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Individual glow bands of Mn^{2+} ions photoluminescence in plastically deformed ZnS single crystals

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Abstract. The spectra of a photoluminescence (PL) in plastically deformed (PD) ZnS:Mn single crystals are investigated. It is shown that the PD processes cause change of a quantitative ratio between separate types of glow manganese centres (MC) as a result of their local symmetry rearrangement. After decomposing of PL integral spectra by individual PL bands using the cumulative distribution Gauss function, the nature of a ratio change between PL MC of different types is established. The individual with the peaking in the range 618–620 nm is discovered.

Keywords: spectra of photoluminescence, plastical deformation, manganese centres, individual band, decomposition of integral spectra.

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The photoluminescence (PL) researches of ZnS:Mn single crystals at small plastical deformations (PD) ($\varepsilon \sim 1\ldots2\%$) have shown that there is an increase of PL integral spectrum intensity by 10…15 % from an intensity level of a undeformed single crystal with a shift of the peak position into short wave side by 2…3 nm. At further increase of up to 5.3 %, there is a decrease of the glow intensity with the shift of PL peak into long wave range by 5…7 nm (Fig. 1).

This experimental fact predetermines more detail analysis of manganese centres (MC) glow behaviour in ZnS single crystals in the range of values $0 < \varepsilon < 5.3$ % in PD process. Each of them is characterised by the intrinsic local symmetry of Mn^{2+} ions and features of excitation causing MC glow. The types of these centres were offered after electroluminescence (EL) and PL researches of spectra in ZnS:Mn single crystals under different conditions of excitation [1–6]. Being based on the obtained data, individual bands are interpreted as follows: the band $\lambda_{max} = 557$ nm – ions Mn^{2+} in tetrahedrons of the cubic grating; $\lambda_{max} = 578$ nm – ions Mn^{2+} near to dislocations or dot defects; max = 600 nm – ions Mn^{2+} in octahedral interstices. The band peaking at $\lambda_{max} = 635$ nm is connected to formation of α-MnS phase in ZnS. If somehow it will be possible to execute decomposing of integral PL spectra and to receive the information on a behaviour of individual PL bands at various values of PD, it means, that we shall receive the information on change of a ratio between different types of MC glow, and consequently we shall obtain some comprehension of changes taking place in the crystalline structure of ZnS:Mn chips as a whole. Now there are some methods enabling to make similar decomposition. The most effective of them are based on the analysis of integral spectra changes accompanying variations in experimental conditions: the intensity [7] or wavelength [7, 8] of excitation, concentrations of centres of glow [9], the temperature [10], the additional illumination from damping area of one bands [11]. Using the results obtained with the Alentsev-Fok method [11] allows to determine, in a number of cases, the shape of an contour of a individual band, quantity of these bands in an integral spectrum without any prior assumption about their form. The application of modulation methods [12] enables to find a feeble structure of composite bands. At the same time, it is necessary to note that for today there is no universal method to decompose integral spectra of the different form. Moreover, from [11, 12] it follows that obtaining unambiguous and authentic results about the structure of an integral PL spectrum decomposed is practically impossible. Each of listed methods has both number of advantages and a number of lacks and can be correctly applied only in specific conditions. Some methods are tolerant to very feeble and narrow bandwidths located inside the broad and intensive

