

DOI: 10.5604/01.3001.0012.7982

## ANALYSIS OF THE SEPARATION METHODS OF OPTICAL SPECTRA FOR INDIVIDUAL COMPONENTS

**Victor Makhniy, Oksana Kinzerska, Illia Senko**

Yuriy Fedkovich Chernivtsi National University, PTC SI

**Abstract.** A comparative analysis of various methods for the decomposition of broad bands into individual components has been carried out. It is shown that the most universal are the methods of modulation spectroscopy and direct differentiation of conventional spectral characteristics, which, unlike the widely used Alentsev-Fock method, are applicable to spectra of any type (luminescence, transmission, absorption, etc.). The features and capabilities of the direct differentiation method are used to identify the structure in the emission spectra and transmission of ZnSe <Al> single-crystal substrates.

**Keywords:** optical spectra, separation methods, luminescence, transmission

### ANALIZA METOD SEPARACJI WIDM OPTYCZNYCH DLA INDYWIDUALNYCH SKŁADNIKÓW

**Streszczenie.** Przeprowadzono analizę porównawczą różnych metod dekompozycji szerokich pasm na poszczególne składniki. Pokazano, że najbardziej uniwersalne są metody spektroskopii modulacyjnej i bezpośrednie różnicowanie konwencjonalnych charakterystyk spektralnych, które w przeciwieństwie do powszechnie stosowanej metody Alentsewa-Focka mają zastosowanie do widm dowolnego rodzaju (luminescencja, transmisja, absorpcja itp.). Cechy i możliwości bezpośredniej metody różnicowania są stosowane do identyfikacji struktury w widmach emisyjnych i transmisyjnych monokrystalicznych składników ZnSe <Al>.

**Słowa kluczowe:** widma optyczne, metody separacji, luminescencja, transmisja

### Introduction

Measurement and study of optical spectral characteristics are widely used in the emission of the energy structure of the allowed bands and local centers of semiconductors, since they largely determine their physical properties and areas of practical use [3]. At the same time, the composition of local centers of real semiconductor materials is rather complicated due to the fact that they are formed by various types of point defects – intrinsic, impurity, and their associates [7]. This in turn leads to the formation of wide structureless bands in the optical spectra, which causes certain difficulties in interpreting of the experimental results. Note that the interaction of free or bound charge carriers also causes the expansion of narrow bands, the structure of which is difficult to reveal even at cryogenic temperatures.

In this regard, the separation of integral spectra into individual components is an urgent task. Today there are many ways to solve it, however, not every way leads to the desired results when used in real conditions.

Among the best-known ones, we should highlight the Alentsev-Fock method [2], which is based on the deformation of complex luminescence bands when the excitation conditions change and it does not require information on the shape and position of the maxima of their components. Meanwhile, this method is applicable only to the analysis of the emission spectra, and only in case of their noticeable reaction to the level of excitation. In addition, a serious problem is to take into account the overlap of individual bands, especially when there are many of them and the selection of individual horizontal sections becomes almost impossible. These deficiencies are devoid of modulation spectroscopy methods based on transformations of spectra caused by small periodic changes in the physical parameters of a sample or a light wave [4]. The effectiveness of the use of various structural methods requires the fulfillment of conditions, among which we can single out the following [8]. First, usually, for standardization, special samples are required, the creation of which in some cases presents certain difficulties. Secondly, mechanical devices that modulate the parameters of the light beam (amplitude, wavelength, phase or degree of polarization) must ensure a high temporal stability of the modulation frequency. This requirement becomes even more stringent when using higher harmonics of the fundamental modulation frequencies. This is due to the fact that the application of the latest strong effects, as well as another - the deterioration of the signal-to-noise ratio after a sharp decrease in the level of the useful signal.

Many proposed physical problems that can be reliably measured at sufficiently high signal levels. In particular, by this method the author [1] with high accuracy determined the width of the forbidden zone  $E_g$  of a series of indirect-gap semiconductors –Si and SiGe solid solutions. Meanwhile, despite the fact that in this work the differential method was applied only to the spectra of the edge luminescence, it can be very promising for analyzing the spectral characteristics of other types (transmission, absorption, photoconductivity, etc.), and more wide range of energies.

