

## Smoothing photoluminescence spectra and their derivatives for identification of individual bands

*A.V.Kovalenko, S.M.Vovk, Ye.G.Plakhtii*

Oles Honchar Dnipro National University,  
72 Gagarin Ave., 49010 Dnipro, Ukraine

*Received November 19, 2019*

Methods for smoothing the experimental photoluminescence spectra and their derivatives, which are based on the Tikhonov regularization method, are proposed. The performances of the proposed methods and Savitzky-Golay's method are compared by numerical simulations of photoluminescence spectra and their derivatives. Effective smoothing of the experimental curves made it possible to carry out the decomposition of the photoluminescence spectra of ZnO and ZnO:Mn nanocrystals using the derivative spectroscopy method into elementary bands. Thus, the possibility to detect individual photoluminescence bands on the basis of a single measurement is shown. It was found that the experimental photoluminescence spectra of ZnO and ZnO:Mn contain two separate bands:  $E_{max} = 2.13$  eV ( $\lambda_{max} = 583$  nm) and  $E_{max} = 2.30$  eV ( $\lambda_{max} = 540$  nm), which are associated with oxygen vacancies or oxygen interstitials and zinc interstitials, respectively. Three individual bands are also detected in the experimental photoluminescence spectra of ZnO:Mn nanocrystals with  $E_{max} = 2.34$  eV ( $\lambda_{max} = 530$  nm),  $E_{max} = 2.19$  eV ( $\lambda_{max} = 567$  nm) and  $E_{max} = 1.97$  eV ( $\lambda_{max} = 630$  nm), which are associated with the Mn dopant.

**Keywords:** photoluminescence, emission band, Savitzky-Golay method, Tikhonov regularization, derivative spectroscopy.

Предложены методы сглаживания экспериментальных спектров фотолюминесценции и их производных, основанные на методе регуляризации Тихонова. Характеристики предложенных методов и метода Савицкого-Голея сравниваются путем численного моделирования спектров фотолюминесценции и их производных. Эффективное сглаживание экспериментальных кривых позволило в дальнейшем с помощью метода производной спектроскопии провести разложение спектров фотолюминесценции нанокристаллов ZnO и ZnO:Mn на элементарные полосы. Таким образом, показана возможность выявления индивидуальных полос фотолюминесценции на основании одного измерения. Установлено, что экспериментальные спектры фотолюминесценции ZnO и ZnO:Mn содержат две отдельные полосы:  $E_{max} = 2.13$  eV ( $\lambda_{max} = 583$  nm) и  $E_{max} = 2.30$  eV ( $\lambda_{max} = 540$  nm), связанные с кислородными вакансиями или междоузельным кислородом и междоузельным цинком, соответственно. Обнаружены также три отдельные полосы в экспериментальных спектрах фотолюминесценции нанокристаллов ZnO:Mn с  $E_{max} = 2.34$  eV ( $\lambda_{max} = 530$  nm),  $E_{max} = 2.19$  eV ( $\lambda_{max} = 567$  nm) и  $E_{max} = 1.97$  eV ( $\lambda_{max} = 630$  nm), связанные с легирующей добавкой Mn.

**Згладжування спектрів фотолюмінесценції та їх похідних для ідентифікації окремих смуг.** *О.В.Коваленко, С.М.Вовк, Є.Г.Плахтії*

Запропоновано методи згладжування експериментальних спектрів фотолюмінесценції та їх похідних, що базуються на методі регуляризації Тихонова. Запропоновані методи та метод Савицького-Голея порівнюються за чисельним моделюванням спектрів

фотолюмінесценції та їх похідних. Ефективне згладжування експериментальних кривих дозволило надалі за допомогою методу похідної спектроскопії провести розкладання спектрів фотолюмінесценції нанокристалів ZnO і ZnO:Mn на елементарні смуги. Таким чином, показано можливість виявлення індивідуальних смуг фотолюмінесценції на підставі одного виміру. Встановлено, що експериментальні спектри фотолюмінесценції ZnO і ZnO:Mn містять дві окремі смуги:  $E_{max} = 2.13$  eV ( $\lambda_{max} = 583$  nm) і  $E_{max} = 2.30$  eV ( $\lambda_{max} = 540$  nm), які пов'язані з вакансіями кисню або міжвузловим киснем і міжвузловим цинком відповідно. Виявлено також три окремі смуги в експериментальних спектрах фотолюмінесценції нанокристалів ZnO:Mn з  $E_{max} = 2.34$  eV ( $\lambda_{max} = 530$  nm),  $E_{max} = 2.19$  eV ( $\lambda_{max} = 567$  nm) та  $E_{max} = 1.97$  eV ( $\lambda_{max} = 630$  nm), які пов'язані з легуючою домішкою Mn.

## 1. Introduction

The phenomenon of photoluminescence (PL) is widely used in various optoelectronic devices, among them: emitting LEDs, lasers, white light sources, means of information display [1–4], etc. Furthermore, PL analysis is an effective method of nondestructive testing, which is applied in chemistry, biology, medicine, physics, archeology, criminalistics [5–8]. Due to this method, the individual emission bands are detected which are associated with intrinsic lattice defects, impurity centers, associations of point defects, as well as the presence of additional chemical phases in the object under study. In order to increase the efficiency of the PL analysis method, it is necessary to improve the equipment designed for registration of the initial PL spectra and to use the methods of smoothing the experimental data for subsequent identification of individual emission bands in the integrated spectrum and establishing of the nature of the emitting center.

