On the 75th anniversary of Associate Member of the ASM I.I. Geru

Ivan Ivanovich Geru and Kazan

I.I. Geru devoted all his scientific activity of many years to the development of radiospectroscopy methods and their application for studying the magnetic phenomena in condensed media.

The electron paramagnetic resonance (EPR) as a method of research originated in Kazan as a result of the discovery of microwave energy resonance absorption by the substance in a magnetic field, which was made by assistant professor of the Kazan State University E.K. Zavoisky in 1944. The Kazan scientific school of magnetic radiospectroscopy has won the world recognition, so it is no wonder that the life of I.I. Geru is connected with Kazan and Kazan's physicists. It was in Kazan where he was directed by the head of the Institute of Chemistry of the Academy of Sciences of MSSR, academician of the Academy of Sciences of MSSR A.V. Ablov. In conjunction with collaborator of the Kazan Physico-Technical Institute Yurii Vasil'evich Yablokov, he carried out experimental research into a number of coordination compounds. These results were published in 1961 in the journal "The Reports of the Academy of Sciences" with the recommendation being given by academician A.E. Arbuzov, and this was the first publication on EPR of structurally ordered dimmer cluster in the URSS. The joint work in the field of EPR spectroscopy of coordination compounds of scientists of the Kazan PhTI and the Institute of Chemistry of the ASM, initial steps on which were taken by I.I. Geru, is successfully continued nowadays.

The second thread that connects the Kazan PhTI and I.I. Geru is the phenomenon of a double electron-nuclear acoustic resonance, which was theoretically predicted by I.I. Geru in 1967. This phenomenon was experimentally discovered in the Kazan PhTI in 1969 under the supervision of V.A. Golenishchev-Kutuzov.

In the life of every scientist, the recognition of his merits by his colleagues is of great importance. Formally, it is expressed in the awarding of scientific degrees of candidate and doctor of sciences. In this respect, Kazan has played an important role in the life of I.I. Geru. It was at the Council for the Thesis Defense where he was awarded the degree of doctor habilitate in physics and mathematics.

During all these years of communication in creative work and in human contracts, we have had immense respect for Ivan Ivanovich. We are always happy to meet him. We also see that Ivan Ivanovich is not indifferent to Kazan physicists and to Kazan. It is difficult to remember an important Russian or international conference on the problems of magnetic resonance in which Ivan Ivanovich has not taken part. There is no necessity to name all Kazan conferences in which Ivan Ivanovich participated during 50 years of his scientific activity. Let us mention just a few of them: the XII All-Union meeting on low temperature physics held in 1965, the All-Union jubilee conference on paramagnetic resonance dedicated to the 25th anniversary of the discovery of EPR held in 1969, the XXVI Congress AMPERE in 1994, the International Conference "Modern Development of Magnetic Resonance" dedicated to 60 years since the discovery of EPR held in 2004, and the International conference "Resonances in Condensed Media" dedicated to the centenary of one of the founders of Kazan school of radiospectroscopy S.A. Al'tshuler held in 2011.

We know I.I. Geru as an actively working scientist and a very pleasant person to communicate with. We wish him every success in the implementation of new scientific projects, health, well-being, and many years ahead.



In the photo: I.I. Geru and one of the participants of the conference dedicated to the centenary of S.A. Al'thsuler.

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SCIENTIST ION GERU IS A WILLING LIFELONG CAPTIVE OF THE MIRACULOUS WORLD OF CONDENSED MATTER



Having involved in the world of modern physics for over 50 years, associate member of the Academy of Sciences of Moldova, professor Ion Geru can be rightfully considered to be one of the first descendants of the "golden generation" of physics in Moldova, which is represented by academicians Moskalenko, Ghitu, Radautan, Andries, and others. He has grown and formed with them and in other research laboratories in Russia, Ukraine, and other countries. Creatively assimilating the new areas of condensed matter physics, which was developed in the 1960s and 1970s, he seeks for his own paths of research, which later would become full-fledged highways. A convincing example is radiospectroscopy of excitons and biexcitons, a pioneer research in which was conducted by professor Ion Geru. Another direction which is promoted for the first time in the world by his participation is related to semimagnetic semiconductors. Extensive research in these two domains has led to results of an incontestable value. They include: the development of a method for narrowing the exciton absorption lines and high-density exciton recombination radiation; the theoretical prediction of a double radio-optical resonance in the Wannier-Mott exciton system, which was subsequently confirmed in experiments; the theoretical interpretation of the giant spin splitting of exciton states that leads to giant magneto-optical effects in semimagnetic semiconductors; the excitonic Knight shift of NMR lines and its sudden increase in the exciton transition to a Bose-Einstein condensed state (a new method for verifying the existence of the Bose-Einstein condensation of excitons). The list can be extended, and bare listing would fill dozens of book pages.

It is well known that the paradigm of modern physics in general and condensed matter physics in particular is based on the symmetry principles and their violation is the driver of new phases and phenomena. Professor Ion Geru, being a consummate researcher, in his basic investigations could not but try to promote his own concepts of this fine and profound field of condensed matter physics. In this context, we should mention his generalizations about magnetic symmetry groups and time reversal symmetry. In fact, the "magnetic line" runs like a scarlet thread through most of the studies that he carried out guided by the "magic compass" of his research talent. In this field of studies, his activities are as follows: he demonstrates that the magnetic properties of clusters with half-integer spin must be described using four-color magnetic point groups, unlike the conventional concept according to which all point groups of magnetic symmetry are two-color symmetry groups; he identifies the structural distortions in magnetic clusters with half-integer spin that are caused by the existence of time-reversal symmetry, which were experimentally confirmed for a large number of coordination compounds of transition metal ions; he develops a general method for transforming the ferromagnetic ordering to the antiferromagnetic one and vice versa in magnetic dimers with the determination of the ground state type for all possible magnetic dimers based on iron group ions and rare earth group ions; he reveals a new type of degeneration of quasi-energy levels and bands caused by the noncommutation of the time-reversal operator and time translation operators. This brief listing makes it possible to classify these results as new directions in addition to those mentioned above.

Scientific research of Prof. I. Geru is well known worldwide. His significant ingenious contribution to the development of modern condensed state physics and its applications to multiple devices and electronic components has been appreciated and recognized. He touched the fine aspects of the miraculous world of condensed matter that had been inaccessible for his predecessors. He was invited as a "visiting professor" to prestigious foreign universities, such as Catholic University, Leuven, Belgium; Florida State University, USA; Kazan Physico-Technical Institute, Russia; University of Cluj, Romania, and many others.

Having implemented a valuable research and having reached the age of maturity, he continues to be optimistic about the life as a teenager. He has reasonable grounds for this, because he is only 75 years old. Fanciful ideas still make him restless; he is captivated by the toils of paradox in physics. He is constantly on the go trying on the ideas of time travel, which appeared simultaneously with Albert Einstein's theory of relativity, according to which the passage of time is relative and depends on the velocity of the object. As far as researchers are concerned, we would like to add that it also depends on the speed of processing the new ideas and concepts. Prof. I. Geru accelerates his thinking and processing and thus makes his own time pass more slowly and catches new facets of physics. Unfortunately, this method works only for travels to the past. No matter how fast you move, the time will never flow backwards. However, the effect of time reversal can be advantageously used as a concept in analyzing the phenomena as evidenced by many studies of the celebrated scientist.

Riding a wave of time reversal in our retrospective discussions about our native land, i.e., his Cotiujenii Mari (Big Cotiujeni) and my Zahorna Mica (Small Zahorna) in Soldanesti district, every time he comes with thoughts of gratitude for the sacrifice of his parents to whom he is indebted for his ascension to the light of books, being conscious that the values we share here have their vigorous roots at home.

By writing this essay, we render homage to three-quarters of a century of life and more than 50 years of creative work; we wish our Physicist with capital letter an Everest of health, a flow of happiness as wide as the Nile or at least the Dniester, a cartful of new significant achievements and sincere traditional HAPPY BIRTHDAY!

Acad. Valeriu Kantser, editor-in-chief of the MJPS

NONLINEAR DYNAMICS OF AN OPTICAL PARAMETRIC EXCITON–POLARITON OSCILLATOR IN A MICROCAVITY

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Abstract

The system of nonlinear evolution equations was obtained for describing the time evolution of densities of pump, signal, and idler microcavity polaritons. It was shown that the period and amplitude of oscillations of the polariton densities essentially depend on the initial densities of polaritons, initial phase difference, and resonance detuning. For the definite relation between the parameters, the aperiodic evolution of the system is also possible; it represents the conversion of only the part of pump polaritons, by which the evolution of the system is finished. The significant dependence of the period and amplitude of polariton oscillations on the initial phase difference evidences the possibility of the phase controlling of the polariton dynamics. The damping of the system of coherent polaritons leads to the oscillatory decay of polariton density in time, the rate of which is defined by the polariton damping constants.

1. Introduction

Semiconductor microcavities have attracted a special attention because of the discovery of a strong light-matter coupling regime. The first observation of strong coupling between light and excitons in a semiconductor quantum microcavity was demonstrated by Weisbuch et al. [1]. They experimentally demonstrated that the interaction of a confined light mode with an exciton state in a microcavity can lead to the appearance of two new eigenstates that have different energies other than the bare exciton and photon states. These new modes are associated with microcavity exciton-polaritons. Houdre et al. [2, 3] published the results of the experimental measurements of the cavity polariton dispersion curve from angle-resolved photoluminescence experiments and the studies of saturation of the polariton resonance.

In a strong coupling regime, the exciton and photon modes are pushed apart and, consequently, the upper and lower microcavity polariton determines its small effective mass, whereas the exciton component of the polariton is responsible for the effective polariton–polariton interactions, owing to which the polaritons can be scattered from one another. Two pump polaritons can scatter into the signal and idler modes with the energy and momentum conservation. The specific features of the processes of polariton–polariton scattering, which provide the parametric amplification and parametric oscillations, have been investigated in a number of articles [4-5]. Savvidis et al. [6] observed stimulated parametric scattering in pump–probe experiment. They observed a resonance at the inflection point of the polariton dispersion. Another experiment with a single cw pump [7] showed the same resonance at the so-called

"magic angle." The parametric scattering process was experimentally studied in detail under both cw pumping [8-11] and pulsed excitation [12-14]. By using the pump-probe method, Savvidis et al. [6] and Baumberg et al. [15] were the first who observed the parametric amplification in a semiconductor microcavity under excitation of the lower polariton branch by a picosecond pump pulse. After a further excitation (with a short delay) of the lower polariton branch by a weak test pulse at a normal angle of incidence, it was revealed that this pulse in reflection was amplified by a factor of more than 70. In this case, there also appeared the idler mode at an angle of 35° . It is these angles that satisfy the resonance conditions. The results of the experiments performed in [6, 15] were also reproduced by Saba et al. [16] and simulated by Ciuti et al. [17, 18] with the use of polariton-polariton scattering mechanism. Similar processes were observed by Huang et al. [19], who used two beams incident at angles of $\pm 45^{\circ}$ and a test beam incident at an angle of 0° . The parametric oscillator mode was observed by Baumberg et al. [15] and Stevenson et al. [7] under continuous excitation of the lower polariton branch by pumping at a "magic" angle of 16° without a test pulse. Above the threshold intensity, these authors observed intense beams of the signal and idler modes at the angles of incidence of 0^{0} and 35^{0} , respectively. Recently, Tosi et al. [20] have visualized the formation of a spontaneously oscillating quantum fluid using twodimensional polariton condensates on semiconductor microcavity and observed stable quantum oscillator wavefunctions in a real space. This system was created on the fly by injecting polaritons at two spatially separated pump spots. It was announced [21] that the macroscopic quantum pendulum has now been created by confining a polariton condensate in a parabolic optical trap.

The description of polariton parametric oscillators and amplifiers was presented in a number of papers. Shelykh et al. [22] derived a closed set of the kinetic equations describing a system of interacting bosons, which was applied to the investigation of the dynamics of a three state polariton parametric oscillator taking into account the incoherent photon dynamics and the coherent nature of the polariton–polariton scattering process in the presence of macroscopically occupied polariton modes. In the framework of the three-level model, Ciuti et al. [17] investigated the dynamics of the pump, signal, and idler modes, which were considered to be coherent and macroscopically populated. In [23, 24] we present some preliminary results of investigation of the dynamics of parametric oscillations of polaritons in a microcavity that consists of a periodic and aperiodic conversion of pairs of pump polaritons into polaritons of signal and idler modes and vice versa.

Further investigation in this field is an important problem. A complete theoretical description of the optical parametric oscillation dynamics in a semiconductor microcavity is very important from the point of view of the optimization of the device operation and also of the fundamental interest of nonlinear dynamics.

2. Statement of the problem and basic equations

The purpose of the present paper is to investigate the dynamics of exciton-polaritons in the parametric oscillator model. We consider the situation where polaritons are excited on the lower branch of the dispersion law at a "magic" angle. A schematic sketch of the pumping is shown in Fig.1: a coherent pump is incident on the microcavity at such an angle that the wave vector $\vec{k_p}$ lies in the vicinity of the inflection point of the lower polariton branch. Due to the interactions, polaritons are scattered into a pair of other modes $p + p \leftrightarrow s + i$, which represent the signal and

idler modes with the wave vectors $\vec{k_s}$ and $\vec{k_i}$. The peculiar dispersion relation of excitonpolaritons in the strong coupling regime allows us to satisfy the resonance condition for the pump, signal, and idler modes. The scattering processes in the bosonic systems can be stimulated by existing populations in the initial and final states. When the pump intensity is strong enough for the stimulated scattering rate to overcome losses, a new regime with a macroscopic occupation of signal and idler modes is achieved and a pair of coherent signal and idler beams is emitted with a narrow distribution in the energy and a in-plane wave vector.



Fig. 1. Energies of the polaritons of the upper and lower branches (ω_{\pm}) ; ω_{cav} and ω_{ex} are the dispersions of the microcavity and exciton, respectively. Two pump polaritons (closed circles) are scattered into polaritons of the signal (open circle) and idler (open rhombus) modes.

We consider the simplest model based on the assumption that the process of excitonpolariton parametric oscillation may be described by only three quantum states, such as the pump, signal and idler states. Under the assumption that the dynamics takes place in the lower polariton branch and the population of the upper polariton branch remains negligible, the description can be simplified by restricting it to the lower polariton only. It was shown in [17, 22] that, upon excitation of exciton-polaritons on the lower branch of the dispersion law, the process of parametric scattering of two pump polaritons (p) into polaritons of signal (s) and idler (i) modes and vise versa is described by the Hamiltonian of the following form

$$H = \hbar \omega_{p} \hat{a}_{p}^{+} \hat{a}_{p}^{-} + \hbar \omega_{s} \hat{a}_{s}^{+} \hat{a}_{s}^{-} + \hbar \omega_{i} \hat{a}_{i}^{+} \hat{a}_{i}^{-} + \hbar \mu \left(\hat{a}_{p}^{+} \hat{a}_{p}^{+} \hat{a}_{s}^{-} \hat{a}_{i}^{-} + \hat{a}_{s}^{+} \hat{a}_{i}^{+} \hat{a}_{p}^{-} \hat{a}_{p}^{-} \right)$$
(1)

where ω_p , ω_s and ω_i are the frequencies of the pump, signal and idler modes respectively, μ is the constant of parametric process, \hat{a}_p , \hat{a}_s and \hat{a}_i are the annihilation Bose operators of polaritons of corresponding modes. The first term in brackets describes scattering from the pump into the signal and idler, and the last term accounts for the reverse process. We postulate here the existence of coherent coupling between pump, signal and, idler modes. In this case, their phases may be synchronized, which is achieved by the coherent transfer of polaritons between three modes. A detailed analysis of the blueshifts due to the interparticle interactions lies beyond the scope of the present paper, because we consider the peculiarities of the simplest parametric interaction between two pump polaritons and a pair of signal and idler polaritons.

Using (1), we can obtain a system of Heisenberg equations for these operators. Averaging this system of equations and applying the mean field approximation [25] yield a system of nonlinear evolution equations for the complex amplitudes $a_{p,s,i} = \langle \hat{a}_{p,s,i} \rangle$ in the form

$$i\dot{a}_p = (\omega_p - i\gamma_p)a_p + 2\mu a_p^*a_s a_i,$$

$$i\dot{a}_{s} = (\omega_{s} - i\gamma_{s})a_{s} + \mu a_{i}^{*}a_{p}a_{p},$$

$$i\dot{a}_{i} = (\omega_{i} - i\gamma_{i})a_{s} + \mu a_{s}^{*}a_{p}a_{p},$$
(2)

where γ_p , γ_s and γ_i are the phenomenological damping constants of the respective mode, which are due to leaving of polaritons from the coherent states. System of equations (2) should be supplemented by the initial conditions, which can be written in the form

$$a_{p|t=0} = a_{p0} \exp(i\varphi_{p0}), \ a_{s|t=0} = a_{s0} \exp(i\varphi_{s0}), \ a_{i|t=0} = a_{i0} \exp(i\varphi_{i0}),$$
(3)

where $a_{p0} = \sqrt{N_{p0}}$, $a_{s0} = \sqrt{N_{s0}}$, $a_{i0} = \sqrt{N_{i0}}$ and φ_{p0} , φ_{s0} , φ_{i0} are the real amplitudes and phases of polaritons at the initial moment of time, respectively. Further we will introduce the polariton densities $N_p = a_p^* a_p$, $N_s = a_s^* a_s$, $N_i = a_i^* a_i$ and two functions $Q = i \left(a_p a_p a_s^* a_i^* - a_s a_i a_p^* a_p^* \right)$ and $R = a_p a_p a_s^* a_i^* + a_s a_i a_p^* a_p^*$. Using (2) it is easy to obtain a new system of nonlinear differential equations for these functions:

$$\dot{N}_{p} = -2\gamma_{p}N_{p} + 2\mu Q, \quad \dot{N}_{s} = -2\gamma_{s}N_{s} - \mu Q, \quad \dot{N}_{i} = -2\gamma_{i}N_{i} - \mu Q,$$

$$\dot{Q} = \Delta R - (2\gamma_{p} + \gamma_{s} + \gamma_{i})Q + 2\mu (4N_{p}N_{s}N_{i} - N_{p}^{2}N_{s} - N_{p}^{2}N_{i}),$$

$$\dot{R} = -\Delta Q - (2\gamma_{p} + \gamma_{s} + \gamma_{i})R, \quad (4)$$

where

$$\Delta = 2\omega_p - \omega_s - \omega_i \tag{5}$$

is the resonance detuning. The initial conditions for system of equations (4) can be written as follows:

$$N_{p|t=0} = N_{p0}, \ N_{s|t=0} = N_{s0}, \ N_{i|t=0} = N_{i0},$$
$$Q_{|t=0} = 2N_{p0}\sqrt{N_{s0}N_{i0}}\sin\theta_0, \ R_{|t=0} = 2N_{p0}\sqrt{N_{s0}N_{i0}}\cos\theta_0,$$
(6)

where $\theta_0 = \varphi_{s0} + \varphi_{i0} - 2\varphi_{p0}$ is the initial phase difference. We suppose that we can produce the initial conditions by the action of supershort (δ -shaped) pulses of laser radiation.

It follows from equations (4) that there is no possibility to obtain exact analytical solutions of this system. Therefore, we consider the two limit cases. One of them is the limit γ_p , γ_s , $\gamma_i \rightarrow 0$. This is the case of the evolution at the times which are small in comparison with the exciton-polariton relaxation times. In this case, the process of relaxation does not come into action and the evolution of the system represents the limit of the optical exciton-polariton nutation after the action of supershort pulse of laser radiation, which is responsible for the generation of the initial state of the system. Assuming that $\gamma_p = \gamma_s = \gamma_i = 0$, we obtain the conservative system of equations:

$$\dot{N}_{p} = 2\mu Q, \ \dot{N}_{s} = -\mu Q, \ \dot{N}_{i} = -\mu Q, \dot{Q} = \Delta R + 2\mu \left(4N_{p}N_{s}N_{i} - N_{p}^{2}N_{s} - N_{p}^{2}N_{i} \right), \ \dot{R} = -\Delta Q.$$
(7)

The second case is the limit of the equal damping constants of the polaritons $\gamma_p = \gamma_s = \gamma_i \equiv \gamma$ and the equal constants of elastic collisions. For $\Delta = 0$ in this case we have the following system of equations:

$$\dot{N}_p = -2\gamma N_p + 2\mu Q, \ \dot{N}_s = -2\gamma N_s - \mu Q, \ \dot{N}_i = -2\gamma N_i - \mu Q$$

$$\dot{Q} = -4\gamma Q + 2\mu \left(4N_p N_s N_i - N_p^2 N_s - N_p^2 N_i\right), \quad R = -4\gamma R.$$
(8)

In both cases (7) and (8), we can obtain exact analytical solutions.

3. Evolution in the absence of damping

We now consider in detail the time evolution of the system for the case $\gamma_p = \gamma_s = \gamma_i = 0$, i.e., in the absence of damping. Using system of equations (7), we obtain the following integrals of motion:

$$N_{p} + 2N_{s} = N_{p0} + 2N_{s0}, N_{p} + 2N_{i} = N_{p0} + 2N_{i0},$$

$$Q^{2} + R^{2} = 4N_{p}^{2}N_{s}N_{i}, \quad R = R_{0} + \frac{\Delta}{2\mu} (N_{p0} - N_{p}).$$
(9)

It follows from (9) that nontrivial evolution of the system can take place in the case if only two of the initial densities of particles are nonzero. This is due to the complicated stimulation of the process of four-wave interaction, since we take into account only the stimulated transitions. It is more comfortable to carry out the further consideration for the normalized values of the density of pump polaritons $y = N_p/N_{p0}$. Then we can represent system of equations (7) as a single nonlinear differential equation

$$\frac{1}{2}\left(\frac{dy}{d\tau}\right)^2 + W(y) = 0, \qquad (10)$$

where

$$W(y) = W_{1}(y) + W_{2}(y),$$

$$W_{1}(y) = -2y^{2} (1 + 2\overline{N}_{s0} - y) (1 + 2\overline{N}_{i0} - y), \quad W_{2}(y) = 2 (2\sqrt{\overline{N}_{s0}}\overline{N}_{i0} \cos \theta_{0} + \alpha (1 - y))^{2}.$$
(11)

Here

$$\overline{N}_{s0} = N_{s0} / N_{p0}, \ \overline{N}_{i0} = N_{i0} / N_{p0}, \ t = \tau \tau_0, \ \tau_0^{-1} = \mu N_{p0}, \ \alpha = \Delta / (2\mu N_{p0}).$$
(12)

Equation (10) describes the evolution of the nonlinear oscillator, where W(y) plays the role of the potential energy of this oscillator and $\frac{1}{2}(dy/d\tau)^2$ is the kinetic energy. Now it is easy to determine the qualitative behavior of the function $y(\tau)$, investigating the dependence of the potential energy W(y) on y for the different values of the parameters. The evident form of function $y(\tau)$ is determined by the roots of the algebraic equation W(y)=0, which depend on the parameters \overline{N}_{s0} , \overline{N}_{i0} , θ_0 , α , τ_0 .

3.1. Evolution in the case $\theta_0 = \pi/2$

At first, we will consider the time evolution of the system for the initial phase difference $\theta_0 = \pi/2$. Then the equation W(y) = 0 has four real roots, which we arrange in the order of decrease in their values and designate them $y_1 > y_M > y_m > y_4$, respectively. In the limit of small values of α they change with respect to α : $y_1 = 1 + 2\overline{N}_{s0} + \frac{2\alpha^2 \overline{N}_{s0}^2}{(\overline{N}_{s0} - \overline{N}_{s0})(1 + 2\overline{N}_{s0})^2}$,

$$y_{M} = 1 + 2\overline{N}_{i0} - \frac{2\alpha^{2}\overline{N}_{i0}^{2}}{\left(\overline{N}_{s0} - \overline{N}_{i0}\right)\left(2\overline{N}_{i0} + 1\right)^{2}}, \quad y_{m} = \frac{|\alpha|}{\sqrt{\left(1 + 2\overline{N}_{s0}\right)\left(1 + 2\overline{N}_{i0}\right)}}, \quad y_{4} = -y_{m}. \text{ Here the roots } y_{M}$$

and y_m have the meaning of maximal and minimal normalized densities of pump polaritons, which they can have during the evolution process. Further, for definiteness, we will assume that $\overline{N}_{i0} > \overline{N}_{s0}$. Evolution of roots depending on parameter α is presented in Fig. 2. We can see that the roots y_1 and y_m increase, but y_M and y_4 decrease with the increase of α . Then the solution of equation (10) has the form

$$y = \frac{y_M(y_1 - y_m) - y_1(y_M - y_m) \operatorname{sn}^2(\sqrt{(y_1 - y_m)(y_M - y_4)}\tau \pm f(\varphi_0, k))}{y_1 - y_m - (y_M - y_m) \operatorname{sn}^2(\sqrt{(y_1 - y_m)(y_M - y_4)}\tau \pm f(\varphi_0, k))},$$
(13)

where $\operatorname{sn}(x)$ is the elliptic $\operatorname{sin}[26, 27]$, $f(\varphi_0, k) = F(\varphi_0, k) - K(k)$, $F(\varphi_0, k)$ is the incomplete elliptic integral of the first kind with the modulus k and parameter φ_0 , K(k) is the complete elliptic integral of the first kind [26, 27]. The quantities k and φ_0 are determined by the expressions

$$k^{2} = \frac{(y_{1} - y_{4})(y_{M} - y_{m})}{(y_{1} - y_{m})(y_{M} - y_{4})}, \quad \varphi_{0} = \arcsin \sqrt{\frac{(y_{M} - y_{4})(1 - y_{m})}{(y_{M} - y_{m})(1 - y_{4})}}.$$
(14)



Fig. 2. Dependence of the roots y_i (i = 1, 2, 3, 4) of the equation W(y) = 0 on the parameter α for $\overline{N}_{s0} = 0.1$, $\overline{N}_{i0} = 0.05$ and different values of θ_0 , equals to $\pi/2$, 0 and π .