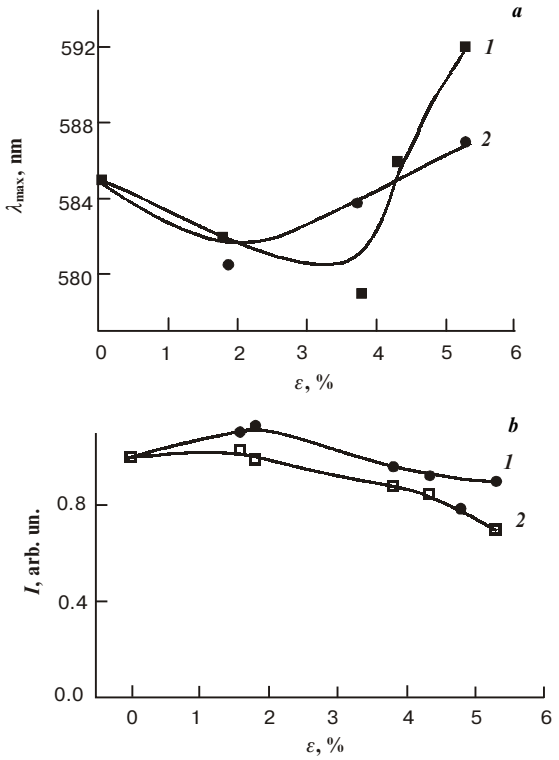

Fig. 1. Relation of a peak position (*a*) and emission power (*b*) of the integral PL spectrum in ZnS:Mn single crystals at different degrees of plastic deformation ε. C_{Mn} = $1 \cdot 10^{-2}$ (1) and C_{Mn} = $5 \cdot 10^{-3}$ (2) *g* MnS / *g* ZnS (*g*/*g*).

individual bands [7, 8–11]. Besides, the known Alentsev-Fok method is rather complex in operational use, as it demands considerable changes of an integral spectrum, which is often impossible without considerable changes of experimental conditions. If we have large a number of individual bands in intermediate spectra, it is very difficult to determine horizontal segments bound with coefficients of decomposition. Other methods [12], being super-sensitive, allow to find out even phonon repetitions [7, 13], thus the number of features in a differential luminescent spectrum can be larger then quantity of independent centres of glow [12]. As a result, we have to carry out additional experiments. Therefore, selecting this or that method of decomposing, or creating a new one, it is necessary to aim it at specific features of integral PL spectra and special conditions of experiment.

As the spectral shape of individual PL bands of Mn^{2+} ions is close to the form of a cumulative distribution of the Gauss function, in our view, for decomposing similar spectra it is convenient to use the following function:

$$y = y_0 + A\exp[-(x - x_{max})^2 / 2w^2], \qquad (1)$$

where A is the amplitude of a maximum, w is the width of a peak at the half of its amplitude, x_{max} – the maximum position, y_0 – level of zero point (Fig. 2).

The area under the curve, $S = \int_{x_1}^{x_2} y(x)dx$ will be proportional to quantity of glow MC, accountable for radiation of an integral spectrum. The limits of integrating x_1 and x_2 belong to a segment, where function $y(x) \neq 0$. As at the analysis of PL spectra, the area under a spectral curve between the ordinate $y = 0$ and y_0 level characterises the noise signal and has no useful information, we can accept $y_0 = 0$.

It is known that any "Gaussian" can be decomposed by components also depicted by a cumulative distribution of the Gauss function, so

$$y(x) = y_1(x) + y_2(x) + y_3(x) + \ldots + y_n(x), \qquad (2)$$

where $y_1\, y_2\, y_3 \ldots y_n$ are functions determining separate individual bands included into a structure of an integral PL spectrum.

In our case, the number of such components should be limited by the number of individual bands shaped close to "Gaussian" and found other methods [11, 14, 15]. As the form of experimental spectra nevertheless differs a little from the form of an approximating function, it is necessary to allow for error of this approximation. So, it is necessary to decide a return problem by having established how great is the deviation of the sum of approximating functions describing individual bands, from an experimental PL spectrum. As this relation has composite nature, we shall designate it as some function $f(x)$. Allowing the said above, we should obtain

$$y(x) = y_1(x) + y_2(x) + y_3(x) + y_4(x) + f(x). \qquad (3)$$

In original sign of experimental PL spectra this formula will accept the following view:

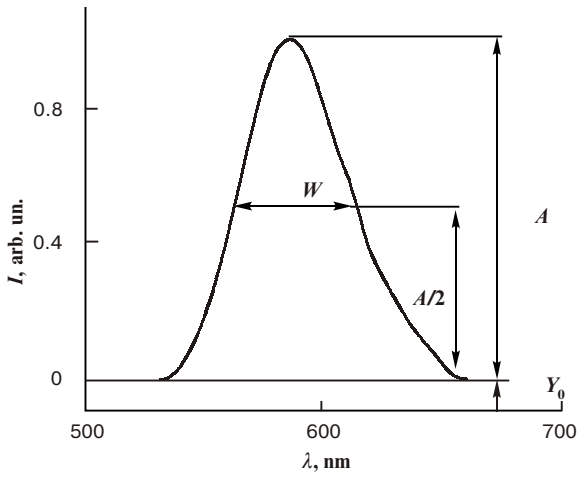

Fig. 2. PL spectra of ZnS:Mn single crystals with parameters serving as constants of decomposition of an integral spectrum by individual bands.

$$I(\lambda) = A_1\exp[-(\lambda-\lambda_{1\max})^2/2w_1^2] + A_2\exp[-(\lambda-\lambda_{2\max})^2/2w_2^2] + A_3\exp[-(\lambda-\lambda_{3\max})^2/2w_3^2] + A_4\exp[-(\lambda-\lambda_{4\max})^2/2w_4^2] + \Delta A(\lambda), \quad (4)$$

where $I(\lambda)$ is the function describing the experimental spectrum, A_1, A_2, A_3, A_4 – amplitudes; w_1, w_2, w_3, w_4 – half widths; $\lambda_{1\max}$, $\lambda_{2\max}$, $\lambda_{3\max}$, $\lambda_{4\max}$ – abscissas of individual peaks, accordingly; $\Delta A(\lambda)$ - some function describing how great is the deviation of the sum of approximating functions from an experimental PL spectrum – "function of an error".

So, the problem of decomposing the integral PL spectrum is reduced to finding the functions $y_1(\lambda) = A_1 \times \exp[-(-\lambda_{1\max})^2/2w_1^2]$, $y_2(\lambda) = A_2\exp[-(-\lambda_{2\max})^2/2w_2^2]$, $y_3(\lambda) = A_3\exp[-(-\lambda_{3\max})^2/2w_3^2]$, $y_4(\lambda) = A_4\exp[-(-\lambda_{4\max})^2/2w_4^2]$, at some optimal value $\Delta A(\lambda)$. This problem can be solved using mathematical methods of optimization, for example, the least square method [16, 17]. In essence, it is the minimisation of a special object function, which, using directly the experimental notations, looks like:

$$\Phi(A_{ij}, w_{ij}) = \sum_{i=1}^{4}\sum_{j=1}^{200}[I_j(\lambda_j) - [y_i(\lambda_j)]]^2 = \min. \quad (5)$$

Allowing that w_{ij} values are in indexes of exponents (4) and are carried up in a quadratic degree, the solution of the given problem represents the minimization of a non-linear model. In this case, the formula (5) has set of solutions, the optimal of which should be selected. It is rather difficult problem that often has no unequivocal solutions. Therefore, it is better to make some assumptions.

From mathematical statistics [18], it is known that for construction of normal "Gaussian" distribution of probability:

$$P(x) = \frac{1}{\sqrt{2\pi}m\exp[(x-x_{\max})^2/2m^2]}, \quad (6)$$

it is enough to know two constants: a maximum position $x_{\max}$ and parameter of half width – m. For the given function, up to date vast tables are compounded [19]. If we change only constants xmax the plot of the function displaces along the abscissa axis by some value without any changes of the form. As we need the information on the relative contribution of individual bands into radiation of an integral PL spectrum, we have to know also the behaviour of the third value – amplitudes of the maxima A_i versus PD degree.

The shape of integral spectra changed only with redistribution between the intensities of individual bands in PD process. The temperature was fixed and half width of PL spectra practically did not change (Fig. 2). So, there are no basis to consider that the half width of PL individual bands will be changed essentially. Therefore, we attempt to fix this value and we shall assume that all bands are elementary, are subject to distribution (1) and have approximately identical half widths. It means that $w_1 \approx w_2 \approx w_3 \approx w_4 = constant$, and

$$w_i \approx 2w/n, \quad (7)$$

where n is the number of bands.