In this paper, we study the possibility of applying of the above mentioned methods to identify the structure of complex bands in the optical spectra of ZnSe<Al> and ZnSe <Al>:Gd semiconductor substrates.

### 1. Samples and research methods

The choice of objects for research is due to several reasons. First, zinc selenide for many decades has continued to remain one of the most promising materials for functional electronics. Secondly, Al is widely used as an alloying element for ZnSe, since, unlike many other donor impurities, it does not exhibit amphotericity and does not form deep centers. Third, the dependence of the form of a wide low-energy luminescence band of ZnSe <Al> crystals on the level of excitation allows the use of the Alentsev-Fock method for its separation. Fourth, studies show that this band is also present in the spectra of pure ZnSe crystals annealed in a zinc melt containing 0.01–5 mol%. Al [11] At the same time, its shape depends on the aluminum content, annealing time, cooling modes and the “biography” of the original crystal, which indicates the redistribution of the roles of the recombination centers included in an ensemble of ZnSe<Al> crystals, whose composition apparently remains unchanged.

Finally, a feature of the ZnSe<Al>:Gd samples is that, while maintaining a wide low-energy band, a narrower band of edge radiation also appears in them [9]. This allows a comparative analysis of the results obtained using the same separation methods for spectra of different nature and complexity.

Spectral studies were carried out on substrates cut from a bulk crystal grown from the melt stoichiometric composition by the Bridgman method with an additive of ~0.1 mol % Al. The doping technology of zinc selenide substrates with rare-earth impurities, including Gd, is described in detail [10]. Optical transmission  $T_{\omega}$  and luminescence  $N_{\omega}$  spectra were measured at room temperature on a universal installation containing

an MDG-23 monochromator, a PEM-79 photodetector, and radiation sources – a halogen lamp and an N<sub>2</sub>-laser. Their differentiation was carried out on a computer using a special program.

## 2. Results and discussion

First, we will carry out a general analysis of the usual photoluminescence spectrum of ZnSe <Al> crystals, which is shown in Fig. 1 at 300 K.

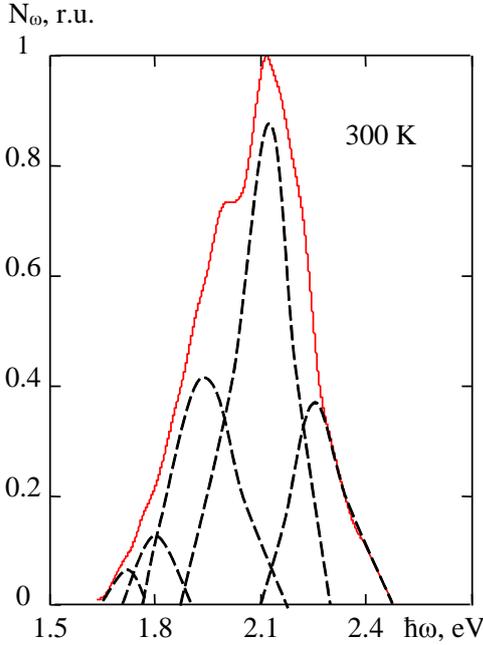


Fig. 1. The ordinary photoluminescence spectrum of ZnSe <Al> crystals is a solid line, the dotted line is the individual bands calculated by the Alentsev-Fock method

Its abnormally large half width ( $\Delta\hbar\omega_{1/2} \approx 0.45$  eV) as well as the presence of a clear maximum and a bend in the energy range of 2.0 and 2.1 eV, respectively, indicate that this band is not elementary. In this regard, there is a need for its decomposition into components, which was carried out according to the Alentsev-Fock method [2]. As a result of this procedure, it was possible to distinguish 5 bands with maxima near 1.70, 1.80, 1.95, 2.10 and 2.25 eV, which are shown in Fig. 1 (dotted line). Meanwhile, a detailed analysis showed that the half-width of all selected bands is about the same and at 0.20–0.22 eV, which significantly exceeds  $kT \approx 0.026$  eV.