From (13) we can obtain the amplitude A and period T of oscillations of the density of pump polaritons:

$$A = y_M - y_m, \ T = 2K(k) / \sqrt{(y_1 - y_m)(y_M - y_4)}.$$
(15)

Here the amplitude A is determined as the difference between the second and the third roots of the equation W(y)=0 (Fig. 2a). In the limit $\alpha \to 0$ we obtain from (13)

$$y = \frac{2N_{i0} + 1}{1 + \frac{2(\overline{N}_{s0} - \overline{N}_{i0})}{2\overline{N}_{s0} + 1} \operatorname{sh}^{2} \left(\sqrt{(1 + 2\overline{N}_{s0})(1 + 2\overline{N}_{i0})}\tau \pm \operatorname{arsh} \sqrt{\frac{\overline{N}_{i0}(2\overline{N}_{s0} + 1)}{\overline{N}_{s0} - \overline{N}_{i0}}}\right)}.$$
 (16)

In the arguments of the functions $\operatorname{sn}(x)$ in (13) and $\operatorname{sh}(x)$ in (16) there are phase shifts with the sign (+) or (-), which does not depend on time. The sign determines the direction of the change of the initial velocity $\dot{y}(\tau)_{|\tau=0}$ of the function $y(\tau)$ and does not influence the amplitude or period of oscillations. This is due to the fact that the initial value of $y_{|\tau=0} = 1$ for $\overline{N}_{i0} \neq 0$ is placed between the roots y_m and y_M . Therefore, there are two possible directions for the initial displacement: in the direction of the root y_m or in the direction of y_M .

The time evolution of the density of the pump polaritons is presented in Fig. 3 for the case of $\alpha = 0$. We can see that the solution with the sign (+) monotonously decreases to zero. This means that all initial pump polaritons convert into signal and idler polaritons. As for the solution with the sign (-), we see that it initially increases, at the moment of

$$\tau = \frac{1}{\sqrt{\left(2\overline{N}_{s0} + 1\right)\left(2\overline{N}_{i0} + 1\right)}} \operatorname{arsh} \sqrt{\frac{\overline{N}_{i0}\left(2\overline{N}_{s0} + 1\right)}{\overline{N}_{s0} - \overline{N}_{i0}}}$$
(17)

achieves its maximal value of $2\overline{N}_{i0}+1$ and then monotonously decreases, and asymptotically tends to zero at the long times (Fig. 3). Hence, in this case, all polaritons of the idler mode and the same value of the signal polaritons at first convert into pump polaritons and then at the time $\tau > \tau_0$ all existing pump polaritons convert into the equal values of signal and idler polaritons, by which the evolution finishes. Both solutions in (13) at the times $\tau >> \tau_0$ have asymptotically the same behavior.



Fig. 3. Aperiodic evolution of the normalized density of pump polaritons y for $\theta_0 = \pi/2$, $\alpha = 0$ and $\overline{N}_{s0} = 0.1$, $\overline{N}_{i0} = 0.05$.

The periodic evolution of the density of pump polaritons is presented in Fig. 4a. The polariton density changes periodically in time between the values y_m and y_M . Hence, there is no total conversion of the pump polaritons into the signal and idler polaritons; that is, the density oscillations take place without complete depletion of pump polaritons. The amplitude and period of the oscillations monotonously decrease with an increase in α for the fixed values of \overline{N}_{s0} and \overline{N}_{i0} (Figs. 4b, 4c). We point out that, in the absence of idler ($\overline{N}_{i0} = 0$) or signal ($\overline{N}_{s0} = 0$) polaritons, at the initial moment, the root y_M of the equation W(y)=0 is equal to one for any α . Therefore, solution (13) is also true for the case $\overline{N}_{i0} = 0$ or $\overline{N}_{s0} = 0$ taking into account that $y_M = 1$.



Fig. 4. (a) Time evolution of the normalized density of pump polaritons for $\overline{N}_{s0} = 0.1$, $\overline{N}_{i0} = 0.05$ and different values of α and the dependence (b) of the amplitude A and (c) of the period T of the oscillations of the density of pump polaritons on the value of \overline{N}_{s0} for $\theta_0 = \pi/2$ and fixed value of $\overline{N}_{i0} = 0.05$.

3.2. Evolution in the case of $\theta_0 = 0$ and π

Next, we will consider the evolution of the system for the phase difference $\theta_0 = 0$. It is evident from (9) that, in this case, one of the roots of the equation W(y)=0 coincides with the initial condition $y = y_0 = 1$ (Fig. 2b). Therefore, the solution will not include the phase shift. In the case where the expression

$$4\overline{N}_{s0}\overline{N}_{i0} + 2\alpha\sqrt{\overline{N}_{s0}\overline{N}_{i0}} = \overline{N}_{s0} + \overline{N}_{i0}$$
⁽¹⁸⁾

is satisfied, the second root also equals unity (Fig. 2b). Moreover, the solution of equation (10) in this case is $y(\tau) = y_0 = 1$; that is, it coincides with the initial condition too, which is due to the crossing of two middle roots depending on α . This means that a nontrivial evolution of the system is impossible in the case of nonzero initial densities of all polaritons if expression (18) is satisfied. On the phase plane (y, \dot{y}) this solution corresponds to the phase center. The system is at rest if $\theta_0 = 0$. In the plot of the potential energy W(y) of the nonlinear oscillator depending on y the rest corresponds to the phase point of particle, which locates in the minimum of the potential energy without kinetic energy. The particle in this case does not move from the initial state, since its velocity is equal to zero.

Two different cases of evolution are possible, if expression (18) is not true. The equation W(y)=0 has four real roots. Depending on the relation between the parameters \overline{N}_{s0} , \overline{N}_{i0} , and α in the first case, the roots are arranged in the order $y_1 > y_0 = 1 > y_m > y_4$; in the second case, $y_1 > y_M > y_0 = 1 > y_4$ (Fig. 2b). In the first case, the density of pump polaritons changes within the limits $y_m \le y \le y_0 = 1$; in the second case, within the limits $y_0 = 1 \le y \le y_M$. Therefore, depending on the values of parameters, the oscillations of the density of pump polaritons are possible under the background with the amplitude $A = 1 - y_m$ in the first case and $A = y_M - 1$ in the second, where the background density is equal to the initial density of the pump polaritons $y_0 = 1$. We point out that the aperiodic regime of evolution is absent for $\alpha = 0$ if $\theta_0 = 0$.

The solution of equation (10) for the first case has the form

$$y = \frac{y_1 - y_m - y_1(1 - y_m) \operatorname{sn}^2 \sqrt{(y_1 - y_m)(1 - y_4)\tau}}{y_1 - y_m - (1 - y_m) \operatorname{sn}^2 \sqrt{(y_1 - y_m)(1 - y_4)\tau}},$$
(19)

where modulus k of the elliptic function, and amplitude A and period T of oscillations are equal to

$$k^{2} = \frac{(y_{1} - y_{4})(1 - y_{m})}{(y_{1} - y_{m})(1 - y_{4})}, \ A = 1 - y_{m}, \ T = 2K(k)/\sqrt{(y_{1} - y_{m})(1 - y_{4})}.$$
(20)

For the second case we obtain

$$y = \frac{y_M - y_4 - y_4(y_M - 1)\operatorname{sn}^2 \sqrt{(y_1 - 1)(y_M - y_4)}\tau}{y_M - y_4 - (y_M - 1)\operatorname{sn}^2 \sqrt{(y_1 - 1)(y_M - y_4)}\tau},$$
(21)

where

$$k^{2} = \frac{(y_{1} - y_{4})(y_{M} - 1)}{(y_{1} - 1)(y_{M} - y_{4})}, \ A = y_{M} - 1, \ T = 2K(k)/\sqrt{(y_{1} - 1)(y_{M} - y_{4})}.$$
(22)

If we put $y_m = 1$ in (19) or $y_M = 1$ in (21), we obtain the solution $y(\tau) = 1 = const$ again.

It follows from (19) and (21) that the density of pump polaritons evolves periodically (Fig. 5a). As we pointed out, the oscillations of the density take place both under background (for small values of α) and above background (for great α). The amplitude of oscillations, which is defined as the difference of two middle roots of the equation W(y) = 0, for fixed \overline{N}_{s0} and \overline{N}_{i0} at first decreases with an increase in α , tends to zero at $\alpha = \alpha_c = (\overline{N}_{i0} + \overline{N}_{s0} - 4\overline{N}_{i0}\overline{N}_{s0})/(2\sqrt{\overline{N}_{i0}\overline{N}_{s0}})$, if two middle roots (y_m and $y_0 = 1$) coincide, and then increases and rapidly goes to saturation (Fig. 5b). Period of oscillation T essentially depends on the parameters \overline{N}_{s0} , \overline{N}_{i0} (Fig. 5c). For small \overline{N}_{s0} period T at first increases, achieves a maximal value at $\alpha = \alpha_c$, and then rapidly decreases. At a high value of \overline{N}_{s0} the period of oscillations monotonously decreases with an increase in α (Fig. 5c).



Fig. 5. The same as in Fig. 4, but for $\theta_0 = 0$.

If the initial phase difference $\theta_0 = \pi$, then the roots of the equation W(y) = 0 for $\alpha \ge 0$ as before are arranged in the order $y_1 > y_M > y_m > y_4$ (Fig. 2c), where y_M and y_m as before play

the role of the maximal and minimal density of pump polaritons. It follows from Fig. 2c that at $\theta_0 = \pi$ a crossing between the roots y_4 and y_m appears with an increase in α . The degeneration of these roots brings about to the appearance of the aperiodic evolution of the system similar to the case where $\theta_0 = \pi/2$. Hence, at $\theta_0 = \pi$ the periodic and aperiodic regimes of evolution are possible. In the case here all four roots are different, the evolution of the system is described by equation (13); hence, the density of pump polaritons periodically changes between the values y_m and y_M (Fig. 6a). If two least roots coincide ($y_4 = y_m$) the solution of equation (10) has the form

$$y = y_m + \frac{y_M - y_m}{1 + \frac{y_1 - y_M}{y_1 - y_m}} sh^2 \left(\sqrt{(y_M - y_m)(y_1 - y_m)} \tau \pm \operatorname{arsh} \sqrt{\frac{(y_M - 1)(y_1 - y_m)}{(1 - y_m)(y_1 - y_M)}} \right).$$
(23)

In this case, the density of pump polaritons monotonously decreases beginning from the initial state $y_0 = 1$ till the asymptotic value $y = y_m$ for solution (23) with sign (+). The solution with sign (-) at first increases, it achieves the maximal density y_M in the moment $\tau = \frac{1}{\sqrt{(y_M - y_m)(y_1 - y_m)}} arsh \sqrt{\frac{(y_M - 1)(y_1 - y_m)}{(1 - y_m)(y_1 - y_M)}}$, then decreases monotonously and achieves

asymptotically the value $y = y_m$ in the limit $\tau \to \infty$. It follows from Fig. 6a that the periodic regime of evolution transits into aperiodic and vice versa.

If we put $y_m = 0$ in (23), as it took place under the conditions of degeneration of two least roots of the equation W(y) = 0 at $\theta_0 = \pi/2$ (Fig. 2a), then we again obtain solution (16).

As for the amplitude A and period T of the oscillations of the pump polariton density, we can see from Figs. 6b and 6c that, with an increase in α , the amplitude of oscillation at first increases, achieves unity, and then monotonously decreases, while the period of oscillations at first increases too with an increase in α , but then it diverges at the value of α at which both least roots (y_4 and y_1) occur to be equal, and then monotonously decreases.



Fig. 6. The same as in Fig. 4, but for $\theta_0 = \pi$.

3.3. Evolution for arbitrary θ_0

Thus, the results obtained for $\theta_0 = 0, \pi/2$ and π are different. Therefore, further on, we will consider the case of arbitrary initial phase difference θ_0 and will elucidate the possibility of phase controlling the process without changing the initial density of polaritons. In this case, we arrange the roots of the equation W(y)=0 in the order of their diminishing $y_1 > y_M > y_m > y_4$ too. They essentially depend on the parameters \overline{N}_{s0} , \overline{N}_{i0} , α , θ_0 . We can easily get convinced in it considering the "degenerate" case (in the sense of $\overline{N}_{s0} = \overline{N}_{i0} \equiv \overline{N}_0$), where the roots are

expressed by the formulae:
$$\overline{N}_0 + \frac{1-\alpha}{2} \pm \sqrt{\left(\overline{N}_0 + \frac{1+\alpha}{2}\right)^2 - 2\overline{N}_0(\alpha + \cos\theta_0)}$$

$$\overline{N}_0 + \frac{1+\alpha}{2} \pm \sqrt{\left(\overline{N}_0 + \frac{1-\alpha}{2}\right)^2 - 2\overline{N}_0(\alpha + \cos\theta_0)}, \text{ which evidently depends on } \overline{N}_0, \alpha, \text{ and } \theta_0. \text{ In }$$

a general case for arbitrary \overline{N}_{s0} , \overline{N}_{i0} , α and θ_0 the solution of equation (10) is expressed as before by formula (13); the period and amplitude of oscillations, by formulae (15). For $\theta_0 \neq 0, \pi$ $(k\pi, k = 0,1,2,...)$ relation (18) does not take place, but the roots can cross each other and this will prove the appearance of the aperiodic evolution. Figure 7 presents the time evolution of the density of pump polaritons depending on the initial phase difference θ_0 for three values of α . We can see that there are both periodic and aperiodic regimes of evolution. At $\alpha = 0.01$ there are two crossings of the two least roots (Fig. 7a) in accordance with which two transitions appear from the periodic regime to aperiodic one at different θ_0 , which are described by solution (23). For $\alpha = 0.14$ there exists only one transition at $\theta_0 = \pi$. For the fixed values of \overline{N}_{s0} and \overline{N}_{i0} , a further increase in α does not lead to the appearance of aperiodic regimes because the crossings of both least roots of the equation W(y)=0 are absent.



Fig. 7. Time evolution of the normalized density of pump polaritons on the initial phase difference θ_0 for three values of the parameter α and $\overline{N}_{s0} = 0.1$, $\overline{N}_{i0} = 0.05$.

In Fig.8, we plotted the amplitude A and period T of the oscillations of the density of pump polaritons depending on the initial phase difference θ_0 for the different values of α . We can see that the both functions are changed over broad intervals and these changes can be nonmonotonous too. In particular, the period of oscillations T tends to infinity if two least roots of the equation W(y)=0 are equal (Fig. 2c).



Fig. 8. Dependence of the amplitude A and the period T of the oscillations of the density of pump polaritons on the initial phase difference θ_0 for different values of α : (1) 0.01,

(2) 0.14, (3) 0.3, and (4) 0.9.

4. Evolution with damping

Let us consider the time evolution of the system for the case of exact resonance $(\Delta = 0)$ and of the equal polariton dampings $(\gamma_p = \gamma_s = \gamma_i \equiv \gamma)$. In this case, we can obtain exact analytical solutions of the system of equations. We introduce new functions $N_{p,s,i} = n_{p,s,i} \exp(-2\gamma)$, $Q = q \exp(-4\gamma)$ and $R = r \cdot \exp(-4\gamma)$ and new variable $\xi = \frac{1 - \exp(-2\gamma)}{2\gamma}$. Then, system (8) is

reduced to the form

$$\frac{dn_p}{d\xi} = 2\mu q , \ \frac{dn_s}{d\xi} = \frac{dn_i}{d\xi} = -\mu q , \ \frac{dq}{d\xi} = 2\mu \Big(4n_p n_s n_i - n_p^2 n_s - n_p^2 n_i\Big), \ \frac{dr}{d\xi} = 0.$$
(24)

Considering the variable ξ as the time, we can regard system of equations (24) as a "conservative" one. From (24), we obtain the following integrals of motion

 $n_p + 2n_s = N_{p0} + 2N_{s0}, n_p + 2n_i = N_{p0} + 2N_{i0}, r^2 + q^2 = 4n_p^2 n_s n_i, r = R_0$, (25) which are similar to (9).

Using (24) and (25) we can obtain the nonlinear equation for the density of pump polaritons, similar to equation (10). Since equation for n (24) and integrals of motion (25) are the same as equation (8) and for integrals (9), we can state that the previously obtained solutions for $y(\tau)$ retain the form depending on variable ξ . Therefore, we will present the solution for the general case, where four real roots of the equation W(y)=0 are arranged in decreasing order as follows: $y_1 > y_M > y_m > y_4$. Here y_m and y_M again are the minimal and maximal values of the function Y, which it acquires in the course of its evolution. This solution has the form

$$\frac{N_{p}}{N_{p0}} = \exp(-2\gamma) \frac{y_{m}(y_{M} - y_{4}) - y_{4}(y_{M} - y_{m})sn^{2} \left(\sqrt{(y_{1} - y_{m})(y_{M} - y_{4})} \frac{1 - \exp(-2\gamma)}{2\gamma} \pm F(\varphi_{0}, k)\right)}{y_{M} - y_{4} - (y_{M} - y_{m})sn^{2} \left(\sqrt{(y_{1} - y_{m})(y_{M} - y_{4})} \frac{1 - \exp(-2\gamma)}{2\gamma} \pm F(\varphi_{0}, k)\right)}$$
(26)

where

$$k^{2} = \frac{(y_{1} - y_{4})(y_{M} - y_{m})}{(y_{1} - y_{m})(y_{M} - y_{4})}, \quad \varphi_{0} = \arcsin \sqrt{\frac{(y_{M} - y_{4})(1 - y_{m})}{(y_{M} - y_{m})(1 - y_{4})}}.$$
(27)

From (26), we can see that the density of the pump polaritons oscillating decreases in time. The rate of decay is defined by the damping constants. At a long time, the argument of the elliptic functions hardly depends on time, since it turns constant and all time evolution consists in the exponential decreasing of the density of pump polaritons. The time evolution of the density of pump polaritons for different values of parameters is plotted in Figs. 9–11. At long times, the transformation of the oscillator regime of evolution displays into an exponential decay and the periodicity of the evolution disappears. An interval between two nearest maxima of the oscillating curve $N_p(t)$ is changed in time.



Fig. 9. Time evolution of the density of pump polaritons for the initial phase difference $\theta_0 = 0$, different values of the parameter γ and the initial densities (a) $\overline{N}_{s0} = 0.7$, $\overline{N}_{i0} = 0.5$; (b) $\overline{N}_{s0} = 0.1$, $\overline{N}_{i0} = 0.05$.



Fig. 10. Time evolution of the density of pump polaritons depending on the initial phase difference θ_0 for different values of the parameter γ , equal to (*a*) 0.01 and (*b*) 0.03.



Fig. 11. Time evolution of the density of pump polaritons for the initial phase difference $\theta_0 = 0$ and for $\overline{N}_{s0} = 0.1$, $\overline{N}_{i0} = 0.05$ and different values of parameter γ : (1) $\chi = \chi = \chi = 0.01$; (2) $\chi = \chi = 0.01$; $\chi = 0.06$; (3)

(1)
$$\gamma_p = \gamma_i = \gamma_s = 0.01$$
, (2) $\gamma_p = \gamma_s = 0.01$, $\gamma_i = 0.06$, (3)
 $\gamma_p = 0.05, \gamma_s = 0.06, \gamma_i = 0.07$; and (4) $\gamma_p = 0.03, \gamma_s = 0.02, \gamma_i = 0.01$

5. Conclusions

In conclusion, we point out that the dynamics of polaritons in the regime of parametric oscillator represents the periodic conversion of pairs of pump polaritons into polaritons of the signal and idler modes and vice versa. The period and amplitude of oscillations of the polariton density depend on the initial densities of polaritons, initial phase difference, and resonance detuning. For the definite relation between the parameters, the aperiodic evolution of the system is also possible, which represents the conversion only of the part of pump polaritons into the signal and idler polaritons, by which the evolution of the system is finished. The significant dependence of the period and amplitude of oscillations of polaritons on the initial phase difference suggests the possibility of the phase controlling of the polariton dynamics. A similar effect was predicted earlier for the process of atomic–molecular conversion in a Bose–Einstein condensate [28-31]. The damping of the system of coherent polaritons leads to the oscillatory decay of polariton densities in time, the rate of which is defined by polariton damping constants.

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ELECTRIC RESISTIVITY AND THERMOELECTRIC COEFFICIENT IN LAYERED STRUCTURES WITH AN ANISOTROPIC ENERGY SPECTRUM

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Abstract

The temperature dependence of resistivity ρ and thermoelectric coefficient α is studied in terms of the Mott-Davies theory for electronic processes in quasi two-dimensional disordered systems. The existence of a peak in the electron state density and narrow energy bands makes it possible to describe the anomalies in the temperature dependence of α and ρ in high temperature superconducting cuprates based on *FeAs*.

1. Introduction

Intensive researches on HTSC iron-based compounds (ferropnictides) have been conducted for last years. The great interest in these compounds is determined, first of all, by the possibility of obtaining a high temperature of superconducting transition $(T_c \sim 55K)$ [1]. This fact equates iron-based compounds to HTSC cuprates. Despite intensive researches of cuprates which began in 1986, the main problem, i.e., the determination of HTSC appearance mechanism, has not been solved. A detailed description of these two classes of materials—compounds obtained on the basis of *FeAs* and cuprates on the basis of CuO— (their common and distinctive features) is given in reviews [2-4].

Note that, from the point of view of electronic properties, the both classes of above mentioned materials are quasi two-dimensional (layered) systems; this fact leads to their strong anisotropy. Owing to this, in some cases, it is possible to neglect the existence of a direction perpendicular to layers. The consideration of the third direction in the case of a weak overlapping of intervals in this direction does not change the peculiarity in electronic state density (see Fig. 3 in [5]).

We will also emphasize that a series of phase transitions, for example, to magnetic and superconducting states, takes place in the both mentioned classes of materials. But firstly it is necessary to know their physical properties in the normal state. In this sense the determination of kinetic coefficients and their temperature dependence represents a special interest. In particular, a number of anomalies in the temperature dependence of thermoelectric coefficient α and electric resistivity ρ are observed in the compounds $YBa_2Cu_3O_4$ and $La_{2-x}(SrBa)_xCuO_4$. In some works [5-7] these anomalies are explained based on phenomenological models which assume that a peak exists on the Fermi surface and the energy bands are narrow.

From our point of view, it is interesting to determinate the above mentioned quantities α and ρ without assuming the existence of a peak on the Fermi surface of any origin. These

quantities should be determined considering the real electron state density, which is inherent in quasi two-dimensional systems. It will give us the possibility to compare the results obtained on phenomenological approach [5-7], temperature dependence of α and ρ in cuprates and in new materials based on *FeAs*. The application of same approach to cuprates and new *FeAs* materials is justified because they both are quasi two-dimensional and, from our point of view, the peculiarities in the electron state density which are characteristic of two-dimensional systems must manifest themselves in the properties of kinetic coefficients of both classes of materials.

The thermoelectric coefficient α and electric resistivity ρ are calculated in this work. We proceed from the determination of these coefficients on the basis of the Mott-Davies theory of electronic processes in two-dimensional disordered systems with anisotropic energy spectrum [8, 9].

In the expressions for the electron state density $g(\varepsilon)$, conductivity σ and α , in order to simplify the numerical calculations, a number of transformations are performed. Numerical calculations are performed and the obtained temperature dependence of σ and α is compared with experimental data both for cuprates and new materials based on *FeAs*.

2. Determination of conductivity σ and thermoelectric coefficient α

We use the Mott and Davies theory [8, 9] for electronic processes in the noncrystalline state. According to this theory, in the case of strong dispersion $\frac{\hbar}{\tau} \approx \varepsilon_F$, the quantities σ and α will be represented in the form

$$\sigma = \int \sigma(\varepsilon) \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon, \qquad (1)$$

$$\alpha = \frac{k_{\rm E}}{e\sigma} \int \sigma\left(\varepsilon\right) \left(-\frac{\partial f}{\partial\varepsilon}\right) \frac{\varepsilon - \mu}{k_{\rm E}T} \,d\varepsilon,\tag{2}$$

Here the conductivity $\sigma(\epsilon)$ is described by the Kubo-Greenwood formula:

$$T(\varepsilon) = M |D(\varepsilon)|^2_{av} g^2(\varepsilon),$$
(3)

where *M* is a constant, $D(\varepsilon)$ is the matrix element of electron interaction in an acyclic field, $f=1/\{1+exp \ [\beta \ (\varepsilon - \mu)]\}\$ is the function of Fermi distribution, $g(\varepsilon)$ is the electron state density. Further we choose the approximation $|D(\varepsilon)|_{\alpha\nu} = const$, which corresponds to the approximation with constant relaxation time τ . According to (1) and (2), we introduce the condition defining the chemical potential:

$$n = \int f(\varepsilon)g(\varepsilon)d\varepsilon / \int g(\varepsilon)d\varepsilon, \qquad (4)$$

where n is the degree of filling the energy band by quasiparticles.