The classic method for analyzing the PL spectrum is the decomposition of the PL spectrum into individual bands by the Alentsev-Fock method [9, 10]. However, it is difficult to apply this method in practice because several PL spectra which differ essentially from each other should be obtained. These spectra should be measured at various temperatures, with different PL excitation sources, etc. [9]. When the PL spectra change insignificantly, the application of the Alentsev-Fock method is practically impossible. It should be noted that this situation often occurs, for example, during the investigation of the PL spectra of nanocrystals which change slightly with changing temperatures and excitation conditions. For this reason, approaches that do not require multiple measurements under various environmental conditions, are of practical importance for solving the problem of analyzing the PL spectra; this makes possible to carry out the analysis of the PL spectrum

on the basis of a single measurement. One of these methods is the derivative spectroscopy method (DSM) [11, 12] which is based on the requirement of the presence of "correct" fixed order derivatives from the measured spectrum. As the differentiation operation is unstable, its numerical implementation can lead to a significant increase of noise in the initial data. Therefore, with an increase in the order of the derivative, a situation may occur when very small random changes in the elements of the initial data lead to such large errors that this result will be unacceptable for use. Thus, the necessary condition for the use of DSM is the presence of a correctly smoothed experimental PL spectrum and its derivatives; in this connection, the problem consists in the study of methods of effective smoothing of experimental data and its derivatives based on the Savitzky-Golay method [13, 14] and the Tikhonov regularization method [15, 16]. Comparatively similar results were obtained using the smoothing methods based on the Tikhonov regularization and the Savitzky-Golay method for smoothing the experimental PL spectra without taking into account derivatives [17].

To date, insufficient attention has been paid to the effective smoothing of experimental PL spectra. Traditionally, the smoothing of the initial data is performed either using the moving average method or the Savitzky-Golay method. Infrared PL spectra of biological objects and their first and second derivatives, which are smoothed by the Savitzky-Golay method, as well as by the standard normal variate transformation and multiplicative scatter correction were considered in [18]; however, no smoothing parameters were specified (window width, polynomial order of smoothing). In [19], absorption spectra of organic compounds and their first and second derivatives obtained by the Savitzky-Golay method of smoothing and differentiation were studied. The smoothing parameters were not specified in

this paper. In [20], PL spectra of biological objects and their second-order derivatives were smoothed by means of the Savitzky-Golay method; the smoothing parameters were not given as well. In [21], absorption spectra of chemical objects and their derivatives up to the eighth order were studied; the derivatives were smoothed by the Savitzky-Golay method, a polynomial of the second degree was used with a window of 15, 19, 23 points. However, in this work, the obtained half-widths of derivatives of the spectra of 2, 4, and 8th orders turned out to be the same, which, in principle, is not entirely correct. In [22], absorption spectra of chemical objects and their derivatives up to 8th order were considered; it was concluded that the derivatives should be smoothed by the Savitzky-Golay method using a polynomial of the second degree and a window from 13 to 21 points. Also the authors concluded that the smoothing by a polynomial of the fourth degree is more preferable than by a polynomial of the second degree. In [23], the Savitzky-Golay method was used to smooth IR spectra of biological objects and their derivatives up to the second order. A polynomial of the second degree and a window of 7 points were used for the smoothing. In [24], dielectric spectra of biological and chemical objects and their derivatives up to the fourth order were studied; it was shown that for smoothing the spectra, the method of locally weighted regression is more preferable than the Savitzky-Golay method. However, smoothing parameters were not indicated in this paper. In [25], spectra similar to IR emission of organic objects and their fractional derivatives up to the second order with a step of 0.25 were considered. The Savitzky-Golay method, a second-order polynomial, and a window of 11 points were used in order to smooth the spectrum and derivatives. The given information indicates that the smoothing procedure is not precisely defined. This, in turn, involves the development of the recommendations of the smoothing procedure that would allow obtaining the most accurate results.

The issues of smoothing of the initial spectra are usually highly specialized and are not considered fully. In the present work, the Savitzky-Golay method is described as a method of a local smoothing of experimental data by means of a sliding polynomial of a given degree; as well, the description of the proposed method of global smoothing based on the Tikhonov

regularization method is given. The proposed method is represented by two variants: the first is the method of smoothing of the initial data and the second is the method of smoothing their derivatives. In this paper it is substantiated that for the analysis of the PL spectra, the second variant which is based on the Tikhonov regularization method is optimal. Within the framework of the DSM, the smoothing procedure is obligatory due to the fact that the experimental PL spectra always contain noise components associated with both the thermal noise of the registration system and the amplitude of the recorded signal. It is noted that the second variant of this method generalizes the first one. In the end of the work we present the results of numerical modeling of the smoothing problem of the noisy PL spectrum and its derivatives. Also we present the results of the analysis of the experimental PL spectra of ZnO and ZnO:Mn nanocrystals (NC) obtained by decomposing these spectra by the DSM method into individual emission bands.

## 2. Methods and materials

The smoothing of experimental data is the problem of their approximating by a smooth function. The concept of the smooth function means that this function has a continuous derivative in the entire domain of its definition. If for a given function, its continuous derivatives exist up to the  $r$ -th order inclusive, then the smooth function with an order of smoothness is implied. Further we consider the issues of smoothing the experimental data and constructing their smooth derivatives.

The problem of smoothing the experimental data  $g(x)$  by a smooth function  $f(x)$  can be formulated on the basis of the least squares criterion as:

$$\min_{f(x)} \int_X |g(x) - f(x)|^2 dx, \quad (1)$$

where  $X$  means the observation interval. The requirement to the smoothness of the  $f(x)$  can be implemented in various ways, including the replacement of the requirement for global smoothness by the requirement for local smoothness. In the latter case, the observation interval  $X$  can be divided into some sub-intervals  $X_j$ ;  $j = 1, 2, \dots$ . At each of them the function  $f(x)$  is chosen in the form of a polynomial with a low

degree  $k$  and with unknown coefficients  $a_0, \dots, a_k$ , i.e.

$$f(x) = a_0 + \dots + a_k(x - x_0)^k, \quad (2)$$

where  $x_0$  is the middle point of the subinterval  $X_j$ . Substituting (2) into (1) and taking into account that (1) must be satisfied at each subinterval  $X_j$ , one can obtain the minimization problem:

$$\min_{a_0, \dots, a_k} \int_{X_j} |g(x) - [a_0 + \dots + a_k(x - x_0)^k]|^2 dx. \quad (3)$$

