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# AIM AND SCOPE

The scope of the journal includes all areas of nano-sciences. Papers devoted to basic problems of physics, chemistry, material science and mathematics inspired by nanosystems investigations are welcomed. Both theoretical and experimental works concerning the properties and behavior of nanosystems, problems of its creation and application, mathematical methods of nanosystem studies are considered.

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### Quantum graphs with the Bethe-Sommerfeld property

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In contrast to the usual quantum systems which have at most a finite number of open spectral gaps if they are periodic in more than one direction, periodic quantum graphs may have gaps arbitrarily high in the spectrum. This property of graph Hamiltonians, being generic in a sense, inspires the question about the existence of graphs with a finite and nonzero number of spectral gaps. We show that the answer depends on the vertex couplings together with commensurability of the graph edges. A finite and nonzero number of gaps is excluded for graphs with scale invariant couplings; on the other hand, we demonstrate that graphs featuring a finite nonzero number of gaps do exist, illustrating the claim on the example of a rectangular lattice with a suitably tuned  $\delta$ -coupling at the vertices.

Keywords: periodic quantum graphs, gap number,  $\delta$ -coupling, rectangular lattice graph, scale-invariant coupling, Bethe-Sommerfeld conjecture, golden mean.

Quantum graphs [1] have attracted much attention both from the practical point of view as models of nanostructures as well as a tool to study the properties of quantum systems with a nontrivial topology of the configuration space. The topological richness of quantum graphs allows them to exhibit properties different from those of the 'usual' quantum Hamiltonians; examples are well known, for instance, the existence of compactly supported eigenfunctions on infinite graphs [1, Sec. 3.4] or the possibility of having flat bands only as is the case for magnetic chain graphs with a half-of-the-quantum flux through each chain element [2].

In this letter, we are going to consider another situation where quantum graphs are known to behave unusually. Our problem concerns the gap structure of the spectrum of periodic quantum graphs. Recall that the finiteness of the open gap number for periodic quantum systems in dimension two or more was conjectured in the early days of quantum theory by Bethe and Sommerfeld [3]. The validity of the conjecture was taken for granted even if its proof turned out to pose a mathematically difficult problem. It took a long time before it was rigorously established for the 'usual' periodic Schrödinger operators [4–8]. Nevertheless, the situation appears to be different for quantum graphs, as we will see below.

The traditional reasoning behind the Bethe-Sommerfeld conjecture relies on the behavior of the spectral bands identified with the ranges of the dispersion curves or surfaces which, in contrast to the one-dimensional situation, typically overlap, making opening of gaps more and more difficult as we proceed to higher energies. The situation with graphs might be similar [1, Sec. 4.7] but the spectral behavior need not be the same, one reason being the possibility of resonant gaps. The existence of gaps coming from a graph decoration was first observed in the discrete graph context [9] and the effect is present for metric graphs as well [1, Sec. 5.1]. In addition, the recently discovered universality property of periodic graphs [10], valid in the generic situation when the graph edges are incommensurate and the vertex coupling is the simplest possible, usually called Kirchhoff, shows that the occurrence of infinitely many open gaps is quite typical.

This prompts one to ask whether there are quantum graphs with the band spectrum similar to that of the 'usual' multidimensional periodic systems, i.e. a nonzero and finite number of open gaps; for the sake of brevity, we shall speak of the *Bethe–Sommerfeld property*. With this question in mind, our aim in this letter is twofold. On the one hand we will show that the answer depends on the vertex coupling and there are classes of couplings for which such a behavior is excluded. On the other hand, using a simple example we shall demonstrate that periodic graphs with Bethe–Sommerfeld property do exist.

Consider an infinite graph  $\Gamma$  periodic in  $\nu$  directions, with a slight abuse of notation we will speak of a  $\mathbb{Z}^{\nu}$ -periodicity,  $\nu \geq 2$ . The Hamiltonian is supposed to act as  $-d^2/dx^2$  on each edge; to make it a self-adjoint operator, one has to impose appropriate coupling conditions at each vertex. The most general form of them [11,12] is  $(U - I)\Psi + i(U + I)\Psi' = 0$ , where  $\Psi$ ,  $\Psi'$  are vectors of the function and derivative values at the vertex, respectively, and U is a unitary  $n \times n$  matrix for n denoting the degree of the vertex. According to the eigenvalues of U one can split the coupling into the Dirichlet, Neumann, and Robin parts [1, Sec. 1.4]. Equivalently, the coupling can be written in so-called ST-form [13],

$$\begin{pmatrix} I^{(r)} & T \\ 0 & 0 \end{pmatrix} \Psi' = \begin{pmatrix} S & 0 \\ -T^* & I^{(n-r)} \end{pmatrix} \Psi$$
(1)

for certain r, S, and T, where  $I^{(r)}$  is the identity matrix of order r and S is a Hermitian matrix that refers to the Robin part. A coupling is called *scale-invariant* if the matrix U has no eigenvalues other than  $\pm 1$ ; it is easy to see that this happens if and only if S = 0 [14]. Recall that the on-shell scattering matrix S(k) for the vertex in question is in the ST-formalism given by

$$S(k) = -I^{(n)} + 2\left(\frac{I^{(r)}}{T^*}\right)\left(I^{(r)} + TT^* - \frac{1}{ik}S\right)^{-1}\left(I^{(r)} - T\right)$$

and it is obvious that S(k) is independent of k iff S = 0.

The spectrum is obtained using the Bloch-Floquet theory [1, Sec. 4.2]. We cut from  $\Gamma$  its elementary cell  $\Gamma_{\text{per}}$  which is assumed to be a finite graph with a family of pairs of 'antipodal' vertices related mutually by the conditions  $\psi(v_+) = e^{i\vartheta_l}\psi(v_-)$  and  $\psi'(v_+) = e^{i\vartheta_l}\psi'(v_-)$  with some  $\vartheta_l \in (-\pi, \pi]$ , where  $l = 1, \ldots, \nu$  with  $\nu$  being the dimension of translation group associated with graph periodicity; the pair of edges with the endpoints  $v_{\pm}$  can be turned into a single edge by identifying these endpoints, and the acquired phase  $\vartheta_l$  coming from the Bloch conditions can be also regarded as being induced by a suitable magnetic potential.

The spectral problem can be solved in the usual way, cf. [1, Sec. 2.1] or [10]. Assuming that  $\Gamma_{per}$  has E edges, we consider three  $2E \times 2E$  matrices. The diagonal matrix **L** is determined by the lengths of the directed edges (bonds) of  $\Gamma_{per}$ , the diagonal matrix **A** has the entries  $e^{i\vartheta_l}$  or  $e^{-i\vartheta_l}$  at the positions corresponding to the edges created by the mentioned vertex identification, and all its other entries are zero, and finally, the matrix **S** is the bond scattering matrix, which contains directed edge-to-edge scattering coefficients. Using them, we define

$$F(k;\vec{\vartheta}) := \det\left(\mathbf{I} - e^{i(\mathbf{A}+k\mathbf{L})}\mathbf{S}(k)\right);$$
<sup>(2)</sup>

then  $k^2 \in \sigma(H)$  holds iff there is a  $\vartheta \in (-\pi, \pi]^{\nu}$  such that the secular equation  $F(k; \vec{\vartheta}) = 0$  is satisfied.

Suppose now that the couplings at all the vertices of  $\Gamma$  are scale-invariant. This, in particular, means the matrix **S** entering formula (2) is independent of k, hence the value  $F(k; \vec{\vartheta})$  depends on the vectors  $\vec{\vartheta}$  and  $k\ell_0, k\ell_1, \ldots, k\ell_d$ , where  $\{\ell_0, \ell_1, \ldots, \ell_d\}, d \leq E - 1$ , is the set of mutually different edge lengths of  $\Gamma$ , and  $F(k; \vec{\vartheta})$  is obviously  $2\pi$ -periodic in the terms  $k\ell_0, k\ell_1, \ldots, k\ell_d$ . The secular equation can be then written as

$$F(\{k\ell_0\}_{(2\pi)}, \{k\ell_1\}_{(2\pi)}, \dots, \{k\ell_d\}_{(2\pi)}; \vec{\vartheta}) = 0,$$
(3)

where  $\{x\}_{(2\pi)} := 2\pi \{x/(2\pi)\}$ , for  $\{\cdot\}$  denoting the difference between the number and its nearest integer. This allows us to prove that

- (i) if  $\sigma(H)$  has a gap, then it has infinitely many gaps,
- (ii) the gaps can be divided into series with asymptotically constant lengths with respect to k, and
- (iii) in particular, if all the edge lengths are commensurate, the momentum spectrum is periodic.

The easiest part to verify is (iii). In that case there is an elementary length L > 0 and integers  $m_j \in \mathbb{N}$  such that  $\ell_j = m_j L$  holds for j = 0, 1, ..., d, and consequently, the left-hand side of (3) is  $2\pi/L$ -periodic with respect to k. Parts (i) and (ii) are more involved and we just sketch the argument referring to [15] for the full proof.

To prove (i) we consider a k > 0 satisfying  $k^2 \notin \sigma(H)$  and use it to prove the existence, for any given C > 0, a k' > C such that  $(k')^2 \notin \sigma(H)$ . Due to the continuity of F, it is sufficient to find a k' so that the values  $k'\ell_j$  are arbitrarily close to  $k\ell_j$  up to an integer multiple of  $2\pi$ . To this aim, we denote  $\alpha_j = \ell_j/\ell_0$  and employ the simultaneous version of the Dirichlet's approximation theorem by which for any  $N \in \mathbb{N}$  there are integers  $p_1, \ldots, p_d, q \in \mathbb{Z}, 1 \leq q \leq N$ , such that

$$\left|\alpha_j - \frac{p_j}{q}\right| \le \frac{1}{qN^{1/d}} \,. \tag{4}$$

Choosing integers  $m > \ell_0 C/2\pi$  and  $N > (2\pi m/\delta)^d$ , and putting  $k'_{\delta} := k + 2\pi mq/\ell_0$ , it is straightforward to see that  $k'_{\delta} > C$  and, using (4), to check that  $|\{k'_{\delta}\ell_j - k\ell_j\}_{(2\pi)}| < \delta$  for all j. Moreover, the latter inequality in combination with the argument used to prove (i) yields the claim (ii).

