SOME INVESTIGATIONS ON LUMINESCENCE CENTRES OF (ZnCd)S:Cu, Cl

By

L. SZÖLLŐSY and GY. GARAB

Institute of Experimental Physics, Attila József University, Szeged

(Received June 20, 1971)

Luminescence emission spectra and decay characteristics of (ZnCd)S:Cu, Cl phosphors as a function of temperature were measured. Certain regions of the spectrally resolved decay characteristics cannot be explained by the accepted donor-acceptor pair emission mechanism.

Recent investigations on the luminescence of ZnS crystal phosphors [1—3] demonstrated that the so-called donor-acceptor model of PRENER and WILLIAMS [4, 5] can be well used for the interpretation of the green luminescence band emitted by the G—Cu centre. This has been verified experimentally by SHIONOYA *et al.* [1, 2], chiefly by detailed investigations on the decay characteristics.

On the basis of analogous properties of (ZnCd)S mixed crystals it is supposed that luminescence centres of the same type are formed in these crystals as those found in ZnS. Though numerous data on the luminescence of (ZnCd)S mixed crystals are to be found in literature, investigations on the validity of the donor-acceptor pair model are not known. The papers published up to now predominantly dealt with the effect of changes in CdS concentration on the emission spectra and on the spectrally unresolved decay characteristics [6, 7]. With increasing CdS concentration the nearest-neighbour distances increase and the band gap decreases [8] in consequence of the distortion of the valence band [9], therefore the emission is shifted towards lower energies. The present paper deals with some results of our investigations on (ZnCd)S luminescence, chiefly with respect to the validity of the PRENER—WILLIAMS-model.

Experimental

The material used was $(Zn_{0.9}Cd_{0.1})S:Cu, Cl$ (with $2 \cdot 10^{-2}$ g/g Cu of 5 μ particle size). The powder was placed in the sample-holder without binding material and smoothed.

In measuring emission spectra the 366 and 406 nm bands of the light of a HBO 200 high pressure mercury lamp were selected with a quartz prism monochromator (Zeiss SPM-2). The luminescence light incident on the multiplier (EMI type 9558 AQ) passed through another monochromator SPM-2; the photocurrent of the multiplier was recorded by a compensograph (Zeiss G1B1).

The same optical arrangement was used for measuring the spectrally resolved

decay characteristics,— with the difference that the exciting light was periodically interrupted by a rotating disk, and the time dependent changes in the luminescence intensity were observed and photographed with an oscilloscope EMG type 4401. The measurements were made between 90°K and 520°K in both cases. Spectrally unresolved decay characteristics were also investigated; a similar mechanical phosphoroscope as described above was built up for this sake. The spectrally unresolved characteristics were determined between 300°K and 520°K.

Results and discussion

The emission spectra of the (ZnCd)S:Cu, Cl, measured and normalized for two exciting wavelengths at seven different temperatures, are to be seen in Fig. 1. The spectra N° 1, 2, 3, 4, 5, 6, 7 belong to the temperatures 90, 190, 300, 320, 420, 470, and 520°K, respectively. As it can be seen from the figure, at 90°K a second band appears besides the principal band, more distinctly with exciting light of 366 nm, less expressed in case of excitation with 406 nm. This additional band is weak at 190°K; it cannot be observed at room-temperatures. According to [6] the principal band can be ascribed to G—Cu centres; this is supported by the temperature dependence of the spectra. The thermally unstable additional band can be attributed to the blue luminescence of the so-called B—Cu centres.

The shift of the emission peak of the principal band (see Fig. 2a) is similar but somewhat less as that of the emission peak of the G—Cu band of ZnS. The same can be said of the changes in halfbandwidth (see Fig. 2b). (Because of the additional band, the half values of the half-band width are plotted in the figure.)

The shape of the spectrally unresolved decay characteristics can be approximated by two hyperbolas, as suggested in [7]; this also indicates the presence of a complex mechanism. From our results, the temperature dependence of the decay times $\tau_{1/2}$ and $\tau_{1/5}$ are shown in Fig. 3. The decay times decrease exponentially with increasing temperatures; then, from about 450°K, a much steeper exponential dependence is valid. To our knowledge, exponential dependence of the τ-values on temperature has not been found hitherto; the temperature dependence of the spectrally unresolved decay characteristics is, however, in good accordance with earlier results [6].