This problem is that (3) should be minimized by the unknown coefficients  $a_0, \dots, a_k$ . It is seen from (2) that the value of the approximating polynomial in the middle point of the subinterval (i.e., at the point  $x = x_0$ ) is equal to the value of the coefficient  $a_0$ . Moreover, the value of its first derivative in the middle point of the interval is equal to  $a_1$ , etc. Thus, the described approach leads to the local smoothing of the initial data at each subinterval, and the "global" smoothing of the data is achieved by enumerating all possible subintervals of the observation interval (although this does not guarantee that the resulting function will be smooth over the entire observation interval). In addition, note, that this approach performs not only local smoothing of the initial data, but also it gives their derivatives, the order of which will be not higher than the degree of the polynomial  $k$ . In the discrete case this approach forms the basis of the Savitzky-Golay method.

The Savitzky-Golay method is obtained from (3) by discretization of  $g(x)$  and  $x$  with a constant step and by choosing a subinterval (slide window)  $X_j$  in such a way that the number of discrete samples included in it is an odd number greater than  $k$ . If these samples are numbered from  $-M$  to  $M$ , then the Savitzky-Golay method can be described as:

$$f_i = \frac{\sum_{m=-M}^M \omega_m g_{i+m}}{\sum_{m=-M}^M \omega_m}, \quad (4)$$

where  $M < i \leq N - M$  and the coefficients  $\omega_m$  can be either found in the proper tables for various window widths and given polynomial degrees [14] or obtained from the discrete version of the problem (3) under assumption of a single step of  $x$ . In particu-

lar, if the window width is equal to  $(2M + 1) = 5$  and the polynomial degree is  $k = 2$ , then (4) takes the form:

$$f_i = \frac{1}{35}(-3g_{i-2} + 12g_{i-1} + 17g_i + 12g_{i+1} - 3g_{i+2}) \quad (5)$$

It should be noted that at the border of a discrete sequence of  $g_i$ ;  $i = 1, \dots, N$  (4) should be replaced by the other formula, which allow smoothing the first  $M$  and last  $M$  of discrete samples.

The moving average method is a special case of (4) under the assumption that  $\omega_m = const$  for all  $m = -M, \dots, M$ . In such a case the calculations are:

$$f_i = \frac{1}{2M+1} \sum_{m=-M}^M g_{i+m} \quad (6)$$

Another way to implement the requirement of the smoothness of  $f(x)$  is to add a regularizing term to the problem (1). This approach leads to the problem of constrained optimization known as the Tikhonov regularization method [15, 16]. Further, we use the integral of the square of the first derivative of the solution as the regularizing term; this physically reflects the requirement to the "power (energy) of the derived spectrum". Then instead of (1) we have the problem:

$$\min_{f(x)} \int_X |g(x) - f(x)|^2 dx + \alpha \int_X |D_1[f(x)]|^2 dx, \quad (7)$$

where  $D_1[f(x)] = df(x)/dx$  is a differentiation operator, and  $\alpha$  is a regularization parameter which stands a compromise between first and second terms in (7). If we use, as a constraint, the integral of the square of the  $r$ -th solution derivative of the desired solution, then instead of (1) we have the problem:

$$\min_{f(x)} \int_X |g(x) - f(x)|^2 dx + \alpha \int_X |D_r[f(x)]|^2 dx, \quad (8)$$

where  $D_r[f(x)] = d^r f(x)/dx^r$  is the  $r$ -th order differentiation operator. It should be noted that if  $\alpha = 0$ , then from (7) we obtain a trivial solution  $f(x) = g(x)$ ;  $x$  in  $X$  when the smoothing is not performed. But if  $\alpha \rightarrow \infty$  then we get a zero solution, since in this case, the minimized functional does not depend on  $g(x)$ . Therefore a practically useful value of  $\alpha$  lies within the interval  $(0, \infty)$ .

Using (8) for the discrete case leads to the problem:

$$\min_f (\|g - f\|^2 + \alpha \|D_r f\|^2), \quad (9)$$

where the vectors  $g$  and  $f$  correspond to the functions  $g(x)$  and  $f(x)$  accordingly, and the matrix  $D_r$  corresponds to the differentiation operator  $D_r$ . This problem (9) has an obvious solution:

$$f = (I + \alpha D_r^T D_r)^{-1} g, \quad (10)$$

where  $I$  is the identity matrix, and  $D_r^T$  is the transposed matrix  $D_r$ . One can note the following: if  $r = 0$ , then  $D_0 = I$  with the size of  $N \times N$  of elements. The first-order derivative operator  $r = 1$  is described by a two-diagonal matrix with the size of  $N \times (N - 1)$ , which is:

$$D_1 = \begin{pmatrix} -1 & 1 & 0 & 0 & \dots \\ 0 & -1 & 1 & 0 & \dots \\ 0 & 0 & -1 & 1 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}, \quad (11)$$

The second-order derivative operator is described by a tridiagonal matrix with the size of  $N \times (N - 2)$ , which is:

$$D_2 = \begin{pmatrix} 1 & -2 & 1 & 0 & \dots \\ 0 & 1 & -2 & 1 & \dots \\ 0 & 0 & 1 & -2 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}, \quad (12)$$

The third-order derivative operator is described by a four-diagonal matrix with the size of  $N \times (N - 3)$ :

$$D_3 = \begin{pmatrix} -1 & 3 & -3 & 1 & 0 & \dots \\ 0 & -1 & 3 & -3 & 1 & \dots \\ 0 & 0 & -1 & 3 & -3 & \dots \\ 0 & 0 & 0 & -1 & 3 & \dots \\ 0 & 0 & 0 & 0 & -1 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}, \quad (13)$$

etc. However, the matrix  $D_r^T D_r$  always has the size of  $N \times N$ .