In fact, one can exclude the Bethe–Sommerfeld property for a wider class of graphs. Given a vertex coupling described by condition (1), we consider the *associated scale-invariant* one obtained by replacing the Robin part S by zero. The vertex scattering matrix can be then written as  $S(k) = S_0 + S_1(k)/k$ , where  $S_0$  is the scattering matrix of the associated scale-invariant vertex coupling. Then the function  $F(k; \vec{\vartheta})$  in the secular equation is

$$F_0(\{k\ell_0\}_{(2\pi)},\{k\ell_1\}_{(2\pi)},\ldots,\{k\ell_d\}_{(2\pi)};\vec{\vartheta})+\frac{1}{k}F_1(k;\vec{\vartheta}),$$

where the subscript zero at  $F_0$  refers to the Hamiltonian  $H_0$  of the graph in which all the couplings have been replaced by the associated scale-invariant ones. Using the fact that the leading behavior of  $F(\cdot; \vec{\vartheta})$  at high energies comes from the scale-invariant term, it is not difficult to see that [15]

- (i) if  $\sigma(H_0)$  has an open gap, then  $\sigma(H)$  has infinitely many gaps,
- (ii) if all the edge lengths of  $\Gamma$  are commensurate, then the gaps of  $\sigma(H)$  asymptotically coincide with those of  $\sigma(H_0)$ .

Let us turn to our second topic, the existence of graphs with the Bethe-Sommerfeld property. To this goal, we revisit the *lattice Kronig-Penney model* introduced in [16] and further discussed in [17, 18]. In this case,  $\Gamma$  is a rectangular lattice graph in the plane with edges of lengths a and b, cf. Fig. 1.



FIG. 1. The rectangular-lattice graph

The Hamiltonian  $H = H_{\alpha,a/b}$  is the negative Laplacian with the  $\delta$  coupling condition in each vertex, i.e. the functions are continuous there and satisfy  $\sum_{j=1}^{4} \psi'(v) = \alpha \psi(v)$  with a fixed parameter  $\alpha \in \mathbb{R}$ .

According to [17], a number  $k^2 > 0$  belongs to a gap if and only if k > 0 satisfies the gap condition, which reads

$$\tan\left(\frac{ka}{2} - \frac{\pi}{2}\left\lfloor\frac{ka}{\pi}\right\rfloor\right) + \tan\left(\frac{kb}{2} - \frac{\pi}{2}\left\lfloor\frac{kb}{\pi}\right\rfloor\right) < \frac{|\alpha|}{2k}$$
(5)

for  $\alpha > 0$  and the analogous one with tan replaced by cot if  $\alpha < 0$ ; we neglect the case  $\alpha = 0$  where the spectrum is trivial,  $\sigma(H) = [0, \infty)$ . For  $\alpha < 0$  the spectrum extends to the negative part of the real axis and may have a gap there, but since such a gap always has a positive part [18], we may restrict our attention to examining gaps in the positive spectrum.

The crucial quantity is the ratio  $\theta = a/b$ . It is obvious that  $\sigma(H)$  has infinitely many gaps once  $\alpha \neq 0$  and  $\theta$  is rational, and the same is true for the 'well approximable' irrationals [17]. We thus focus on the other irrationals, called *badly approximable*, i.e those to which there is a c > 0 such that

$$\left|\theta - \frac{p}{q}\right| > \frac{c}{q^2}$$

for all  $p, q \in \mathbb{Z}$  with  $q \neq 0$ . These numbers form a set of zero Lebesgue measure. Alternatively they can be characterized as irrationals for which the sequence in the continued-fraction representation,  $\theta = [c_0; c_1, c_2, ...]$ , is bounded [19], or as numbers whose *Markov constant*  $\mu(\theta)$ , defined [20] for  $\theta \in \mathbb{R}$  as

$$\mu(\theta) = \inf\left\{c > 0 \mid \left(\exists_{\infty}(p,q) \in \mathbb{N}^2\right) \left(\left|\theta - \frac{p}{q}\right| < \frac{c}{q^2}\right)\right\},\tag{6}$$

is strictly positive. It is convenient to introduce a one-sided analog  $v(\theta)$  of the Markov constant, with the last inequality in (6) replaced by  $0 < \theta - p/q < c/q^2$ . We have  $\mu(\theta) = \min\{v(\theta), v(\theta^{-1})\}$ ; the number  $v(\theta)$  may or may not coincide with the Markov constant [21].

To obtain the existence claim, we focus on the situation where  $\theta$  is the 'worst approximable' irrational, the golden mean,  $\phi = (\sqrt{5} + 1)/2$ . Our result about the golden-mean lattice is the following:

- (i) If  $\alpha > \pi^2/(\sqrt{5}a)$  or  $\alpha \le -\pi^2/(\sqrt{5}a)$ , the spectrum has infinitely many gaps.
- (ii) If  $-2\pi/a \tan\left((3-\sqrt{5})\pi/4\right) \le \alpha \le \pi^2/(\sqrt{5}a)$  there are no gaps in the spectrum.
- (iii) If  $-\pi^2/(\sqrt{5}a) < \alpha < -2\pi/a \tan((3-\sqrt{5})\pi/4)$ , there is a nonzero and finite number of gaps in the spectrum.
- (iv) Moreover, put  $A_j := 2\pi \left( \phi^{2j} \phi^{-2j} \right) / \sqrt{5} \tan \left( \pi \phi^{-2j} / 2 \right)$ , then there are exactly N gaps in the spectrum if  $-A_{N+1} \le \alpha < -A_N$ .

Note that the window in which Bethe–Sommerfeld property occurs in this example (statement (iii)), is rather narrow, roughly  $4.298 \leq -\alpha a \leq 4.414$ .

The proof of these claims is rather involved and we limit ourselves with mentioning its key elements referring to [15] for the full exposition. The central notion is that of the *Diophantine approximation of third type from below* (from above, respectively). The former is a number p/q with  $p, q \in \mathbb{Z}$  such that

$$0 < q(q\theta - p) < q'(q'\theta - p') \tag{7}$$

holds for all  $p'/q' \ge \theta$  with  $p'/q' \ne p/q$ ,  $p', q' \in \mathbb{Z}$  and  $0 < q' \le q$ ; the approximation from above has (7) replaced by  $0 < q(p-q\theta) < q'(p'-q'\theta)$ . We note that  $v(\theta)$  is the infimum of those  $q(q\theta - p)$  for which p/q is a best approximation from below to  $\theta$ . These approximations are also closely related to *convergents* obtained from truncated continued-fraction representation of  $\theta$ . Specifically, every best approximation from above is either  $\lceil \theta \rceil$  or a convergent of  $\theta$ , where  $\lceil \cdot \rceil$  is the ceiling function.

The described Diophantine approximation in combination with the gap condition allows us to estimate the number of gaps for a given ratio  $\theta = a/b$  and coupling parameter  $\alpha$ . This has to be done for each sign of  $\alpha$  separately. If  $\alpha > 0$ , condition (5) yields that

- if α < π<sup>2</sup> · min {v(θ)/b, v(θ<sup>-1</sup>)/a}, the spectrum has at most finitely many gaps. If the opposite (sharp) inequality holds true, the number of gaps is infinite;
- if  $\alpha \leq \gamma_+$  for  $\gamma_+$  given by

$$\gamma_{+} := \min_{\eta=\theta,\theta^{-1}} \inf_{m\in\mathbb{N}} \left\{ 2\pi m \sqrt{\frac{\eta}{ab}} \tan\left(\frac{\pi}{2}(m\eta - \lfloor m\eta \rfloor)\right) \right\},\tag{8}$$

the spectrum has no gaps. If  $\alpha > \gamma_+$ , there are gaps in the spectrum;

• in particular, if  $\gamma_+ < \alpha < \pi^2 \cdot \min \{ v(\theta)/b, v(\theta^{-1})/a \}$ , there is a nonzero and finite number of gaps in the spectrum.

The golden mean  $\phi$  in our example has continued-fraction representation  $\phi = [1; 1, 1, ...]$ , therefore, its convergents are ratios  $F_{n+1}/F_n$  of the Fibonnaci numbers  $F_n = (\phi^n - (-\phi)^{-n})/\sqrt{5}$ , and we have  $\mu(\phi) = \nu(\phi) = 1/\sqrt{5}$  in view of the Hurwitz theorem [22]. Hence, we get

$$\gamma_{+} = \frac{\pi^2}{\sqrt{5}a} \quad \text{and} \quad \pi^2 \cdot \min\left\{\frac{\upsilon(\phi)}{b}, \frac{\upsilon(\phi^{-1})}{a}\right\} = \frac{\pi^2}{\sqrt{5}a}$$

which implies for all positive  $\alpha$  either infinite number of spectral gaps or none at all. Alternatively, for  $\alpha < 0$  the gap condition implies that

- if  $|\alpha| < \pi^2 \cdot \min \{ v(\theta)/a, v(\theta^{-1})/b \}$ , the number of gaps in the positive spectrum is at most finite. By contrast, for  $|\alpha|$  greater than the right-hand side of the above inequality, there are infinitely many spectral gaps, while
- if |α| ≤ γ<sub>-</sub> for γ<sub>-</sub> given by the relation analogous to (8) in which mη ⌊mη⌋ is replaced by ⌈mη⌉ mη, the spectrum has no gaps. If |α| > γ<sub>-</sub>, there are gaps in the spectrum;
- in particular, if  $\gamma_{-} < |\alpha| < \pi^{2} \cdot \min \{ v(\theta)/a, v(\theta^{-1})/b \}$ , there is a nonzero and finite number of gaps in the spectrum.

The last of these results, together with the easily verifiable formula

$$\gamma_{-} = \frac{2\pi}{a} \tan \frac{(3-\sqrt{5})\pi}{4}$$

proves the claim (iii) above, demonstrating thus the existence of graphs with the Bethe–Sommerfeld property. To prove (iv), the first step consists in showing that the number of gaps in the golden-mean lattice graph is equal to the number of solutions  $m \in \mathbb{N}$  of

$$\frac{2\pi m}{a} \tan\left(\frac{\pi}{2}\left(\lceil m\phi \rceil - m\phi\right)\right) < |\alpha|$$

If  $-A_{N+1} \leq \alpha < -A_N$ , one can verify that the inequality is satisfied only for  $m = F_n$  with n = 2, 4, 6, ..., 2N; this implies the existence of exactly N gaps.

Since a finite nonzero number of gaps occurred in the above example only for attractive vertex couplings, it is natural to ask whether the attractivity of the coupling is always a necessary condition for the Bethe–Sommerfeld property. It appears that it is not the case, a more thorough analysis of the gap condition [15] shows that, for instance, the edge ratio

$$\theta = \frac{2t^3 - 2t^2 - 1 + \sqrt{5}}{2(t^4 - t^3 + t^2 - t + 1)} \quad \text{with } t \in \mathbb{N}, \ t \ge 3,$$

which has the continued-fraction representation [0; t, t, 1, 1, 1, 1, ...], yields the lattice graph spectrum with the said property for a certain  $\alpha > 0$  and for a certain  $\alpha < 0$  as well. This observation can be stated more generally [15] and allows one to explicitly construct ratios to achieve the Bethe–Sommerfeld property.