From our measurements concerning the spectral changes in decay time at 90°*K*, we found that the $\tau_{1/2}$ and $\tau_{1/5}$ values of the B—Cu band are lower by about 1.5 orders of magnitude than those of the G—Cu band. The results of our measurements at 190°K are presented in Fig. 4. At this temperature, as a comparison with Fig. 1. shows, the role of the B—Cu band is insignificant. The sudden breakdown of the curve, which, at the first sight, could be attributed to the effect of the B—Cu band, is however to be found at temperatures up to 420°K, where the B—Cu band cannot be observed at all.

According to the PRENER—WILLIAMS model the following relations hold for the energy of emission and the probability of radiative transition, respectively:

$$E(r) = E_g - (E_a + E_d) + \frac{e^2}{Kr}$$

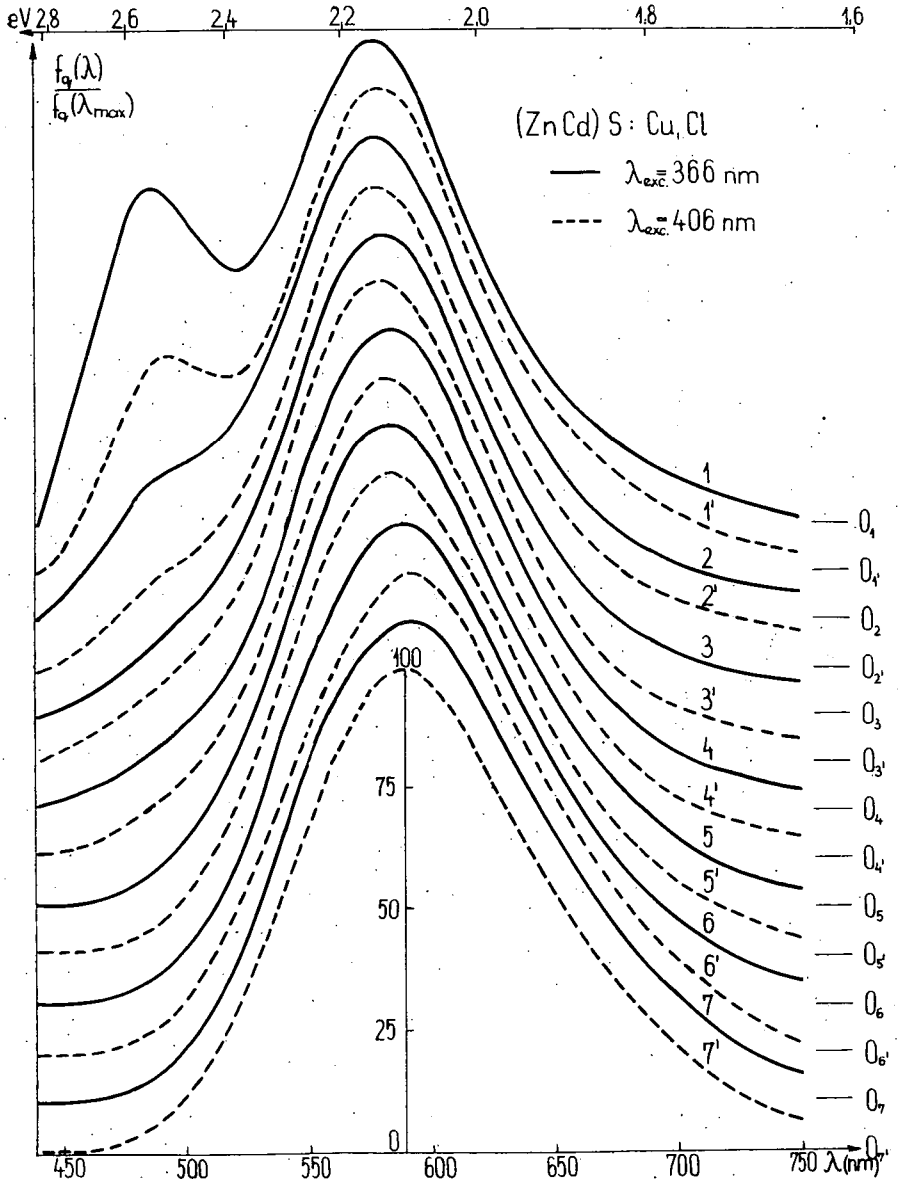
eV 2,8 2,6 2,4 2,2 2,0 1,8 1,6
$f_q(\lambda)$ / $f_q(\lambda_{max})$
(Zn Cd) S : Cu, Cl
$\lambda_{exc.}$ = 366 nm
$\lambda_{exc.}$ = 406 nm
1 1' 2 2' 3 3' 4 4' 5 5' 6 6' 7 7'
O_1 $O_{1'}$ O_2 $O_{2'}$ O_3 $O_{3'}$ O_4 $O_{4'}$ O_5 $O_{5'}$ O_6 $O_{6'}$ O_7 $O_{7'}$
100 75 50 25 0
450 500 550 600 650 700 750 λ(nm)