This assumption is in accord to the same interaction with crystal for different types of MC glow. However, taking into account that this difference is shown that only in the third layer of their local symmetry, in our opinion, in this case we shall not make the big mistake. Finally, we may correct this parameter by using experimental data, keeping in such a manner the mathematical identity of the decomposition for all spectra.

The values $\lambda_{i\max}$ are found in [11, 14, 15], where four steady individual bands with $\lambda_{\max}$ = 557, 578, 600 and 635 nm were described. If these bands are individual, the values $\lambda_{i\max}$ should be stable during decomposing. Now our object function $\Phi(A_i)$ depends only on four variables A_1, A_2, A_3 and A_4 – amplitudes of individual band maxima that are vary within the limits from 0 up to $y_i(\lambda_{i\max})$. In this case, the least square criterion demands that the factors Ai should be selected from the condition of a minimum value for $\Phi(A_i)$ [16, 17]. Therefore,

$$\Phi(A_i) = \sum_{j=1}^{200}[I_j(\lambda_j) - [y_1(\lambda_j) + y_2(\lambda_j) + y_3(\lambda_j) + y_4(\lambda_j)]]^2 = \min, \quad (8)$$

$$\frac{\partial\Phi(\vec{a})}{\partial a_k} = 0. \quad (9)$$

After that we use selected values w_i, $y_i(\lambda_{i\max})$, A_i from the indicated interval, parameter $\lambda_{i\max}$ from [11, 14, 15] and we calculate values of functions $y_i(\lambda)$ using (8). For this aim, after introducing the following notations we will have the relations:

$$\vec{A} = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \end{bmatrix}, \quad \begin{bmatrix} \exp[\frac{-(\lambda-\lambda_{1\max})^2}{2w_1^2}] & \exp[\frac{-(\lambda-\lambda_{2\max})^2}{2w_2^2}] & \exp[\frac{-(\lambda-\lambda_{3\max})^2}{2w_3^2}] & \exp[\frac{-(\lambda-\lambda_{4\max})^2}{2w_4^2}] \\ \exp[\frac{-(\lambda-\lambda_{1\max})^2}{2w_1^2}] & \exp[\frac{-(\lambda-\lambda_{2\max})^2}{2w_2^2}] & \exp[\frac{-(\lambda-\lambda_{3\max})^2}{2w_3^2}] & \exp[\frac{-(\lambda-\lambda_{4\max})^2}{2w_4^2}] \\ \vdots & \vdots & \vdots & \vdots \\ \exp[\frac{-(\lambda-\lambda_{1\max})^2}{2w_1^2}] & \exp[\frac{-(\lambda-\lambda_{2\max})^2}{2w_2^2}] & \exp[\frac{-(\lambda-\lambda_{3\max})^2}{2w_3^2}] & \exp[\frac{-(\lambda-\lambda_{4\max})^2}{2w_4^2}] \end{bmatrix} = B \quad \vec{f} = \begin{bmatrix} y_{\lambda 1} \\ y_{\lambda 2} \\ \vdots \\ y_{\lambda n} \end{bmatrix}$$

In a vectorial form, we discover optimum values of the matrix A conforming to minimum value $\Phi(A_i)$ in (8):

$$\vec{BA} = \vec{f}$$

$$B^t B\vec{A} = B^t \vec{f} \qquad (10)$$

$$\vec{A} = (B^t B)^{-1} B^t \vec{f}$$

where B^t – transpose of the matrix B.

Using a personal computer, it is possible to take any values $y_i(\lambda_{i\max}) = A_i$ from the indicated interval sequentially from the smaller to greater ones. However, allowing the form of experimental PL spectra of ions Mn^{2+} in ZnS:Mn chips and the plenty of the experimental results of decomposing, obtained by us, the optimal ratio – $y(\lambda_{\max})/\, y(\lambda_{i\max}) \approx 1.14$.