In conclusion, we have proved and demonstrated on concrete examples that there are periodic quantum graphs, the spectrum of which contains a nonzero and finite number of open gaps. We have also described how this property depends on the type of the vertex coupling; in particular, we showed that a quantum graph cannot be of the Bethe–Sommerfeld type if its couplings are scale invariant or associated with scale-invariant ones.

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# Finiteness of discrete spectrum of the two-particle Schrödinger operator on diamond lattices

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We consider a two-particle Schrödinger operator H on the d-dimensional diamond lattice. We find a sufficiency condition of finiteness for discrete spectrum eigenvalues of H.

Keywords: two-particle Hamiltonian on lattice, Birman-Schwinger principle, discrete spectrum.

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#### 1. Introduction

The spectrum of the many particle Schrödinger operator is closely connected to the spectrum of two-particle Schrödinger operator. To obtain the two-particle Schrödinger operator (in the continuous case) from the total Hamiltonian, we can separate the energy of motion of the center of mass such that the one-particle "bound states" are eigenvectors of the energy operator with separated total momentum (in this case, such an operator is indeed independent of the total momentum values) [1]. On the lattice case, the "separation of the center of mass" of a system is associated with the realization of the Hamiltonian as a "laminated operator", i.e., as the direct integral of the family  $h(k), k \in \mathbb{T}^d$  (where  $\mathbb{T}$  is a one dimensional torus), of the energy operators of two particles, where k is the value of the total quasi-momentum [2].

Conditions for the finiteness of the negative spectrum and for the absence of positive eigenvalues of the twoparticle continuous Schrödinger operator H were presented in [3]. The finiteness of the number of bound states for two-particle cluster operators at some values of the clustering parameter was established in [4]. The sufficient condition of finiteness of discrete spectrum of two-particle lattice Schrödinger operators was given in [5]. An example one-dimensional lattice Schrödinger operator having at the same time an infinite number of discrete and embedded eigenvalues was given in the paper [6]. The existence conditions for eigenvalues of the family h(k)depending on the energy of interaction and quasi-momentum k have been investigated in [7].

The models which can be obtained investigating differential operators on graphs have already been used by physicists, a good review of such publications can be found, for example, in [8,9]. Two particle scattering theory on graphs was studied in [9]. The obtained results are applied to the qualitative description of a simple three-electrode nanoelectronic device. In [10] and [11], the problem of quantum particle storage in a nanolayered structure was considered. The authors numerically solved an eigenvalue problem of the corresponding Hamiltonian.

K. Ando et al. [12] described the Schrödinger operators on square, triangular, hexagonal, Kagome, diamond, subdivision lattices and the spectral properties of these Schrödinger operators were studied with compactly supported potentials. Conditions for the finiteness of the discrete spectrum and the non-existence of embedded eigenvalues of these Schrödinger operators with compactly supported potentials were given. The inverse scattering for discrete Schrödinger operators with compactly supported potentials on  $\mathbb{Z}^d$  and on the hexagonal lattice were studied in [13,14] in part, in these papers, the discreteness of embedded eigenvalues of these operators was proved.

We consider a discrete Schrödinger operator H on the d-dimensional diamond lattice with any continuous potential Q, i.e. a perturbation of discrete Laplacian with compact operator. The aim of the present paper is to prove the finiteness of the discrete spectrum of H. To show this, we use the technique proposed in [15]. First, we, using the well-known Birman-Schwinger principle, we reduce the study number of discrete spectrum  $N_{-}(z)(N_{+}(z))$  of H, lying to the left (right) from z to the study of the number of eigenvalues  $n(1, T_{\mp}(z))$  of the compact operator  $T_{\mp}(z)$ , lying to the right from 1, i.e. we prove the equalities  $N_{\mp}(z) = n(1, T_{\mp}(z))$ . Further, we show that the operator-valued function  $T_{\pm}(\cdot)$  is well defined at the limits of the essential spectrum and apply the Weyl inequality.

#### 2. Statement of the Main Results

We first give descriptions of the d-dimensional diamond lattice and a discrete Schrödinger operator on the d-dimensional diamond lattice [12].

Discrete Laplacian on the graph. We denote by G = (V(G), E(G)) the graph that consists of a vertex set V(G), whose cardinality is at most countable, and an edge set E(G), each element of which connects a pair of vertices. We assume that the graph is simple, i.e. there are neither self-loop, which is an edge connecting a vertex to itself, nor multiple edges, which are two or more edges connecting the same vertices. Let  $v, u \in V(G)$ , and  $e \in E(G)$ . We denote by  $v \sim u$ , when v is adjacent to u by e; by  $N_v$  the set of vertices which are adjacent to v, i. e.  $N_v = \{u \in V(G) : u \sim v\}$ . We denote by  $\deg(v) = \#N_v$  the degree of v. We assume that the graph G is connected, which implies that deg(v) > 0 for any  $v \in V(G)$ .

The discrete Laplacian  $\triangle_d$  on G is defined as (see [16])

$$(\triangle_d \hat{f})(v) = \frac{1}{\deg(v)} \sum_{u \in N_v} [\hat{f}(u) - \hat{f}(v)],$$

for the function  $\hat{f}$  on V(G). It is well known that  $-\Delta_d$  is bounded, self-adjoint on

$$\ell_2(G) = \Big\{ \widehat{f}: \quad \sum_{v \in v \in V(G)} |\widehat{f}(v)|^2 \deg(v) < \infty \Big\}.$$

Higher-dimensional diamond lattice. Let  $\mathbb{Z}^d, d \geq 2$ , be a d-dimensional integer lattice,  $(\mathbb{Z}^d)^2 = \mathbb{Z}^d \times \mathbb{Z}^d$  be the Cartesian power of  $\mathbb{Z}^d$ , and  $l_2((\mathbb{Z}^d)^2)$  be the Hilbert space of square-integrable functions defined on  $(\mathbb{Z}^d)^2$ . Let  $A_d$  be a subset of  $\mathbb{Z}^{d+1}$  defined as follows

$$A_d = \left\{ x \in \mathbb{Z}^{d+1} : \sum_{i=1}^{d+1} x_i = 0 \right\}$$

and  $\mathbf{e}_1 = (1, 0, \dots, 0)$ ,  $\mathbf{e}_2 = (0, 1, 0, \dots, 0)$ ,  $\dots$ ,  $\mathbf{e}_{d+1} = (0, \dots, 0, 1)$ ,  $\mathbf{v}_i = \mathbf{e}_{d+1} - \mathbf{e}_i$ ,  $i = 1, \dots, d$ . Then,  $A_d$  is a lattice (see [12]) of rank d in  $\mathbb{R}^d$  with basis  $\mathbf{v}_i$ ,  $i = 1, \dots, d$ , i.e.

$$A_d = \left\{ \mathbf{v}(n) : \quad \mathbf{v}(n) = \sum_{j=1}^d n_j \mathbf{v}_j, \ n = (n_1, \cdots, n_d) \in \mathbb{Z}^d \right\}.$$

The lattice  $A_d$  is called d-dimensional diamond lattice. We put

$$\mathcal{V} = A_d \cup (p + A_d), \quad p = \frac{1}{d+1}(\mathbf{v}_1 + \dots + \mathbf{v}_d).$$

The set  $\mathcal{V}$  is vertex set of d-dimensional lattice  $A_d$ .

The set of adjacent points of  $\mathbf{v}(n) \in A_d$  and  $p + \mathbf{v}(n') \in P + A_d$  are defined by

$$N_{\mathbf{v}(n)} = \left\{ p + \mathbf{v}(n') : n - n' = (0, \dots, 0), (1, 0, \dots, 0), \dots (0, \dots, 0, 0) \right\},\$$

$$N_{p+\mathbf{v}(n')} = \left\{ \mathbf{v}(n) : n - n' = (0, \dots, 0), (1, 0, \dots, 0), \dots (0, \dots, 0, 0) \right\}$$

Hence  $\deg(v) = d + 1$  for  $v \in N_{\mathbf{v}(n)}$  or  $v \in N_{p+\mathbf{v}(n)}$ .

Discrete Laplacian on higher-dimensional diamond lattice. Using the definition of Discrete Laplacian on Graph from the definition of adjacent sets on  $\mathcal{V}$  Discrete Laplacian  $\triangle_d$  on  $\mathcal{V}$  is defined by

$$((d+1)(\triangle_d+1)f)(v) = (\hat{g}_1(n), \hat{g}_2(n)),$$

where

$$\hat{g}_1(n) = \hat{f}_2(n) + \hat{f}_2(n - \mathbf{e}_1) + \dots + \hat{f}_2(n - \mathbf{e}_d),$$
  
$$\hat{g}_2(n) = \hat{f}_1(n) + \hat{f}_1(n + \mathbf{e}_1) + \dots + \hat{f}_1(n + \mathbf{e}_d).$$

Any function  $\hat{f}$  on  $\mathcal{V}$  is written as  $\hat{f}(n) = (\hat{f}_1(n), \hat{f}_1(n)), n \in \mathbb{Z}^d$ , where  $\hat{f}_1(n) := \hat{f}_1(\mathbf{v}(n)), f_2(n) := \hat{f}_2(p + 1)$  $\mathbf{v}(n)$ ). Hence  $\ell_2(\mathcal{V})$  is the Hilbert space equipped with the inner product

$$(\hat{f}, \hat{g})_{\ell_2(\mathcal{V})} := \sum_{v \in A_d} \hat{f}_1(v) \overline{\hat{g}_1(v)} \operatorname{deg}(v) + \sum_{v \in (p+A_d)} \hat{f}_2(v) \overline{\hat{g}_2(v)} \operatorname{deg}(v).$$

The discrete Schrödinger operator. Let  $\mathbb{T}^d = \mathbb{R}^d/(2\pi)^d$ . We denote by  $L_2^{(2)}(\mathbb{T}^d)$  the Hilbert space with inner product

$$(f,g)_{L_2^{(2)}} = (f_1,g_1) + (f_2,g_2), \quad (f_j,g_j) = \int_{\mathbb{T}^d} f_j(x)\overline{g_j(x)}dx.$$

We then define a unitary operator  $\mathcal{U}:\ell_2(\mathcal{V})\to L_2^{(2)}(\mathbb{T}^d)$ 

$$(\mathcal{U}\hat{f})_j = (2\pi)^{-d/2}\sqrt{d+1}\sum_{n\in\mathbb{Z}^d}\hat{f}_j(n)e^{n\cdot x}.$$

Passing to the Fourier series, we rewrite  $-(\triangle_d + 1)$  into the following form:

$$(\mathcal{U}(-(\triangle_d+1))\mathcal{U}^{-1}f)(x) = (\mathbf{H}_0f)(x), \quad f \in L_2^{(s)}(\mathbb{T}^d),$$

where  $\mathbf{H}_0$  is a matrices operator for a  $2 \times 2$  matrix  $\mathbf{H}_0(x)$ 

$$\mathbf{H}_0(x) = \left(\begin{array}{cc} 0 & E(x) \\ \overline{E(x)} & 0 \end{array}\right),$$
$$E(x) = \frac{1}{d+1} \left(1 + e^{ix_1} + \dots e^{ix_d}\right).$$

Note that

$$|E(x)|^2 = \frac{1}{(d+1)^2} \left[ d+1 + 2\sum_{j=1}^{n} \cos x_1 + 2\sum_{i< j} \cos(x_i - x_j) \right], \quad j = 1, \cdots, d.$$

Hence

$$\min_{p} |E(p)| = 0, \quad \max_{p} |E(p)| = 1,$$

and the point  $\mathbf{0} = (0, \dots, 0) \in \mathbb{T}^d$  is a unit degenerated maximum point of function  $|E(\cdot)|^2$ .