So great values  $\Delta\hbar\omega_{1/2}$  of these components indicate a strong electron-phonon interaction of the centers that are involved in their formation. In this case, the shape of the bands can be described using the ratio obtained in [5, 6]. So great values of these components indicate a strong electron-phonon interaction of the centers that are involved in their formation. In this case, the shape of the bands can be described using the ratio obtained in [5, 6]

$$I(y) = I_0 \theta^{1/4} e^{-\frac{E_0}{kT(1-\delta)}} y \psi \left[ \frac{3}{4}, \frac{1}{2}, \frac{(1-y)^2}{\theta} \right] e^{-\frac{(1-y-2\delta)^2}{\theta}} \quad (1)$$

where  $I_0$  – constant;  $y = \hbar\omega / E_0$ ;  $E_0$  – optical energy of ionization or neutralization of the center of the glow;

$\theta = \left( \frac{a^* \hbar\Omega}{E_0} \right)^2 \text{cth} \left( \frac{\hbar\Omega}{2kT} \right)$ ;  $\delta = \theta E_0 / 4kT$ ;  $a^*$  – electron-phonon

interaction constant;  $\hbar\Omega$  – oscillation energy localized at the center;  $\psi(a, c, x)$  – degenerate hypergeometric function. Due to the complexity of the expression (1), in practice, its simplified variants are used much more often, they are discussed below.

Formula (1) shows that the shape of the luminescence band is determined mainly by the exponent  $e^{-\frac{(1-y-2\delta)^2}{\theta}}$  and is almost gaussian.

The condition is used to determine the position of the maximum emission band

$$\left. \frac{dI(y)}{dy} \right|_{y=y_m} = 0$$

Since the exponent in (1) determines the dependence  $I(y)$ , for a successful solution of the problem, it suffices to take the derivative only of the exponential part of the equation, that is,

the exponent  $\left( e^{-\frac{(1-y-2\delta)^2}{\theta}} \right)' = 0$  At the same time we get

$y_m \approx (1-2\delta)$  or taking into account the ratio for  $\delta$  and  $\theta$  will have

$$\hbar\omega_m = E_0 \left[ 1 - \frac{E_0}{2kT} \left( \frac{a^* \hbar\Omega}{E_0} \right) \text{cth} \left( \frac{\hbar\Omega}{2kT} \right) \right] \quad (2)$$

at temperature, when  $\hbar\Omega \ll 2kT$ , will get

$$\hbar\omega_m \approx E_0 - a^{*2} \hbar\Omega \quad (3)$$

From (3) it is clear that the derivatives  $a^{*2} \cdot \hbar\Omega$  are equal to energy which is actually Stokes displacement  $\Delta$ .

The width of the emission band at the level  $1/e$  will be determined by the condition  $\ln(I_m / I_{1/e}) = 1$ . Given only the exponential factor in (1), we obtain

$$(y_{1/e} - y_m)^2 = \theta \quad (4)$$

On the other side,

$$y_{1/e} - y_m = \frac{E_{1/e}}{2E_0} \quad (5)$$

Equating the right sides of (5) and (6), we get  $E_{1/e} = 2E_0 \theta^{1/2}$ , and given the ratio for  $\theta$

$$E_{1/e} = 2a^* \hbar\Omega \left[ \text{cth} \left( \frac{\hbar\Omega}{2kT} \right) \right]^{1/2} \quad (6)$$

at temperature, when  $\hbar\Omega \ll 2kT$ ,

$$E_{1/e} = 2a^* (2kT \hbar\Omega)^{1/2}$$

It should be noted that (2) and (6) are approximate, since in the corresponding calculations we took into account only the exponential multiplier of the dependence  $I(y)$ .