3. Electron state density

As noted above, we examine layered structures (quasi two-dimensional systems). In this case, we assume that the overlapping intervals in the third direction are small, which makes it possible to represent the dispersion law for the energy of quasiparticles (see, for example, [10, 11]) in the form

$$\varepsilon\left(\vec{k}\right) = \varepsilon_1 - W_1 \cos(k_x \alpha) - W_2 \cos(k_y b), \tag{5}$$

where $(W_1 + W_2)$ is the half breadth of the energy band: *a*, *b* are the lattice constants.

This formula is obtained in the strong bound approximation of the band theory, which in a

semi quantitative way would describe the properties of electrons near the Fermi surface. In order to simplify the task, we considered only the nearest neighbors in (5).

The electron state density is defined by the expression

$$g(\varepsilon) = \sum_{k_x, k_y} \delta\left[\varepsilon - \varepsilon\left(\vec{k}\right)\right].$$
(6)

Substituting (5) into (6) and integrating over k_x and k_y , we transform the density of electron states $g(\varepsilon)$ (see Appendix and [12, 13]) to the following form:

$$g(\varepsilon) = \frac{1}{\pi^2 a b} \left\{ \frac{\theta \left[(\varepsilon - \varepsilon_1)^2 - (W_1 - W_2)^2 \right]}{\sqrt{W_1 W_2}} K(k_1) + \frac{2\theta \left[(W_1 - W_2)^2 - (\varepsilon - \varepsilon_1)^2 \right]}{\sqrt{(W_1 + W_2)^2 - (\varepsilon - \varepsilon_1)^2}} K(k_2) \right\}.$$
 (7)

where

$$\Theta(x) = \begin{cases} 1 & for \ x > 0 \\ 0 & for \ x < 0 \end{cases};$$

$$k_1^2 = \frac{(W_1 + W_2)^2 - (\varepsilon - \varepsilon_1)^2}{4W_1 W_2};$$

$$k_2^2 = \frac{4W_1 W_2}{(W_1 + W_2)^2 - (\varepsilon - \varepsilon_1)^2},$$
(8)

K(k) is the first kind elliptic integral. At $W_1 = W_2$ we will obtain the expression for a twodimensional isotropic system:

$$g_{is}(\varepsilon) = \lim_{W_1 \to W_2} g(\varepsilon) = \frac{1}{\pi^2 a b} \frac{K(k_1)}{\sqrt{W_1 W_2}}.$$
(9)

In a limiting case when $W_2=0$, we obtain the electron state density for a quasi onedimensional system with the root peculiarity

$$g_{one}\left(\varepsilon\right) = \frac{1}{\pi a} \frac{1}{\sqrt{W_1^2 - (\varepsilon - \varepsilon_1)^2}}.$$
(10)

In a two-dimensional case, formula (7) has a logarithmic peculiarity as follows:

$$K(k) \xrightarrow[k \to 1]{} \ln \frac{4}{\sqrt{1-k^2}}.$$
 (11)

Substituting expression (7) into formulas (1), (2) and (4), we will transform these functions in a form convenient for calculation. To this end, we will analyze the electron state density $g(\varepsilon)$. There are three features in the calculated quantity $g(\varepsilon)$ which is present in (7):

1) $g(\varepsilon)$ limits the definition domain of ε with two finite limits $[\varepsilon_a, \varepsilon_b]$, where $\begin{cases} \varepsilon_a \\ \varepsilon_b \end{cases} = \varepsilon_1 \mp (W_1 + W_2);$

2) $g(\varepsilon)$ has a logarithmic divergence at the points $[\varepsilon_c, \varepsilon_d]$, where $\begin{cases} \varepsilon_c \\ \varepsilon_d \end{cases} = \varepsilon_1 \mp (W_1 - W_2);$

3) the first term in (7) is different from zero on the segments $[\epsilon_{\alpha}, \epsilon_{c}]$ and $[\epsilon_{d}, \epsilon_{b}]$; the second one, on the segment $[\epsilon_{c}, \epsilon_{d}]$.

We represent the quantities $\sigma(T)$, $\alpha(T)$, and $n(\delta)$ through the integrals of the type

$$C_{\gamma}^{(\beta)} = \int_{\varepsilon_{\alpha}}^{\varepsilon_{\beta}} F_{\gamma}(\varepsilon) g^{\beta}(\varepsilon) d\varepsilon, \qquad (12)$$

$$\bar{\sigma} = C_1^{(2)} \text{ where } F_1(\varepsilon) = \frac{1}{4 k_b T} \frac{1}{c h^2 \frac{\varepsilon - \mu}{2k_b T}}$$
(13)

$$\alpha = \frac{k_B}{e} \frac{C_2^{(2)}}{C_1^{(2)}}, \quad \text{where } F_2\left(\varepsilon\right) = \frac{1}{4 k_B T} \frac{\frac{\varepsilon - \mu}{k_B T}}{ch^2 \frac{\varepsilon - \mu}{2k_B T}}$$
(14)

$$n(\delta) = \frac{C_3^{(1)}}{C_4^{(1)}}, \text{ where } F_3(\varepsilon) = \frac{1}{1 + \exp \frac{\varepsilon - \mu}{k_b T}}; F_4(\varepsilon) = 1.$$
 (15)

Let us represent expression (12) in the form:

$$C_{\gamma}^{(\beta)} = I + II, \tag{16}$$

where

$$I = \int_{\varepsilon_a}^{\varepsilon_c} F_{\gamma}(\varepsilon) g^{\beta}(\varepsilon) d\varepsilon + \int_{\varepsilon_d}^{\varepsilon_b} F_{\gamma}(\varepsilon) g^{\beta}(\varepsilon) d\varepsilon.$$
(17)

Introducing a new variable $x^2 = (W_1 + W_2)^2 - \frac{(\varepsilon - \varepsilon_1)^2}{4W_1W_2}$, we will represent expression (17) in the form

$$I = \int_0^1 \mathbf{K}^\beta(\mathbf{x}) \mathbf{x} \, \Phi_\gamma(\mathbf{x}) d\mathbf{x},\tag{18}$$

where

$$\Phi_{\gamma}(\mathbf{x}) = \frac{F_{\gamma}\left(\varepsilon_{1} - \sqrt{(W_{1} + W_{2})^{2} - 4W_{1}W_{2}\mathbf{x}^{2}}\right) + F_{\gamma}\left(\varepsilon_{1} + \sqrt{(W_{1} + W_{2})^{2} - 4W_{1}W_{2}\mathbf{x}^{2}}\right)}{\sqrt{(W_{1} + W_{2})^{2} - 4W_{1}W_{2}\mathbf{x}^{2}}}.$$
 (19)

In the same way, by introducing a new variable $x^2 = \frac{4W_1W_2}{\{(W_1+W_2)^2 - (\varepsilon - \varepsilon_1)^2\}}$, the second term from (16), which has the form

$$II = \int_{\varepsilon_c}^{\varepsilon_1} F_{\gamma}(\varepsilon) g^{\beta}(\varepsilon) d\varepsilon + \int_{\varepsilon_1}^{\varepsilon_d} F_{\gamma}(\varepsilon) g^{\beta}(\varepsilon) d\varepsilon$$
(20)

will be modified into

$$II = \int_{\frac{2\sqrt{\eta}}{1+\eta}}^{1} K^{\beta}(x) x^{\beta-3} \Phi_{\gamma}(1/x) dx, \eta = W_1/W_2.$$
(21)

Based on (18) and (21), we get

$$C_{\gamma}^{(\beta)} = \int_{0}^{1} K^{\beta}(x) x \Phi_{\gamma}(x) dx + \int_{\frac{2\sqrt{\eta}}{1+\eta}}^{1} K^{\beta}(x) x^{\beta-3} \Phi_{\gamma}(1/x) dx.$$
(22)

Substituting (22) into (12)-(14), we obtain expressions for $\overline{\sigma}$, α and n, which are convenient for numerical calculations:

$$\bar{\sigma} = \sigma \frac{\pi^4 a^2 b^2 W_1^2}{MD} = \frac{1}{\bar{T}} \left\{ \int_0^1 \frac{K^2(x) x dx}{\varphi(\eta, x)} \left[\frac{1}{ch^2 \frac{\delta - \varphi(\eta, x)}{2\bar{T}}} + \frac{1}{ch^2 \frac{\delta + \varphi(\eta, x)}{2\bar{T}}} \right] + \frac{1}{ch^2 \frac{\delta + \varphi(\eta, x)}{2\bar{T}}} \right\} + \frac{1}{ch^2 \frac{\delta + \varphi(\eta, x)}{2\bar{T}}} = \frac{1}{\bar{T}} \left\{ \int_0^1 \frac{K^2(x) x dx}{\varphi(\eta, x)} \left[\frac{1}{ch^2 \frac{\delta - \varphi(\eta, x)}{2\bar{T}}} + \frac{1}{ch^2 \frac{\delta + \varphi(\eta, x)}{2\bar{T}}} \right] + \frac{1}{ch^2 \frac{\delta - \varphi(\eta, x)}{2\bar{T}}} \right\}$$

$$+ \int_{\frac{2\sqrt{\eta}}{1+\eta}}^{1} \frac{K^{2}(x)dx}{x\varphi(\eta,1/x)} \left[\frac{1}{ch^{2}\frac{\delta-\varphi(\eta,1/x)}{2\overline{T}}} + \frac{1}{ch^{2}\frac{\delta+\varphi(\eta,1/x)}{2\overline{T}}} \right] \right\}; \qquad (23)$$

$$\alpha = \frac{k_{\overline{b}}}{e \ \overline{\sigma} \ \overline{T}} \left\{ \int_{0}^{1} \frac{K^{2}(x)x \, dx}{\varphi(\eta,x)} \left[\frac{\delta-\varphi(\eta,x)}{\overline{T}ch^{2}\frac{\delta-\varphi(\eta,x)}{2\overline{T}}} + \frac{\delta+\varphi(\eta,x)}{\overline{T}ch^{2}\frac{\delta+\varphi(\eta,x)}{2\overline{T}}} \right] + \frac{1}{\overline{T}ch^{2}\frac{\delta+\varphi(\eta,x)}{2\overline{T}}} \right] + \frac{1}{\overline{T}ch^{2}\frac{\delta-\varphi(\eta,1/x)}{2\overline{T}}} + \frac{1}{\overline{T}ch^{2}\frac{\delta+\varphi(\eta,1/x)}{2\overline{T}}} \right] \right\}; \qquad (24)$$

$$n = \left\{ \int_{0}^{1} \frac{K^{2}(x)xdx}{\varphi(\eta,x)} \left[\frac{1}{1+exp\frac{\delta-\varphi(\eta,x)}{\overline{T}}} + \frac{1}{1+exp\frac{\delta+\varphi(\eta,x)}{\overline{T}}} \right] + \frac{1}{1+exp\frac{\delta+\varphi(\eta,x)}{\overline{T}}} \right] + \frac{1}{1+exp\frac{\delta+\varphi(\eta,x)}{\overline{T}}} + \frac{1}{1+exp\frac{\delta+\varphi(\eta,x)}{\overline{T}}} \right] + \frac{1}{1+exp\frac{\delta+\varphi(\eta,x)}{\overline{T}}} + \frac{1}{\overline{T}} + \frac{1}{2\sqrt{\eta}} + \frac{1}{$$

where we denoted

$$\delta = \frac{\varepsilon_1 - \mu}{W_1}; \quad \bar{T} = \frac{k_b T}{W_1}; \quad \frac{W_2}{W_1} = \eta \le 1;$$

$$\varphi(\eta, x) = \sqrt{(1+\eta)^2 - 4\eta x^2}; \quad |D(\varepsilon)|_{av}^2 = D = const.$$
(26)

The system of equations (23)-(25) describes the temperature dependence of the quantities in question: thermoelectric coefficient α and electric resistivity ρ . In the presented form, this system of equations is more convenient for numerical calculations.

4. Numerical calculations and discussion

Note that the electron state density $N(\varepsilon)$ plays an important role in the obtained formulas. Expression (7) can be transformed into the form

$$\frac{N(\varepsilon)}{N_0} = \frac{\theta (1+\eta)^2 - \lambda^2}{\sqrt{\eta}} \left\{ \theta \left(\lambda^2 - (\eta - 1)^2 \right) K(k) + \frac{\Theta \left((\eta - 1)^2 - \lambda^2 \right)}{k} K\left(\frac{1}{k}\right) \right\}, \quad (27)$$
where

where

$$\lambda = \frac{\varepsilon}{W_1}, \quad K = \frac{\sqrt{(1+\eta)^2 - \lambda^2}}{(2\sqrt{\eta})}, \quad \eta = \frac{W_1}{W_2},$$
 (28)

The dependence of $N(\varepsilon)/N_0$ on λ for different values of the parameter η is given in Fig.1. The calculations were made on the base of formula (7), which requires the consideration of logarithmic peculiarity of the elliptic function K(k) [11]. This approach in the calculation of electron state density is adequate and can be used for the calculation of the kinetic coefficients of quasi two-dimensional systems. This conclusion results from the comparison of Fig. 1 with the results obtained earlier [13], where the elliptic function was calculated precisely.



Fig. 1. Electron states density $N(\varepsilon)$ as a function of $\lambda = \varepsilon/W_I$ in the approach taking into account the logarithmic peculiarity of the function $K(\kappa)$.

According to this, the values of the theoretical parameters play an important role, especially, the energy band width. The examined compounds based on FeAs are metals, and, at the first sight, the energy bands cannot be narrow. But there are a lot of works stating that the energy bands are narrow at strong and medium electron correlations. For example, the review of Sadovskii [2] examines the influence of electron correlations on the energy spectrum of electrons and gives references to works where the band structure of *FeAs* compounds is calculated by using different methods. The LDA method, which is usually applied for the calculation of band structure, does not consider potentially strong effects of inter-electron correlations (Hubbard repulsion between electrons), which is naturally to expect in the bands created in the main d-state of Fe in the FeAs layers. Nowadays, the Dynamic Middle Field Theory (DMFT) is the most consecutive approach in dealing with these correlations. The calculations on LDA basis give an important divergence with the modern methods. This fact is determined by the omission within LDA of the role of inter-electron correlations. In a number of works (references to them can be found in [2]) it is shown that the inter-electron correlations lead to considerable increasing of effective masses

(2-5 times) and essential damping of quasiparticles. The conduction bands are essentially narrowed (compared with the results given by LDA), and, at an energy of about 0.5 *eV*, these conduction bands are completely destroyed, so we have a kind of energy gap. In such a way, we can conclude that the examined systems with intermediate electronic correlation are close to the state of Mott dielectric, which makes them similar to HTSC cuprates. Unlike cuprates, they are metals rather than Mott-type dielectrics.

The question about the role of inter-electron correlations in the new superconductors remains debatable. The most probable is that the correlations in these systems are intermediary between typical metals and Mott-type dielectrics. Thus we deal with the state of correlated metal. Here we examine a simple model of strong electron interaction in a layered system. However,

this approach does not forbid us to consider the band width taking into account these correlations. As was specified above, in the new *FeAs* materials this band width can be very narrow.

The calculations of the quantities α and ρ are performed based on system (23)-(25) within the above mentioned approach for electron state density, which has a peak on the Fermi surface and narrow energy bands.

Thus, the chosen density of states in the phenomenological model (see [5-7]) and expression (7) used by us have important similarities, namely, a peak in the state density on the Fermi surface and the assumption concerning the narrow pattern of energy bands. This fact in common cases leads to the appearance of similar anomalies in the behavior of α and ρ .

The temperature dependence of thermoelectric coefficient α and electric resistivity ρ are presented in Figs. 2a and 2b, respectively. The theoretical dependences are represented by continuous lines, and the experimental data for the YBa₂Cu₃O₄ compound are shown by small circles and shaded numbers. The theory parameters *n* and η are chosen so that the theoretical and experimental dependences gave qualitative conformity. Case 1a (the dependence of α on *T*) corresponds to cases (1,1[']), (2,2[']), and (4,4[']).



Fig. 2. (a) Dependence of thermoelectric coefficient α on temperature; (b) dependence of electric resistivity ρ on temperature. Continuous curves correspond to theoretical results; dashed ones, to experimental data. Case a) Continuous curves 1-4 correspond to the parameters n=0.513, $\eta=0.9$, n=0.481, $\eta=0.9$; n=0.457, $\eta=0.9$ respectively. Curves 1', 2' are experimental data for YBa₂Cu₃O_x with oxygen content x = 7.02; x = 6.88 [7], curve 4': x = 5.34 [6]. Case b) Curves 1-4 for the parameter n=0,499 and various values of η : 1; 0.9; 0.4; 0.6, respectively. Curves 1' and 3' are experimental data for x=0.12 and x=0.53, respectively [6].

Hereinafter, the values of theory parameters *n*, η and the content of oxygen or impurity in the examined compounds [6, 7, 22, 23] are given in the explanations to figures. In Fig. 2b, we have the quantities ρ and $\bar{\rho}$ as functions of temperature. The curves are marked similarly to the ones from Fig. 2a. Here we emphasize the conformity of our theoretical results with the experimental data for compound YBa_2Cu_3Ox (1, 1[/]) and (3, 3[/]).

In such a way, for both quantities $\alpha(T)$ and $\rho(T)$, we have qualitative conformity between the theory developed by us and experimental data. We emphasize that this conformity takes place in the case of narrow energy bands ($W_1 \sim 0.08 \ eV$). Note that the same order of band width was chosen in [5-7], where the abnormal behavior of kinetic coefficients is explained on the basis of a phenomenological model with a peak in electron state density.

It follows from Figs. 2a and 2b that the temperature dependence of coefficients α and ρ is quite various and is defined by the values of chemical potential (filling degree numbers *n*) and the parameter $\eta = W_2/W_1$. The thermoelectric factor α quickly grows forming a maximum in the low temperature range and slowly decreases with increasing temperature. The resistivity $\bar{\rho}$ grows linearly when temperature increases. More complicated dependences are possible (see Fig. 3 in [12]) in the range of low temperatures when local indistinct maxima appear at $\eta = 0.2$; 0.4 and at least at $\eta=0.6$. Apparently, to examine the superconducting phase in the low temperature range, the parameter η should be considered to be temperature dependent, as in HTSC ceramics the dimensionality of the system can change from two-dimensional in the range of high temperatures to one-dimensional in the case when $T \rightarrow 0$ (formation of chains of O - Cu - O [15]). This unusual behavior is determined by the asymmetrical interaction of the nearest neighbors.

The dependences of thermoelectric coefficient α and electric resistivity ρ on temperature are presented in Figs. 3a and 3b. In this case, the values of theoretical parameters *n* and η are different from those in Figs. 2a and 2b. This was done in order to describe the behavior of these quantities in the case of new materials based on *FeAs*. The dependence $\alpha(T)$ in the case of the compound $Ba(Fe_{1-x}Co_x)As_2$ is given in Fig. 3a and the dependence $\bar{\rho}$ on *T* is given in Fig. 3b for the same compound.



Fig. 3. Case a) Dependence of thermoelectric coefficient α on temperature: curve 1 corresponds to n=0,523, η=0.9, curve 2 to n=0.545, η=0.9. Curves 1', 2' correspond to the experimental data for the compound Ba(Fe_{1-x}Co_x)As₂ at x=0.4 and x=0.3, respectively [22].
Case b) Dependence of electric resistivity ρ on temperature: curves 1-3 are for the parameter n=0.499 and various values of η (0.38; 0.7; 0.85, respectively). Curves 1' – 3' correspond to the experimental data for Ba(Fe_{1-x}Co_x)As₂ at x=0.06, 0.08, and 0.15, respectively [23].

Figures 3a and 3b show a quality coincidence of our proposed theory with the experimental data both for $\alpha(T)$ and $\rho(T)$. In both figures, we have the following compliance: (1, 1'), (2, 2'), (3, 3'). As in the case of cuprates, this consistency between theory and experiment takes places in the

presence of narrow energy bands. We emphasize that at more careful selection of theory parameters it is possible to achieve closer values for theoretical and experimental dependences for the examined quantities α and ρ .

5. Conclusions

- 1. Based on the Mott–Davies theory of electron processes in disordered quasi two-dimensional systems, the experimentally observed behavior of electric resistance $\rho(T)$ and thermoelectric coefficient $\alpha(T)$ is possible to describe qualitatively. This is realizable thanks to the existence of a peak in the electron state density and narrow pattern of energy bands in quasi two-dimensional systems, which was observed earlier in cuprates and recently in the compounds based on *FeAs* [2].
- 2. The behavior of the dependence of thermoelectric coefficient α and electric resistance ρ on temperature is quite various and determined by the value of chemical potential (parameter *n*, which defines the filling degree of energy band) and the parameter of the anisotropy of energy spectrum $\eta = W_I/W_2$. Selecting these parameters in a proper way, we can achieve consistency between the theoretical dependences $\alpha(T)$ and $\rho(T)$ and the experimental data. Based on the application of theory [10] to quasi two-dimensional systems, the behavior of the quantities α and ρ in cuprates and in new *FeAs* materials is described using the example of *YBa*₂*Cu*₃*O*_x and *Ba*(*Fe*_{1-x}*Co*_x)*As*₂.
- 3. A variation in the parameters *n* and η has a more essential impact on $\alpha(T)$ than on $\rho(T)$. In particular, we obtain $\alpha(T) > 0$ for all temperatures 0 < T < 300K at n < 0.5 and $\alpha(T) > 0$ at n > 0.5 (Fig. 4). As it was mentioned earlier, in the above given calculations, we assume that the energy bands are very narrow due to strong and medium electron correlations. But the question about the energy bands width in the materials based on *FeAs* remains debatable. We believe that these materials with medium electron correlation are close to the state of Mott dielectrics and this fact makes them similar to HTSC cuprates [24].



Fig. 4. Dependence of thermoelectric coefficient α on the filling degree of the n^{th} - energy band. Curve 1 corresponds to $\eta=1$ and T=120 K; curve 2, to $\eta=0.8$ and T=140 K.

Appendix

Here the calculation of electron state density in the examined systems is given. For this

purpose, in formula (2), we will pass from summation over \vec{k} to two-dimensional integration according to the following formula

$$\sum_{k_x,k_y} \delta\left[\varepsilon - \varepsilon\left(\vec{k}\right)\right] = \frac{1}{(2\pi)^2} \int_{-\pi/a}^{\pi/a} dk_x \int_{-\pi/b}^{\pi/b} dk_y \delta\left[\varepsilon - \varepsilon\left(\vec{k}\right)\right]. \tag{A.1}$$

Substituting expression (1) into (A.1) and passing to new variables $x=cos(k_x a)$, $y=cos(k_y b)$, we obtain

$$g(\varepsilon) = \frac{1}{\pi^2 a b W_1} \int_{-1}^{1} \frac{ay}{\sqrt{1 - y^2}} \frac{\theta \left[1 - \left(\frac{\varepsilon - \varepsilon_1}{W_1} + \frac{W_2}{W_1}y\right)^2\right]}{\sqrt{1 - \left(\frac{\varepsilon - \varepsilon_1}{W_1} + \frac{W_2}{W_1}y\right)^2}}$$
(A.2)

This expression can be reduced to the sum of four integrals of the following type:

$$\int_{y_3}^{y_2} \frac{dy}{\sqrt{(y-y_1)(y-y_2)(y-y_3)(y-y_4)}}, \quad (y_1 > y_2 > y_3 > y_4) \quad (A.3)$$

Here y_1 , y_2 , y_3 , y_4 are the points where the denominator from (A.2) becomes zero. Introducing a new variable φ [15] according to the following relation

$$y = \frac{y_3(y_2 - y_4) - y_4(y_2 - y_3)sin^2\varphi}{(y_2 - y_4) - (y_2 - y_3)sin^2\varphi}$$
(A.4)

we obtain

$$\mu \int_{\varphi(y_3)}^{\varphi(y_2)} \frac{d\varphi}{\sqrt{1 - k^2 \sin^2 \varphi}}, \qquad (A.5)$$

where

$$\mu = \frac{2}{\sqrt{(y_1 - y_3)(y_2 - y_4)}}; \quad k^2 = \frac{y_1 - y_4}{y_1 - y_3} \frac{y_2 - y_3}{y_2 - y_4}$$

In order to define the integration limits in (A.5), $sin^2 \phi(y)$ from (A.4), we will express through y:

$$\sin^{2}[\varphi(y)] = \frac{(y_{2} - y_{4})(y - y_{3})}{(y_{2} - y_{3})(y - y_{4})}.$$
 (A.6)

It follows from (A.6) that $sin^2[\varphi(y_3)]=0$, $sin^2[\varphi(y_2)]=1$, then the lower integration limit in (A.5) is $\varphi(y_3)=0$, and the upper one is $\varphi(y_2)=\pi/2$. Thus, (A.5) is transformed into the following integral:

$$\mu \int_{0}^{M/2} \frac{d\varphi}{\sqrt{1 - k^2 \sin^2 \varphi}} = \mu K(k) \tag{A.7}$$

where K(k) is the (k) first kind elliptic integral.