Let  $\widehat{\mathbf{Q}}$  be the potential on  $\ell_2(\mathcal{V})$  defined as multiplication operator by real valued, diagonal  $2 \times 2$  matrices

$$(\hat{\mathbf{Q}}\hat{f})(n) = \begin{pmatrix} \hat{Q}_1(n) & 0\\ 0 & \hat{Q}_2(n) \end{pmatrix} \begin{pmatrix} \hat{f}_1(n)\\ \hat{f}_2(n) \end{pmatrix},$$

where

$$\hat{Q}_1(n) := \hat{Q}_1(\mathbf{v}(n)), \quad \hat{Q}_2(n) := \hat{Q}_2(p + \mathbf{v}(n)), \quad n \in \mathbb{Z}^d.$$

Throughout the paper, we shall assume that

$$\sum_{n \in \mathbb{Z}^d} |\hat{Q}_j(n)| < \infty, \quad j = 1, 2.$$

$$(2.1)$$

The discrete Schrödinger operator is denoted by

$$\widehat{\mathbf{H}} = -(d+1)(\Delta_d + 1) + \widehat{\mathbf{Q}}.$$

Passing to the Fourier series, we rewrite  $\hat{H}$  into the following form

$$\mathbf{H}=\mathbf{H}_{0}+\mathbf{Q},$$

where

$$(\mathbf{Q}f)(x) = \begin{pmatrix} (Q_1f_1)(x)\\ (Q_2f_2)(x) \end{pmatrix}, \quad f \in L_2^{(2)}(\mathbb{T}^d),$$
$$(Q_jf_j)(x) = \int_{\mathbb{T}^d} Q_j(x-t)f_j(t)dt, \quad j = 1, 2,$$
$$Q_j(x) = (\mathcal{U}\hat{Q}_j)(x), \quad j = 1, 2.$$

The Main Results. Note that from (2.1), it follows that the function  $Q_j(\cdot)$  is continuous on  $\mathbb{T}^d$ . Hence the operator  $\mathbf{Q}$  is a compact operator. By the Weyl theorem, the essential spectrum  $\sigma_{ess}(\mathbf{H})$  of the operator  $\mathbf{H}$  coincides with the spectrum of the unperturbed operator  $\mathbf{H}_0$ .

**Lemma 2.1.** The spectrum  $\sigma(\mathbf{H}_0)$  of  $\mathbf{H}_0$  coincides with the set

$$\{\lambda : |E(x)|^2 = \lambda^2 \text{ for some } x \in \mathbb{T}^d\},\$$

i.e.,

$$\sigma(\mathbf{H}_0) = [-1, 1].$$

**Theorem 2.1.** Let  $\widehat{\mathbf{Q}}$  satisfy (2.1). Then, the number of eigenvalues of  $\mathbf{H}$  lying in  $(-\infty, -1) \cup (1, \infty)$  is finite, *i.e. the discrete spectrum of*  $\mathbf{H}$  *is a finite set.* 

The proof of Theorem 2.1 implies the following theorem.

**Theorem 2.2.** Let  $v_{ij}$ , i, j = 1, 2 be continuous functions on  $(\mathbb{T}^d)^2$  and  $\mathbf{V} = \left(V_{ij}\right)_{i,j=1}^2$ , where  $V_{ij}$  is an integral operator with kernel  $v_{ij}(x, y), x, y \in \mathbb{T}^d$ ,  $d \ge 2$ . Then the discrete spectrum of  $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}$  is finite set.

#### 3. Proof of the Main results

Resolvent of  $\mathbf{H}_0$ . Proof of the Lemma 2.1. The operator  $\mathbf{H}_0 - \lambda \mathbf{I}$  has a matrix form

$$\left(\begin{array}{cc} -\lambda I & E \\ \overline{E} & -\lambda I \end{array}\right),$$

where I is an identity operator and E is operator multiplication by function E(x).

Therefore, the inverse of this matrix has the form

$$\left(\begin{array}{cc} -\lambda I & E \\ \overline{E} & -\lambda I \end{array}\right)^{-1} = \left(\begin{array}{cc} L^{-1}(\lambda) & 0 \\ 0 & L^{-1}(\lambda) \end{array}\right) \left(\begin{array}{cc} -\lambda I & -\overline{E} \\ -E & -\lambda I \end{array}\right),$$

where  $L(\lambda)$  is operator multiplication by function  $L(\lambda, x)$ ,  $L(\lambda, x) = \lambda^2 - |E(x)|^2$ .

Let us denote by  $\mathbf{L}_{\lambda}$  and  $\mathbf{A}_{\lambda} \ 2 \times 2$  matrix operators

$$\mathbf{L}_{\lambda} = \begin{pmatrix} L(\lambda) & 0\\ 0 & L(\lambda) \end{pmatrix}, \quad \mathbf{A}_{\lambda} = \begin{pmatrix} -\lambda I & -\overline{E}\\ -E & -\lambda I \end{pmatrix}.$$

Then the resolvent  $\mathbf{R}_0(\lambda) = (\mathbf{H}_0 - \lambda \mathbf{I})^{-1}$  of  $\mathbf{H}_0$  has the form

$$\mathbf{R}_{\mathbf{0}}(\lambda) = \mathbf{L}_{\lambda}^{-1} \mathbf{A}_{\lambda}$$

It follows from this that the operator  $\mathbf{R}_0(\lambda)$  exists if and only if  $L(\lambda, x) \neq 0$  for all  $x \in \mathbb{T}^d$ , i.e iff  $\lambda \notin \{y = |E(x)| : x \in \mathbb{T}^d\} = [-1, 1]$ . Hence, we have  $\sigma(\mathbf{H}_0) = [-1, 1]$ .

The lemma is thus proven.

Remember that  $L(\lambda, x) > 0$  as  $|\lambda| > 1$  for all  $x \in \mathbb{T}^d$ . Therefore  $L(\lambda)$  is a positive operator for all real  $\lambda$  with  $|\lambda| > 1$ . Hence  $\mathbf{L}_{\lambda}$  is a positive operator for all real  $\lambda$  with  $|\lambda| > 1$ . A positive root  $\mathbf{L}_{\lambda}^{-1/2}$  of  $\mathbf{L}_{\lambda}^{-1}$  has the form

$$\mathbf{L}_{\lambda}^{-1/2} = \begin{pmatrix} L^{-1/2}(\lambda) & 0\\ 0 & L^{-1/2}(\lambda) \end{pmatrix},$$

where  $L^{-1/2}(\lambda)$  is an operator multiplication by function  $1/\sqrt{L(\lambda, \cdot)}$ ,  $|\lambda| > 1$ . Let

$$\mathbf{A}_{\lambda}(x) = \begin{pmatrix} -\lambda & -\overline{E(x)} \\ -E(x) & -\lambda \end{pmatrix}.$$

For any fixing  $x \in \mathbb{T}^d$  the eigenvalues of the matrices  $\mathbf{A}_{\lambda}(x)$  are  $\xi_{-}(\lambda, x) = -\lambda - |E(x)|$  and  $\xi_{+}(\lambda, x) = -\lambda + |E(x)|$ . The numbers  $-\lambda \pm |E(x)|$  are positive as  $\lambda < -1$  and negative as  $\lambda > 1$ . Then,  $\mathbf{A}_{\lambda} \ge 0$  as  $\lambda < -1$  and  $-\mathbf{A}_{\lambda} \ge 0$  as  $\lambda > 1$ . Since the operator  $\mathbf{L}_{\lambda}^{-1}$  is commutative with  $\mathbf{A}_{\lambda}$ , the operator  $\mathbf{L}_{\lambda}^{-1}\mathbf{A}_{\lambda}$  is self-adjoint and  $\mathbf{L}_{\lambda}^{-1}\mathbf{A}_{\lambda} \ge 0$  as  $\lambda < -1$ ,  $-\mathbf{L}_{\lambda}^{-1}\mathbf{A}_{\lambda} \ge 0$  as  $\lambda > 1$ .