The Tikhonov regularization method can be also applied to the problem of constructing the first derivative of the spectrum, which can be either limited in the magnitude or satisfy the smoothness requirement. Indeed, let  $u(x) = D_1[f(x)]$  be the first derivative of the  $f(x)$ . Then we can write  $f(x) = (D_1)^{-1}[u(x)] = A[u(x)]$ , where  $A$  is an anti-differentiation operator [26], which can be specified by the matrix:

$$A = \begin{pmatrix} 1 & 0 & 0 & 0 & \dots \\ 1 & 1 & 0 & 0 & \dots \\ 1 & 1 & 1 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}. \quad (14)$$

Using the constraint on the square of the norm of the desired first derivative, in this case, we obtain the problem:

$$\min_u (\|g - Au\|^2 + \alpha \|u\|^2). \quad (15)$$

The solution of the problem (15) allows us to find  $f(x)$  [26]. Here we can note, if we search for  $f(x)$ , then the problem (15) is equivalent to the problem (9) for  $r = 1$ . On the other hand, using the requirement of smoothness of derivatives up to the  $r$ -order, for the discrete case, we can pose the problem relative to the first derivative:

$$\min_u (\|g - Au\|^2 + \alpha \|D_r u\|^2), \quad (16)$$

or derivatives of higher orders:

$$\min_{u_q} (\|g - A_q u_q\|^2 + \alpha \|D_r u_q\|^2), \quad (17)$$

where  $u_q$  denotes the vector that corresponds to the continuous derivative of the  $q$  order for the function  $f(x)$ , and  $A_q$  is the antidifferentiation operator of the  $q$  order. It can be seen, when  $q = 0$ , the problem (17) is transformed into the problem (9). The solution of the problem (17) can be written as:

$$u_q = (A_q^T A_q + \alpha D_r^T D_r)^{-1} A_q^T g. \quad (18)$$

Thus, (18) can be used as a basis for both the spectrum smoothing procedure and the procedure for calculating smooth derivatives, which are necessary for the spectrum analysis within the framework of the DSM. The success of this approach depends on the noise level in the initial data and on the used values of the regularization parameter  $\alpha$ .

ZnO and ZnO:Mn NC were synthesized by means of ultrasonic spray pyrolysis [27]. The ZnO:Mn NC samples were synthesized with a manganese concentration of 2 at. % according to the method described in [28]. The size of NC particles was  $d \sim 40$  nm according to the XRD analysis. An ultraviolet LED ( $\lambda_{max} = 375$  nm) was used as the source of the excitation light. The PL spectra were registered according to a standard methodology at room temperature ( $T = 300$  K); a photoelectronic multiplier 136 (PEM-136) was used as an emission detector.

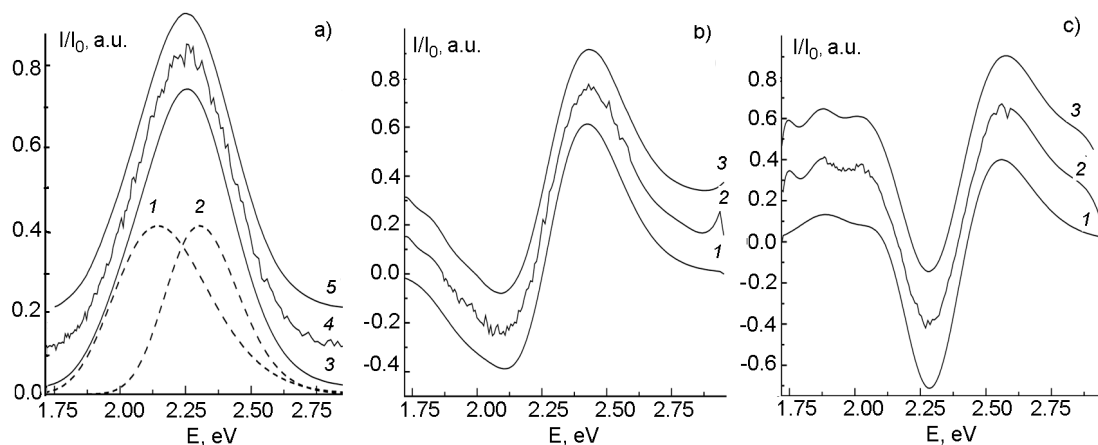


Fig. 1. Results of modeling and smoothing of the PL spectra and their first and second derivatives: a — the synthesized PL spectrum (3), consisting of two Gaussians (1–2), the synthesized PL spectrum with the addition of noise dependent of the signal and thermal noise (4), smoothed by the Savitzky-Golay method with the smallest total error (5); b — veritable the first derivative of the synthesized PL spectrum (1), the first derivative of the smoothed PL spectrum by the Savitzky-Golay method with the smallest total error (2), the smoothed first derivative by the Savitzky-Golay method (3); c — veritable the second derivative of the synthesized PL spectrum (1), the second derivative of the smoothed first derivative of the PL spectrum by the Savitzky-Golay method with the smallest total error (2), the smoothed second derivative by the Savitzky-Golay method (3); all the curves in the presented figures are shifted relative to each other along the vertical axis for better presentation of the results.

### 3. Results and discussion

To demonstrate the capabilities of the smoothing methods under study, we performed a numerical modeling of a non-elementary PL spectrum mathematically synthesized from two Gaussian elementary bands with different positions of maxima ( $E_{max}$ ), standard deviations ( $\sigma$ ), and amplitudes ( $I$ ). The modeling task was to simulate the noise in the synthesized PL spectra, which was characteristic to the measurements of PL spectra, and to establish optimal smoothing methods. In this case, for the Tikhonov method, the parameters  $r = 5$  and  $m = 1$  were fixed, and only the parameter  $\alpha$  was subject to tuning. For the Savitzky-Golay method, polynomials were searched up to the eighth order; if we used a larger polynomial order, an error occurred in the Matlab shell. The number of points in the window changed up to  $N/2 + 1$ , where  $N$  is the number of discrete samples in the spectrum. All the calculations were performed in the Matlab shell using 100 noise realizations. As a measure of effectiveness of the smoothing method we apply the mean square deflection of the smoothed curve from the true one which is an rms error of the solution. We will consider, that the smaller the value of this error, measured in

arbitrary units, the more effective the method.