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ELECTROCHEMICAL NANOSTRUCTURING OF CuInSe₂ BULK CRYSTALS

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Abstract

We show that chalcopyrite $CuInSe_2$ crystals can be nanostructured by electrochemical treatment in an aqueous HCl solution. To make the crystals suitable for electrochemical nanostructuring, they are subjected to thermal treatment either in vacuum or in Zn vapors. The morphology of the produced material and the diameter of pores are found to be a function of the resistivity of the samples attained after thermal treatment. The pore diameter can vary in a range of 100 nm to 1 μ m. The influence of thermal treatment and electrochemical etching on the photoluminescence spectra is analyzed.

1. Introduction

Solar cell technologies using I-III-VI₂ direct band-gap chalcopyrite semiconductors as the absorber layer have attracted great interest [1]. CuInSe₂-based solar cells are currently demonstrating the leading performance amongst thin-film technologies: 20% conversion efficiency [2] and excellent stability. CuInSe₂ is a semiconductor with the direct band gap near 1.05 eV and an absorption coefficient exceeding 10^5 cm⁻¹ [3]. In spite of the high value, the reached conversion efficiency of 20% is still far from the theoretical limit for a one-junction solar cell [4]. This is indicative of the importance of further technological improvements.

One way of boosting the performance of solar cells consists in coating them with a textured layer. The idea is to trap more light so that it bounces around inside the cell instead of reflecting back out, since reflection means the loss of the light, which is absorbed to solar cell and generates electric power. Light trapping regimes were implemented in thin-film silicon solar cells with a photonic pattern [5], in textured multicrystalline silicon [6], in GaAs solar cells textured with dielectric 1D and 2D nanopatterns [7], etc. Nanopatterning of solar cells was produced by nano-imprint lithography [8, 9], by surface etching processes [10], or by the formation of a porous silicon layer on a textured silicon wafer [11]. A porous layer can be produced by anodization [11]. Electrochemical treatment proved to be a powerful tool for the preparation of a variety of porous morphologies also in III-V [12] and II-VI [13, 14] materials.

The goal of this paper is to demonstrate that electrochemical treatment can be also applied for the nanostructuring of $CuInSe_2$ crystals, particularly for patterning the surface of the samples to reduce the reflection at the surface in the case of their implementation in solar cells.

2. Sample preparation and experimental results

CuInSe₂ single crystals were grown by chemical vapor transport (CVT) in a closed system

using iodine as a transport agent. The polycrystalline material preliminary synthesized in iodine atmosphere at a temperature of about 800°C from a stoichiometric mixture of the elemental constituents was used as the raw charge in the CVT. The iodine concentration was approximately 5 mg cm⁻³. The source temperature and the growth temperature were about 820 and 770°C, respectively. The system was cooled down slowly at a rate of 10°C/h to avoid straining of the crystals after crystal growth.

Electrochemical treatment for nanostructuring was performed in an electrochemical cell as described elsewhere [15]. A fourPt electrode configuration was used: a reference electrode in the electrolyte, a reference electrode on the sample, acounter electrode and a working electrode. The area of the sample exposed to the electrolyte solution was 0.1 cm². The anodic etching was carried out in a 5% HCl:H₂O electrolyte in the potentiostatic regime at room temperature. The resulting morphology of the etched samples was studiedusing a TESCAN scanning electron microscope (SEM). The photoluminescence (PL) wasexcited by a LD Pumped all-solid state MLL-III-532 laser andanalyzed through a double spectrometer. The resolution wasbetter than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

3. Results and discussions

The as-grown CuInSe₂ crystals are n-type with resistivity in the order of 10^5 - $10^6 \Omega$ ·cm. In is known that low resistivity crystals are required for nanostructuring by electrochemical treatment. For decreasing the resistivity of the as-grown CuInSe₂ crystals, several types of thermal treatment have been applied. Crystals with the resistivity down to 0.2 Ω ·cm were produced by annealing of crystals in vacuum. For a further decrease in resistivity, the samples were subjected to annealing in Zn vapors. The samples were subjected to annealing during 30 h. The parameters of samples as a function of the technological conditions are presented in the table.

Sample	As	Annealed	Annealed	Annealed	Annealed in	Annealed in
treatment	grown,	in vacuum	in vacuum	in vacuum	Zn vapors at	Zn vapors at
conditions		at 500°C,	at 600°C,	at 700°C,	600°C,	700°C,
	#1	#2	#3	#4	#5	#6
ρ	$10^{5} \div 10^{6}$	12	0.6	0.2	0.06	0.03
$(\Omega \cdot cm)$						
n	-	$2 \cdot 10^{15}$	$5 \cdot 10^{16}$	$2.1 \cdot 10^{17}$	$1.1 \cdot 10^{18}$	$7 \cdot 10^{18}$
(cm^{-3})						
μ	-	250	210	140	90	30
$(cm^2/V \cdot s)$						

Table. Electrical parameters of CuInSe₂ crystals subjected to different thermal treatment

The PL spectra of the samples #1 to #6 with parameters from the table are presented in Fig. 1. The spectrum of the as-grown sample consists of several near-band-edge lines and several deeper PL band at 0.99, 0.97, and 0.96 eV. Among the near-band-edge lines, two most intensive lines at 1.036 and 1.028 eV assigned previously as M2 amd M5 lines [3] are attributed to the recombination of bound excitons [16, 17], while the band at higher photon energies (1.042 eV) is due to the recombination of free excitons [3]. The bands at 0.99 and 0.97 eV have been previously attributed to donor-acceptor transitions involving shallow donor and different

acceptors [18], such as [Cu_{In}-Cu_i] complex and V_{Cu} center [19-21].

The annealing of crystals in vacuum at 500° C leads to a decrease in the luminescence intensity by a factor of 10, to a broadening of the lines related to the recombination of bound excitons, and to the disappearance of the band associated with the recombination of free excitons. An increase in the annealing temperature to 600° C leads to the quenching of the exciton lines and the emergence of a new broad and asymmetric PL band in the near-band-edge region (at 1.056 eV). The intensity of this band decreases with the increase in the annealing temperature to 700° C, while it is broadened and its maximum shifts to higher energies. This PL band is attributed to the band-to-band transitions, since the shift of the maximum and its broadening correlates with the shift of the equilibrium Fermi level. A similar behavior was observed for the near-band-edge PL band in CuInS₂ crystals subjected to similar thermal treatment [22] and in ZnSe single crystals annealed in Zn melt containing Al impurity [23].



Fig. 1. PL spectra of CuInSe₂ crystals measured at T = 10 K. The numbers of curves correspond to the number of samples in the table.

The annealing of crystals in Zn vapors instead of vacuum leads to a further increase in the carrier concentration. At the same time, taking into account the decrease in carrier mobility, one can suggest that a partial compensation of conductivity occurs due to the formation of acceptor centers in addition to donors. As a result, the near-band-edge PL band is shifted to lower photon energies in the samples annealed in Zn vapors as compared to the samples annealed in vacuum (compare curves 4 and 5 in Fig. 1). This behavior is explained in terms of the theory of heavily doped semiconductors developed by Shklovskij, Efros, Levanyuk, and Osipov in the early 1970s [24, 25]. According to this theory, the asymmetric shape of PL bands is caused by the potential fluctuations in the material. These fluctuations are probably caused by high concentrations of charged defects. It should be mentioned that in ternaries compositional fluctuations can also give rise to disorder and cause very similar fluctuations of the bandgap energy.

In the case of heavy doping, the defects do not constitute a discrete distribution of defect levels inside the bandgap. Instead, the energy levels form a continuous distribution function. Consequently, the distribution function of shallow states overlaps the distribution function of conduction and valence band states. As a result, the so-called band tails are developed. Therefore, the PL band on curve 5 in Fig. 5 can be attributed to band-to-tail (BT) electronic transitions.

The increase in the annealing temperature in Zn vapors from 600 °C to 700 °C leads to a

further shift of the PL band to lower photon energy and its splitting into two bands (see curve 6 in Fig. 1). This splitting is explained by the fact that in heavily doped semiconductors the recombination between the conduction band and an impurity level can occur via two channels. The first so called tail-to-impurity (TI) recombination takes place between the electrons that are localized in the conduction band tails and the holes that are localized at the acceptor state (the PL band at 0.98 eV in curve 6 in Fig. 1). The second so-called band-to-impurity (BI) recombination takes place between the free electrons in the conduction band and the holes that are localized at the acceptor state (the PL band at 1.00 eV in curve 6 in Fig. 1). Similar electronic transitions have been observed in other heavily doped chalcopyrite materials [26-28].

The conductivity of samples directly influences the processes of electrochemical etching. The morphology of surface of samples #3, #4, and #5 from the table after electrochemical treatment under the applied voltage of 0.7 V in aqueous HCl electrolyte is shown in Fig. 2. One can realize the formation of porous layers with various diameters of pores, it being around 200 nm for sample #5, 300-400 nm for sample #4, and around 1 μ m for sample #3. Therefore, the diameter of pores sharply decreases with increasing the conductivity of the material. One can see also from Fig. 2 that in sample #4 some pore merging occurs, while in sample #3 several pores merge into a larger unit. Apart from that, the pore formation in the sample with high resistivity (sample #3) is highly inhomogeneous, porosification was found to occur only in separate regions. Probably the resistivity is not uniform in this sample. In samples #1 and #2 no electrochemical reaction occurs under the voltage up to 1 V, while material decomposition occurs at a higher voltage.



Fig. 2. SEM images of surfaces of CuInSe₂ crystals with numbers #5 (a) #4 (b) and #3 (c) in the table subjected to electrochemical treatment at 0.7 V in an aqueous HCl electrolyte.

In the sample #6 with lowest resistivity, a uniform porous structure is formed with a mean dimension of pores around 100 nm as shown in Fig. 3.

Figure 4 compares the PL spectra of $CuInSe_2$ samples before and after electrochemical treatment. One can see that electrochemical etching leads to the increase in the PL intensity. Apart form that, in sample #3 the electrochemical treatment leads to narrowing the band-to-band emission and the increase in the intensity of lines related to the recombination of bound excitons. This suggests a good passivation of the porous skeleton surface and the increase in the material quality as a result of treatment.



Fig. 3. SEM images in cross section of $CuInSe_2$ crystals with numbers #6 in the table subjected to electrochemical treatment at 0.7 V in an aqueous HCl electrolyte.



Fig. 4. PL spectra of #3 (a) and #6 (b) CuInSe₂ samples before (curve 1) and after (curve 2) electrochemical etching. The spectra are measured at T = 10 K.

4. Conclusions

The results of this study demonstrate possibilities of producing nanostructured layers and nanopatterned surfaces on $CuInSe_2$ crystals. In order to reduce the resistivity of the as-grown crystals and make them suitable for electrochemical etching, they should be subjected to annealing in vacuum or in Zn vapors. The analysis of PL spectra demonstrates that passivation of the porous skeleton surface and increase in the material quality occurs as a result of electrochemical treatment which is also important in the development of solar cells.

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INTERBAND OPTICAL TRANSITIONS IN THE REGION OF EXCITON RESONANCES IN In_{0.3}Ga_{0.7}As/GaAs QUANTUM WELLS

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Abstract

Reflectance spectra of quantum wells (QWs) with 8-nm-thick $In_{0.3}Ga_{0.7}As$ layers with a 9-nm-thick GaAs barrier layer up and a 100-nm-thick barrier layer down were investigated in the spectral range of 0.5–1.6 eV in S- and P- polarizations at an incidence angle close to the normal (7°) as well as at a Brewster angle (76°). Narrow lines at 0.9021; 1.0161; 1.1302; 1.1973; and 1.2766 eV were observed in the reflectance and absorption spectra, which are due to hh,lh1-e1(1s), hh1,lh1-e2(1s), hh2,lh2 -e2(1s), and hh3,lh3,-e3(1s) transitions, as well as features due to quantum dotes (QDs) formed at the interface of nanolayers and the buffer. The contours of reflectance and absorption spectra are calculated with a single-oscillator, and many-oscillator models. The oscillator strength and the damping parameter are estimated for the optical transitions in QWs and QDs. The radiative life time of the exciton in a QW and a QD was found to be $\tau_0 = (2\Gamma_0)^{-1} \approx 2x10^{-12}$ s.

1. Introduction

The optical properties of heterostructures with $In_{0.3}Ga_{0.7}As/GaAs$ quantum wells (QWs) are determined mainly by the high efficiency of interaction of the quasi-two-dimensional exciton subsystem with the light. The investigation of semiconductor nano-heterostructures is important from the point of view of both the determination of fundamental properties of excited QW and QD states and the development of a new generation of optoelectronic and microelectronic devices [1-3]. Nowadays, injection lasers based on quantum dotes QDs have been demonstrated with an ultra-high thermal stability of the threshold current J_{th}, a low value of the J_{th} [4–6], and generating in a continuum wave mode at room temperature with a high output power above 3 W [7-12]. One of the advantages of using structures with QDs is the possibility to extend the optical diapason of the emission as compared to structures with QWs. Thus, structures with In(Ga)As/(Al)GaAs QDs allow one to obtain emission in the range of 1–1.6 µm [8–12]. In particular, the structures with QDs are promising for the development of devices generating at wavelength of 1.3 µm [9–11].

In this study, we investigate the interband optical transitions in the region of exciton resonances in $In_{0.3}Ga_{0.7}As/GaAs$ QWs. The contours of reflectance and absorption spectra related to the ground exciton polariton states in QWs are calculated.

2. Experimental

The optical reflectance and transmission spectra were measured with MDR-2 and JASCO-670 at temperatures of 10 and 300 K in s- and p- polarizations at different incidence angles of the light at the surface of the hetero-nanostructure. When necessary, the fine structure of spectra was measured with a high-aperture (1:2) double-grating high-resolution SDL-1 spectrometer. An InGaAsP photodiode was used as photodetector. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system for cooling. The back-side surface of the structure was polished to a mirror-state for the investigation of transmittance spectra $T(\omega) = |t(\omega)|^2$.

3. Results and discussion

3.1 Reflectance and transmission spectra of $In_{0.3}Ga_{0.7}As/GaAs$ heterostructures with QWs

The transitions induced by the light with photon energies $\hbar \omega > \text{Eg}$ between different subbands of the V-band to subbands of the C-band produced by dimensional quantization in QWs can generate a whole family of electronic transitions, i.e., interband reflection, absorption and luminescence bands [13-15]. The reflection $R(\omega) = |r(\omega)|^2$ and transmission $T(\omega) = |t(\omega)|^2$, as well as the luminescence, are versatile techniques for investigating QWs in heterostructures. For the determination of absorption $A(\omega)$ in structures with QWs, it is necessary to measure the reflection *R* and transmission *T*

$$A(\omega) = 1 - R(\omega) - R(T)$$
(1)

The nonideality of the structure influences the optical reflection and absorption spectra, leading to inhomogeneous broadening of the resonance frequency of excitons in heterostructures. The inhomogeneity can lead to a smooth dependence of ω_0 upon the coordinate in the plane of the QW, or in the volume of the super-lattice, which results in the broadening of absorption and reflection lines.

From the experimental point of view, the narrow absorption and reflection lines indicate on the high quality of the QW structure. The simplest way to take into account the inhomogeneous broadening when calculating the reflection coefficient is to substitute in the respective formula the non-radiative damping Γ by the effective non-radiative damping $\Gamma_{eff} = \Gamma + \Gamma_0$, where Γ_0 is the broadening parameter. Figure 1 shows a structure consisting of two In_{0,3}Ga_{0,7}As QW layers with a thickness of 8 nm separated by GaAs barrier layers with a thickness of 9 nm. The reflections spectra shown in Fig. 1 were measured at an angle of incidence of the light of 7°, while absorption spectra were measured at normal incidence of the light on the surface of the In_{0,3}Ga_{0,7}As/GaAs QW heterojunction. Since the spectra were measured with a high resolution spectrometer, and the maxima in the absorption spectra as well as the minima in the reflection spectra have a FWHM around 2 – meV, one can conclude that the energies of the minima in the reflection spectra.

The reflection spectra from a $In_{0,3}Ga_{0,7}As/GaAs$ structure with QWs measured at 300 K at incidence angles of 7° and 76° (the Brewster angle) in S-S (A) and P-P (B) polarizations of the light are shown in Fig. 2. The path of the light rays is shown in insets *a* and *b*. Reflection minima b1-b6 are observed in the S-S polarization at an angle of incidence of 7°, these minima being highly broadened at an Brewster angle of incidence.

The same b1-b6 minima are observed in the reflection spectra measured in P-P polarization at the angle of incidence of 7° . The minima in the reflection spectra are observed at energies

a1-a6 at a Brewster angle incidence of 76°; that is, they are shifted. The shift is nearly the same for all the minima. The peak-to-peak amplitude of the reflection spectra is also by a factor of two lower in this polarization. The geometry of the reflection is shown in Fig. 2b. A plane monochromatic wave $E(r,t) = E_0 \exp(-i\omega t + i\kappa r)$ is incident on a $In_{0.3}Ga_{0.7}As$ QW placed between two identical GaAs barriers with a real dielectric permittivity ε_b . The wave vector of the light, related to the frequency ω according to the relation $k = \left(\frac{\omega}{c}\right)\sqrt{\varepsilon_b}$ (where c is the speed of the light in vacuum), is also real.



Fig. 1. Reflection and absorption spectra of In_{0.3}Ga_{0.7}As/GaAs heterojunctions. The structure consisting of two In_{0.3}Ga_{0.7}As QW layers with a thickness of 8 nm separated by GaAs barrier layers with a thickness of 9 nm is shown in the inset.

The amplitude of the light wave E_o lies in the plane of the interfaces (x,y) at a normal incidence of the light, when the wave vector is parallel to the main structure axis z. Since the system has an axial symmetry with reference to the z-axis, the electrical vectors of the incident, reflected and transmitted light waves are parallel to each other. Therefore, one can use the scalar amplitudes E_0 , E_{Γ} and E_t instead of vector ones. The amplitude coefficients of reflection and transmission of the light are $r=E_r/E_0$, $t=E_t/E_0$, respectively. When there is no energy dissipation inside the QW, the energy conservation law imposes the following restriction to these coefficients: $|r|^2 + |t|^2 = 1$. The percentage of the absorbed energy inside the QW structure is $1-|r|^2 + |t|^2$.



Fig. 2. Reflection spectra of an $In_{0.3}Ga_{0.7}As/GaAs$ structure with QWs measured at 300 K at angles of incidence of 7° and 76° (the Brewster angle) in S-S (A) and P-P (B) polarization of the light. The path of the light rays is shown in insets (*a*) and (*b*).

Figure 3 presents the reflection spectra of a QW structure at different polarizations of the incident and the reflected light waves. No features are observed in the S-S light polarization, while intense bands are observed at 0.9 eV and 1.0 eV in P-P and S-P polarizations.

The reflection, absorption and transmission of an electromagnetic wave which interacts with discrete levels of electron system in a QW in the frequency range corresponding to interband transitions have been investigated in different quantum structures [17, 18]. The results of these investigations are valid for narrow QWs where the following inequality is satisfied

$$Kd \ll 1, \tag{2}$$

where d is the width of the QW, K is the module of the wave vector **k** of the light wave. For wide QWs, the parameter Kd can be ≈ 1 . For a heterolaser on the basis of GaAs with a QW with the width of 500 Å, generating at the wavelength of 0.8 µm, the parameter Kd is 1.5. For the determination of the electromagnetic field in QWs for which the inequality d >> a₀ (a₀ is the lattice parameter) is satisfied, one can use the Maxwell equations for a continuous medium [17-19]. This approach allows one to take into account the difference of the refraction coefficients of the barrier and the well. The spatial dispersion of the electromagnet wave is taken into account in these structures, since its amplitude changes significantly across the well width. The theory which takes into account the spatial dispersion of the electromagnetic wave passing through a QW is described elsewhere [17-19]. An excited level (i.e., an interband transition) has been considered, and refraction coefficients of barriers and QWs for both the monochromatic [18] and the pulsed [19] excitations have been introduced in addition to the spatial dispersion.



Fig. 3. Reflection spectra measured at different polarizations of the incident and the reflected light waves.

For the structure considered in this paper, the optical characteristics of the QW and the barrier (the coefficients of refraction and exctinction, as well as the real and imaginary parts of the dielectric constant) were calculated from the reflection coefficient by means of the Kramers-Kronig relations. The spectral dependence of the refraction coefficient for different light wave polarizations is shown in Fig. 4. The obtained results suggest that the highest value of the real part of the refraction coefficient is observed in the P-P polarization at the resonance energy of 1.085 eV.



Fig. 4. The spectral dependence of the refraction coefficient for different light wave polarizations calculated from the reflection spectra by means of the Kramers-Kronig relations.

Figure 5 presents the spectral dependences of the refractive index n, the extinction coefficient k, the real ε_1 and the imaginary ε_2 parts of the dielectric constant for S-P and P-P light wave polarization calculated from the reflection spectra by means of the Kramers-Kronig relation. ε_2 reaches a value near 270 at the energy of 1.085 eV in the P-P light wave polarization, which suggests that the highest absorption is observed at the resonance value of e1-hh1(1s) transitions.



Fig. 5. Spectral dependence of the refraction coefficient n, the excitonctions coefficient k, the real ε_1 and the imaginary parts of the dielectric constant for the S-P and P-P light wave polarizations calculated from the reflection spectra by means of Kramers-Kronig relations.

3.2 The influence of temperature on the absorption spectra of $In_{0.3}Ga_{0.7}As/GaAs$ heterojunctions.

The knowledge of semiconductor band structure parameters, particularly the effective mass of carriers, as well as the dependence of these parameters on the composition of layers and temperature is necessary for the determination of parameters of QW structures. The valence band of III-V compounds is four-fold degenerated at k=0. The application of an axial deformation leads to the appearance of two maxima of the valence band with a small energy separation (the heavy and the light holes). The different maxima (minima) shift to a different degree with the application of an axial deformation in an arbitrary direction. These extremums shift to a higher degree with the temperature change. It is difficult to determine the temperature coefficient of the heavy and light holes valence bands shift. These difficulties are partially overcome in bulk semiconductors by investigating the exciton absorption spectra and the interband magneto-optic effect. For the determination of the temperature coefficient of the heavy and light holes valence bands in $In_{0,3}Ga_{0,7}As/GaAs$ heterostructures, we measured the transmission spectra of QW structures at temperatures of 3 and 300 K (Fig. 6).

The digital values on Fig. 6 indicate energy position of the observed transitions in the investigate QW structure. The temperature coefficients of the quantized energy levels as well as the electron and hole bands responsible for these transitions were estimated from these data. The results presented in the table show that the light holes valence bands have a large value of the temperature coefficient, for which $\beta=\Delta E/\Delta T$ varies in the limits of $(5.7-7.9)\times10^{-5}$ eV/K. The temperature coefficient of the heavy holes valence bands varies in the limits of $(4.4-5.0)\times10^{-5}$ eV/K. The splitting of the 1S states of light and heavy holes (ΔE_1 =lh1-hh1) at 300 K is 1.7 meV, while it is 3.7 meV at 30 K. The splitting of the ΔE_{12} =lh2-hh2 is 4.3 meV

and 10.1 meV at 300 and 30 K, respectively. The same value of splitting is observed for the ΔE_2 =lh2-hh2 interval at both temperatures. The splitting of the ΔE_{33} =lh3-hh3 transitions is larger: 7.6 and 16.6 meV at 300 and 30 K, respectively (Fig. 7).



Fig. 6. Transmission spectra of an In_{0.3}Ga_{0.7}As/GaAs QW structure measured at 30 and 300 K, and the energy of electronic transitions in QWs. The high-energy part of the spectrum is presented in a larder scale for the sake of clarity.

Transition	E _i (300K)	E _i (30K)	$\Delta E = E_i^{30K} - E_i^{300K}$	$B = \Delta E_i / \Delta T$
(1s)	eV	eV		eV/K
lh1 - e1	1.0249	1.0405	0.0156	5.8x10 ⁻⁵
hh1 - e1	1.0232	1.,0368	0.0136	5.0x10 ⁻⁵
$\Delta E_1 = lh1 - hh1$	1.7 meV	3.7 meV		
lh1-e2	1.1472	1.1654	0.0182	6.7x10 ⁻⁵
hh1-e2	1.1429	1.1553	0.0124	4.6x10 ⁻⁵
ΔE_{12} =lh1-hh1	4.3 meV	10.1 meV		
lh2-e2	1.2148	1.2301	1.0153	5.7x10 ⁻⁵
hh2-e2	1.2105	1.2191	0.0086	3.2×10^{-5}
$\Delta E_2 = lh2 - hh2$	4.3 meV	11.0 meV		
lh3-e3	1.2949	1.3164	0.0215	7.9x10 ⁻⁵
hh3-e3	1.2878	1.2998	0.0120	4.4×10^{-5}
$\Delta E_3 = lh3 - hh3$	7.0 meV	16.6 meV		

Table. Energy of electronic transitions in QWs of a In_{0.3}Ga_{0.7}As/GaAs structure



Fig. 7. Dependence of energy position of hh, lh bands and the difference ΔE =hh-eh on the quantum number n (left part of the graph), and the scheme of electron transitions and the energy intervals between the energy levels in QWs (right part of the graph).