The positive roots  $[\mathbf{R}_0(\lambda)]^{1/2}$ ,  $\lambda < -1$  and  $[-\mathbf{R}_0(\lambda)]^{1/2}$ ,  $\lambda > 1$  of the operators  $\mathbf{R}_0(\lambda)$ ,  $\lambda > 1$  and  $-\mathbf{R}_0(\lambda)$ ,  $\lambda < 1$  have the following forms, respectively:

$$\mathbf{R}_{0}(\lambda)^{1/2} = \mathbf{L}_{\lambda}^{-1/2} \mathbf{A}_{\lambda}^{-1/2} \quad \text{as} \quad \lambda > 1$$
(3.1)

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$$[-\mathbf{R}_{0}(\lambda)]^{1/2} = \mathbf{L}_{\lambda}^{-1/2} [-\mathbf{A}_{\lambda}]^{-1/2} \quad \text{as} \quad \lambda < -1.$$
(3.2)

**Lemma 3.1**. The positive roots  $[\mathbf{A}_{\lambda}(x)]^{-1/2}$  and  $[-\mathbf{A}_{\lambda}(x)]^{-1/2}$  of the matrix  $\mathbf{A}_{\lambda}(x)$ ,  $\lambda < -1$  and  $-\mathbf{A}_{\lambda}(x)$ ,  $\lambda > 1$  are given, respectively, by

$$\mathbf{A}_{\lambda}^{-1/2} = \frac{1}{2} \begin{pmatrix} \sqrt{\xi_{-}(\lambda,x)} + \sqrt{\xi_{+}(\lambda,x)} & \left[\sqrt{\xi_{-}(\lambda,x)} - \sqrt{\xi_{+}(\lambda,x)}\right] \frac{\overline{E(x)}}{|\overline{E(x)}|} \\ \left(\sqrt{\xi_{-}(\lambda,x)} - \sqrt{\xi_{+}(\lambda,x)}\right) \frac{E(x)}{|\overline{E(x)}|} & \sqrt{\xi_{-}(\lambda,x)} + \sqrt{\xi_{+}(\lambda,x)} \end{pmatrix} \end{pmatrix}$$

and

$$[-\mathbf{A}_{\lambda}]^{1/2}(x) = \frac{1}{2} \begin{pmatrix} \sqrt{-\xi_{-}(\lambda, x)} + \sqrt{-\xi_{+}(\lambda, x)} & \left[\sqrt{-\xi_{-}(\lambda, x)} - \sqrt{-\xi_{+}(\lambda, x)}\right] \frac{\overline{E(x)}}{|\overline{E(x)}|} \\ \left(\sqrt{-\xi_{-}(\lambda, x)} - \sqrt{-\xi_{+}(\lambda, x)}\right) \frac{\overline{E(x)}}{|\overline{E(x)}|} & \sqrt{-\xi_{-}(\lambda, x)} + \sqrt{-\xi_{+}(\lambda, x)} \end{pmatrix} \end{pmatrix}.$$

*Proof.* The eigenvectors of the matrix  $\mathbf{A}_{\lambda}(x)$  corresponding to the eigenvalues  $\xi_{-}(\lambda, x)$  and  $\xi_{+}(\lambda, x)$  are  $\varphi_{-} = 1/\sqrt{2} (1, E(x)/|E(x)|)$  and  $\varphi_{+} = 1/\sqrt{2} (\overline{E(x)}/|E(x)|, -1)$ , respectively, with  $||\varphi_{\pm}|| = 1$ . Therefore the matrix  $\mathbf{A}_{\lambda}(x)$  in a sense operator can be represented as

$$\mathbf{A}_{\lambda}(x) = \xi_{-}(\lambda, x)(\cdot, \varphi_{-})_{\mathbb{C}^{2}}\varphi_{-} + \xi_{+}(\lambda, x)(\cdot, \varphi_{+})_{\mathbb{C}^{2}}\varphi_{+},$$

where  $(\cdot, \cdot)_{\mathbb{C}^2}$  is a usual scalar product of  $\mathbb{C}^2$ . Therefore the positive roots  $[\mathbf{A}_{\lambda}(x)]^{1/2}$ ,  $\lambda < -1$  and  $[-\mathbf{A}_{\lambda}]^{1/2}(x)$ ,  $\lambda > 1$  of the matrices  $\mathbf{A}_{\lambda}(x)$ ,  $\lambda < -1$  and  $-\mathbf{A}_{\lambda}(x)$ ,  $\lambda > 1$  have the forms

$$[\mathbf{A}_{\lambda}(x)]^{1/2} = \sqrt{\xi_{-}(\lambda, x)}(\cdot, \varphi_{-})_{\mathbb{C}^{2}}\varphi_{-} + \sqrt{\xi_{+}(\lambda, x)}(\cdot, \varphi_{+})_{\mathbb{C}^{2}}\varphi_{+}, \quad \lambda < 1,$$
$$[-\mathbf{A}_{\lambda}(x)]^{1/2} = \sqrt{-\xi_{-}(\lambda, x)}(\cdot, \varphi_{-})_{\mathbb{C}^{2}}\varphi_{-} + \sqrt{-\xi_{+}(\lambda, x)}(\cdot, \varphi_{+})_{\mathbb{C}^{2}}\varphi_{+}, \quad \lambda > 1$$

These equalities prove the desired results of the lemma.

Note that the Lemma 3.1 shows that the matrix valued function  $[\mathbf{A}_{\lambda}(\cdot)]^{1/2}$ ,  $\lambda \leq -1$   $([-\mathbf{A}_{\lambda}(\cdot)]^{1/2}$ ,  $\lambda \geq 1)$  is bounded for all  $x \in \mathbb{T}^d$  and  $\lambda \leq -1$   $(\lambda \geq 1)$ .

The Birman-Schwinger principle. We define the self-adjoint compact operators  $\mathbf{T}_{\mp}(z)$ , acting in the Hilbert space  $L_2^{(2)}(\mathbb{T}^d)$  determined by

$${\bf T}_-(z)={\bf R}_0^{1/2}(z){\bf Q}{\bf R}_0^{1/2}(z) \quad {\rm for} \quad z<-1$$

and

$$\mathbf{T}_{+}(z) = -\left[-\mathbf{R}_{0}(z)\right]^{1/2} \mathbf{Q} \left[-\mathbf{R}_{0}(z)\right]^{1/2} \text{ for } 1 < z.$$

By  $N_{-}(z)$  and  $N_{+}(z)$ , we denote the number of eigenvalues of the operator **H** lying to the left from z < -1 and lying to the right from z > 1, respectively.

Let A be a self-adjoint operator acting in a Hilbert space  $\mathcal{H}$ , and let  $\mathcal{H}_A(\lambda)$ ,  $\lambda > \sup \sigma_{ess}(A)$ , be the subspace consisting of the vectors  $f \in \mathcal{H}$  satisfying the condition  $(Af, f) > \lambda(f, f)$ . We set

$$n(\lambda, A) = \sup_{\mathcal{H}_A(\lambda)} \dim \mathcal{H}_A(\lambda).$$

By definition, we have  $N_{-}(z) = n(-z, -\mathbf{H}), -z > 1$  and  $N_{+}(z) = n(z, \mathbf{H}), z > 1$ .

The following lemma is a modification of the well-known Birman–Schwinger principle for the operator H (see [17, 18]).

**Lemma 3.2**. For the numbers  $N_{-}(z)$  and  $N_{+}(z)$  of eigenvalues (counted with multiplicities) of the operator **H** we have the equalities, respectively,

$$N_{-}(z) = n(1, \mathbf{T}_{-}(z)), \quad z < -1,$$
(3.3)

and

$$N_{+}(z) = n(1, \mathbf{T}_{+}(z)), \quad z > 1.$$
 (3.4)

*Proof.* We suppose that  $u \in \mathcal{H}_{\mathbf{H}}(-z)$ , i.e.,

$$(\mathbf{H}u, u) < z(u, u)$$

or

$$((\mathbf{H}_0 - z\mathbf{I})u, u) < -(\mathbf{Q}u, u).$$

Then we have

$$(y,y) < -\left(\mathbf{R}_0^{1/2}(z)\mathbf{Q}\mathbf{R}_0^{1/2}(z)y,y\right), \quad y = (\mathbf{R}_0 - z\mathbf{I})^{1/2}u.$$

Therefore,  $N_{-}(z) \le n \left( 1, \mathbf{R}_{0}^{1/2}(z) \mathbf{Q} \mathbf{R}_{0}^{1/2}(z) \right).$ 

By analogous arguments, we obtain the converse statement:

$$N_{-}(z) \ge n\left(1, \mathbf{R}_{0}^{1/2}(z)\mathbf{Q}\mathbf{R}_{0}^{1/2}(z)\right).$$

Hence inequality (3.3) follows. The equality (3.4) can be proven similarly.

Proof of Theorem 2.1. To prove the theorem, we use the technique proposed in [15], i.e., we show that the operator-valued function  $T_{\pm}(\cdot)$  is well defined at the limits of the essential spectrum and we also use Lemma 3.2 and apply the Weyl inequality [19]

$$n(a+b, A+B) \le n(a, A) + n(b, B),$$

which holds for compact operators A and B.

Let us first show that the operator-valued functions  $T_{-}(\cdot)$  and  $T_{+}(\cdot)$  are continuous in the norm,  $(-\infty, 0]$  and  $[1,\infty)$  respectively.

Note that since **0** is a unite maximum point of  $|E(\cdot)|^2$ , we have

$$C_1 x^2 \le |E(x)|^2 \le C_2 x^2$$
 for all  $x \in \mathbb{T}^d$ .

From this, we get the estimation

$$\frac{1}{\sqrt{L(z,x)}} = \frac{1}{\sqrt{z^2 - |E(x)|^2}} \le \frac{C}{|x|}, \quad \forall |z| \ge 1.$$
(3.5)

Using (3.1) and (3.2) we rewrite  $\mathbf{T}_{-}(z)$  and  $\mathbf{T}_{+}(z)$  as

$$\mathbf{T}_{-}(z) = \mathbf{L}_{z}^{-1/2} \mathbf{A}_{z}^{-1/2} \mathbf{Q} \mathbf{A}_{z}^{-1/2} \mathbf{L}_{z}^{-1/2}, \quad z < -1$$

and

$$\mathbf{T}_{+}(z) = \mathbf{L}_{z}^{-1/2} [-\mathbf{A}_{z}]^{-1/2} \mathbf{Q} [-\mathbf{A}_{z}]^{-1/2} \mathbf{L}_{z}^{-1/2}, \quad z > 1.$$

We denote by  $q_{ij}^{\pm}(z)$  the entries of the matrix operator

$$[\pm \mathbf{A}_{\lambda}]^{-1/2} \mathbf{Q} [\pm \mathbf{A}_{\lambda}]^{-1/2}.$$

Then  $q_{ij}^{\pm}(z)$  are integral operators. Since  $Q(\cdot, \cdot)$  and  $\xi_{\pm}(z, \cdot)$  are continuous functions, respectively on  $(\mathbb{T}^d)^2$  and  $\mathbb{T}^d$  as  $|z| \ge 1$ , the kernel  $q_{ij}^{\pm}(z; \cdot, \cdot)$  of the integral operator  $q_{ij}^{\pm}(z)$  are bounded functions on  $(\mathbb{T}^d)^2$ . It follows from (3.5) that the kernel  $t_{ij}^{\pm}(z; x, y) = \frac{1}{\sqrt{L(z, x)}} q_{ij}^{\pm}(z; x, y) \frac{1}{\sqrt{L(z, y)}}$  of  $\mathbf{T}_{\pm}(z)$  estimated by

$$|t_{ij}^{\pm}(z;x,y)| \leq \frac{C}{|x||y|} \quad \text{as} \quad x,y \in \mathbb{T}^d,$$

where the constant C does not depend of  $z, |z| \ge 1$ . This implies that the functions  $t_{ij}^-(z;\cdot,\cdot), z < -1$  and  $t_{ij}^+(z;\cdot,\cdot), z > 1$  are square-integrable on  $(\mathbb{T}^d)^2$  and  $t_{ij}^{\mp}(z;\cdot,\cdot)$  converges almost everywhere to  $t_{ij}^{\mp}(\mp 1;\cdot,\cdot)$  as  $z \to \mp 1 \mp 0$ . By the Lebesgue theorem, the operator  $\mathbf{T}_{\mp}(z)$  then converges in the norm to  $\mathbf{T}_{\mp}(\mp 1)$  as  $z \to \mp 1 \mp 0$ . Further, using the Weyl inequality, from (3.3) and (3.4) we obtain

$$N_{-}(z) \le n\left(\frac{1}{2}, \mathbf{T}_{-}(z) - \mathbf{T}_{-}(-1)\right) + n\left(\frac{1}{2}, \mathbf{T}_{-}(-1)\right), \quad z < -1$$
$$N_{+}(z) \le n\left(\frac{1}{2}, \mathbf{T}_{+}(z) - \mathbf{T}_{+}(1)\right) + n\left(\frac{1}{2}, \mathbf{T}_{+}(1)\right), \quad z > 1.$$

Since the operator  $T(\pm 1)$  is compact,

$$n\left(\frac{1}{2},\mathbf{T}(\pm 1)\right) < \infty.$$

For small |z+1| and |z-1| we have the equalities, respectively,

$$n\left(\frac{1}{2}, \mathbf{T}_{-}(z) - \mathbf{T}_{-}(-1)\right) = 0$$

and

$$n\left(\frac{1}{2},\mathbf{T}_{+}(z)-\mathbf{T}_{+}(1)\right)=0.$$

Hence, by Lemma 3.2, the number of eigenvalues of H in  $(-\infty, -1) \cup (1, \infty)$  must be finite.