Fig. 1

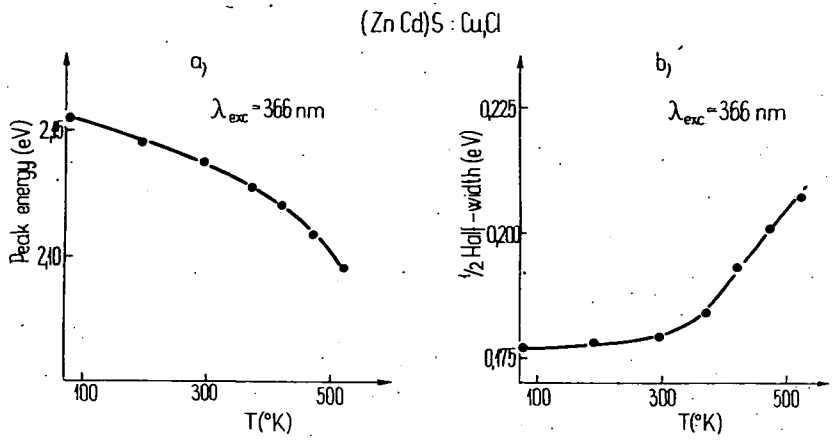

Fig. 2

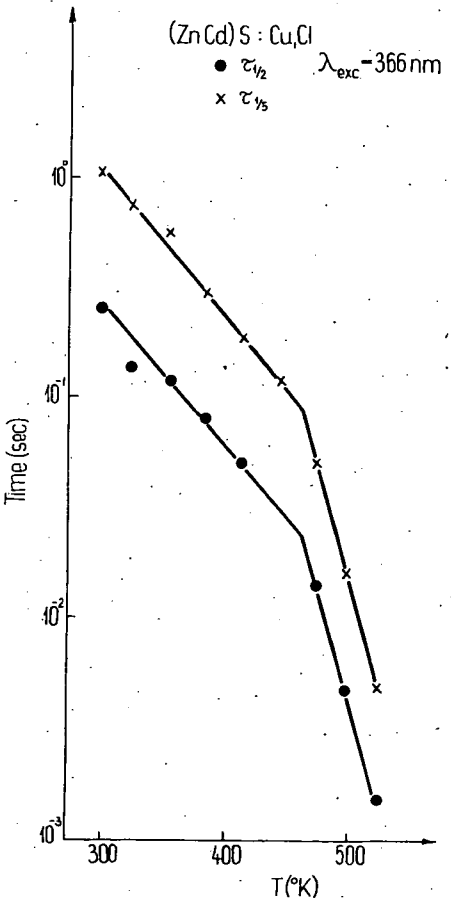

Fig. 3

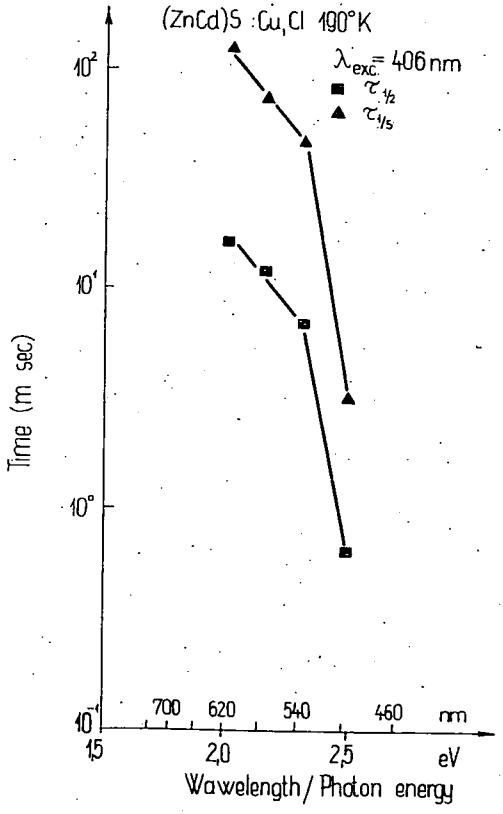

Fig. 4

and

$$W(r) = W_{\max} \exp\left(-\frac{r}{r_d}\right),$$

where E_g is the band-gap width, E_a and E_d the distance of the acceptor and donor levels from the respective bands, e the elementary charge, K the static dielectric constant, r the distance between donor and acceptor, r_d the half of the Bohr radius of the donor.