The positions of its maximum

$$\hbar\omega_m \approx E_0 (1-2\delta) \quad (7)$$

Using expert value  $E_{1/e} - \hbar\omega_m$  from formulas (2) and (6) it is easy to determine the parameters  $\theta$  and  $E_0$ , which also allow to calculate the Frank-Condon displacement

$$\Delta = \frac{a^{*2} \hbar\Omega}{2} \quad (8)$$

and the activation energy of the glow centers

$$E_a = E_g - \hbar\omega_m - \Delta \quad (9)$$

Table 1. Parameters of the centers responsible for the "elementary" luminescence bands of ZnSe <Al> crystals

$\hbar\omega$ , eV	$E_0$ , eV	$\Delta$ , eV	$E_a$ , eV
2.25	2.54	0.18	0.32
2.10	2.46	0.18	0.42
1.95	2.30	0.18	0.56
1.80	2.16	0.18	0.70
1.70	2.0	0.18	0.86

Values  $E_0$ ,  $\Delta$  and  $E_a$ , characterizing centers responsible for the formation of bands with maximum  $\hbar\omega_m$  at 300 K, are shown in Table 1. Let's pay attention to the same values of the Franck-Condon offset for all the above bands, which is a consequence of the proximity of their widths at the level  $1/e$ .

Thus, the application of the Alentsev-Fock method together with the Kopylov-Pikhtin model made it possible not only to isolate individual components in a wide luminescence band of ZnSe <Al> crystals, but also to determine the main parameters of recombination centers. On the other hand, the "elementary" bands calculated by the Alentsev-Fock method are structureless symmetric gaussian curves (dotted line in Fig. 1), which do not always correspond to reality. In most cases, their shape is usually asymmetric due to the interaction of recombination centers with phonons. This should lead to the appearance of a certain structure on the "wings" of individual bands. The latter is simply inevitable in our case, since the Kopylov-Pikhtin model used to calculate the model is based on the assumption of a strong electron-phonon interaction.

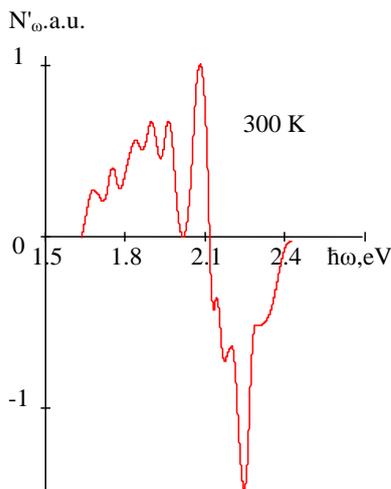


Fig. 2. The first derivative of the usual photoluminescence spectrum of ZnSe <Al> crystals

One of the ways to solve this problem is to use the method of direct differentiation mentioned earlier, the result of which is applied to the usual luminescence spectrum (Fig. 1), it is shown in Fig. 2. Despite the rather complex shape of the curve, its analysis allows us to identify some features of the "elementary" bands. So, in particular, the intersection point of the curve with abscissa axis corresponds to the maximum of the normal spectrum  $N'_\omega$ , and minima - the energy position of the maxima of the corresponding "elementary" bands, Table 1. Equidistant peaks on the curve  $N'_\omega$  located to the left of the minima near 1.95 and 2.25 eV are caused by scattering by LO-phonons, since the distance between them is  $\sim 30$  meV and is consistent with the energy of the longitudinal optical phonon of ZnSe [3, 11]. The interaction of these centers with LO-phonons is also confirmed by the presence of sections

with an equidistant structure on the curve (Fig. 4) obtained by differentiating the usual optical transmission spectrum, Fig. 3. The result is in favor of the wider possibilities of differential methods (which include modulation [4, 8]) as compared with the Alentsev-Fock method, which is not applicable to optical transmission spectra at all.