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# To the qualitative properties of solution of system equations not in divergence form of polytrophic filtration in variable density

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In this paper, the properties of solutions for the nonlinear system equations not in divergence form:

$$\begin{split} |x|^n \frac{\partial u}{\partial t} &= u^{\gamma_1} \nabla \left( |\nabla u|^{p-2} \nabla u \right) + |x|^n u^{q_1} v^{q_2} \,, \\ |x|^n \frac{\partial v}{\partial t} &= v^{\gamma_2} \nabla \left( |\nabla v|^{p-2} \nabla v \right) + |x|^n v^{q_4} u^{q_3} \,, \end{split}$$

are studied. In this work, we used method of nonlinear splitting, known previously for nonlinear parabolic equations, and systems of equations in divergence form, asymptotic theory and asymptotic methods based on different transformations. Asymptotic representation of self-similar solutions for the nonlinear parabolic system of equations not in divergence form is constructed. The property of finite speed propagation of distributions (FSPD) and the asymptotic behavior of the weak solutions were studied for the slow diffusive case.

**Keywords:** nonlinear system of equations, not in divergence form, global solutions, self-similar solutions, asymptotic representation of solution. *Received: 20 February 2017* 

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#### 1. Introduction

Consider in  $Q = \{(t, x): t > 0, x \in \mathbb{R}^N\}$  parabolic system of nonlinear equations not in divergence form:

$$|x|^{n} \frac{\partial u}{\partial t} = u^{\gamma_{1}} \nabla \left( |\nabla u|^{p-2} \nabla u \right) + |x|^{n} u^{q_{1}} v^{q_{2}},$$

$$|x|^{n} \frac{\partial v}{\partial t} = v^{\gamma_{2}} \nabla \left( |\nabla v|^{p-2} \nabla v \right) + |x|^{n} v^{q_{4}} u^{q_{3}},$$
(1)

$$u|_{t=0} = u_0(x) \ge 0, \ v|_{t=0} = v_0(x) \ge 0, \ \forall x \in \mathbb{R}^N$$
(2)

where  $n, p, \gamma_i$   $(i = 1, 2), q_i$  (i = 1, 2, 3, 4) the numerical parameters,  $\nabla(\cdot) = \text{grad}_x(\cdot), t$  and  $x \in \mathbb{R}^N$  – respectively, the temporal and spatial coordinates,  $u = u(t, x) \ge 0, v = v(t, x) \ge 0$  are the solutions.

Such systems arise in various applications, such as the spatial segregation of interacting species [1], chemotactic cell migration in tissues [2], and ion transport through biological and synthetic channels (nanopores) [3].

In [4], the Cauchy problem (1)–(2) was studied for p = 2, n = 0 and the absence of absorption, proved the existence of a single viscous solutions, and in [5] investigated the existence and uniqueness of a classical solution of the Cauchy problem for p = 2, n = 0.

In previous research [6], a degenerate nonlinear parabolic system with localized source was considered  $u_t = u^{\alpha} (\Delta u + u^p (x, t) v^q (x_0, t)), v_t = v^{\beta} (\Delta v + v^m (x, t) u^n (x_0, t))$ . In that work [6], the authors investigated blowup properties for a degenerate parabolic system with nonlinear localized sources subject to homogeneous Dirichlet boundary conditions. The main aim of [6] was to study the blow-up rate estimate and the uniform blow-up profile for the blow-up solution. At the end, the blow-up set and blow up rate with respect to the radial variable was considered when the domain Q is a ball.

In [7], the nonlinear degenerate parabolic system  $u_t = v^{\gamma_1} (u_{xx} + au)$ ,  $v_t = u^{\gamma_2} (v_{xx} + bv)$  with Dirichlet boundary conditions was studied. The regularization method and upper-lower solutions technique were employed to show the local existence of a solution for the nonlinear degenerate parabolic system. The global existence of a solution was discussed. The finite time blow-up results, together with an estimate of the blow-up time, were found. The blow-up set with positive measure was analyzed in some detail.

In [8] Chunhua and Jingxue were concerned with the self-similar solutions of the form:

$$u(t,x) = (t+1)^{-\alpha} f\left((t+1)^{\beta} |x|^2\right),\,$$

for the following degenerate and singular parabolic equation in non-divergence form:

$$\frac{\partial u}{\partial t} = u^m \operatorname{div} \left( |\nabla u|^{p-2} \nabla u \right), \quad m \ge 1, \, p > 1.$$

They first established the existence and uniqueness of solutions f with compact supports, which implies that the self-similar solution shrinks. On that basis, the convergent rates of these solutions on the boundary of the supports were also established. Conversely, the convergent speeds of solutions were also considered and compared with the Dirac function as t tends to infinity.

In [9], Raimbekov studied some properties of solutions for the Cauchy problem for nonlinear parabolic equations in non-divergence form with variable density  $|x|^n \frac{\partial u}{\partial t} = u^m \operatorname{div} \left( |\nabla u|^{p-2} \nabla u \right)$ , p > 1,  $0 \le m < \frac{(p-2)(N+n)+p+n}{p-N}$  where they obtained a self-similar solution of the Barenblatt–Zeldovich–Kompaneets type and compared solution methods that proved the asymptotic behavior of solutions in the fast and slow diffusion cases. In this article, some comparative numerical results were also given for the case m = 0, m = 1 and m = 1.5. Using this result, the author discussed the properties for the finite speed of heating propagation for divergent equations and localization for non-divergent case.

In [10] and [11], the authors studied the asymptotic behavior of self-similar solutions of a parabolic system:

$$|x|^{n} \frac{\partial u}{\partial t} = v^{\alpha_{1}} \nabla \left( |x|^{k} u^{m_{1}-1} \nabla u \right) + |x|^{n} u^{\beta_{1}},$$
$$|x|^{n} \frac{\partial v}{\partial t} = u^{\alpha_{2}} \nabla \left( |x|^{k} v^{m_{1}-1} \nabla v \right) + |x|^{n} v^{\beta_{2}}.$$

The Zeldovich–Barenblatt type solution of the Cauchy problem was obtained for a cross-diffusion parabolic system not in divergence form with a source and a variable density. Based on the comparison method, the properties of finite speed perturbation of distribution is considered.

This paper is devoted to constructing a Zeldovich–Barenblatt type solution for the system equation (1). Based on comparing solution methods the properties of FSPD of the Cauchy problem for a parabolic system not in divergence form is established. The asymptotic behavior of a self-similar solution for a nonlinear parabolic system of equations in non-divergence form for slow diffusion case (depending on value of the numerical parameters) is discussed.

#### 2. The self-similar system of equations

Below, a method of nonlinear splitting [13] is provided to construct a self-similar system of equations. For construction of the self-similar solutions of the system (1) in the form:

$$u(x,t) = (t+T)^{-\alpha_1} f(\xi),$$
  

$$v(x,t) = (t+T)^{-\alpha_2} \varphi(\xi),$$
  

$$\xi = (t+T)^{-\gamma} |x|,$$
(3)

where  $\alpha_1 = -\frac{1+q_2-q_4}{(1-q_1)(1-q_4)-q_2q_3}$ ,  $\alpha_2 = -\frac{1+q_3-q_1}{(1-q_1)(1-q_4)-q_2q_3}$ ,  $\gamma = \frac{1-\alpha_1(p+\gamma_1-2)}{p+n}$ , T > 0,  $\alpha_1 (p+\gamma_1-2) = \alpha_2 (p+\gamma_2-2)$ , it can be a self-similar system of equations:

$$f^{\gamma_1}\xi^{1-N}\frac{d}{d\xi}\left(\xi^{N-1}\left|\frac{df}{d\xi}\right|^{p-2}\frac{df}{d\xi}\right) + \alpha_1\xi^n f + \gamma\xi^{n+1}\frac{df}{d\xi} + \xi^n f^{q_1}\varphi^{q_2} = 0,$$

$$\varphi^{\gamma_2}\xi^{1-N}\frac{d}{d\xi}\left(\xi^{N-1}\left|\frac{d\varphi}{d\xi}\right|^{p-2}\frac{d\varphi}{d\xi}\right) + \alpha_2\xi^n\varphi + \gamma\xi^{n+1}\frac{d\varphi}{d\xi} + \xi^n f^{q_3}\varphi^{q_4} = 0.$$
(4)

In [12], the qualitative properties of solutions for system (4) in divergence form were studied based on the self-similar and approximately self-similar approaches.