The PL spectrum was modeled in the wavelength range of 1.72 to 2.95 eV (420–720 nm), with a step  $\Delta E \approx 0.008$  eV ( $\Delta\lambda = 2$  nm), which corresponded to  $N = 151$  discrete samples. The spectrum model was designed for the real PL spectrum imitation of ZnO nanocrystals and was specified by the sum of two Gaussian functions with parameters:  $A_1 = 1300$ ,  $m_1 = 60\Delta\lambda$ ,  $\sigma_1 = 16\Delta\lambda$ ;  $A_2 = 1300$ ,  $m_2 = 80\Delta\lambda$ ,  $\sigma_2 = 24\Delta\lambda$ . A constant amplitude background  $A_0 = 50$  and noise were added to the sum of the Gaussian functions; thus the noise of a photoelectronic multiplier was simulated as a sum of noises dependent on the signal amplitude and thermal noise. This noise was modeled by the relation:  $\xi_i = |g(x_i)|^{1/2}\eta_i + 15\zeta_i$ , where  $\eta_i$  and  $\zeta_i$  are the values of Gaussian random variables with unit dispersion and zero mathematical expectation. A similar model was used in [26]. The smoothing results of the synthesized PL spectrum and its first two derivatives by the methods of Savitzky-Golay and Tikhonov are presented in Fig. 1 and Fig. 2, respectively.

Fig. 1 shows: the initial PL spectrum smoothed by means of the Savitzky-Golay method with a seventh degree polynomial. With an optimal window with a length of

Table 1. The initial parameters and parameters found to solve the inverse problem of individual Gaussian bands in the synthesized PL spectrum

No.	The parameters of the initial Gaussian bands, arb.u.			The parameters of the found Gaussian bands, arb.u.			Deviation values, %		
	$E$	$\sigma$	$I$	$E$	$\sigma$	$I$	$E$	$\sigma$	$I$
1	60	16	1300	61.6	16.2	1268	2.6	1.25	2.5

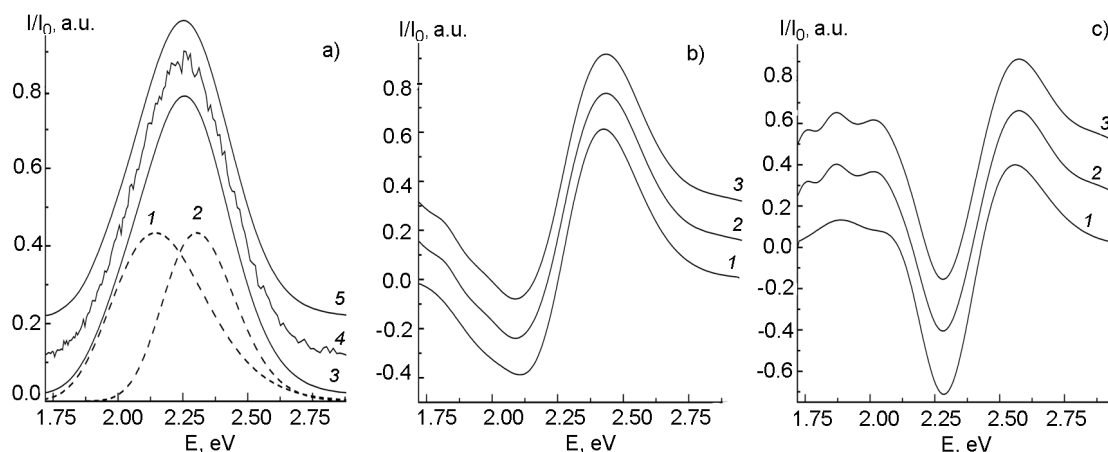


Fig. 2. Results of modeling and smoothing of the PL spectra and their first and second derivatives: a — the synthesized PL spectrum (3), consisting of two Gaussians (1-2), the synthesized PL spectrum with the addition of noise dependent of the signal and thermal noise (4), smoothed by the Tikhonov method with the smallest total error (5); b — veritable the first derivative of the synthesized PL spectrum (1), the first derivative of the smoothed PL spectrum by the Tikhonov method with the smallest total error (2), the smoothed first derivative by the Tikhonov method (3); c — veritable the second derivative of the synthesized PL spectrum (1), the second derivative of the smoothed first derivative of the PL spectrum by the Tikhonov method with the smallest total error (2), the smoothed second derivative by the Tikhonov method (3); all the curves in the presented figures are shifted relative to each other along the vertical axis for better presentation of the results.