The PL spectra of ZnS:Mn single crystals, $C_{Mn} = 5\times$ $\times 10^{-3}$ and $1\cdot 10^{-2}$ gMnS/gZnS (g/g), at different values of a degree of PD were used for checking the given method. The obtained results are submitted in Fig. 3. According to them, the most considerable changes of an emission power in PD process is characteristic for the band with $\lambda_{\max}$ =578 nm. The general change of an emission power of remaining individual bands is comparable to changes of the given band. Let is take into account, that this personal band is connected with MC of glow arranged near to defective places of crystal lattice – of dislocations and dot defects undergoing the most considerable change in PD process. The results of decomposition correlate well with the known data [20-23].

The analysis of the "function of an error" – $\Delta A(\lambda)$ view (Fig. 4) gives the completely definite result. This function has the large values in a wavelength interval λ = 510÷560 and 650÷670 nm conforming to boundaries of an integral PL spectrum. The most likely, it is connected with some little changes of the ratio "signal to noise" during the experiment. The view of $\Delta A(\lambda)$ function completely coincides with the view of the Gauss function having a maximum in the range of 618÷620 nm, in the interval of λ = 605÷630 nm. Also, we obtained the appearance of the second maximum in PL spectra of the deformed ZnS:Mn single crystals at λ = 606÷608 nm, the temperature of experiment T = 77 K and concentration of manganese $C_{Mn} = 1\cdot 10^{-2}$ g/g. Most legibly, it was observed at λ_{exit} = 396 nm (Fig. 5). All that gives the basis to suppose availability in the given place at least one more individual band.

The data of other works about existence of this band are rather various. In [4], the given band observed at EL and cathodoluminescence with a maximum in the range

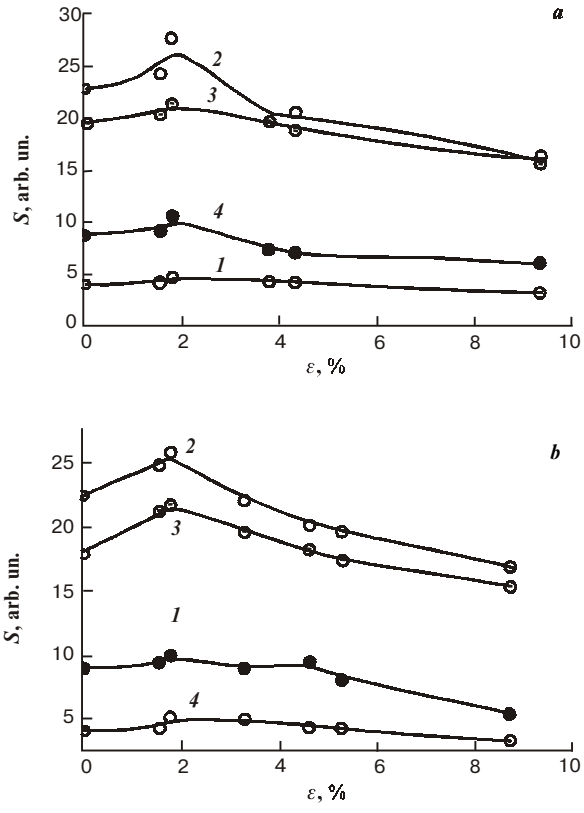

Fig. 3. Relations of integral brightness of individual bands of ions Mn^{2+} in ZnS:Mn single crystals at a different degree of PD – ε. $C_{Mn} = 5\cdot 10^{-3}$ g/g (a) and $1\cdot 10^{-2}$ g/g (b), λ_{exit} = 557 (1), 578 (2), 600 (3), 635 nm (4).