#### 3. Slow diffusion (case $p + \gamma_i - 2 > 0$ , i = 1, 2). A global solvability of solutions

The properties of a global solvability for weak solutions of the system (1) were proved using a comparison principle [14]. For this goal, a new system of equations was constructed using the standard equation method as in [13]:

$$u_{+}(t,x) = (t+T)^{-\alpha_{1}} \overline{f}(\xi),$$
  

$$v_{+}(t,x) = (t+T)^{-\alpha_{2}} \overline{\varphi}(\xi),$$
(5)

where  $\alpha_1 = -\frac{1+q_2-q_4}{(1-q_1)(1-q_4)-q_2q_3}, \ \alpha_2 = -\frac{1+q_3-q_1}{(1-q_1)(1-q_4)-q_2q_3}, \ \gamma = \frac{1-\alpha_1(p+\gamma_1-2)}{p+n}, \ T > 0,$  $\xi = (t+T)^{-\gamma} |x|.$ 

In case,  $\alpha_1 (p + \gamma_1 - 2) = \alpha_2 (p + \gamma_2 - 2)$ ,

$$\overline{f}(\xi) = A_1 \left( a - \xi^{\frac{p+n}{p-1}} \right)_+^{\frac{p-1}{p+\gamma_1 - 2}}, \quad \overline{\varphi}(\xi) = A_2 \left( a - \xi^{\frac{p+n}{p-1}} \right)_+^{\frac{p-1}{p+\gamma_2 - 2}}, \tag{6}$$

where a > 0,  $A_i = \left(\frac{\gamma(p + \gamma_i - 2)}{(1 - \gamma_i)(p + n)}\right)^{\frac{1}{p + \gamma_i - 2}} \left|\frac{p + n}{p + \gamma_i - 2}\right|^{\frac{2-p}{p + \gamma_i - 2}}$ , (i = 1, 2),  $b_+ = \max(0, b)$ . The following notations can be introduced:

$$k_{i} = \frac{(p-1)q_{2i-1}}{p+\gamma_{1}-2} + \frac{(p-1)q_{2i}}{p+\gamma_{2}-2} - \frac{p-1}{p+\gamma_{i}-2}, \quad h_{i} = \frac{n(p-1)+N(p+\gamma_{i}-2)}{(n+p)(\gamma_{i}-1)} - \frac{p}{n+p}, \ i = 1, 2$$
$$m_{1} = A_{1}^{q_{1}-1}A_{2}^{q_{2}}, \quad m_{2} = A_{1}^{q_{3}}A_{2}^{q_{4}-1}.$$

**Theorem 1.** (A global solvability). Let the conditions of  $p + \gamma_i - 2 > 0$ ,  $k_i \ge 0$ ,

$$-\frac{N+n}{(n+p)(1-\gamma_i)} - h_i \alpha_i + m_i a^{k_i} \le 0, \quad i = 1, 2,$$

$$u_+(0, x) \ge u_0(x) \quad v_+(0, x) \ge v_0(x) \quad x \in \mathbb{R}^N$$

$$u_{+}(0,x) \ge u_{0}(x), \ v_{+}(0,x) \ge v_{0}(x), \ x \in \mathbb{R}^{2}$$

Then, for sufficiently small  $u_0(x)$ ,  $v_0(x)$ , the followings holds:

$$u(t,x) \le u_{+}(t,x), \quad v(t,x) \le v_{+}(t,x) \quad in \ Q,$$
(7)

where the functions  $u_+(t, x)$ ,  $v_+(t, x)$  defined as above.

**Proof.** Theorem 1 is proved by the comparing solution method [14]. Hence, comparing solution methods it is taken the functions  $u_+(t, x)$ ,  $v_+(t, x)$ . Substituting (5) in (1) the following inequality can be obtained:

$$\overline{f}^{\gamma_1}\xi^{1-N}\frac{d}{d\xi}\left(\xi^{N-1}\left|\frac{d\overline{f}}{d\xi}\right|^{p-2}\frac{d\overline{f}}{d\xi}\right) + \alpha_1\xi^n\overline{f} + \gamma\xi^{n+1}\frac{d\overline{f}}{d\xi} + \xi^n\overline{f}^{q_1}\overline{\varphi}^{q_2} \le 0,$$

$$\overline{\varphi}^{\gamma_2}\xi^{1-N}\frac{d}{d\xi}\left(\xi^{N-1}\left|\frac{d\overline{\varphi}}{d\xi}\right|^{p-2}\frac{d\overline{\varphi}}{d\xi}\right) + \alpha_2\xi^n\overline{\varphi} + \gamma\xi^{n+1}\frac{d\overline{\varphi}}{d\xi} + \xi^n\overline{f}^{q_3}\overline{\varphi}^{q_4} \le 0.$$
(8)

If the specific form (6) is given for the functions  $\overline{f}(\xi)$ ,  $\overline{\varphi}(\xi)$ , inequality (8) can be rewritten as follows:

$$-\frac{N+n}{(n+p)(1-\gamma_1)} - h_1\alpha_1 + m_1\left(a - \xi^{\frac{p+n}{p-1}}\right)^{k_1} \le 0,$$
$$-\frac{N+n}{(n+p)(1-\gamma_2)} - h_2\alpha_2 + m_2\left(a - \xi^{\frac{p+n}{p-1}}\right)^{k_2} \le 0.$$

It is easy to check that  $m_1\left(a-\xi^{\frac{p+n}{p-1}}\right)^{k_1} \le m_1 a^{k_1}, m_2\left(a-\xi^{\frac{p+n}{p-1}}\right)^{k_2} \le m_2 a^{k_2}.$ 

Then, according to the hypotheses of Theorem 1 and comparison principle, it will be:  $u(t,x) \le u_+(t,x)$ ,  $v(t,x) \le v_+(t,x)$  in Q, if  $u_+(0,x) \ge u_0(x)$ ,  $v_+(0,x) \ge v_0(x)$ ,  $x \in \mathbb{R}^N$ .

The proof of the theorem is completed.

#### 4. Asymptotic of the self-similar solutions

Next, the asymptotic behavior of the self-similar solutions of the system (4) is studied. Self-similar solution of system equations (4) will be searched for in the form:

$$f(\xi) = \overline{f}(\xi)y(\eta), \quad \varphi(\xi) = \overline{\varphi}(\xi)z(\eta), \quad \eta = -\ln\left(a - \xi^{\frac{p+n}{p-1}}\right), \tag{9}$$

where  $\overline{f}(\xi) = \left(a - \xi^{\frac{p+n}{p-1}}\right)^{\frac{p-1}{p+\gamma_1-2}}, \, \overline{\varphi}(\xi) = \left(a - \xi^{\frac{p+n}{p-1}}\right)^{\frac{p-1}{p+\gamma_2-2}}, \, a > 0.$ 

Then, substituting (9) into (4) for the function  $y(\eta) > 0$ ,  $z(\eta) > 0$ , the following system of nonlinear equations is obtained:

$$y^{\gamma_{1}}\frac{d}{d\eta}(L_{1}y) + a_{11}(\eta)y^{\gamma_{1}}(L_{1}y) + a_{12}(\eta)\left(\frac{dy}{d\eta} + a_{10}(\eta)y\right) + a_{13}(\eta)y^{q_{1}}z^{q_{2}} + a_{14}(\eta)y = 0,$$

$$z^{\gamma_{2}}\frac{d}{d\eta}(L_{2}z) + a_{21}(\eta)z^{\gamma_{2}}(L_{2}z) + a_{22}(\eta)\left(\frac{dz}{d\eta} + a_{20}(\eta)z\right) + a_{23}(\eta)y^{q_{3}}z^{q_{4}} + a_{24}(\eta)z = 0.$$
(10)

Here, 
$$a_{i0}(\eta) = -\frac{p-1}{p+\gamma_i-2}$$
,  $a_{i1}(\eta) = \frac{(N+n)(p-1)}{p+n} \frac{e^{-\eta}}{a-e^{-\eta}} - \frac{(p-1)(1-\gamma_i)}{p+\gamma_i-2}$ ,  $a_{i2}(\eta) = \gamma \left(\frac{p-1}{p+n}\right)^{p-1}$ ,  
 $a_{i4}(\eta) = \alpha_i \left(\frac{p-1}{p+n}\right)^p$ ,  $a_{i3}(\eta) = \left(\frac{p-1}{p+n}\right)^p \frac{e^{-s_i\eta}}{a-e^{-\eta}}$ ,  $s_i = 1 + \frac{(p-1)q_{2i-1}}{p+\gamma_1-2} + \frac{(p-1)q_{2i}}{p+\gamma_2-2} - \frac{p-1}{p+\gamma_i-2}$   $(i = 1, 2)$ ,  
 $L_1y = \left|\frac{dy}{d\eta} + a_{10}(\eta)y\right|^{p-2} \left(\frac{dy}{d\eta} + a_{10}(\eta)y\right)$ ,  $L_2z = \left|\frac{dz}{d\eta} + a_{20}(\eta)z\right|^{p-2} \left(\frac{dz}{d\eta} + a_{20}(\eta)z\right)$ .  
There, it is assumed that  $\xi \in [\xi_0, \xi_1)$ ,  $0 < \xi_0 < \xi_1$ ,  $\xi_1 = a^{\frac{p-1}{p+n}}$ .

There, it is assumed that  $\xi \in [\xi_0, \xi_1), 0 < \xi_0 < \xi_1, \xi_1 = a^{p+n}$ . Therefore, the function  $\eta(\xi)$  has the properties:  $\eta'(\xi) > 0$  at  $\xi \in [\xi_0, \xi_1), \eta_0 = \eta(\xi_0) > 0, \lim_{\xi_0 \to \xi_1} \eta(\xi) = +\infty$ . Further, the self-similar system of equations (10) is investigated in the following limitations:  $\lim_{\eta \to +\infty} a_{ij}(\eta) = a_{ij}^0$ ,

 $0 < \left|a_{ij}^{0}\right| < +\infty, (i = 1, 2; j = 0, 1, 2, 3, 4).$ 

Through the introduction of transformations (3), (9) and properties  $\eta \to +\infty$ , study of the solutions of (1) is reduced to the study of the solutions of (10), each of which is in the vicinity  $+\infty$  and satisfies the inequalities:

$$y(\eta) > 0, \quad y' + a_{10}(\eta)y \neq 0,$$
  
 $z(\eta) > 0, \quad z' + a_{20}(\eta)z \neq 0.$ 

Now, the asymptotic behavior of the positive solutions of (10), having a nonzero a finite limit as  $\eta \to +\infty$  is studied.

#### 5. The main results

Here, we introduce the notations:

$$c_{i1} = \frac{1 - \gamma_i}{(p + \gamma_i - 2)^p}, \quad c_{i2} = \frac{1}{(p + n)^{p-1}} \left(\frac{\alpha_i}{p + n} - \frac{\gamma}{p + \gamma_i - 2}\right), \quad c_{i3} = \frac{1}{(p + n)^p a} \quad (i = 1, 2)$$

Let  $y(\eta) = y^0 + o(1), z(\eta) = z^0 + o(1)$  at  $\eta \to +\infty$  and the equality  $(1 + q_1)(\gamma_1 + p - 2) = (1 + q_2)(\gamma_2 + p - 2)$ is performed.