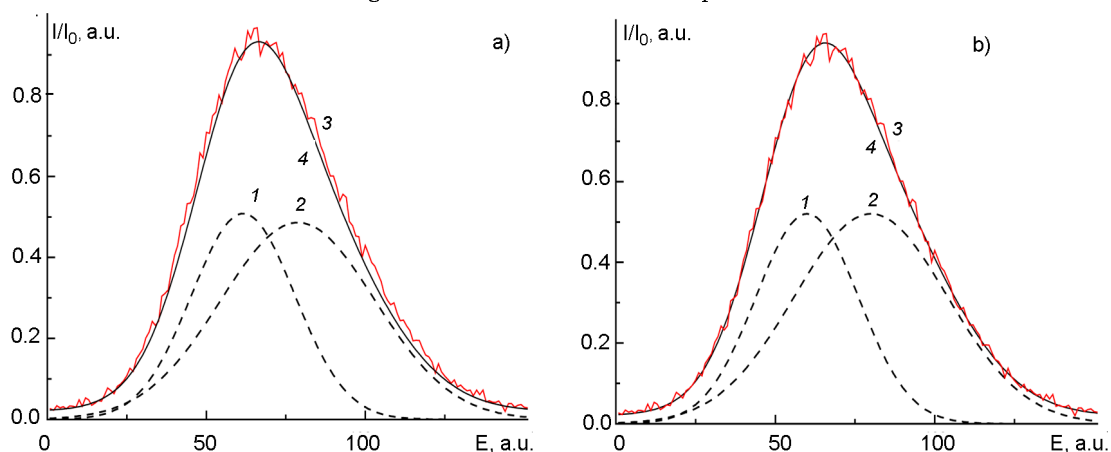


Fig. 3. Modeling results: a — the mathematical sum is dash line (3) of two Gaussian curves (1-2), the mathematical sum (3) with the addition of noise dependent on the signal and thermal noise (4); b — mathematical sum with the addition of noise dependent on the signal and thermal noise (3), the result of the decomposition of the signal (1-2), the mathematical sum of two Gaussian curves is dash line (4).

Table 2. The parameters of the found individual Gaussian bands in the experimental PL spectra of ZnO and ZnO:Mn nanocrystals

	Parameters of the found Gaussian bands in ZnO NC				Parameters of the found Gaussian bands in the ZnO:Mn NC	
	$E_{max}$	eV	$\sigma$ , eV	$I/I_0$	$E_{max}$	eV
1	2.13	0.17	0.294	1.97	0.09	0.232
2	2.30	0.18	0.780	2.13	0.11	0.268
3	–	–	–	2.19	0.12	0.287
4	–	–	–	2.30	0.13	0.324
5	–	–	–	2.34	0.13	0.314

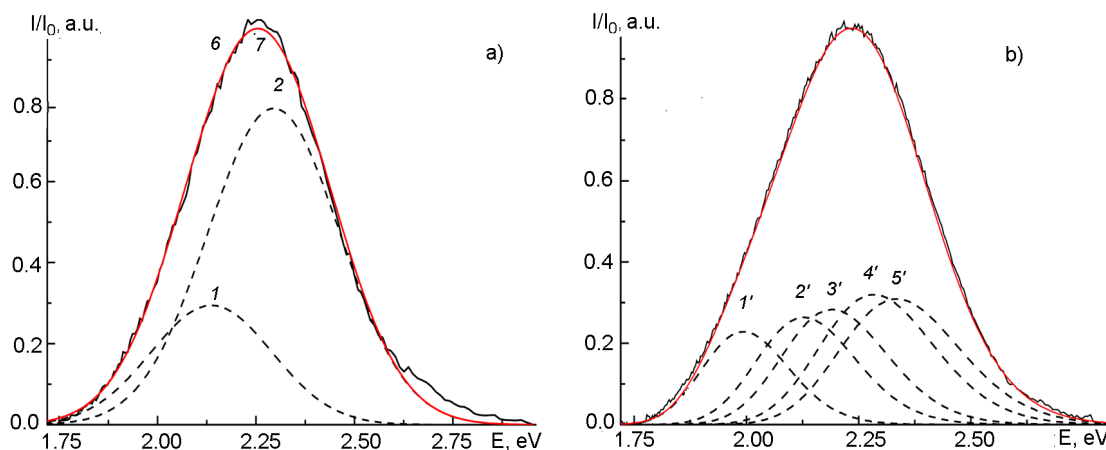


Fig. 4. Results of the decomposition of the experimental PL spectra into individual bands: a — experimental PL spectrum of ZnO nanocrystals smoothed by the Tikhonov method and individual bands revealed in it by the derivative spectroscopy method:  $E_{max} = 2.13$  eV — 1,  $E_{max} = 2.30$  eV — 2; 6 — experimental PL spectrum at  $T = 300$  K; 7 — integral PL spectrum (sum of individual bands) is dash line; b — experimental PL spectrum of ZnO:Mn nanocrystals smoothed by the Tikhonov method and individual bands revealed in it by derivative spectroscopy:  $E_{max} = 1.97$  eV — 1';  $E_{max} = 2.13$  eV — 2';  $E_{max} = 2.19$  eV — 3';  $E_{max} = 2.30$  eV — 4';  $E_{max} = 2.34$  eV — 5'; 6 — 197 experimental PL spectrum at  $T = 300$  K; 7 — integral PL spectrum (sum of individual bands) is dash line.

59 discrete samples, this method gave a minimum total error of 16907 arb. u. The first and second derivatives of the PL spectrum which were smoothed by the Savitzky-Golay method by the seventh degree polynomial, with optimal windows of 61 and 57 discrete samples, gave minimal total errors of 384 and 15 arb.u., respectively.

Fig. 2 shows: the initial PL spectrum smoothed by the Tikhonov method with  $\alpha = 7.9 \cdot 10^5$  regularization coefficient. It gave a minimum total error equal to 15924 arb. u. The first and second derivatives of the PL spectrum, smoothed by the Tikhonov method with regularization coefficients  $\alpha = 0$  and  $\alpha = 0$ , gave minimal total errors of 295 and 7 arb.u., respectively. Zero values of the regularization coefficients mean that when smoothing the initial signal with the smoothing parameter  $r = 5$

by the Tikhonov method, the derivatives are smoothed up to the fifth order automatically. Comparing the values of the obtained errors with different smoothing methods, we can conclude that the Tikhonov regularization method is more efficient than the Savitzky-Golay method. In addition, the Tikhonov regularization method for obtaining smoothed derivatives is characterized by a higher operation speed and a simpler calculation procedure.

Fig. 3a shows a noisy spectrum composed of two elementary Gaussian bands with the parameters of the elementary bands presented in Table 1. Figure 3b shows the results for solving the inverse problem: decomposition of the synthesized PL spectrum into elementary components of the Gaussian form by the derivative spectroscopy method using 4–6th orders derivatives. It was previously shown that when smoothing the ex-



perimental PL spectra by the Tikhonov method, derivatives up to 6–8th orders of magnitude can be used in DSM [29].