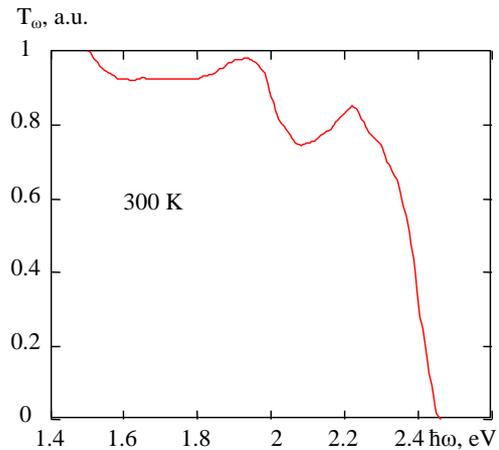


Fig. 3. The usual transmission spectrum of single-crystal ZnSe <Al> substrates with a thickness of 1 nm

We also pay attention to the presence in the spectra  $T'_\omega$  and another intense band with a peak near 2.4 eV, which is absent on the curve  $N'_\omega$ , Fig. 2. Meanwhile, the clarification of the nature of the centers responsible for its appearance requires additional research beyond the scope of this work.

The results obtained above confirm the legitimacy and perspective of applying the method of direct differentiation of broad optical spectra for separation into components. At the same time, the efficiency of its use decreases with the expansion of the studied spectral range, due to the substantial complication of the energy structure of the obtained curves and the overlap of individual bands. The transition from the first to higher derivatives, although it increases the separation capacity, further aggravates the situation due to the appearance of additional structural elements.

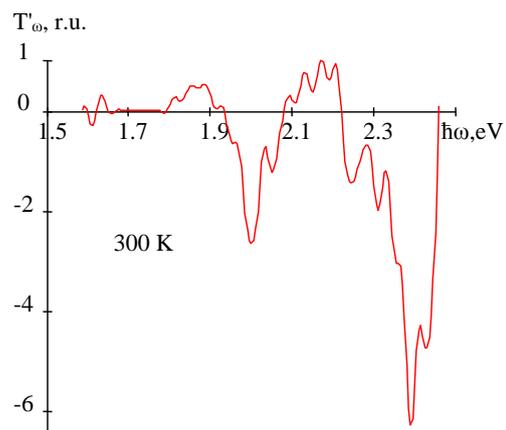


Fig. 4. The first derivative of the usual transmission spectrum of the ZnSe <Al> substrates shown in Fig. 3

Considering the above mentioned, it is reasonable to assume that the direct differentiation method is more appropriate to use for the analysis of relatively narrow bands, as which we chose the edge luminescence  $B$  band of the substrates ZnSe<Al>:Gd, Fig. 5.

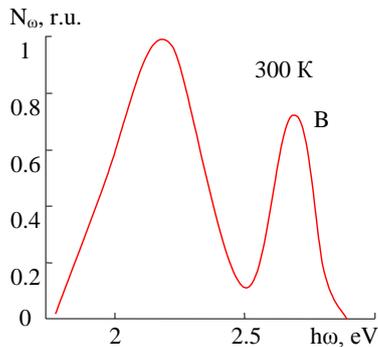


Fig. 5. The usual photoluminescence spectrum of ZnSe <Al>: Gd crystals

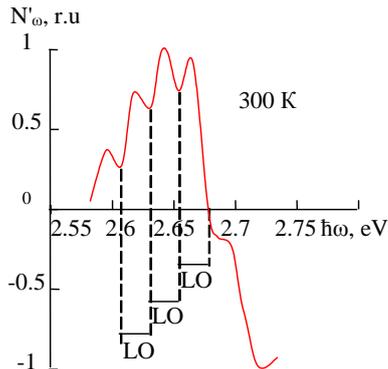


Fig. 6. The first derivative of the edge band of the usual photoluminescence spectrum of ZnSe <Al>: Gd crystals

As a result of its differentiation, a complex curve is obtained (Fig. 6), on which a number of equidistant minima are observed with an energy distance corresponding to the energy of the LO-phonon ZnSe. Intersection of  $N'_\omega$  curve with the abscissa axis at 2.68 eV, corresponds to the maximum emission of a free exciton, and the bend at 2.7 eV corresponds to the band gap of ZnSe at 300 K [3, 11]. We note that the edge luminescence spectra of the ZnSe<Al>:Gd samples measured in [9] by the modulation method, unlike their direct differentiation (Fig. 6), do not exhibit phonon replications. This demonstrates the advantage of using the differential method for detecting and isolating the fine structure of optical spectra.