A change in the crystal temperature as well as in QW structures leads to a change in the crystal lattice parameter. A change in the lattice parameter (at low deformation potentials) leads a change in electronic energy levels which are described by the deformation potential tensor. The change of the level energy at point \mathbf{r} of the crystal is given by the following expression [20, 21]:

$$\delta E(\mathbf{r}) = \sum_{ij} E_{ij} W_{ij}(\mathbf{r}) \tag{3}$$

where $W_{ij}(\Gamma)$ is the deformation tensor. Uniaxial or biaxial deformation can cause complicated effects due to the change of the crystal symmetry. In the case of uniaxial deformation, the energy of the band edges E_c and E_v of a cubic crystal subjected to the deformation Δ , can be written in the following form

$$E_{l}(\Delta) = E_{l}(0) + E_{l}(\Delta). \tag{4}$$

At a given temperature and pressure,

$$E_i(T,P) = E_i(T) + E_1 \Delta(P), \tag{5}$$

where $\Delta(P)$ is the deformation caused by the applied pressure *P*, and *E*_l(*T*) is the energy of the band edge at normal pressure, which is given by the following expression

$$E_{l}(T) = E_{l}(0) + E_{5l}(T) + E_{l}\Delta(T).$$
(6)

Here $E_{s,l}$ are the energy levels, and $\Delta(T)$ is the temperature deformation. One can write further $E_l(T, P) = E_l(0) + E_{s,l}(T) + E_l\Delta(T, P)$. (7)

For the energy levels determining the bandgap, we have

$$E_{g}(T,P) = E_{B}(0) + [E_{s,c}(T) - E_{s,v}(T)] + (E_{1,c} - E_{1,v}) \Delta(T,P),$$
(8)

where
$$\Delta(T, P) = \int_{0}^{T} \left(\frac{\partial \Delta}{\partial T}\right)_{P_0} dT + \left(\frac{\partial \Delta}{\partial P}\right)_{T} (P - P_0)$$

Here the first partial derivative is the temperature coefficient of expansion, and the second partial derivative is the compressibility taken with a negative sign. These macroscopical values have been measured for some semiconductors. From the last equation we have

$$\left(\frac{\partial Eg}{\partial T}\right)_{P} = \left(\frac{\partial E_{s,c}}{\partial T}\right)_{P} - \left(\frac{\partial E_{s,v}}{\partial T}\right)_{P} + \left[E_{1,c} - E_{1,v}\right] \left(\frac{\partial \Delta}{\partial T}\right)_{P}$$
(9)

$$\left(\frac{\partial Eg}{\partial P}\right)_{T} = \left[E_{1,c} - E_{1,v}\right] \left(\frac{\partial \Delta}{\partial P}\right)_{T}$$
(10)

Therefore, the temperature coefficient of the energy level shift consists of the electronphonon and the deformation components. Different temperature coefficients of the QW exciton energy level shift were found from optical transmission spectra of the investigated heterojunctions. This is due to different temperature coefficients of the light and heavy holes bands shift as well as difference of the light and heavy holes effective masses. The energy of the QD transition is 0.9056 and 0.9289 eV at 300 and 30 K, respectively. The temperature coefficient of the QD energy shift $\beta=\Delta E/\Delta T$ is 8.3x10-5 eV/K. This value does not differ from the temperature coefficient of the energy level shift in QW in the limits of the experimental errors (± 1 meV). This observation suggests that, in this structure, the shift of the light and heavy holes bands is determined mainly by the temperature component, rather than by the deformation one. There is an ambiguity in the literature concerning the determination of band parameters in the In_yGa_{1-y}As–GaAs system. The published data concerning the conduction band offset at the InyGa1- y As–GaAs interface $\Delta E_c/\Delta E_g$ (ΔE_c is the difference of the conduction band bottoms of GaAs and In_yGa_{1-y}As, ΔE_g is the difference of their bandgaps) are different: 0.52 [22], 0.6 [23], 0.7 [24, 25], 0.83 [26].

The situation with the data about the heavy holes effective mass in GaAs is similar: 0.62m0 [22], 0.52m0 [24], 0.51m0 [26], and 0.36m0 [25] (m0 is the free electron mass). There is also a discrepancy concerning the dependence of the bandgap $E_g(y)$ of stressed $In_yGa_{1-y}As$ layers in the GaAs– $In_yGa_{1-y}As$ –GaAs system on the In content (y) [23, 28, 29].

In considering the energy spectrum of QW based on the GaAs– $In_yGa_{1-y}As$ –GaAs system, we used a mean value of $E_c/E_g=0.7$ and a linear approximation of the dependence of electron and hole effective masses on the In content (y). The electron effective mass of $In_xGa_{1-x}As$ solid solutions was determined from the relation $m_e^*/m_0 = 0.067-0.0603+0.0163x^2$. The effective masses of electrons m_e^* , heavy m_{hh}^* and light m_{lh}^* holes are $0.050m_0$, $0.312m_0$, and $0.074m_0$, respectively, at x = 0.3. The bandgap at 300 K was estimated from the relation $E_g = 1.425-1.501x + 0.436 x^2$ [30,31], and it was found to be 1.014 eV for an $In_xGa_{1-x}As$ layer with x=0.3. At 10 K, the bandgap was determined from the relation $E_g = 1.515 - 1.584x + 0.489x^2$, which is used for the determination of the bandgap at 0 K [30,31]. The bandgap of an $In_xGa_{1-x}As$ layer with x=0.3 was determined to be 1.024 eV at 10 K.

The temperature coefficient β of the quantum levels hh2-e2 and hh1-e2 is 3.2×10^{-5} and 4.6×10^{-5} eV/K, respectively. The value of $\Delta\beta = \beta(hh1-e2) - \beta(hh2-e2) = 1.4 \times 10^{-5} [eV/K]$ means that the level hh1 lies below the top of the valence band with an energy separation of 3.7 meV. The energy interval E(hh1-e1) - E_g is 0.011 eV. Consequently, taking into account the energy position of the hh1 level, one can deduce that the ellevel is situated 7.3 meV above the conduction band. One can find from the data presented in the table that the energy interval hh1-hh2 is 119 meV, while the interval e1-e2 is 187 meV.

3.3 Calculation of the line shape of the QD oscillator, and the 1s state of excitons in QW of an $In_{0.3}Ga_{0.7}As/GaAs$ structure.

The excited states with a frequency close to ω_0 in QWs of semiconductor heterostructures have a mixed exciton-photon nature including both the electromagnetic and the exciton

components [13-15]. These waves in structures with QWs are analogous to exciton polaritons widely investigated in bulk crystals. In the absence of dissipative processes (i.e., at $\Gamma = 0$), the exciton polariton propagates limitless far, supporting continuous coherent transformations from the exciton to the photon and vise-versa. As a result, the dispersion of the hybrid wave is different from the dispersion of non-interacting photons and excitons; that is, a characteristic anticrossing occurs near the point of the intersection between the initial dispersion branches. The dispersion equation for exciton polaritons in a periodic structure with QWs has been previously deduced [13, 14]. A wave propagating in the direction of the main axis of the structure Z, where the component of the wave vector k_{\parallel} in the plane of the interface (x,y) is zero and the electric field as well as the dielectric polarization of the medium lay in this plane, was considered. A frequency range $\Delta \omega$ which is wide as compared to the inverse value of the exciton life time, but narrow as compared to the distance $|\omega_0 - \omega_0^*|$ from another nearest exciton resonance ω_0^* was considered by specifying one of isolated exciton states in the QW (the level e1- hhl(ls), and designating the resonance frequency of the specified exciton as ω_0 [13-15]. It was shown that an exciton with non-zero two-dimensional wave vector, i.e., $K_x = K_y = 0$, is excited at a normal incidence of the light. The amplitude coefficients of reflection and transmission are determined according to the relations $r_{OW} = E_r/E_0$, $t_{OW} = E_t/E_0$. The amplitude coefficient of the reflection from a real four-layered structure "vacuum (0)-coating layer (1)-singular QW (2)-semi-infinite barrier (3)" is related to r_{OW} according to the following expression:

$$\mathbf{r} = \mathbf{r}_{01} + \frac{t_{01} t_{10} e^{2i\varphi_1}}{1 - r_{10} r_{QW} e^{2i\varphi_1}} \qquad \mathbf{r}_{QW} = \frac{r_{01} + r_{QW} e^{2i\varphi_1}}{1 - r_{10} r_{QW} e^{2i\varphi_1}}.$$
 (11)

Here r_{ij} (= - r_{ji}) and t_{ij} are the amplitude coefficients of reflection and transmission of the light at the incidence from a semi-infinite medium i (i = 0 in the vacuum, i = 1 in the layer 1) on a semiinfinite medium j. In equation (12) we have $\varphi_1 = K(d_1 + a/2)$, where K is the polariton wave vector, and d_1 is the thickness of the layer 1. Therefore, the problem of calculation of the reflection spectrum $R = |r|^2$ is reduced to the determination of the linear response $r_{QW}(\omega)$, which is a complex function of the frequency cBeTAW. The physical meaning of parameters is as follows: $\tau_0 = (2\Gamma_0)^{-1}$ is the radiative damping of the 2D exciton, ω_0 is the resonance exciton frequency, and ϖ_0 is its renormalized resonance frequency [13, 14]. These parameters describe the transformation of the complex frequency of the exciton from $\omega_0 - i\Gamma$ to $\varpi_0 - 1(\Gamma + \Gamma_0)$ induced by the exciton-photon interaction. Previously [13, 14], an analysis has been performed of the reflection and transmission coefficients of heterostructures with QWs, where the reflection r_{QW} is defined as

$$r_{QW(\omega)} = \frac{i\Gamma_0}{\varpi_0 - \omega - i(\Gamma + \Gamma_0)}; \quad t_{QW}(\omega) = \frac{\varpi_0 - \omega - i\Gamma}{\varpi_0 - \omega - i(\Gamma + \Gamma_0)}$$
(12)

$$\omega_0^* = \omega_0 + \Gamma_{10} \Gamma_0 \sin 2\phi, \qquad \Gamma_0 = \Gamma_0 (1 + r_{10} \cos 2\phi).$$
(13)

Here ω_0^* , $\Gamma o = (2\tau_0)^{-1}$, $\Gamma = (2\tau)^{-1}$ are the resonance frequency the radiative, and non-radiative exciton damping parameters, respectively, renormalized taking into account the interaction of the exciton with the light wave induced by this exciton and reflected from the external surface. After a number of transformations of the reflection and absorption coefficients, the following expression is obtained for the reflection coefficient [13, 14]:

$$R(\omega) = |r(\omega)|^2 = R_0 + \frac{A + Bx}{1 + x^2}$$

$$X = \frac{\omega - \omega_0^*}{\Gamma}, \quad R_0 = r_{01}^2$$
(14)

where

$$A = t_{01}t_{10}S[t_{01}t_{10}S - 2r_{01}(1 + S^*)\cos 2\varphi]$$

$$B = 2r_{01}t_{01}t_{10}S\sin 2\varphi, \ S = \frac{\Gamma_0}{\Gamma}, \ S^* = \frac{\Gamma_0^*}{\Gamma}$$

According to the Fresnel's formula, at normal incidence of the light on the crystal surface we have:

$$r_{10} = -r_{01} = \frac{n_b - 1}{n_b + 1}, \quad t_{01} t_{10} = \frac{4n_b}{(n_b + 1)^2}.$$
 (15)

The A and B coefficients can take values of different signs depending on the distance between the center of the QW and the external surface, and, particularly, they can alternately vanish. At A = 0, B<0, the resonance contour consists of a maximum at $\omega < \omega_0^*$ and a minimum at $\omega > \omega_0^*$. At B = 0, there is a maximum (A > 0) or a minimum (A < 0) in the spectrum. According to previous results [13, 14], the best agreement between the calculations and the experimental spectra is obtained at $\Gamma \approx \Gamma_0$, $\Gamma_0 = (60\pm15) \ \mu eV$, which corresponds to the radiative life time of the exciton $\tau_0 = (2\Gamma_0)^{-1} \approx 2x10^{-12}$ s. The value of $\hbar\Gamma_0$ lies in the limits of 0.02–0.2 meV for typical structures, for instance, $\hbar\Gamma_0 = 0.12 \ meV$ in a CdTe/Cd_{0.11}Zn_{0.87}Te QW with the thickness of 100Å [12] and $\hbar\Gamma_0 \approx 27 \ \mu eV$ in a In _{0.04}Ga_{0.96} As/GaAs QW with thickness of 85Å [13, 14].

In the technological process of producing GaAs– $In_yGa_{1-y}As$ –GaAs heterojunctions with QWs, QDs are also formed at the interface of heterojunction layers. The technology of producing QW structures is prospective for the elaboration of optoelectronic devices for the infrared spectral range [4-7]. The process of QDs growth in InAs/GaAs heterostructures with a high value of d_{eff} thickness was previously investigated [4-12], and in was shown that with increasing the d_{eff}, apart from the inrease in QD density, the scatter of the QD sizes occurs, and the number of large relaxed clusters of InAs defects increases. This leads to a broadening of the photoluminescence lines of QD and to a decrease in their intensity.

The deepest minimum (strong oscillator) is observed at the energy of 1.0859 eV (Fig. 8) in the reflection and absorption spectra of $In_{0.3}Ga_{0.7}As/GaAsheterojunctions$ with QWs. This minimum is due to the hh1-e1(1s) transitions. As mentioned above, the bandgap of the $In_XGa_{1-X}As$ layer with x=0.3 is 1.014 eV. A weaker minimum at the energy of 0.85 eV is due to QDs formed at the interface of heterojunctions. The calculation of the experimental reflection spectra is performed for the 1s states of the hh1-e1 transitions (as a singular oscillator) as well as for two oscillators (one oscillator of QDs and the other oscillator of QWs). A good coincidence of experimental and experimental contours (Fig. 8) is obtained with the following parameters: $\omega_0(QD) = 0.985$ eV and $\omega_0(hh1-e1,1s) = 1.086$ eV, $\varepsilon_b = 10.0$, $\omega_{LT} = 75$ meV, and $\Gamma = \Gamma + \Gamma_0 = 7.6 \ \mu eV$, where ω_{LT} is the longitudinal-transverse splitting of the polariton in QW, and Γ is the damping parameter. Unfortunately, the value of the effective mass $M=m_v^*+m_c^*$ was impossible to be determined. The M parameter, as well as the thickness of the deal layer, does not significantly influence the contours of the investigated spectra.

The experimental values of the optical density (D = 1-R-T) were determined from the measured reflection (R) and transmission (T) spectra of the In_{0.3} Ga_{0.7}As/GaAs quantum structure. The calculations of spectra were also performed taking into account two oscillators of QD and QW (hh1-e1,1s). The calculated and experimental curves of the optical density (Fig. 9) are in satisfactory concordance with the following parameters: $\omega_0(QD) = 0.975$ eV and $\omega_0(hh1-e1,1s) = 1.076$ eV. The value of $\varepsilon = \varepsilon_b + \varepsilon_a$ is (10.0+0.07) for the QD oscillator and QW level. The longitudinal-transverse splitting of the polariton in the QW ω_{LT} is 45 meV, and the damping parameter is $\Gamma_{eff} = \Gamma + \Gamma_0 = (2.0+40.5) \ \mu eV$ for the QD and (1.0+44.5) μeV for the $\omega_0(hh1-e1,1s)$ level of the QW. One can see from these data that $\Gamma_{eff} \approx \Gamma_0$ and, consequently, the

radiative exciton life time in the QD and in the QW are nearly equal to $\tau_o = (2\Gamma)^{-1} \approx 2x10^{-12}$ s.



Fig. 8. Spectral dependence of the contour of measured (exp.) and calculated (cal.) reflections spectra of an $In_{0.3}$ Ga_{0.7}As/GaAs quantum structure.



Fig. 9. Experimental (Exp.) and calculated (Cal.) optical densities obtained from the measured reflection (R) and transmission (T) spectra as well as from the calculations of an $In_{0.3}Ga_{0.7}As/GaAs$ quantum structure.

4. Conclusions

The experimental investigations of $In_{0.3}Ga_{0.7}As/GaAs$ heterojunctions with QWs revealed the presence of narrow and intensive lines in optical absorption and reflection spectra which are due to the ground states of exciton polaritons in QWs. Features caused by QDs formed at the interface of nanolayers and the buffer were observed in the optical spectra. The contours of the reflection and transmission lines were calculated both with a single-oscillator, and many-oscillator models. The oscillator strength and the damping parameter of QWs and QDs were estimated from these calculations. These data demonstrate that $\Gamma_{eff} \approx \Gamma_0$ and, consequently, the radiative life time of the exciton in the QD and in the QW are nearly equal to $\tau_0 = (2\Gamma_0)^{-1} \approx 2x10^{-12}$ s.

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TUNABILITY OF HEXAGONAL AND TRIANGULAR PHOTONIC CRYSTALS

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Abstract

With the aid of numerical simulations, we study the tunability of photonic structures by evidencing the band gaps (BGs) of two interesting particular hexagonal and triangular photonic crystals. Several runs were performed for different values of the dielectric constant ranging from $\varepsilon = 15$ to $\varepsilon = 150$. Results showed that the BGs cover large intervals. The numerical model used for the simulations is presented. We conclude these configurations could be used for a tunable high-reflectivity and high-directionality antenna. The analogy between electronic waves in the crystal and light waves in a three-dimensionally periodic structure and the evidencing of a complete photonic band gap led to further studies, which cover a large range of domains.

1. Introduction

Photonic crystals (PCs) are one of the major recent revolutions in integrated optics. In 1987 E. Yablonovitch [1] and S. John [2] proposed the possibility to build a material able to forbid the propagation of electromagnetic waves in order to control the spontaneous emission and to generate interesting quantum electrodynamics effects. This idea relies on the basic concepts of the solid-state physics and proposes a periodic arrangement of dielectric materials as a means of obtaining the photonic bandgaps. The investigation of other interesting effects derived from this one, such as strong photon localization, is a fascinating phenomenon [3]. Since these pioneering works, novel exciting phenomena related to the richness of the dispersion relation of PCs [4] have been found out. These include the superprism, self-guiding, and negative refraction effects. In 1990, Ho et al. [5], using a plane-wave expansion method, solved the Maxwell's equations for the propagation of electromagnetic waves in a periodic lattice of dielectric spheres in a uniform dielectric background and found that, unlike experiment, a fcc dielectric structure does not have a full photonic band-gap. In 1991, Yablonovitch [6] demonstrated the first three-dimensional photonic band gap in the microwave regime.

Ferroelectrics have many unusual properties; one of them, namely the nonlinear optical response, can be widely exploited for designing tunable photonic crystals [7]. An external quasistationary electric field can cause a substantial nonlinear response especially in the microwave range [8].

As mentioned before, the aim of this paper is to demonstrate, with the aid of numerical simulations, large intervals of BGs in two particular photonic crystals: one with hexagonal symmetry and the other with triangular symmetry. The paper is organized as follows: Section 2

describes the numerical model with which the results are obtained together with our methodology, **Section 3** presents the construction of the lattices, **Section 4** contains results and discussion, and **Section 5** contains some conclusions.

2. Numerical model and methodology

The **MIT Photonic-Bands** (**MPB**) package is a free program for computing the band structures (dispersion relations) and electromagnetic modes of periodic dielectric structures using both serial and parallel computers. This program computes definite-frequency eigenstates (harmonic modes) of Maxwell's equations in periodic dielectric structures for arbitrary wavevectors, using fully-vectorial and three-dimensional methods. It is especially designed for the study of photonic crystals (photonic band-gap materials), but is also applicable to many other problems in optics, such as waveguides and resonator systems. (For example, it can be used for the modes of waveguides with arbitrary cross-sections). Some of the main design goals of this package are the followings:

(a) Fully vectorial, three-dimensional calculations for arbitrary Bloch wavevectors (the only approximation is the spatial discretization, or equivalently the planewave cutoff.)

(b) Flexible interface. Readable, extensible, scriptable.

(c) Parallel (can run on a single-processor machine, but is also supports parallel machines with MPI.)

(d) "Targeted" eigensolver: find modes nearest to a specified frequency, not just the lowest-frequency bands (for defect calculations.)

(e) Modularity. The eigensolver, Maxwell's equations, user interface, and so on, should be oblivious to each other as much as possible. This way, they can be debugged separately, combined in various ways, replaced, and used in other programs (all the usual benefits of modular design).

(f) Take advantage of inversion symmetry in the dielectric function, but don't require it (this means that we have to handle both real and complex fields.)

Calculation of the dispersion relation and the associated band gaps in an ideal photonic material is well understood. The periodicity of the medium allows using the Bloch's theorem leading to an eigenvalue problem. For the numerical solutions of the eigenvalue problem, we used the free available MPB package developed by Joannopoulos and associates. Their description of this package reads "Fully vectorial eigenmodes of Maxwell's equations with periodic boundary conditions were computed by preconditioned conjugate – gradient minimization of the block Rayleigh quotient in a plane wave basis using a freely available software package" [9]. The source of the electromagnetic field has the form: $E(x,t) = A(x)B\exp(i\omega t)$, with A(x) = 1 and $\omega = 2\pi c/\lambda$. As it is well known, the numerical code of Joannopoulos et al. works with adimensional units.

3. Lattices

The elementary cell of the hexagonal symmetric structure (Fig. 1a) consists of six rods of radius 0.2*a*, where *a* is the lattice constant. For the other photonic crystal (Fig. 1b), a 2D triangular lattice consisting of holes of ferroelectric was envisaged. The elementary cell consists of three holes of radius 0.5*a*, where *a* is the lattice constant, a = 5 cm.



Fig. 1. Photonic crystals structures (top view): (a) hexagonal symmetry and (b) triangular symmetry.

4. Results and Discussion

4a. Hexagonal photonic crystal

Several runs were performed, for the dielectric constant taking different values (only three of them shown in this study). In the following, we present the BGs structures for $\varepsilon = 25$ (Fig. 2), $\varepsilon = 50$ (Fig. 3), and $\varepsilon = 100$ (Fig. 4).



Fig. 2. BGs ($(2\pi c/a)$ units) for $\varepsilon = 25$.



Fig. 3. BGs($(2\pi c/a)$ units) for $\varepsilon = 50$.



Fig. 4. BGs ($(2\pi c/a)$ units) for $\varepsilon = 100$.

In this scope, we could fabricate a photonic crystal on ferroelectric materials and then apply an electric field. It is clear that the voltage applied to the structure must be appropriatelly triggered by an antenna in order to obtain the corresponding band gap, which can be quite simply implemented in actual practise, because a field of a few hundreds of V/cm must be applied depending on the ferroelectric structure.

4b. Triangular Photonic Crystal

In this case, ten runs were performed for the dielectric constant taking different values (only three of them shown in this study). Only the results of three runs are presented in Figs. 5a,b - 7a,b below, namely the band structures for both TE and TM modes, for dielectric constant values of $\varepsilon = 15$, 25, and 75.



Fig. 5. (a) TE mode for $\varepsilon = 15$ and (b) TM mode for $\varepsilon = 15$.

From the above figures, we observe the band gaps for TE mode between ~ 0.45 to 0.55 (in $2\pi c/a$ units), and for the TM mode between ~ 0.4 and 0.6 (in the same units).



Fig. 6. (a) TE mode for $\varepsilon = 25$ and (b) TM mode for $\varepsilon = 25$.

Figures 7a and 7b show band gaps for TE mode between ~ 0.5 and 0.55, and for the TM

mode between ~ 0.4 and 0.6 (in the same units).



Fig. 7. (a) TE mode for $\varepsilon = 75$ and (b) TM mode for $\varepsilon = 75$.

The band gap for TE mode between ~ 0.4 and 0.45, and for TM mode between ~ 0.2 and 0.35 (in the same units as above).

5. Conclusions

We studied the possibility of tuning the band gap of a photonic crystal in radar range by numerical simulations. In this scope, a hexagonal lattice of rods and a 2D triangular lattice consisting in holes of ferroelectric were envisaged. The dielectric constant can be varied in practice by an external electrical field. For dielectric constant between 15 and 200, the entire range of ~ 10–60 GHz is covered with band gaps. So, the first application comes from manufacturing tunable antennas.

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PHOTONIC BAND STRUCTURES OF 2D PHOTONIC CRYSTALS WITH HALF-ELLIPTICAL HOLES

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Abstract

In recent years, periodic photonic crystal structures have attracted much attention due to potential application in controlling electromagnetic wave propagation [1]. In this paper, the photonic band gaps in two-dimensional photonic crystal with square lattice composed of half-elliptical rods in air are studied using the plane-wave expansion method. The refractive index of the rods is n = 3.47. In order to analyze the effects of the above-mentioned rod structure on photonic band gaps, we vary the ellipticity. The obtained results are compared with calculations for circular and elliptical rods with the same filling factor. It is observed that the size of the photonic band gap changes with changing ellipticity of the constituent rods and it is bigger than in the case of circular and elliptical rods. These results were obtained using the OptiFDTD 8.0.0.428 software.