The almost complete coincidence of curves 3 and 4 in Fig. 3b, as well as small deviations between the parameters of the initial individual bands and the parameters of these bands were obtained as a result of solving the inverse problem (Table 1); the results indicate the effectiveness of this method. As we can see, deviations are possible in the amplitude of the found Gaussian function. This is most likely due to the small number of points of the synthesized spectrum. In order to find the parameters of individual bands more accurately, it is recommended to register experimental PL spectra with a step as small as possible; this will increase the number of discrete samples and thereby facilitate the search for parameters of individual bands.

The smoothing procedure by Tikhonov regularization method and searching for individual PL bands with DSM were also tested on real experimental PL spectra of ZnO and ZnO:Mn nanocrystals. The results of decomposition of the experimental PL spectra of ZnO and ZnO:Mn NC into individual bands shown in Fig. 4 indicate that the individual bands with  $E_{max} = 2.13$  eV ( $\lambda_{max} = 583$  nm) and  $E_{max} = 2.30$  eV ( $\lambda_{max} = 540$  nm) are part of the experimental spectrum of both ZnO and ZnO:Mn nanocrystals. The literature analysis indicates that these individual PL bands are associated with defects in the ZnO crystal lattice: the band  $E_{max} = 2.13$  eV ( $\lambda_{max} = 583$  nm) is associated with oxygen vacancies [30] or oxygen interstitials [31]; the band  $E_{max} = 2.30$  eV ( $\lambda_{max} = 540$  nm) is associated with structural defects in the crystal such as interstitial zinc [30, 32, 33]. Some researchers observed these bands in bulk undoped ZnO. They associated these bands with the presence of defects in ZnO [34]. The PL spectrum of ZnO:Mn nanocrystals is characterized by a larger half-width and greater asymmetry, which indicates the possible appearance of new individual bands. Indeed, DSM of 4–6 orders revealed five individual Gaussian bands in these NC (Table 2). Individual PL bands with  $E_{max} = 2.34$  eV ( $\lambda_{max} = 530$  nm), with  $E_{max} = 2.19$  eV ( $\lambda_{max} = 567$  nm), and  $E_{max} = 1.97$  eV ( $\lambda_{max} = 630$  nm) detected in ZnO:Mn nanocrystals, are associated with the dopant Mn, which could provoke the appearance of new defects.

The analysis of literature shows that the individual band with  $E_{max} = 1.97$  eV

( $\lambda_{max} = 630$  nm) is possibly associated with the transition  ${}^4T_1 \rightarrow {}^6A_1$  of  $Mn^{2+}$  ions in the octahedral environment [35], or with the  $MnO_2$  phase [36]. The individual band with  $E_{max} = 2.19$  eV ( $\lambda_{max} = 567$  nm) is associated with small donors (zinc vacancies) [37], the appearance of which is provoked by an admixture of manganese. The individual band with  $E_{max} = 2.34$  eV ( $\lambda_{max} = 530$  nm) is most likely associated with the transition  ${}^4T_1 \rightarrow {}^6A_1$  of  $Mn^{2+}$  ions in a tetrahedral environment [35].

#### 4. Conclusions

Numerical modeling has shown the efficiency of smoothing the PL spectra both by the proposed method, which is based on Tikhonov's regularization method, and by the Savitzky-Golay method. The best smoothing of the obtained PL spectra is achieved using the proposed method based on the Tikhonov regularization. Using this method, it is possible to obtain smoothed derivatives of the PL spectra up to 6–8th orders. Smoothing coefficients depend on the noise environment. For our proposed noise variant (signal/noise ratio  $\sim 100$ ), the smoothing coefficient of the PL spectra is equal to  $\alpha = 7.9 \cdot 10^5$ . Due to the proposed method, the derivatives of the first to fifth order of the PL spectra become smooth. This gives the opportunity to increase operation speed and simplify the calculation program.

The application of DSM to search for individual PL bands smoothed by the proposed method allows obtaining parameters of individual bands close to those that were laid in the model spectrum. The results of smoothing by the proposed method and the application of DSM to search for individual bands of the experimental PL spectra of ZnO and ZnO:Mn NC showed that these bands contain individual bands:  $E_{max} = 2.13$  eV due to oxygen vacancies or oxygen interstitials and  $E_{max} = 2.30$  eV, associated with interstitial zinc. In the experimental PL spectra of the ZnO:Mn NC DSM, additional three individual bands were found, which were associated with the dopant Mn. An analysis of the literature suggests that the band with  $E_{max} = 1.97$  eV is probably associated with the transition  ${}^4T_1 \rightarrow {}^6A_1$  of  $Mn^{2+}$  ions in the octahedral environment, or with the  $MnO_2$  phase; the band with  $E_{max} = 2.19$  eV indicates small donors (zinc vacancies), the appearance of which is provoked by a manganese admixture; the band with  $E_{max} = 2.34$  eV is most likely associated with the transition  ${}^4T_1 \rightarrow {}^6A_1$  of  $Mn^{2+}$  ions in a tetrahedral environment.

