^{2+} ion.

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