1. Introduction

In recent years, photonic crystals (PCs), which are a kind of artificial lattice structure, have attracted much attention due to the possibilities and abilities of controlling the flow of photons. The electromagnetic wave propagation inside a PC is forbidden for some specific or all directions for a certain frequency range due to the photonic bandgap (PBG) effect [2].

PBG can suppress vacuum fluctuation and spontaneous emission and can lead to interesting quantum electrodynamics effects [2]. It has potential applications in quantum electronic devices, distributed-feedback mirror, microwave antennae substrate [3], and its unusual optical properties can be exploited to control and guide the propagation of light [4].

Here we report a study of the photonic band gaps in two-dimensional photonic crystal with a square lattice composed of half-elliptical rods in air (Fig. 1) in comparison with a square lattice composed of circular and elliptical rods using the plane-wave expansion method.

The following parameters are used here:

- refractive index of the rods, n = 3.47
- lattice constant, $a = 0.55 \,\mu\text{m}$
- filling factor, $F \approx 0.0314$

The filling factor was the same for all types of lattice structure (circular, elliptical, and half-elliptical).



Fig. 1. a) Square lattice composed of half-elliptical rods; b) band gap structure for half-elliptical rods.

To analyze the effects of the rod structures on photonic band gaps, we vary the radius and the ellipticity, respectively.

For the two-dimensional photonic crystal with square lattice composed of circular rods, the radius was varied from 0.06 to 0.2 μ m. For values higher than 0.2 μ m, no band gaps were found. The maximum of the band gap in this case is achieved for a radius of 0.1 μ m. Furthermore, in some cases the presence of two band gaps was observed.



Fig. 2. Band gap width depending on radius for a circular structure.

The presence of two band gaps can be observed in Fig. 2: the first one for radius values between 0.06 and 0.2 μ m and the second one for values between 0.14 and 0.2 μ m. In both cases, there is an increase to a certain point followed by a decrease. For the first band gap, the maximum is achieved at a 0.1- μ m radius with a width of 47.85% and for the second one the maximum is at a 0.17- μ m radius with a width of 25.21%.

In both cases, there is a maximum and a minimum. For the first band gap, frequency values are smaller than those reported for the second band gap. Frequency of the first band gap is highest at 0.7451 $2\pi c/\mu m$ for a 0.19- μm radius and lowest at 0.4727 $2\pi c/\mu m$ for a 0.17- μm radius. For the second bang gap, frequency is highest at 1.0956 $2\pi c/\mu m$ for a 0.19- μm radius and lowest at 0.8201 $2\pi c/\mu m$ for a 0.17- μm radius.



Fig. 3. Band gap average frequency depending on radius for a circular structure.

In the case of the two-dimensional photonic crystal wit a square lattice composed of elliptical rods, the filling factor was the same as in the case of circular rods. Studies were performed for both vertical and horizontal elliptical rods and showed higher band gap values in the case of vertical elliptical rods, while the average frequencies of the band gap are almost the same in both cases.

As for the two-dimensional photonic crystal with square lattice composed of half-elliptical rods, in each case, studies were carried out both on the left and right side. As a result of the obtained data, it can be stated that the band gap and average frequency values for the left and right side concur. This means that, with respect to the band gap structure, the shape of the dielectric interface is of no importance for electromagnetic radiation. With respect to the vertical and horizontal position of the rods, data showed higher band gaps for the horizontal ones. Frequency values are almost the same in both cases.



Fig. 4. Wave propagation through a photonic crystal with a right side vertical half-elliptical structure for $\lambda = 1 \ \mu m$.

A splitter can be observed in Fig. 4. It is also evident that electromagnetic radiation is well reflected.



Fig. 5. Wave propagation through a photonic crystal with a right side horizontal halfelliptical structure for $\lambda = 1 \ \mu m$.

It is evident from Fig. 5 that the splitter effect is not as intense as it is in the case of the vertical half-elliptical structure.



Fig. 6. Wave propagation through a photonic crystal with a left side horizontal half-elliptical structure for $\lambda = 1 \mu m$.

Although the position of the rods is horizontal, as in Fig. 5, the side of the dielectric interface is different. It can be observed from Fig. 6 that focusing is better in this case.

Therefore, we can conclude that the dielectric interface shape is important to the electromagnetic radiation.



2. Comparative study of elliptical and half-elliptical structures

Fig. 7. Band gap width depending on ellipticity for an elliptical and half-elliptical structure.

It is evident from Fig. 7 that, in the case of vertical elliptical rods, the band gap width data increase more rapidly. However, both structures increase with increasing ellipticity. At the same time, the band gaps appear for elliptical rods at an ellipticity of 0.16 to 0.8151, while band gaps for half-elliptical rods can be seen at an ellipticity of 0.3461 to 0.875.



Fig. 8. Band gap average frequency depending on ellipticity for an elliptical and half-elliptical structure.

In Fig. 8, we see that in both cases the average frequency swings. The values are between 0.6636 and 0.7024 $2\pi c/\mu m$ for the elliptical structure and between 0.6345 and 0.6722 $2\pi c/\mu m$ for the half-elliptical one.

According to Fig. 9, both structures increase with increasing ellipticity. However, in the case of half-elliptical rods, band gap width values are higher, up to 53.98%, instead of 44.15% in the case of elliptical rods.

Figure 10 shows that in both cases the average frequency of the band gap swings. Values are between 0.6175 $2\pi c/\mu m$ and 0.6663 $2\pi c/\mu m$ in the case of elliptical rods and between 0.5461 $2\pi c/\mu m$ and 0.674 $2\pi c/\mu m$ for half-elliptical.



Fig. 9. Band gap width depending on ellipticity for a horizontal elliptical and half-elliptical structure.



Fig. 10. Band gap average frequency depending on ellipticity for a horizontal elliptical and half-elliptical structure.

3. Conclusions

In this paper, we studied the photonic band gaps in a two-dimensional photonic crystal with a square lattice composed of half-elliptical rods in air using the plane-wave expansion method. The results showed that the horizontal elliptical structure leads to much narrower band gaps than the half-elliptical one, which is 20.99% for the elliptical structure and 35.56% for the half-elliptical structure. Both vertical and horizontal half-elliptical structures are shown to increase with increasing ellipticity. As for the average frequency of the band gap, values are almost the same in both cases. We reported that a half-elliptical structure, because of a reduced symmetry in contrast to the circular and elliptical structures, yields higher band gaps and allows a better control of electromagnetic radiation propagation. In the future, the data can contribute to the development of industrial applications, including efficient amplification of the light-emitting diodes and solar cells and biomedical analysis of integrated photonic circuits.

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PHOTOSENSIBLE NANOCOMPOSITES PEPC/ANA-CH: PREPARATION TECHNIQUE AND SOME OPTICAL PROPERTIES

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Abstract

Nanocomposites based on polymers and organic luminophore materials (propenone and coordinated with rare earth elements) are excellent structures for a new generation of devices with high intensity of luminescence in the visible region of the spectrum [1, 2]. The main advantages of nanocomposites are their high stability due to fixation and protection in the polymer matrix; they can be obtained in the form of thin layers on large-area and flexible substrates and in the form of fibers and planar waveguides; they are promising for broad application in optoelectronics and other fields, such as solar cells, gas sensors, medicine, etc. The samples of 3-(anthracene-9-yl)-1-(4-isothiocyanatophenyl)-prop-2-en-1-one (ANA-CH) framed in the polymer matrix of polyepoxypropylcarbazole (PEPC) were prepared and characterized by optical spectroscopic methods. For the ANA-CH and ANA-CH/PEPC nanocomposites, depending on the composition, the photoluminescence peaks at photon energy hv=3.16 eV, hv=2.45 eV and hv=3.18 eV, hv=2.25 eV, respectively, were registered. The peaks in the photoluminescence spectra of the investigated nanocomposites can be attributed to the presence of the CH=CH double bond in the organic luminophore compound with the width of $\Lambda=117$ nm at room temperature and $\Lambda=37$ nm at nitrogen temperature.

1. Introduction

Luminescent organic nanocomposite materials present fundamental and practical interest due to their luminescent properties, such as sharp emission bands, high quantum efficiency, which make them good candidates for application as light emitting diodes (LEDs), laser devices, photonic crystals, optical fibers, planar waveguides, thin film transistors, gas sensors, and in biomedicine [3-7]. Actually, the definition of nanocomposite materials has broadened significantly and includes a large variety of systems and structures, such as one-dimensional, two-dimensional (metal oxides, metal phosphates, chalcogenides), three-dimensional, and amorphous materials. Today the main efforts of scientists are focused on the possibility of controlling the nanoscale structures with required physical and optical characteristics through innovation synthesis approaches. Recent materials include the concept of "plastic light" with the optical, electric, and mechanical characteristics that make it low cost technological in light industries and offers new opportunities for exploitation. In the present paper, we make an effort to synthesize new nanocomposites based on polymers and organic luminophore materials ANA-CH and ANA-CH/PEPC, and to investigate their optical and photoluminescence characteristics.

2. Methodology

2.1. Preparation Technique for ANA-CH and ANA-CH/PEPC Compounds

The organic luminophore compound was prepared in the Department of Organic Chemistry at the State University of Moldova. The preparation method for 3-(anthracene-9-yl)-1-(4-isothiocyanatophenyl)-prop-2-en-1-one (2) consists in removing dimethylamine from 3-(4-(3-(anthracene-9-yl)acryloyl)phenyl)-dimethyl thiourea-1.1 (1) by boiling chloroform acetyl chloride (I) and acetic anhydride (II) according to the following scheme:



Fig. 1. Chemical structure of technological organic compounds and ANA-CH luminophore.

3-(anthracene-9-yl)-1-(4-isothiocyanatophenyl)-prop-2-en-1-one (2) with yields of 94% (II) and 80% (I) was obtained from 3-(4-(3-(anthracene-9-yl)acryloyl)phenyl)-dimethyl thiourea-1.1 (1) by a future condensing reaction in the alkaline (KOH) of 4-N,N-dimethylthiourea acetophenone (dimethilthiourea do acetofenone) with anthracene-9-carbaldehyde. The resulting compound was 3-(4-(3-(anthracene-9-yl)acryloyl)phenyl)-dimethyl thiourea-1.1 (1) with the yield of 83%.

The structure of 3-(anthracene-9-yl)-1-(4-isothiocyanatophenyl)-prop-2-en-1-one (2) was confirmed by C-NMR spectrum (DMSO-d6), ppm: 179.70 (C = O), 139.75 (CN), 149.38 (-CH = CH), 121.49 (-CH = CH-), 137.34 (-C6H4-N = C = S), 125.83, 122.92 [8, 9].

In order to obtain the ANA-CH/PEPC nanocomposite, we studied the properties of the ANA-CH compound organic luminophore in the solid form and dissolved in toluene with different concentrations (0.0045 to 0.9 mg/ml). The solution of ANA-CH/PEPC was measured in quartz sinks.

The ANA-CH/PEPC nanocomposites were prepared from chemicals solutions. Components of the nanocomposites were dissolved in toluene and then carefully folded and shaken for 1 h. Sedimentation was performed on optical glasses by methods of spin-coating and droplets, then the sediment was dried until complete evaporation of the solvent. The samples had five different concentrations (0.2, 1, 5, 9, and 12%) of the ANA-CH nanocomposite. All the nanocomposite samples were yellow-orange, uniform, and transparent and had a flat surface.

2.2. Experimental method

For studying the ANA-CH dust, it was dissolved in toluene and deposited on a glass and subsequently dried. The solutions of toluene with ANA-CH were measured in quartz sinks with a parallelepiped form (the thickness (optical length) of 1cm). The morphological properties of the nanocomposites were investigated using a Linnik MII-4 interferometer microscope. The optical transmission spectra $T=f(\lambda)$ were measured using a Carl Zeiss UV-VIS SPECORD spectrophotometer and a PerkinElmer Spectrum 100 FT-IR instrument.

The photoluminescence spectra were measured using a set of Monochromators based on MDR-23-24 connected to a PC. The excitation of photoluminescence was performed with a

nitrogen laser ($\lambda = 337$ nm) with the radiation intensity of P = 0.1-103 W/cm² and a deuterium lamp in the spectral range of $\lambda = 250-800$ nm.

3. The experimental results

3.1 Morphology of NC ANA-CH/PEPC

Figure 2 represents the images of ANA-CH/PEPC nanocomposite samples on glass substrates obtained by an MII-4 optical microscope in the transmission and reflection modes. Note that, in the initial layer of the nanocomposite, the particles can be observed in clusters of different sizes. This can be seen in images obtained by reflection (Fig. 2 (2; 4)):



Fig. 2. Image of the NC-CH ANA/PEPC (0.2%) samples in the transmission (1, 2) and reflection modes (3, 4) using an MII-4 optical microscope: (1, 3) without UV light treatment; (2, 4) treated with UV light.

The obtained nanocomposite samples are transparent and homogeneous; no bubbles or inclusions are observed in the MII-4 microscope; this shows that the bubbles in the polymer are smaller than $0.1 \mu m$ and uniformly distributed.

3.2. Optical transmission of the nanocomposite solutions

The spectral dependences of optical transmission T=f(v) for the nanocomposite solutions at different concentrations of ANA-CH against toluene (0.0045 - 0.9 mg/ml) are presented in Fig. 3.



Fig. 3. Optical transmission spectra T=f(v) of the nanocomposite solutions at different concentrations of ANA-CH to toluene (0.0045 - 0.9 mg / ml).

Figure 3 also shows the spectral optical transmission dependence for the used solvent, i.e., toluene. Two peaks with the energy of absorption located at $E_1 = 3.17 \text{ eV}$ ($v_1 = 256000 \text{ cm}^{-1}$) and $E_2 = 3.34 \text{ eV}$ ($v_2 = 27000 \text{ cm}^{-1}$) can be observed; they are assigned to the ANA-CH organic luminophore compound. With increasing concentration, a shift of the transmission spectra towards the infrared region was observed in the dependence T=f(v).

Figure 4 represents the transmission spectra of the composite thin layers PEPC/ANA-CH deposited on glass substrates. An increase in the concentration (0.2, 1, 5, 9, and 12%) shifts the transmission spectra T=f(hv) of the ANA-CH nanocomposites in the red region of the spectrum.

Figure 5 represents the dependence of absorption coefficient plotted in the Tauc coordinates $(\alpha \cdot h v)^n = f(h v)$, n = 1/2 of the NC ANA-CH/PEPC nanocomposites. The energy threshold obtained from the approximation of the linear portion to $(\alpha \cdot h v)^{1/2} = 0$ lies in the range of $E_g = 2.24$ eV to $E_g = 2.34$ eV (for samples with concentrations of 0.1 to 9%), and $E_g = 1.96$ eV for the sample with a concentration of 12%.



Fig. 4. Transmission spectra for thin layers of the ANA-CH/PEPC nanocomposites.





To study the structure of the ANA-CH/PEPC polymeric nanocomposite materials with the luminofore organic composite in the solid phase, we measured the infrared (IR) spectra of these compounds from the console ATR-Attenuated Total Reflectance using a Furie Spectrum 100 FTIR spectrometer (PerkinElmer) in a wavenumber region of v = 4000-650 cm⁻¹ ($\lambda = 2.5-15.4 \mu m$). Optical transmission spectra in the IR region for the ANA-CH/PEPC nanocomposite were measured by dust on stand in KBr and presented in Fig. 6. The transmission spectra *T* (λ) for the PEPC polymer were measured in a similar way. From exclusion or difference these spectra have highlighted the maxima of characteristics only for the ANA-CH nanocomposite (Table 1), which is considered to correspond to luminophore compound 3-(anthracene-9-yl)-1-(4-isothiocyanatophenyl)-prop-2-en-1-one in NC. The absorption maxima obtained can probably be attributed to the units of structure (or chemical bonds) of the luminophore compound in NC (NH, NR, CS, NS, N-CH₂).



Fig. 6. Infrared absorption spectra for nanocomposite ANA-CH/PEPC with a mass concentration of 8% organic luminophores: general ANA-CH CN (a) and details (b).

3.3 Photoluminescent nanocomposite

For ANA-CH dust, only the energy spectrum of photoluminescence was measured. From the graph shown in Fig. 7, at the excitation with ultraviolet light of the nitrogen laser, a maximum of photoluminescence was observed mainly at hv=2.45 eV with several peculiarities (hv=2.38 eV and hv=3.02 eV). According to the graph of the energy dependence, the photoluminescence is asymmetric.

Table 1. Infrared absorption maxima for the nanocomposite with a mass concentration of 8% organic luminophore isothiocyanatopropenone-3-(anthracene-9-yl)-1-(4-isothiocyanatophenyl)-prop-2-en-1-one in NC

<i>v</i> , cm ⁻¹	<i>v</i> , cm-1
477	1380
514.9	1453.2
644.2	1465.4
698.4	1493.4
812.1	1524.9
839.7	1578.8
946.4	1634.7
966.7	1720.5
1038.1	2050.4
1072.2	2297.1
1124.2	2873.3
1147.4	2934
1271	2957.3
1302.5	3027.1
1339.4	3041.5









Measurements of photoluminescence were performed for the luminophore compound and the ANA-CH and ANA-CH/PEPC nanocomposite individually and in the toluene solvent.

At the excitation with a nitrogen laser in the spectrum of photoluminescence of the ANA-CH solution (Fig. 7) at low concentrations, a pronounced maximum is observed at hv = 3.16 eV; with increasing concentration, it is attenuated until the maximum disappears and only the maximum at hv = 2.45 eV remains which increases with increasing ANA-CH concentration in the solution.

In the photoluminescence of the ANA-CH/PEPC nanocomposites (Fig. 8) for samples with the ANA-CH concentration of 5–12%, a photoluminescence maximum at hv = 2.25eV is observed; for concentrations of 0.2–1% for the ANA-CH in toluene, the photoluminescence maximum is observed at hv = 3.18 eV.

4. Results and discussion

The results of multiple determinations show that organic luminophores present in the PEPC material considerably shift the luminescence maximum toward the longer wavelengths (Figs. 7, 8). The photoluminescence spectra for the investigated nanocomposites show a shift of photoluminescence maxima in the red region of the spectra from hv=2.45 eV to hv=2.25 eV. The photoluminescence spectra of the nanocomposites in all cases show a well pronounced maximum which is considered to be attributed to the presence of the CH=CH double bond in the organic compound luminophore with widths of $\Lambda=117$ nm at room temperature and $\Lambda=37$ nm at 78 K. It should be noted that the photoluminescence intensity in the nanocomposites is several times higher than that in the individual ANA-CH compound.

The photoluminescence intensity exhibits a Gaussian distribution pattern for the ANA-CH composition of up to 20% in the nanocomposite. The deviation from the Stokes law of the photoluminescence maximum position to the absorption threshold is in a range of hv = 0.1-0.15 eV. This deviation can be explained by the presence of a hydroxyl group in compound ANA-CH. The model proposed for explanation, which describes the photochromic changes in the photoemission spectra of the nanocomposite polymer, envisaged conditions of excitation and proton transfer in ANA-CH molecules. According to this model, the protons are transferred in the excited state of oxygen from nitrogen position. For this excitation, the first singlet status of arousal is considered to be a strictly acidic state and the state of "nitrogen" is strictly basic. Thus, the isomer (S*) is formed, which in this case is more stable than the isomer (S) until the proton transfer. So, the state S* can be considered as an excited vibrational state S. After transition of the molecule in normal state one is emitted a photon. In the result of this process, the proton is transferred back to the state of oxygen, which is more stable state in this case. It can be considered that the reverse state S is also excited by the vibrational state S*.

5. Conclusions

A preparation technique for thin film nanocomposites ANA-CH/PEPC by a chemical method was developed; their physical properties were characterized by microscopic measurements and the transmission and photoluminescence spectra. A model for excitation of photoluminescence was proposed; it describes the photohcromic shift in the spectra of nanocomposite solutions and thin films.

The obtained nanocomposite films are promising materials for the preparation of various fluorescent dyes and devices, in particular, for manufacturing the luminescent fibers. These nanocomposites can be applied in various area of engineering and optoelectronics as indicators of

UV irradiation and rigid irradiation, for converting these energies in the visible spectra, for light amplifiers and modulators, etc.

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PHONON TRANSPORT IN AMORPHOUS SILICON NANOWIRES

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Abstract

Among the perspective research directions in modern physics, an important role is played by the investigation of amorphous nanostructures [1-3]. The effect of the drop in lattice thermal conductivity in these compounds can be used in thermoelectric applications [4, 5]. It is difficult both theoretically and practically to make in fact a distinction between truly amorphous solids and crystalline solids if the crystal sizes are very small [6]. Even amorphous materials have a certain short-range order at the atomic length scale due to the nature of chemical bonding. Furthermore, in very small crystals, a large fraction of the atoms are located at the crystal surface or near it; relaxation of the surface and interfacial effects distort the atomic positions and decrease the structural order.

1. Introduction

The amorphous state of a matter is characterized in general by the atomic structure with a short-range order, because it is characteristic of crystal structures that long-range order is absent [7-9]. One of the most available materials is amorphous silicon (a-Si); it is a noncrystalline allotropic form of silicon [10]. It can be deposited in thin films at low temperatures onto a variety of substrates, as well as, for example, in the form of nanowires. It provides some unique capabilities for a variety of electronics and phononics. Silicon is a fourfold coordinated atom that is normally tetrahedrally bonded to four neighboring silicon atoms. In crystalline silicon (c-Si) this tetrahedral structure continues over a large range, thus forming a well-ordered crystal lattice. In amorphous silicon this long range order is not present. The atoms rather form a continuous random network. Moreover, not all the atoms within amorphous silicon are fourfold coordinated. Due to the disordered nature of the material, some atoms have a dangling bond. These dangling bonds physically represent defects in the continuous random network and may cause anomalous electric and thermal behaviors.

2. VFF model and results on phonon properties

In this study, theoretical researches of phonon transport in amorphous silicon nanowires (NWs) are presented. Phonon energy dispersions are calculated (see Fig. 1) at various degrees of amorphization of these nanometer structures with dimensions of only a few monolayers (MLs). Amorphization of crystalline quasi-one-dimensional compounds was achieved by varying the parameters of interatomic interactions within the Valence Force Field (VFF) model of crystal lattice vibrations [11, 12]. In the calculation of the energy spectrum of amorphous nanowires, the following mechanisms of interatomic interactions was taken into account: the two-particle

"stretching" $(V_r = \frac{\kappa_r}{2} \sum_{j} \delta r_{ij}^2)$, the three-particle "bending" $(V_{\theta} = \frac{\kappa_{\theta} r_0^2}{2} \sum_{j,k} \delta \theta_{ijk}^2)$, "stretchingstretching" $(V_{rr} = \kappa_{rr} \sum_{j,k} \delta r_{ij} \delta r_{jk})$, "stretching-bending" $(V_{r\theta} = \kappa_{r\theta} r_0 \sum_{j,k} \delta r_{ij} \delta \theta_{ijk})$, and the fourparticle "bending-bending" $(V_{\theta\theta} = \kappa_{\theta\theta} r_0^2 \sum_{j,k} \delta \theta_{ijk} \delta \theta_{jkl})$.

In the work as a result, there was used VFF model in phonon energy spectrum calculations, where the atomic force field V describes the short-range covalent bond:

$$V = V_r + V_{rr} + V_{\theta} + V_{r\theta} + V_{\theta\theta} , \qquad (1)$$

the interaction parameters mentioned above κ_r , κ_{rr} , κ_{θ} , $\kappa_{r\theta}$, and $\kappa_{\theta\theta}$ are short-range force constants, r_0 is the equilibrium interatomic distance. In the given expression for the potential energy, subscripts j, k, and l denote the atoms, with which the considered atom i forms various types of interatomic interactions. The force constants $\Phi_{\alpha\beta}(i, j)$ are introduced by

definition $(\Phi_{\alpha\beta}(i,j) = \frac{\partial^2 V}{\partial u_{\alpha}(i)\partial u_{\beta}(j)})$, and they are used to form the equations of motion

$$M\omega^2 u_{\alpha}(\vec{q},i) = -\sum_{\beta} D_{\alpha\beta}(i,i) u_{\beta}(\vec{q},i) + \sum_{j,\beta} D_{\alpha\beta}(\vec{q},i,j) u_{\beta}(\vec{q},j), \qquad (2)$$

where \vec{q} is the wave vector, ω^2 and \vec{u} are eigenvalues and eigenvectors of the confined disordered system, M is the atomic mass, D are elements of the dynamical matrix $D_{\alpha\beta}(i,i) \equiv \sum_{j} \Phi_{\alpha\beta}(i,j); \quad D_{\alpha\beta}(\vec{q},i,j) \equiv \sum_{j} \Phi_{\alpha\beta}(i,j)e^{i\vec{q}\vec{n}(j,i)}$.





Fig. 1. Phonon energy spectra of the crystalline silicon 8MLx8ML nanowire (a) and the same amorphous nanowires (b–d) with different increasing variations of random force distribution in [100] crystallographic direction calculated within VFF model.