## References

1. D.V.Korbutyak, A.V.Kovalenko, S.I.Budzulyak et al., *Ukr. J. Phys.*, **7**, 48 (2012).
2. Q.Zhou, Z.Bai, W.G.Lu et al., *Adv. Mater.*, **41**, 9163 (2016). <https://doi.org/10.1002/adma.201602651>
3. N.Deopa, A.S.Rao, A.Choudhary et al., *Mater. Res. Bull.*, **100**, 206 (2018). <https://doi.org/10.1016/j.materresbull.2017.12.019>
4. S.Adachi, *J. Luminescence*, **202**, 263 (2018). <https://doi.org/10.1016/j.jlumin.2018.05.053>
5. Z.Wang, H.Zeng, L.Sun, *J. Mater. Chem.C*, **3**, 1157 (2015). <https://doi.org/10.1039/C4TC02536A>
6. D.A.Skoog, F.J.Holler, S.R.Crouch, Principles of Instrumental Analysis, Cengage learning, USA (2017).
7. V.Sharma, A.Das, V.Kumar et al., *Physica B*, **535**, (2018). <https://doi.org/10.1016/j.physb.2017.07.019>
8. J.Kaszewski, P.Kielbik, E.Wolska et al., *Opt. Mater.*, **80**, 77 (2018). <https://doi.org/10.1016/j.optmat.2018.04.028>
9. M.V.Fok, *Trudy Fizicheskogo Instituta RAN P.N.Lebedeva Ross. Akad. Nauk*, **59**, 3 (1972).
10. O.M.Bordun, B.O.Bordun, I.Y.Kukharskyy et al., *J. Appl. Spectrosc.*, **84**, 46 (2017). <https://doi.org/10.1007/s10812-017-0425-3>
11. G.Talsky, Derivative Spectroscopy: Low and Higher Order, VCH Publishers, Wiley (1994).
12. H.H.Perkampus, UV-VIS Spectroscopy and its Applications, Springer Science & Business Media, Berlin (2013).
13. A.Savitzky, M.J.Golay, *Anal. Chem.*, **36**, 1627 (1964). <https://doi.org/10.1021/ac60214a047>
14. R.W.Schafer, *IEEE Signal Proc. Mag*, **28**, 111 (2011). <https://doi.org/10.1109/MSP.2011.941097>
15. A.N.Tikhonov, *Dokl. Akad. Nauk*, **151**, (1963).
16. A.N.Tikhonov, A.V.Goncharsky, V.V.Stepanov et al., Springer Science & Business Media (2013).
17. O.V.Kovalenko, S.M.Vovk, Ye.G.Plakhtii, *J. Phys. Electron.*, **26**, 73 (2018). <https://doi.org/10.15421/331828>
18. P.S.Sampaio, A.Soares, A.Castanho et al., *Food Chem.*, **242**, 196 (2018). <https://doi.org/10.1016/j.foodchem.2017.09.058>
19. H.Deng, J.Sun, P.Li et al., *Opt. Appl.*, **46**, 353 (2016). <https://doi.org/10.5277/oal60303>
20. J.Causse, O.Thomas, A.V.Jung et al., *Water Res.*, **108**, 312 (2016). <https://doi.org/10.1016/j.watres.2016.11.010>
21. K.Ichimura, *Bull. Chem. Soc. Jpn.*, **90**, 411 (2017). <https://doi.org/10.1246/bcsj.20160414>
22. K.Ichimura, *Bull. Chem. Soc. Jpn.*, **89**, 549 (2016). <https://doi.org/10.1246/bcsj.20160032>
23. H.Yang, S.Yang, J.Kong et al., *Nat. Protoc.*, **10**, 382 (2015). <https://doi.org/10.1038/nprot.2015.024>
24. R.Olmi, M.Bittelli, *IEEE Trans. Dielectr. Electr. Insul.*, **22**, 3334 (2015). <https://doi.org/10.1109/TDEI.2015.004729>
25. Y.Hong, Y.Chen, L.Yu et al., *Remote Sens.*, **10**, 479 (2018). <https://doi.org/10.3390/rs10030479>
26. S.M.Vovk, *Rad. Electron. Comp. Sci. Control*, **3**, 91 (2017). <https://doi.org/10.15588/1607-3274-2017-3-5>
27. S.C.Tsai, Y.L.Song, C.S.Tsai et al., *J. Mater. Sci.*, **39**, 3647 (2004) <https://doi.org/10.1023/B:JMSE.0000030718.76690.11>
28. V.Yu.Vorovsky, A.V.Kovalenko, A.I.Kushneryov et al., *Functional Materials*, **25**, 61 (2018). <https://doi.org/10.15407/fm25.01.061>
29. A.V.Kovalenko, Ye.G.Plakhtii, S.M.Vovk, *Ukr. J. Phys. Opt.*, **19**, 133 (2018). <https://doi.org/10.3116/16091833/19/3/133/2018>
30. P.Rodnyi, K.Chernenko, O.Klimova et al., *Radiat. Meas.*, **90**, 136 (2016). <https://doi.org/10.1016/j.radmeas.2016.01.021>
31. C.Chandrinou, N.Boukos, C.Stogios et al., *Microelectron J.*, **40**, 296 (2009). <https://doi.org/10.1016/j.mejo.2008.07.024>
32. C.Ton-That, L.Weston, M.R.Phillips, *Phys. Rev. B*, **86**, 115205 (2012). <https://doi.org/10.1103/PhysRevB.86.115205>
33. A.K.Singh, V.Viswanath, V.C.Janu, *J. Luminescence*, **129**, 874 (2009). <https://doi.org/10.1016/j.jlumin.2009.03.027>
34. M.A.Reshchikov, H.Morkoc, B.Nemeth et al., *Physica B*, **401–402**, 358 (2007). <https://doi.org/10.1016/j.physb.2007.08.187>
35. A.J.Reddy, M.A.Kokila, Y.Nagabhushana et al., *Spectrochim. Acta A*, **79**, 476 (2011). <https://doi.org/10.1016/j.saa.2011.03.014>
36. X.T.Zhang, Y.C.Liu, J.Y.Zhang et al., *J. Cryst. Growth*, **254**, 80 (2003). [https://doi.org/10.1016/S0022-0248\(03\)01143-6](https://doi.org/10.1016/S0022-0248(03)01143-6)
37. N.X.Sang, L.Ph.Sang, N.M.Quan et al., *VNU J. Sci. Math. Phys.*, **34**, 37 (2018). <https://doi.org/10.25073/2588-1124/vnumap.4273>