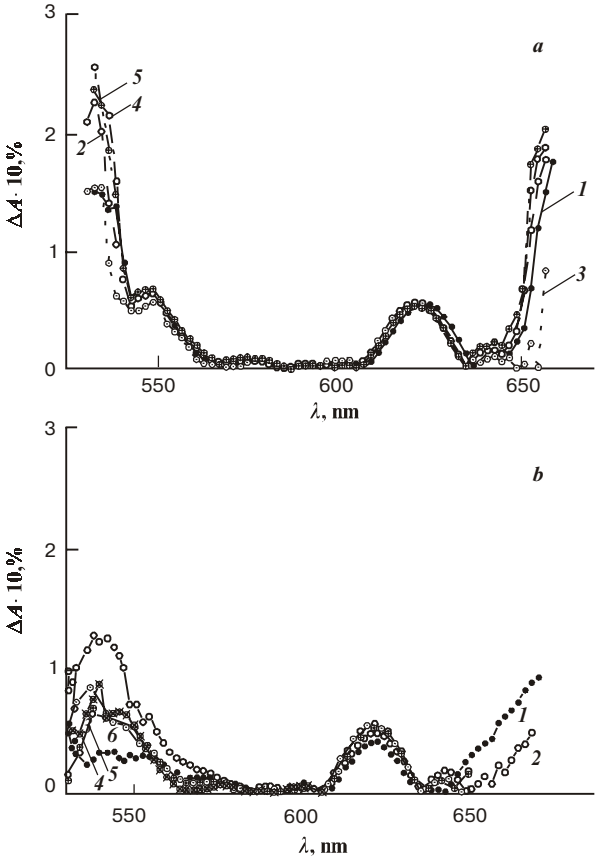

Fig. 4. The deviation of the sum of approximating functions from an experimental PL spectrum of ZnS:Mn single crystals for various degree of PD. $C_{Mn} = 5\cdot 10^{-3}$ g/g (a), ε = 0 (1); 1.57 (2); 1.8 (3); 3.8 (4); 4.33 (5); 9.35 % (6) and $C_{Mn} = 1\cdot 10^{-2}$ g/g, ε =0 (1); 1.57 (2); 1.78 (3); 3.8 (4); 4.63 (5); 8.7%(6) (b).

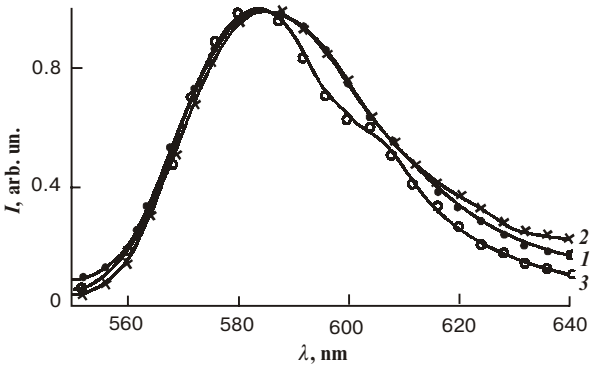

Fig. 5. PL spectra of ZnS:Mn single crystals – λ_{exit} = 396 nm, T = 77 K, $C_{Mn} = 1 \cdot 10^{-2}$ *g/g* at a different degree of PD: ε = 0 (1), 1.57 (2); 1.78 % (3).

of 616±2 nm. In the authors opinion, it is conditioned by the glow of MCs arranged in the bulk of the crystal lattice with a small concentration of dot defects obtaining excitation energy due to direct absorption. In [24], the given band was secured with a maximum close to λ = 606÷610 nm. According to [24], the glow in this area of PL spectrum is conditioned by complex centres consisting of two or more defects, structure of which could include vacancy of sulphur. Here it is necessary to allow that in [24] samples differed a little from the samples used in [4] and in our researches. So, according to the data [24], during growth of crystals ZnS:Mn from melt by the Bridgeman method of the, the manganese was added into the melt as MnS_2. Its concentration was much larger (1.9 mass %) than in our case. Therefore, formation of complex centres at such activator concentrations is quite possible.

Binding the obtained experimental results and data of works [4, 11, 24] with results of our decomposition, it is possible to say that in the spectral range including λ_{max} = = 618…620 nm without doubts exists at least one new elementary individual emission band. This indicates a view of a "function of an error" close to the normal cumulative distribution Gauss function in the range λ = 605…630 nm and presence of the second peak in PL spectra.

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