It can first be noted from Fig. 1 that the maximum energy of optical phonons increases from about 64 meV in the case of the crystalline nanowire to more than 85 meV for the amorphous nanostructure with 90% disordering independently of the force parameters of interatomic interactions. Thus, in the investigated quasi-one-dimensional nanostructures, the number of the so-called "heavy" low-velocity quanta of vibrational motion of the atoms increases. In addition, on closer inspection, it is clear that, if in the nanowire (a) even phonons with energies around 53 meV have got visible nonzero group velocities, then for the amorphous nanoelement (d) the entire range of the spectrum from about 35 meV and above is almost nondispersive; it will be shown below that this could not but affect the lattice thermal conductivities, their falling in amorphous size-limited nanometer structures.

Calculations showed that for the studied nanostructures the following formulaic (3) and numerical (4) representations of limit repetitions (*rep* in indicated expressions) can be written for reliable determination of the phonon densities of states (subscript notation *DOS*, see Figs. 2, 3) and the lattice thermal conductivities (index κ , see Figs. 4, 5) of amorphous nanowires at the highest studied scatter in force parameters of interatomic interactions (*amorph* \rightarrow 90%). For other degrees of amorphization with weaker disordering of the dynamic matrix, these repetitions are obviously more than sufficient in determining the investigated physical quantities:

$$\lim_{amorph\to 0\%} rep_{DOS}^{for all nanostructures} = \lim_{amorph\to 0\%} rep_{\kappa}^{for all nanostructures} \equiv 1$$
(3)

$$\lim_{amorph\to90\%} rep_{DOS}^{NW\,8x8\,MLs} \approx 120; \quad \lim_{amorph\to90\%} rep_{\kappa}^{NW\,8x8\,MLs} \approx 15$$
(4)



In the calculations of phonon densities of states for a smoother and more accurate stroke of density dependences, it is necessary to increase the partition of the phonon energy's scale and repeated calculations in the case of amorphous nanowires. It is shown (see Fig. 3) that the curves of phonon densities considerably vary in amorphous nanowires compared to crystalline nanowires and get a smoother ride. The acoustic density range slightly varies with increasing degree of amorphization and forms the so-called boson peak at a high disorder of dynamic matrices [1-3], while the optical part of the dependence flattens and broadens to higher energies.





3. Results on thermal conductivity of the disordered system

The thermal conductivity of a system is atomically determined by revealing how the atoms composing the system interact. There is an approach for calculating the thermal conductivity of a system. The approach is based on the relaxation time approach. Due to the anharmonicity within the crystal and amorphous potentials obtained by the variation of dynamical matrixes, the phonons in the system are known to scatter. There are two main mechanisms for scattering: boundary scattering, where the phonon interacts with the boundary of the system, and phonon-phonon scattering, where the phonon breaks into two lower energy phonons or collides with another phonon and merge into one higher energy phonon.

The heat flux along a nanowire can be calculated according to the expression [13-15]

$$\vec{W} = \sum_{s,\vec{q}} \vec{v}(s,\vec{q})\hbar\omega_s(\vec{q})N[\vec{q},\omega_s(\vec{q})] = \sum_{s,\vec{q}} \vec{v}(s,\vec{q})\hbar\omega_s(\vec{q})n[\vec{q},\omega_s],$$
(5)

where $\vec{v}\hbar\omega$ is the energy carried by one phonon and $N(\omega, \vec{q})$ is the number of phonons in the flux.

Taking into account the one-dimensional density of states and switching from summation to integration, we can obtain the phonon thermal conductivity in nanowires in the relaxation time approximation [16, 17]:

$$\kappa_{ph} = \frac{1}{2\pi\hbar k_B T^2 d_x d_y} \sum_{\alpha,s} \int_{0}^{\varepsilon_{\text{max}}} (E_s^{\alpha})^2 \langle V(\omega) \rangle N_b(\omega) \tau_{tot}(\omega_s^{\alpha}) \frac{\exp(\frac{E_s^{\alpha}(q)}{k_B T})}{\left(\exp(\frac{E_s^{\alpha}(q)}{k_B T}) - 1\right)^2} dE,$$
(6)

where $\langle V(\omega) \rangle$ is the average group velocity of phonons, $N_b(\omega)$ is the number of phonon branches crossing frequency ω , and $\tau_{tot}(\omega_s^{\alpha})$ is the total phonon relaxation time. In thermal conductivity calculation, the following phonon scattering mechanisms in nanowires are considered: phonon-phonon scattering and boundary scattering.

The total phonon relaxation time is calculated by the formula:

$$1/\tau_{tot} = 1/\tau_U + 1/\tau_B,$$
(7)

where τ_U is the relaxation time for Umklapp processes; τ_B is the relaxation time for surface scattering generalized for the case of a quantum wire:

$$\frac{1}{\tau_B} = \frac{1-p}{1+p} \left(\frac{1}{d_x} + \frac{1}{d_y}\right) \frac{|v_s^{\alpha}(q)|}{2},\tag{8}$$

where d_x and d_y are the cross-section sizes of the nanowire; $v_s^{\alpha}(q)$ are the group velocities of phonon modes with wave vector q; p is the surface scattering parameter characterizing the surface quality of the nanowire, i.e., its roughness, and calculated by comparing the heat

conduction theory with experimental data.



Thermal conductivity is described by the Boltzmann equation with the relaxation time approximation in which phonon scattering is a limiting factor. The phonon mean free path has been directly associated with the effective relaxation length for processes without directional correlation. Thus, if V_g is the group velocity of a phonon wave packet, then the relaxation length l is defined as follows: $l = V_g \tau$, where τ is the characteristic relaxation time. Thermal conductivity of the silicon nanowire with the square cross-section of 8 x 8 monolayers, which is calculated at room temperature (see Fig. 5), decreases from about 4.5 W/m·K for the crystalline silicon nanowire to 2.8 W/m·K for the amorphous nanowire with a random scatter in values of parameters of interatomic interactions.



Fig. 5. Lattice thermal conductivities of the crystal nanowire 8 x 8 MLs of silicon and nanowires with the following degrees of amorphization: +/- 25, 50, 90 % (samples of 15 attempts).

4. Conclusions

In conclusion it can be summarized that the drop in the lattice thermal conductivity of silicon crystalline nanowires and an even greater effect in amorphous quasi-one-dimensional nanostructures are explained by the quantization of the phonon spectrum and the strong scattering of phonons at the boundaries of nanowires. A stronger modification of the phonon properties can be achieved in silicon amorphous nanowires with disordered bond forces. The obtained results are in good agreement with the experimentally determined vibrational densities of states of disordered systems showing a low-frequency excess, the so-called boson peaks. Finally, it should be noted that, in this paper, the surface phonon scattering in amorphous nanostructures was considered to be approximately identical to crystalline nanowires, and further research will be dedicated to clarifying the effect of this scattering mechanism on the thermal conductivity of these nanostructures.

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GROWTH OF WIDE BAND-GAP II-VI COMPOUND SUBSTRATES WITH CONTROLLED ELECTRIC PARAMETERS

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Abstract

Features of the growth of large ZnSe and ZnS single crystals by a physical vapor transport with subsequent doping by thermal diffusion from Zn+Al melt, as well as ZnO single crystals by the chemical vapor transport technique with the use of HCl as a transport agent and a dopant source, are discussed in the present paper. Based on the investigation of electric and luminescent properties of these samples with various doping level, the prospects of the used techniques for obtaining large-area substrates with controlled electric parameters are estimated.

1. Introduction

Wide band-gap II-VI semiconductors, such as ZnSe, ZnS, and ZnO, are promising materials for application in photonics, optoelectronics, and spintronics, in particular, as solar energy converters, light emitting devices, substrates for obtaining nanoporous materials. Similar nanotemplates have a wide potential to produce sets of nanowires and nanotubes of various materials with defined values of diameter and length [1]. It is necessary to develop new technologies for obtaining these substrates with controlled electric parameters varied in a wide range for more effective usage of these materials.

Commercially available n-ZnSe and n-ZnS substrates have a low conductivity that hampers the preparation of pores of a submicron size on their basis [1]. ZnO crystals with moderate conductivity are usually obtained by hydrothermal methods. However, the presence of mobile Li or K ions in these materials limits their utilization in electronics [2].

In this respect, the growth of large II-VI single crystals with a perfect structure and controlled electric parameters is a topical problem awaiting solution. The present work is dedicated to technological aspects of growing II-VI single crystals by means of vapor transport method in sealed chambers and their doping.

2. Experimental techniques

The growth of ZnSe and ZnS single crystals was carried out by the seeded physical vapor transport method in vacuum. The influence of the growth temperature, undercooling, growth rate, growth chamber construction, and furnace temperature profile on the structural perfection of the grown crystals was investigated. The growth temperature was varied from 975 to 1080°C, undercooling was varied from 0.5 to 10°C, the growth rate changed from 0.5 up to 10 mm/day. Zn annealed in Se (or S) vapors was used as a source. The synthesized material was then purified

by sublimation in sealed ampoules.

Non-seed growth of ZnO single crystals was carried out in evacuated quartz ampoules at 1000°C by the chemical vapor transport method with HCl as a transport agent. The density of loaded HCl was varied between 0.07 and 1.3 mg/cm³. Zn annealed in an O atmosphere was used as a source.

The crystals obtained by the physical transport method were cut into substrates and doped by thermal annealing in a Zn+Al melt at 900°C for 100 h. The Al content in the melt was varied between 0 and 2 at %. The melt was transferred to the other end of the ampoule after annealing, the samples were rapidly cooled and then mechanically and chemically polished (BrCH₃ solution, boiling NaOH).

Electric parameters were determined from the Hall effect measurements using a six-probe method. Photoluminescence (PL) was excited by a nitrogen laser ($E_{excit} \approx 3.68 \text{ eV}$, ~ 10 mW/mm²) and registered in a range between 350 and 800 nm using a monochromator with reciprocal dispersion of 1.4 nm/mm.

3. Experimental results

3.1. ZnSe crystals

The most optimal conditions for the growth of ZnSe single crystals by the physical transport method correspond to a growth temperature of 1050°C and undercooling of 2-3°C, which gives a growth rate of 1-1.5 mm/day. These temperature regimes, as well as the use of seeds free from subgrain boundaries and having a dislocation density of 10^4 cm⁻³ and less, provide the growth of crystals free from voids having a volume up to 4 cm³ (Fig. 1c). Twins and subgrain boundaries in these samples are absent or observed only on the periphery [3].



Fig. 1. Furnace temperature profiles: classical parabola-like (a), with minimum (b). External view of ZnSe crystal grown using temperature profile with minimum (c).

The use of classical parabola-like axial temperature profile of the furnace (Fig. 1a) results in the effect of grown crystal (seed) attachment to a flat ampoule bottom and crystal deformation during cooling [3, 4]. Thus, practically complete destruction of both the seed and the lower part of the crystal on depth up to 5 mm happens. The dislocation density in these strained samples is $10^{5}-10^{6}$ cm⁻².

The specially developed temperature profile of the furnace allows eliminating the attachment of crystals to the walls of the growth chamber and minimizing their deformation in

the post-growth cooling process. As a result, the crystals free from twins and subgrain boundaries with a dislocation density of less than 10^4 cm⁻² are obtained (Figs. 1b, 1c) [3].

Modification of Al shallow donor impurity concentration in the annealing medium allows obtaining uniformly doped substrates with an area of no less than 3 cm² (Fig. 2a) with a controlled charge carrier concentration (n) and electric conductivity (σ) varied in ranges of $2 \cdot 10^{15} - 2 \cdot 10^{18}$ cm⁻³ and $1 \cdot 10^{-2} - 20$ ($\Omega \cdot \text{cm}$)⁻¹, respectively (Fig. 2b). The mobility of charge carriers (μ) in ZnSe:Al samples is about 100 cm²/(Vs). Maximum values of electric parameters and optimum impurity concentration (1 at %) do not coincide with the data given in [5]. The decrease of electric conductivity at the Al concentration of more than 1 at % is attributed to the generation of compensating deep associative acceptors "zinc vacancy–Al impurity", which are responsible for intensive self-activated (SA) PL band (Fig. 3b) [6]. For moderate Al concentrations ≤ 2 at %, the optimized technology of doping annealing and cooling allows eliminating the effect of destruction of the substrates of various areas by Zn+Al melt rest. For higher impurity concentrations, a partial attachment of the melt to the samples and their destruction in the process of cooling take place.



Fig. 2. External view of high-conductive ZnSe substrates (a) and electric parameters for ZnSe samples versus impurity concentration in the annealing Zn+Al melt (b).



Fig. 3. Electric conductivity of n-ZnSe, n-ZnS and n-ZnO single crystals with various doping levels (a); normalized PL spectra of ZnSe:Al:Zn, ZnS:Al:Zn (1 at.% Al in Zn+Al melt) and ZnO:HCl ([HCl] = 0.7 mg/cm³) single crystals (b).

3.2. ZnS crystals

ZnS single crystals are also grown by means of a physical vapor transport method. The structural perfection of the samples grown under the same conditions as ZnSe samples (a growth temperature of 1050°C, a growth rate of 1-1.5 mm/day) is significantly lower (they have a high density of subgrain boundaries). It is attributed to both lower vapor pressure (about 0.3 torr, while this value for ZnSe is about 1 torr [6]) and liability of this material to polytypism [6]. The crystals of higher quality may be obtained at the present temperature for growth rates less than 0.5 mm/day. The most optimal conditions for doping by annealing in Zn+Al melt (900°C, 100 h, 0.5 at % Al) allows obtaining the moderately conductive substrates with charge carrier concentration of $2 \cdot 10^{16}$ cm⁻³ and electric conductivity of 0.3 (Ω ·cm)⁻¹ (Fig. 3a).

PL spectra of ZnS:Al samples consist of the bands of SA emission (Fig. 3b), the intensity of which is 150 times higher relative to the same emission of ZnSe samples.

3.3. ZnO crystals

Owing to the extremely low value of the ZnO saturated vapor pressure, the growth of ZnO single crystals is easier to implement by chemical vapor transport with the use of HCl as a transport agent, for instance. An elementary calculation based on thermodynamic constants of reaction substances [7]:

$ZnO + 2HCl \leftrightarrow H_2O + ZnCl_2$ (gas),

indicates high pressure of reaction products that reaches the value of 14·p(HCl) atm at 1000°C.

The use of HCl is favorable for the non-seed growth of individual single crystals, which have minimal surface area contacted with the walls of growth chamber. As a result, the crystals are not subject to deformations during a post-growth cooling even in the case of classical parabola-like temperature profile. However, one of the disadvantages of this method is a great value of the ratio of the crystal length to its diameter (Fig. 4a).



Fig. 4. ZnO:HCl crystal grown by a non-seed method at 1000°C ([HCl] = 1.3 mg/cm³) (a); electric parameters of the samples versus HCl content on the growth medium (b).

Density variation of loaded HCl, which is a source of Cl and H shallow donor impurities in ZnO crystals [8-10], from 0.07 to 1.3 mg/cm³ allows obtaining the samples with controlled charge carrier concentrations and electric conductivity in the ranges of $(2-6)\cdot10^{17}$ cm⁻³ and 0.5–9 (Ω ·cm)⁻¹ respectively (Fig. 4b). This material is less subject to self-compensation since the

additional annealing in the medium enriched with Zn vapors has no strong influence on charge carrier concentration. A small contribution of SA emission to the total intensity of PL spectra indicates a low density of compensating centers (Fig. 3b).

4. Conclusions

The growth of the single crystals by the physical vapor transport method with the subsequent doping by annealing in Zn+Al melt is an effective procedure for obtaining n-ZnSe substrates with controlled electric parameters. The obtaining of high-conductive n-ZnS substrates using this method is limited by a self-compensation effect.

The use of HCl as a chemical transport agent provides obtaining the n-ZnO single crystals, which are not subject to any substantial destruction in the process of post-growth cooling and exhibit the minimum level of self-compensation. The use of this method is limited to a great value of the ratio of the crystal length to its diameter.

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GROWTH OF ZnO CRYSTALS BY CVT METHODS

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Abstract

Features of the growth of ZnO single crystals by chemical vapor transport with the use of H_2 , HCl, $H_2 + HCl$ mixture, and CO as transport agents and dopant sources are discussed in the present paper. Based on the investigation of electrical, luminescent, and optical properties of these samples with various doping level, the prospects of the used techniques for the obtaining of large-area substrates with controlled parameters are estimated.

1. Introduction

Zinc oxide (ZnO) crystals draw attention due to relatively low price and the prospects of their utilization in various applications. Commercially available crystals and corresponding substrates are usually obtained by hydrothermal methods. However, the presence of mobile Li or K ions in these materials limits their utilization in electronics [1]. In this respect, the elaboration of growth technology for ZnO single crystals with controlled parameters and impurity composition by means of chemical vapor transport in sealed chambers is of great interest.

2. Experimental techniques

ZnO single crystals were grown in evacuated sealed quartz ampoules at 1000°C and undercooling of 10-20°C by means of a chemical vapor transport method. H_2 , HCl, H_2 +HCl mixture, and CO were used as transport agents. The density of loaded HCl was varied from 0.07 up to 1.3 mg/cm³. Hydrogen pressure was maintained at a level of 1 atm. An atmosphere of CO was obtained as a product of reaction between ZnO and carbon. The material synthesized by means of annealing of high pure Zn in an atmosphere of O was used as a source for crystal growth.

Electrical parameters were determined from the Hall effect measurements using a six-probe method. Photoluminescence (PL) was excited by a nitrogen laser ($E_{excit} \approx 3.68 \text{ eV}$, ~ 10 mW/mm²). PL and transmission spectra were registered in a range between 350 and 800 nm using a monochromator with a reciprocal dispersion of 1.4 nm/mm.

3. Experimental results

A ZnO saturated vapor pressure is extremely low even at a temperature close to the softening point of quartz (~1150°C) and is no more than 10^{-2} torr. Due to this fact, the growth of these crystals by the physical transport method is impossible. HCl, H₂, and CO substances can be

used as chemical transport agents. An elementary calculation based on thermodynamic constants (namely, formation enthalpy and entropy) of reaction substances [2]:

$$ZnO + H_2 \leftrightarrow H_2O(gas) + Zn(gas),$$
 (1)

$$ZnO + 2HCl \leftrightarrow H_2O(gas) + ZnCl_2(gas),$$
 (2)

$$ZnO + CO \leftrightarrow CO_2 + Zn(gas)$$
 (3)

indicates high pressure of the products of reactions (1)–(3), which reach the values of $1.7 \cdot (p(H_2))^{1/2}$, $14 \cdot p(HCl)$ and $0.8 \cdot (p(CO))^{1/2}$ (all values of pressure are expressed in atm) at 1000°C, respectively. The high pressure is favorable for crystal growth by the chemical transport method. The factor determining the high rate of mass transport by opposing chemical reactions is a high value of reaction enthalpy [2], which is 54, 5, and 45 kcal/mol for reactions (1)–(3), respectively.

3.1. H₂ transport agent

The use of H_2 as a transport agent provides a high growth rate of the crystals (1-2 mm/day), which compactly fill the growth chamber volume. However, these crystals are characterized by pore formation; the strong mechanical contact between ZnO:H and the quartz walls of the growth chamber leads to the destruction of both ampoules and grown crystals during a post-growth cooling. The effective low-temperature edge PL of these materials exhibits exciton emission caused by shallow hydrogen donors [3, 4] (Fig. 1).



Fig. 1. Low-temperature PL spectra of crystals grown with the use of various chemical agents. ZnO:CO crystals were annealed in vacuum.

3.2. HCl transport agent

The use of HCl as a chemical transport agent is favorable for a growth of individual single crystals in sealed quartz ampoules, which have a minimal surface area contacted with the walls of growth chamber. As a result, the crystals are not subject to deformations during a post-growth cooling (Fig. 2a). The growth of the individual and well faceted crystals is caused by high density of the products of gas-transport reaction (2) (see the beginning of Section 3). Disadvantages of the method are the large ratio between the crystal length and diameter and the low growth rate at a high temperature gradient (~10°/cm). The low growth rate is expected because of the low value of the enthalpy of reaction (2).

Modification of density of loaded HCl, which is a source of shallow Cl and H donor

impurities in ZnO crystals [3-5], in a range of 0.07-1.3 mg/cm³ allows obtaining the samples with controlled parameters such as free electron concentration (n) and electrical conductivity (σ) varied in ranges of (2–6) \cdot 10¹⁷ cm⁻³ and 0.5–9 (Ω ·cm)⁻¹ (Fig. 2c), respectively.

Low-temperature PL spectra of ZnO:HCl crystals consist of long-wavelength emission that can be attributed to intrinsic defects of zinc vacancies (V_{Zn}) [3], which are generated by compensation effect in the presence of shallow H and Cl donors (Fig. 1). Increasing temperature up to 300 K promotes a decrease in the long-wavelength emission contribution to near zero and an increase in the edge radiation contribution. The edge PL intensity decreases with increasing doping level (Fig. 2d). ZnO single crystals are less subject to self-compensation since the additional annealing in the medium enriched with Zn vapors has no strong influence on electrical conductivity, concentration and mobility (μ) of charge carriers (Fig. 3b).



Fig. 2. ZnO:HCl crystals grown with the use of HCl (a) and H₂+HCl mixture (b), electrical parameters versus HCl contents in the growth medium (c) and edge PL spectra of ZnO:HCl crystals with various HCl contents in the growth medium.

3.3. H₂+ HCl transport agent

It is established that the use of H_2 + HCl mixture as a transport agent has the advantages, such as a high growth rate (1–2 mm/day) and compact filling of the ampoule volume with high-conductive n-ZnO:H:Cl crystals, which are not subject to any substantial destruction during post-growth cooling (Fig. 2b). The electric properties of these crystals are comparable to the crystals grown with the use of solely HCl vapors.

3.4. CO transport agent

The rate of mass transport for ZnO is independent on location of loaded carbon in the ampoule; chemical transport agent can be in close vicinity to the source of crystal growth (I) or spatially separated from both the source and the growing crystal (II). If the interaction between ZnO and C was solely limited by the reaction

$$ZnO + C \leftrightarrow CO + Zn(gas),$$
 (4)

the rate of ZnO mass transport by chemical reactions in case II would be even lower than that by the physical transport method because of a long period of time necessary for ZnO vapors to reach the distant source of carbon (the carbon pressure at the experiment temperatures can be neglected). Effective transport of ZnO in the presence of carbon for various configurations of growth volume indicates reaction (3) with participation of CO and CO_2 . The complete equation for ZnO chemical transport reaction in the presence of C is as follows:

$$\{ZnO + C \rightarrow CO + Zn(gas)\} + ZnO \leftrightarrow CO_2 + 2 \cdot Zn(gas).$$
(5)

Reaction (5) differs from reaction (3) by higher concentration of Zn vapors that influences the properties of grown crystals, as seen below.

ZnO crystals grown in the presence of CO have the best structural perfection (they exhibit the absence of microscopic cavities) (Fig. 3a). However, their optical density within the visible spectrum range and PL intensity are extremely low, that can be caused by deep centers based on intrinsic defects of oxygen vacancies (V_0) [3] appeared due to a high Zn vapor pressure in the growth medium. These properties are characteristic for the crystals obtained by other methods and subsequently annealed in a high-density atmosphere of Zn vapors.



Fig. 3. ZnO:CO:vacuum crystal (a), electrical parameters (b), PL spectra (c), and transmission spectra (d) for ZnO:CO crystals before and after annealing in various media.

The optical, PL and, to a certain degree, electrical properties of ZnO:CO crystals can be varied by the deviation from stoichiometry (Fig. 3). Annealing in Zn vapors at the pressure of 1 atm has no essential influence on the properties of ZnO:CO crystals initially saturated with zinc. At the same time, the annealing in vacuum or oxygen leads to an increase of optical transparency and PL intensity (Figs. 3c, 3d); therefore, ZnO:CO:vacuum crystals predominate in these parameters over the crystals grown by other methods. In particular, these crystals are characterized by the greatest contribution of the edge radiation into the low-temperature PL spectra (Fig. 1). An essential decrease in the conductive properties of the samples due to changing concentration of V_0 , V_{Zn} intrinsic defects occurs only in the case of oxygen enrichment of the crystals (Fig. 3b).

4. Conclusions

The use of hydrogen as the chemical transport agent for growing ZnO crystals is limited by low structural perfection of obtained crystals and their destruction during a post-growth cooling because of a strong mechanical contact between the grown material and the quartz walls of the growth chamber.

The use of HCl is limited by a low growth rate at high temperature gradients and the large ratio between the crystal length and diameter.

The use of H₂ + HCl mixture and of CO as transport agents provides the growth of n-ZnO

single crystals characterized by a high growth rate (1-2 mm/day) and compact filling of ampoule volume. Optical, PL and, to a certain degree, electric properties of these crystals can be varied in wide ranges by changing the impurity concentration or the deviation from stoichiometry.