## References

- [1] Emelianov A. M.: Differential method for analyzing the luminescence spectra of semiconductors. *Fizika i tehnika polyprovodnikov* 44(9)/2010, 1170–1175.
- [2] Fok M. V.: Decomposition of complex spectra into individual bands using the Alentsev method. *Trydu FIAN SSUR*. 59/1972, 3–24.
- [3] Gavrilenko V. I., Grehov A. M., Korbytyak D. V., Litovchenko V. G.: Optical properties of semiconductors. *Directory naykova dymka*, Kiev 1987.

- [4] Kardona M.: *Modulation spectroscopy*. Mir, Moscow 1972.
- [5] Kopulov A. A., Pihitin A. I.: The effect of temperature on the optical absorption spectra of deep centers in semiconductors. *Fizika tverdogo tela* 16/1974, 1837–1842.
- [6] Kopulov A. A., Pihitin A. I.: The shape of the absorption and luminescence spectra at deep centers in semiconductors (oxygen in gallium phosphide). *Fizika i tehnika polyprovodnikov* 8/1974, 2390–2403.
- [7] Makhniy V. P.: *Physics and chemistry of point defects in semiconductors*. CHNU, Chernivtsi 2014.
- [8] Makhniy V. P.: *Principles and methods of modulation spectroscopy*. Ruta, Chernivtsi 2001.
- [9] Makhniy V. P., Vakhnyak N. D., Kinzerska O. V., Senko I. M.: Luminescence of crystals ZnSe<Al>:Gd. *Semiconductor Physics, Quantum Electronics and Optoelectronics* 21(1)/2018, 80–82.
- [10] Patent 107292 UA, MPK C30B/2500 (20.16.01) C30B 31/00 Method of doping ZnSe<Te> crystals with rare earth elements. Makhniy V. P., Kinzerska O. V., Senko I. M., Yuriy Fedkovych Chernivtsi National University, 2015, 12805, stated 24.12.2015; posted 25.05.2016, Bul. No. 10, 2016.
- [11] Vaksman Yu.F.: Luminescence of single crystals of zinc selenide and radiating structures based on them. *Diss. of doc. phys. and math. science* 1993.

### Prof. Viktor Makhniy

e-mail: vpmakhniy@gmail.com

Viktor P. Makhniy, born in 1946, defended his Doctoral Dissertation in Physics and Mathematics in 1992 and became full professor in 1994. Professor at the Department of Optics, Publishing and Printing of Yuri Fedkovych Chernivtsi National University, Ukraine. Authored over 450 publications, 40 patents, 9 textbooks and wrote 2 monographies. The area of his scientific interests includes technology, physics and applications of wide-band semiconductor compounds and devices based on them.



ORCID ID: 0000-0002-7073-6860

### Ph.D. Oksana Kinzerska

e-mail: oksanakinzerska@gmail.com

Oksana V. Kinzerska, born in 1980, defended her PhD dissertation in Physics and Mathematics in 2012. Assistant Professor at the Department of Physics of Semiconductors and Nanostructures of Yuri Fedkovych Chernivtsi National University, Ukraine. Authored 44 publications, 3 patents, 2 methodical recommendations. The area of her scientific interests includes technology, physics and the application of wide-band semiconductor compounds of semi-magnetic and rare-earth elements.



ORCID ID: 0000-0003-1722-1216

### M.Sc. Illia Senko

e-mail: senko.illia14@gmail.com

Illia M. Senko, born in 1993, PhD student at the Department of Semiconductors and Nanostructures of Yuri Fedkovych Chernivtsi National University, Ukraine. Authored 11 publication and 1 patent. The area of his scientific interests is the influence of rare-earth elements on physical properties of zinc selenide.



ORCID ID: 0000-0002-4665-6879

otrzymano/received: 1.10.2018

przyjęto do druku/accepted: 15.12.2018