On this basis, the dependence of the decay time, more exactly of its logarithm, on the energy of transition could be calculated, taking the decay time proportional to the inverse of the transition probability. After introducing suitable constants the following relation was obtained:

$$\ln \tau = \frac{1}{(E-E_0)K_0} - W_0, \qquad E - E_0 > 0.$$

This is a hyperbola, which can be considerded as represented by the region 700 to 540 nm in figures 4 and 5; (where the descending branch of the hyperbola is approximated by a straight line). The sharp breakdown of the decay characteristic cannot be interpreted by the PRENER—WILLIAMS model. It may be explained by the following suggestions: 1. In mixed crystals the perturbation levels of the donor can be supposed to overlap the conduction band in consequence of the decrease of the band gap with increasing CdS concentration; this would result in altering the probability of recombination of the electrons.

2. The electrons may get into the conduction band by thermal excitation. Both suppositions are equivalent with the assumption that in this region the SCHÖN—KLASENS model is valid rather than the PRENER—WILLIAMS model.

3. A further possibility of explanation might be sought in SHIONOYA's supposition, according to which the experimentally measured Gauss curve of the emission would result from the sum of Gauss curves corresponding to different pair distances.

Similar results were found in our measurements on (ZnCd)S:Ag, Cl phosphors.

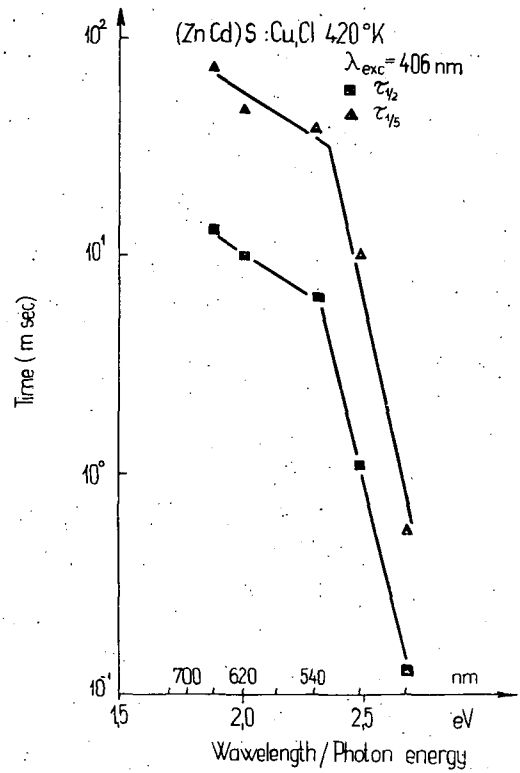

Fig. 5

Further investigations on the emission spectra and decay characteristics of the broad-band luminescence of (ZnCd)S:Cu, Cl phosphors and on connections between luminescence and photoconductivity are in course.

* * *

The authors are indebted to thanks to Prof. I. KETSKEMÉTY, director of the Institute for his interest in their work.

References

[1] *Era, K., S. Shionoya, Y. Washizawa:* J. Phys. Chem. Solids **29**, 1827 (1968).
[2] *Era, K., S. Shionoya, Y. Washizawa, H. Ohmatsu:* J. Phys. Chem. Solids **29**, 1843 (1968).
[3] *Shionoya, S.:* J. Lumin. **1**, **2**, 17 (1970).
[4] *Prener, J. S., F. E. Williams:* J. Electrochem. Soc. **103**, 342 (1956).
[5] *Apple, E. F., F. E. Williams:* J. Electrochem. Soc. **106**, 224 (1959).
[6] *Лёвшин, В. Л.:* Фотолюминесценция жидких твёрдых веществ Гос. изд. техн-теор. Москва 1951 Ленинград
[7] *Leverenz, H. W.:* An Introduction to Luminescence of Solids. John Wiley and Sons, Inc., New York (1950).
[8] *Shionoya, S.:* In: Luminescence of Inorganic Solids (Edited by P. Goldberg) Chap. 4. Academic Press, New York (1966).
[9] *Biter, W. J., F. E. Williams:* J. Lumin. **3**, 395 (1971).

ОБ ИСТОЛЬКОВАНИИ ЦЕНТРОВ ЛЮМИНЕСЦЕНЦИИ (ZnCd)S:Cu, Cl

Л. Сёллёши и *Дь. Гараб*

Исследовались спектры излучения люминесценции и характеристики затухания (ZnCd)S:Cu, Cl фосфоров в зависимости от температуры. На основе спектрально разложенных характеристик затухания показано отличие механизма излучения предлагаемой до сих пор модели донора-акцептора.