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COMPARISON OF UV IRRADIANCE DATA FROM OMI WITH GROUND-BASED OBSERVATIONS AT THE CHISINAU (KISHINEV) SITE, MOLDOVA

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Abstract

Erythemal UV irradiance data obtained from ground-based observations are used for validation of the UV products from overpass nadir measurements performed with the Ozone Monitoring Instrument (OMI) on-board the EOS Aura satellite platform. UV ground data were obtained with using of broadband radiometers (model UV-S-B-C) at the ground-based solar radiation monitoring station in Kishinev (Chisinau), Moldova during the period from 2004 to 2009. OMI UV final products were derived by the OMI's international team with using of the TOMS-like algorithm. Erythemal dose rate at time of overpass (OEDR) and at local noon time (EDR@noon) and erythemal daily dose (EDD) were taken into analysis. Interval of 1-min averaging of erythemal UV irradiance measurements with ground-based broadband radiometer gives an possibility to make quasi-synchronous observations with OMI overpass measurements. Validation showed that OMI overpass UV data underestimate UV data from ground observations for all sky (AS) and cloud-free (CF) conditions. Results of validation showed a bias value of -15.8% under AS and -18.3% under CF conditions. Concerning EDR@noon data bias was -15.8% under AS and -17.7% under CF conditions; taking into account EDD data some increasing in bias was observed (with a value of -21.5% and -19.9% under AS and CF conditions, respectively). The effect of aerosols on UV irradiance was studied in terms of aerosol optical depth (AOD@340 nm) retrieved from the AERONET, NASA/GSFC. It was observed that there is a high correlation of ~ 0.79 and that a larger relative difference corresponds to a larger value of AOD@340 nm.

1. Introduction

The study of variability of the UV radiation levels at the Earth's surface has been of intense interest in the last decades; the key issues were discussed and summarized in report [1]. This interest is due to issues concerning the well-known problem of ozone depletion [2]. The solar UV radiation passing through the atmosphere has a significant impact on human life, flora and fauna, and terrestrial and aquatic ecosystems. This impact may have both a positive and negative effect. For example, a negative effect is that high exposure to UV radiation is fraught with high risk of skin cancers, eye diseases (cataracts), and suppression of human immune system. In addition, UV radiation is involved into the complex chemical reactions with the vehicles exhausts resulting to the formation of smog, which is responsible for eyes and respiratory diseases.

Atmospheric ozone absorption, cloudiness, and aerosols are the main factors that affect UV radiation along the path from the top of the atmosphere to the Earth's surface. It should be noted that these factors demonstrate significant variability on spatial and time scales. To investigate UV irradiance variability on the spatial and temporal scales, both ground-based networks of spectral and broadband photometers and some satellite platforms with unique optical spectral instruments

are used. Ground-based or direct observations can be fulfilled at the small confined areas of Earth's surface. It is a great limitation. At the same time, satellite observations provide daily mapping with a global coverage from a single instrument on-board. The most known among the satellite instruments are the Total Ozone Mapping Spectrometer (TOMS)-like on-board the Earth Probe platform and the Ozone Monitoring Instrument (OMI) on-board the NASA EOS AURA platform. OMI instrument [3, 4] is the successor to the TOMS instruments and is in operation since September 2004.

Reliability of satellite UV irradiance data depends upon the accuracy of measurement by using of the unique spectral optical instruments aboard the satellite, models of atmosphere and atmospheric composition, which are applied in computer modeling and retrieving algorithms for data processing. In addition to instrumental errors, which affect the satellite UV measurements, there are modeling uncertainties in retrieving UV irradiance at the Earth's surface from backscattered UR radiation measured on the satellite orbit. In this connection, validation of satellite data through the ground-based direct UV observations is an extremely important condition of improving the quality and accuracy of UV irradiance data retrieved from satellites. The first thorough validation of the OMI UV products relative to the ground-based UV measurements can be found elsewhere [4]. Results of the study showed a good agreement with the ground spectral UV measurements. Results of validation OMI UV data versus the ground UV observations obtained at a number of stations in Europe can be found elsewhere [5-12]. In most cases, the comparison of OMI UV data with the ground-based UV data showed a good compliance, but having positive biases with values of a variable range for different locations.

Within the framework of this paper, we fulfilled validation of the UV irradiance data retrieved from OMI overpass measurements at the Aura satellite platform with the UV data obtained from direct observations at the ground-based station in the Institute of Applied Physics (IAP), Kishinev (Chisinau), Republic of Moldova in the course of period from 2004 to 2009. Ground-based erythemal UV data from a broadband radiometer were used in validation. Validation of OMI UV data through ground-based measurements will be fulfilled for erythemal UV irradiances or dose rates measured at the time of OMI overpass and at local noon time, and also for erythemal UV daily dose. Uncertainties in validation between OMI and ground-based data due to cloudiness and aerosol variability will be examined.

2. Measurement approach

Erythemal UV data retrieved from measurements of spectral components of solar radiation reflected or backscattered from the Earth's surface or from the top of clouds by using an OMI instrument [4] are utilized in this analysis. OMI is a nadir viewing ultraviolet/visible solar backscatter spectrometer in a wavelength range of 270 to 500 nm, and it is placed on-board the Aura satellite platform. UV irradiance data were retrieved from satellite spectral images of the Earth's surface with high spectral and spatial resolution. The small pixel size of the image corresponds to a dimension of 13 x 24 km² (for nadir viewing) of the area projected onto the Earth's surface. The instrument has a 2600 km wide viewing perpendicular to the line of flight of the space-borne AURA satellite platform. A more detailed description of the OMI instrument, some procedures of data processing, QC/QA procedures, calibration and characterization can be find elsewhere [3, 4]. Theoretical basis of the OMI algorithm for deriving the UV irradiance from spectral radiances scattered and reflected from the Earth's surface reposes on the TOMS-like algorithm (ver.8 is the last version) applied to OMI data processing, and it is described in detail elsewhere [13-16].

UV irradiance datasets retrieved from OMI overpass measurements are compared with the data from ground observations carried out with the UV broadband solar radiometers at the ground-based solar radiation monitoring station in the IAP. Ground observations of UV irradiance are being continuously carried out by the Atmospheric Research Group (ARG), IAP. Global and diffuse UV irradiances are measured with two broadband UV radiometers UV-S-B (Kipp&Zonen) installed at the radiometric complex. The complex is a key element of the groundbased solar radiation monitoring station at the Institute [17]. The station is situated in an urban environment of Kishinev (Moldova) and mounted at the Institute's building roof. Time-series of UV radiance at the ground station (φ =47.00⁰N, λ_{0} =28.82⁰E, h=205 m a.s.l.) started in September 2003. In addition, diffuse, direct, and global broadband solar radiation (280-3000 nm), global and diffuse UV-B (280-315 nm), global UV-A (315-400 nm) and PAR (400-700 nm) radiation, atmospheric IR radiation (4-42 µm), total column ozone content X, DU, and main surface meteorological parameters are measured at the ARG ground station [17]. Aerosol optical characteristics in a column of the atmosphere have been measured by using a Cimel-318 sunphotometer within the framework of the AERONET project, NASA/GSFC [18] since 1999. Datasets of daily means of aerosol optical characteristics are used for evaluation of aerosol effect upon the validation results. UV irradiance data collected over the period of OMI satellite and ARG ground-based observations from 2004 to 2009 are used in this analysis.

3. Data analysis

Respective UV irradiance data from direct ground observations were processed and compiled into the arrays of data; hereinafter, these datasets will be referred to as ARG. Multi-year series of UV data retrieved from the OMI measurements at the Aura satellite platform since October 2004 are utilized in validation. OMI UV final products are available at the Aura Validation Data Center (AVDC) web-site [19].

Summary of statistics concerning the validation of the OMI UV irradiance data in comparison with the ARG ground observations are presented in Table 1. The following parameters are taken in account: n is the number of days representing pairs of ARG and OMI of synchronous observations taken into account in comparison; R is the correlation coefficient between ARG ground and OMI data; the slope of regression line of the scatterplot;

b (in %) is the mean relative difference or bias defined as $b = \frac{1}{n} \sum_{i=1}^{n} (\frac{y_i - x_i}{x_i}) \cdot 100$; the root mean squares (RMS) expressed in mW·m⁻² or J·m⁻², and in % were computed as follows:

$$\sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - x_i)^2}$$
 and $\sqrt{\frac{1}{n}\sum_{i=1}^{n}(\frac{y_i - x_i}{x_i})^2} \cdot 100$, respectively.

Variables y_i and x_i represent the pairs of data from the OMI overpass (y_i) and ARG ground (x_i) observations of UV irradiance. OMI UV products include erythemal dose rate at time of overpass (OEDR) and at local noon time (EDR@noon), and erythemal daily dose (EDD). These datasets for coordinates (ϕ, λ_0) of the ARG ground station were retrieved from the AVDC database [19]. The ARG UV data consist of 1-min averaged measurements of erythemal UV irradiance by using of UV-S-B-C broadband radiometers. These datasets were processed taking into account the respective lookup tables (X,θ) with a matrix of adjustment factors computed for the set of values of total ozone content X and solar zenith angles θ . The EDRs and EDD data were obtained by weighting UV irradiance with the standard erythemal action spectrum CIE-1987 [20] and by integration over the spectral wavelength range of 280-400 nm.

The ARG datasets were collected at the ground station for the period from October 2004 to November 2009 and consist of some parameters, such as instantaneous (OEDR and EDR@noon) and daily doses or daily totals (EDD) of erythemal UV irradiance measured both under all sky (AS) and cloud-free (CF) conditions. The scatter plots and time series presented below consist of data from the OMI overpass measurements versus to the ARG ground-based direct UV irradiance measurements. To keep the condition of spatial homogeneity of ARG and OMI data for validation, we introduce the following criterion of spatial restriction: pairs of ARG and OMI UV data will be taken into consideration only if the normal from a point with coordinates of the ARG ground station to the OMI tracking line is r< 24 km; hereinafter, the measurements will be referred to as point ones. At the same time, it was clearly pointed in [8, 10] that validation results should be considered with caution because of using the different spatial scales: ground-based measurements are fulfilled at a fixed point, whereas the satellite measurements have the spatial resolution of one pixel, which covers different areas from nadir viewing to the edges of swath viewing. Within these areas, UV measurements are affected by cloud and aerosol variability. Meanwhile, the sky condition factor, namely cloudiness variability, remains to be the main source of uncertainties and disagreements in validation of OEDR, EDR@noon, and EDD. This was due to the fact that sky conditions or cloud variability at the time of OMI overpass, as a rule, differ from those at the time of local noon or in the course of all day at which OEDR, EDR@noon, and EDD are measured and calculated. Time sampling with 1-min averaging applied for ground-based measurements of UV irradiance is sufficient to consider ARG ground and OMI overpass observations to be quasi-synchronous within the time window of ± 1 min. To estimate the cloud variability onto validation, two cases were considered: all sky and cloud-free conditions. Optical cloud depth with $\tau_{cld} < 0.1$ and Lambertian Equivalent Reflectivity (LER) at λ = 360 nm with LER < 10% were used as criteria to select datasets corresponding to the cloud-free or cloudless conditions. Values τ_{cld} and LER are also presented in datasets retrieved from AVDC database [19] for coordinates (ϕ , λ_0) corresponding to the ARG ground-based station.

In addition, aerosol variability affects UV irradiance both in time and spatial scales in the same way as for the cloudiness mentioned above. At time of overpass, this characteristic differs from the analogous ones taking place at other time scales, such as local noon time and over the period of a day used in a computer modeling of OMI UV irradiances. It should be mentioned that the effect of aerosol variability is also observed within the satellite pixel area as was noted in [8, 10, 12]. Aerosol optical characteristics, such as aerosol optical depth (AOD) $\tau_a(\lambda)$ and retrieved aerosol single scattering albedo (SSA) from the AERONET observations [18] at the Kishinev site, are used in analysis and evaluation of aerosol effect on uncertainties of validation of OMI data through the ARG ground observations. Cloud and aerosol variability on various time scales, such as at overpass time, at local noon time, and over diurnal interval, are the main sources of uncertainties in validation of OMI UV data with those ones measured at the ground stations.

Scatterplots of the OEDR, EDR@noon, and EDD data derived from direct ARG ground-based observations at the Kishinev site and retrieved from OMI overpass measurements are shown in Figs. 1-3. Equations of regression lines are presented by a solid line in each of the figures. For each of the parameters, i.e., OEDR, EDR@noon, and EDD, the scatterplots are grouped separately by pairs, representing measurements carried out under AS (left side) and CF (right side) conditions, respectively. It is of particular interest to study the OEDR data, because the ARG ground-based observations are quasi-synchronous relative to the OMI overpass measurements, since the time difference is no more than ± 1 min. Comparison between ARG observations and OMI modeled data for parameters EDR@noon and EDD will be burdened with

errors due to the uncertainty of cloudiness and aerosol variability over large time scales apart from overpass. Selection of the case with the CF condition gives the possibility to eliminate the cloudiness uncertainties and to estimate the effect of the aerosols through their optical characteristics.

It should be emphasized that the scatterplots reveal a high correlation between the OMI and ARG UV data both for AS and CF conditions. The scatterplots for CF conditions show a strong mutual dependence between the OMI and ARG UV data with a correlation coefficient of R =0.98. Under the AS condition, the correlation is slightly less than under the CF condition. For each of the parameters, the slopes of regression lines for the two types of sky conditions are different. In the case of the CF condition, the slopes of regression line are larger than the ones computed under the AS condition. At the same time, it should be noted that, for all parameters and sky conditions, the slopes of regression line are less than 1; that is, the OMI derived surface UV data underestimates ARG ground UV data. We note that mean relative differences or biases b are negative values for all parameters and sky conditions under examination. The values of biases are in a range of -15.8% to -21.5%. A comparison of the OMI and ARG OEDRs data at time of overpass taking into account the data under the CF condition shows a negative bias b of -18.3%with a correlation of R = 0.98. For the AS condition, the bias and correlation are b = -15.8% and R = 0.93, respectively. Scatterplots for EDD and EDR@noon data from OMI and ARG observations are shown in Figs. 2 and 3, where (a) and (b) denote the AS and clear sky conditions, respectively. A summary of erythemal OMI UV validation results including the correlation coefficient, slopes, RMS (in %, mWm⁻², and Jm⁻²), and biases (in %) is presented in the table.

Table. Summary of erythemal OMI UV validation results (n is the number of days of observations taken into account in the comparison; r is the correlation coefficient between ARG ground and OMI overpass data; RMS is the root mean squares; b (bias) is the mean relative difference. The data are presented for AS and CF conditions. The bias and RMS are computed for OMI overpass data relative to ARG data acquired from ground observations. Period of observation: October 2004 to November 2009)

		n	R	slope	RMS	<i>b</i> (bias), %
OEDR	(AS)	1144	0.93	0.79	34.8 mW·m ⁻² (44.4%)	-15.8
	(CF)	64	0.98	0.87	28.7 mW·m ⁻² (20.4%)	-18.3
EDD	(AS)	1144	0.97	0.83	783 J·m ⁻² (27.4%)	-21.5
	(CF)	64	0.98	0.85	788 J·m ⁻² (21.9%)	-19.9
EDR@noon	(AS)	1144	0.93	0.79	44.4 mW·m ⁻² (34.8%)	-15.8
	(CF)	64	0.98	0.87	31.5 mW·m ⁻² (20.0%)	-17.7



Fig. 1a. Comparison of the OEDR (in mW^{-m⁻²}) from the ARG radiometer and from OMI at the time of overpass for AS conditions.



Fig. 2a. Comparison of the EDD (in $J \cdot m^{-2}$) from the ARG radiometer and from OMI for AS conditions.



Fig. 3a. Comparison of the EDR@noon (in mW^{-m⁻²}) from the ARG radiometer and from OMI for AS conditions.



Fig. 1b. Comparison of the OEDR (in $mW \cdot m^{-2}$) from the ARG radiometer and from OMI at the time of overpass for CF conditions.



Fig. 2b.Comparison of the EDD (in $J \cdot m^{-2}$) from the ARG radiometer and from OMI for CF conditions.



Fig. 3b. Comparison of the EDR@noon (in $mW \cdot m^{-2}$) from the ARG radiometer and from OMI for CF conditions.



Fig. 4a. Time series of the relative differences or bias (in %) between the ARG ground-based and or OMI OEDR for AS conditions.



Fig. 4b. Time series of the relative differences or bias (in %) between the ARG ground-based and OMI OEDR for CF conditions.

Seasonal variation of relative differences *b* versus day of year (DOY) is shown in Fig. 4 for AS (a) and CF (b) conditions. Time series of biases *b* reveals a seasonal variability. The range of bias variation between winter and summer months is on an average $\sim 26\%$ and $\sim 14\%$ under AS and CF conditions, respectively. This can be indicative of a mismatch between the really existing surface albedo and aerosol models and the ones used in modeling. Meanwhile, the cloudiness remains an important factor resulting in large uncertainties in validation of OMI UV irradiance data through ARG ground-based UV data. A large dispersion in bias data due to cloudiness is observed for AS conditions (see Fig. 4a).



Fig. 5. Relative differences or bias (in %) between the ARG ground-based and OMI OEDR as a function of AOD at 340 nm for CF conditions.

Under CF conditions, the AOD was retrieved from the spectral measurements using the Cimel-318 sun photometer installed at the ground-based station in IAP, Kishinev (Moldova). Aerosol optical properties were measured and retrieved within the AERONET project. For evaluation, we used the data on AOD@340 nm measured at $\lambda = 340$ nm, which is the shortest wavelength in the UV spectral range of the sun photometer. То evaluate the effect of AOD on the relative differences b, the UV OEDR under CF conditions was chosen in order to exclude the effect of cloudiness and to use quasisynchronous measurements at time of overpass. Figure 5 shows the existence of a correlation between relative differences b and AOD@340 nm with respective regression line indicated in the same figure. The larger

relative difference *b* corresponds to the larger value of AOD, and the correlation between *b* and AOD is R = 0.79.





Fig. 6. Relative differences (in %) between the ARG ground-based and OMI OEDR as a function of SSA at 440 nm for CF sky conditions.

Fig. 7. Variation of SSA at 440 nm as a function of aerosol absorption coefficient k for CF sky conditions. The equation of regression line (solid line) is indicated.

Figure 6 shows the dependence between the relative differences *b* and aerosol SSA at $\lambda = 440$ nm (SSA@440 nm) with respective regression lines representing medium SSA < 0.9 and low SSA > 0.9 absorptive aerosols. Respective regression lines are indicated in the same figure. The relationship between SSA@440 nm and aerosol absorption coefficient *k* at $\lambda = 440$ nm is shown in Fig. 7. Figure 7 clearly shows that the aerosol SSA decreases with increasing aerosol absorption coefficient *k*. The correlation coefficient between SSA@440 and *k* is *R* = 0.83. Aerosol SSA@440 nm and *k* at λ =440 nm were retrieved from direct sun and diffuse sky spectral observations with a Cimel-318 sun photometer. The period of observation is October 2004 to November 2009. The dependences shown in Figs. 6 and 7 are derived for CF conditions.

4. Summary and conclusions

The aim of this study was to compare the OMI UV data with the measurements performed by using broadband UV radiometers at the ground-based based solar radiation monitoring station ARG IAP Kishinev (Moldova) for the period of observation from 2004 to 2009. Validation results were summarized in the table in terms of relative differences or biases b, correlation coefficients R, equation of regression lines, and RMS. OEDR, EDR@noon, and EDD parameters were considered in validation. Datasets were subdivided into two main groups of measurements carried out under AS and CF conditions. UV data were complemented with aerosol optical properties, such as AOD, aerosol SSA, and aerosol absorption coefficient k. These characteristics were retrieved from spectral measurements by using a Cimel-318 sun photometer operating at the solar radiation monitoring station within the AERONET project.

Comparisons of the OMI and ARG ground-based UV datasets showed that, on average, OMI data underestimate ARG measurements by more than -16%. It should be noted that, in all cases, the comparison showed negative relative differences or biases *b* with a high correlation between OMI and ARG UV datasets with R > 0.93. The correlation under CF conditions is higher than under AS conditions, and it is R = 0.98. The comparison for OEDR data showed a bias value of -15.8% under AS and -18.3% under CF conditions. Concerning EDR@noon data, the bias

is -15.8% under AS and -17.7% under CF conditions; taking into account the EDD data, an increase in bias is observed (with a value of -21.5% and -19.9% under AS and CF conditions, respectively). Time series of biases *b* reveals a seasonal variability. The range of bias variation between winter and summer months is, on an average, -26% and -14% under AS and CF conditions, respectively.

It was observed that the correlation between relative differences for OEDR data and AOD@340 nm under CF conditions is R = 0.79. The larger relative difference *b* corresponds to the larger value of AOD@340 nm.

The OMI underestimation of the ARG UV data can be partly explained by uncertainties due to aerosol optical-microphysical and climatic surface albedo at 360 nm models, which were applied in modeling of the OMI surface UV radiation from orbital measurements of surface backscattered UV radiation. During the measurement campaign at time of overpass, these models can differ from those existing in reality in the area of observation in the vicinity of the groundbased station. In this connection, another source of uncertainties in validation consists in the fact that ground-based measurements are fulfilled at a single point, where the ground-based station is placed, whereas the satellite output product represents an average over a variable area of the OMI pixel projection onto the Earth's surface.

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Crystallographer Ion Andrei Diacon (1934-2012): Life Dedicated to Science

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Ion Andrei Diacon, well known crystallographer, corresponding member of the Academy of Sciences, doctor habilitate in physical and mathematical sciences, laureate of State Prize in the field of science and engineering (1983), awarded by the Order "Gloria Muncii" (1996) passed away suddenly in the age of 78 on December 23, 2012, following a brief illness.



All his conscious activity during 53 years was related with the Academy of Sciences and the Laboratory of Physical methods of Solid State Investigation "T.I. Malinowski" of the Institute of Applied Physics where he passed the scientific career stages from a laboratory assistant to a principal scientific worker.

Diacon Ion A. was born on September 25, 1934 in a family of peasants in the village Sipoteni, Calarashi district. In 1950 he finished a primary school in Sipoteni; in 1953, Calarashi secondary school, and entered the physico-mathematical department of the Ion Cryanga Pedagogical State University in Kishinev. After graduation in 1957 with an honors degree he was assigned to work as a teacher in a secondary school in his native village Sipoteni. Aspiration for knowledge, self-confidence and the desire to do research led Ion Diacon to the Department of physics and mathematics of the Moldavian branch of the Academy of Sciences of the USSR. December 21, 1959 he was enrolled in the Laboratory of physical methods of solid state investigation and began scientific activities as laboratory assistant. The order for his admission was signed by the Chairman of the Presidium of the Moldavian branch of the USSR, the future

first President of the Academy of Sciences of Moldova Ia. S. Grosul. Two famous scientists, the founders of crystallographic school in Moldova, Anton Ablov and Tadeush Malinowski motivated him to study theory and practice of diffraction methods of crystal structure investigation, taught him crystallography, formulate goals and objectives of research. His first task was related with investigating the crystal structure of coordination compounds with α -amino acids, the biological activity of which made them promising for practice. Specific features of crystallization of these compounds do not allow obtaining monocrystalline samples suitable for the X-ray single crystal diffraction method and inspire young scientist to seek for an adequate method of studying the structure of textured, film-like crystals. It was the method electron diffraction; all further scientific activity of Ion Diacon was related just with this method of crystal structure investigation. In the sixties of the XX century, the A.V.Shubnikov Institute of crystallography of the Academy of Sciences of the USSR was the world-wide known centre of structure investigation by electron diffraction; many famous scientists, such as Boris Vainshtein and Zinovii Pinsker, worked here, and Boris Zvyagin co-operated with them.

After training and following post-graduate courses (supervisor B.Vainshtein) in the Institute of crystallography Ion A. Diacon in 1970 successfully defended his thesis entitled "Structural study of copper salts of glycine and DL - alanine by electron diffraction method" on degree Candidate of physical and mathematical sciences and in 1989 doctor (doctor habilitate) thesis entitled "Electron diffraction investigation and structural crystallography of mixed coordination compounds with α – aminoacids". His investigations of the atomic structure of a number of binary and mixed coordination compounds with α -amino acids by the electron diffraction diffraction method are well known to the scientific community in Moldova and abroad. Ion A. Diacon discovered that the most important structural features of the investigated complex compounds with α -amino acids are related with phenomena of polytypism and polysomatism. Many of above mentioned compounds possess antivirus, antimicrobe, and antitumour activity and can be used as biologically active remedies.

Diacon Ion A. combined his scientific activity with organizing affairs. Starting from 1970 he was a member of the Department of physical, mathematical, and technical sciences and contributes efforts in the organization and development of academic science and preparation research workers. For many years he was the scientific secretary and deputy academician-coordinator of the Department, vice-chairman of the expert commission on physics of the Superior Attestation Commission of Moldova, member of Expert commission on ethics, and the chairman of the Specialized Scientific Council on defense of doctor theses on specialty "Crystallography and crystal physics". On the last day of his life he was going to visit the National Council for Accreditation and Attestation to sign the Diploma of doctor for young crystallographer, who had recently defended dissertation, but fatal disease interfered with his intention. Ion A. Diacon was held in respect, due to benevolence, readiness to help and give a piece good of advice and consultation. He was always involved in the problems of the Laboratory and researchers and deeply experienced the problems of science development in Moldova. He was proud of his family, children, and grandchildren. Laboratory co-workers well remember bouquets of flowers they permanently received from Ion A. Diacon on their birthdays.

All colleagues, disciples, and friends, all those who had the pleasure to get into contact and cooperate with him will certainly remember those days and will keep Ion A. Diacon in grateful memory.