Then, this is validated by the following theorems:

**Theorem 2.** Let  $s_1 = 0$ ,  $s_2 = 0$ . Then, the self-similar solution of system (1) has the asymptotic at  $|x| \rightarrow 1$  $a^{\frac{p-1}{p+n}}(t+T)^{\gamma}$ 

$$u_{A}(t,x) = (T+t)^{-\alpha_{1}} \left( a - \left( \frac{|x|}{(t+T)^{\gamma}} \right)^{\frac{p+n}{p-1}} \right)_{+}^{\frac{p-1}{p+\gamma_{1}-2}} \left( y^{0} + o(1) \right),$$

$$v_{A}(t,x) = (T+t)^{-\alpha_{2}} \left( a - \left( \frac{|x|}{(t+T)^{\gamma}} \right)^{\frac{p+n}{p-1}} \right)_{+}^{\frac{p-1}{p+\gamma_{2}-2}} \left( z^{0} + o(1) \right),$$
(11)

where  $0 < y^0 < +\infty$ ,  $0 < z^0 < +\infty$  and  $y^0$ ,  $z^0$  are the solutions  $w_1$ ,  $w_2$  for the system of nonlinear algebraic equations:

$$c_{i1}w_i^{p+\gamma_i-1} + c_{i2}w_i + c_{i3}w_1^{q_{2i-1}}w_2^{q_{2i}} = 0 \quad (i = 1, 2).$$
(12)

**Theorem 3.** Let  $s_1 = 0$ ,  $s_2 > 0$ . Then, the self-similar solution of system (1) has the asymptotic at  $|x| \rightarrow a^{\frac{p-1}{p+n}}(t+T)^{\gamma}$  form (11), where  $0 < y^0 < +\infty$ ,  $0 < z^0 < +\infty$  and  $y^0$ ,  $z^0$  are the solutions  $w_1$ ,  $w_2$  for the system of nonlinear algebraic equations:

$$c_{11}w_1^{p+\gamma_1-1} + c_{12}w_1 + c_{13}w_1^{q_1}w_2^{q_2} = 0, \quad c_{21}w_2^{p+\gamma_2-1} + c_{22}w_2 = 0.$$

**Theorem 4.** Let  $s_1 > 0$ ,  $s_2 = 0$ . Then, the self-similar solution of equation (1) has an asymptotic at  $|x| \rightarrow a^{\frac{p-1}{p+n}}(t+T)^{\gamma}$  form (11), where  $0 < y^0 < +\infty$ ,  $0 < z^0 < +\infty$  and  $y^0$ ,  $z^0$  are the solutions  $w_1$ ,  $w_2$  the system of nonlinear algebraic equations

$$c_{11}w_1^{p+\gamma_1-2} + c_{12}w_1 = 0, \quad c_{21}w_2^{p+\gamma_2-2} + c_{22}w_2 + c_{23}w_1^{q_3}w_2^{q_4} = 0.$$

**Theorem 5.** Let  $s_1 > 0$ ,  $s_2 > 0$ . Then, the self-similar solution of equation (1) has the asymptotic at  $|x| \rightarrow a^{\frac{p-1}{p+n}}(t+T)^{\gamma}$  form (11), where  $0 < y^0 < +\infty$ ,  $0 < z^0 < +\infty$  and  $y^0$ ,  $z^0$  are the solutions  $w_1$ ,  $w_2$  for the system of nonlinear algebraic equations:

$$c_{11}w_1^{p+\gamma_1-2} + c_{12}w_1 = 0, \quad c_{21}w_2^{p+\gamma_2-2} + c_{22}w_2 = 0.$$

#### The proof. Assuming that the system (10) as:

$$\vartheta_1(\eta) = L_1 y, \quad \vartheta_2(\eta) = L_2 z,$$
(13)

the following identity is obtained:

$$\vartheta_{1}^{'}(\eta) \equiv -a_{11}(\eta)\vartheta_{1}(\eta) - a_{12}(\eta)y^{-\gamma_{1}}\vartheta_{1}^{\frac{1}{p-1}}(\eta) - a_{13}(\eta)y^{q_{1}-\gamma_{1}}z^{q_{2}} - a_{14}(\eta)y^{1-\gamma_{1}},$$

$$\vartheta_{2}^{'}(\eta) \equiv -a_{21}(\eta)\vartheta_{2}(\eta) - a_{22}(\eta)z^{-\gamma_{2}}\vartheta_{2}^{\frac{1}{p-1}}(\eta) - a_{23}(\eta)z^{q_{4}-\gamma_{2}}y^{q_{3}} - a_{24}(\eta)z^{1-\gamma_{2}}.$$
(14)

Now, we consider the function as:

$$g_{1}(\lambda_{1},\eta) \equiv -a_{11}(\eta)\lambda_{1} - a_{12}(\eta)y^{-\gamma_{1}}\lambda_{1}^{\frac{1}{p-1}} - a_{13}(\eta)y^{q_{1}-\gamma_{1}}z^{q_{2}} - a_{14}(\eta)y^{1-\gamma_{1}},$$

$$g_{2}(\lambda_{2},\eta) \equiv -a_{21}(\eta)\lambda_{2} - a_{22}(\eta)z^{-\gamma_{2}}\lambda_{2}^{\frac{1}{p-1}} - a_{23}(\eta)z^{q_{4}-\gamma_{2}}y^{q_{3}} - a_{24}(\eta)z^{1-\gamma_{2}},$$
(15)

where  $\lambda_i \in \mathbb{R}$  (i = 1, 2).

Suppose first that  $s_i = 0$  (i = 1, 2). Then, the functions  $g_i(\lambda_i, \eta)$  (i = 1, 2) preserves sign on some interval  $[\eta_1, +\infty) \subset [\eta_0, +\infty)$  for every fixed value  $\lambda_i$  (i = 1, 2), different from the values satisfying system:

$$-a_{11}^{0}\lambda_{1} - a_{12}^{0}(y^{0})^{-\gamma_{1}}\lambda_{1}^{\frac{1}{p-1}} - a_{13}^{0}(y^{0})^{q_{1}-\gamma_{1}}(z^{0})^{q_{2}} - a_{14}^{0}(y^{0})^{1-\gamma_{1}} = 0, -a_{21}^{0}\lambda_{2} - a_{22}^{0}(z^{0})^{-\gamma_{2}}\lambda_{2}^{\frac{1}{p-1}} - a_{23}^{0}(z^{0})^{q_{4}-\gamma_{2}}(y^{0})^{q_{3}} - a_{24}^{0}(z^{0})^{1-\gamma_{2}} = 0.$$

Now, we let  $s_i > 0$  (i = 1, 2). It is easy to see that the functions  $g_i(\lambda_i, \eta)$  (i = 1, 2), for every fixed value  $\lambda_i$  (i = 1, 2), are different from the values satisfying the system:

$$-a_{11}^{0}\lambda_{1} - a_{12}^{0}(y^{0})^{-\gamma_{1}}\lambda_{1}^{\frac{1}{p-1}} - a_{14}^{0}(y^{0})^{1-\gamma_{1}} = 0, -a_{21}^{0}\lambda_{2} - a_{22}^{0}(z^{0})^{-\gamma_{2}}\lambda_{2}^{\frac{1}{p-1}} - a_{24}^{0}(z^{0})^{1-\gamma_{2}} = 0,$$

which preserves the sign on some interval  $[\eta_2, +\infty) \subset [\eta_0, +\infty)$ .

And in the case  $s_i < 0$  (i = 1, 2), the functions  $g_i(\lambda_i, \eta)$  (i = 1, 2) can be rewritten in the following form:

$$\begin{split} g_1(\lambda_1,\eta) &\equiv -a_{11}(\eta)\lambda_1 - a_{12}(\eta)y^{-\gamma_1}\lambda_1^{\frac{1}{p-1}} - a_{13}(\eta)y^{1-\gamma_1}\left(y^{q_1-1}z^{q_2} - a_{14}(\eta)a_{13}^{-1}(\eta)\right),\\ g_2(\lambda_2,\eta) &\equiv -a_{21}(\eta)\lambda_2 - a_{22}(\eta)z^{-\gamma_2}\lambda_2^{\frac{1}{p-1}} - a_{23}(\eta)z^{1-\gamma_2}\left(y^{q_3}z^{q_4-1} - a_{24}(\eta)a_{23}^{-1}(\eta)\right). \end{split}$$

From here:

$$\lim_{\eta \to +\infty} a_{i1}(\eta) = -\frac{(p-1)(1-\gamma_i)}{p+\gamma_i-2}, \quad \lim_{\eta \to +\infty} a_{i2}(\eta) = \gamma \left(\frac{p-1}{p+n}\right)^{p-1}$$
$$\lim_{\eta \to +\infty} a_{i3}(\eta) = \infty, \quad \lim_{\eta \to +\infty} a_{i4}(\eta) = \alpha_i \left(\frac{p-1}{p+n}\right)^p \quad (i=1,2)$$

implies that the functions  $g_i(\lambda_i, \eta)$  (i = 1, 2) preserve sign on the interval  $[\eta_2, +\infty) \subset [\eta_0, +\infty)$ , where  $\lambda_i \neq 0$  (i = 1, 2). Thus, the functions  $g_i(\lambda_i, \eta)$  (i = 1, 2) for all  $\eta \in [\eta_i, +\infty)$  (i = 1, 2) satisfy one of the inequalities:

$$g_i(\lambda_i,\eta) > 0 \quad \text{or} \quad g_i(\lambda_i,\eta) < 0 \quad (i=1,2).$$

$$(16)$$

Suppose now that for the functions  $\vartheta_i(\eta)$  (i = 1, 2) limit as  $\eta \to +\infty$  does not exist. Consider that case when one of the inequalities (16) is satisfied. As  $\vartheta_i(\eta)$  (i = 1, 2) are oscillating functions around straight line

 $\overline{\vartheta}_i = \lambda_i \ (i = 1, 2)$  its graph intersects this straight line infinitely many times in  $[\eta_i, +\infty) \ (i = 1, 2)$ . However, this is impossible, since on the interval  $[\eta_i, +\infty) \ (i = 1, 2)$  just one of the inequalities (16) is valid, and therefore, from (15), it follows that the graph of the functions  $\vartheta_i(\eta) \ (i = 1, 2)$  intersects the straight lines  $\overline{\vartheta}_i = \lambda_i \ (i = 1, 2)$  only once in the interval  $[\eta_i, +\infty) \ (i = 1, 2)$ . Accordingly, the functions  $\vartheta_i(\eta) \ (i = 1, 2)$  has a limit at  $\eta \to +\infty$ . By assumption,  $y(\eta) = y^0 + o(1), \ z(\eta) = z^0 + o(1)$  at  $\eta \to +\infty$ , and the functions  $\vartheta_i(\eta) \ (i = 1, 2)$  defined

By assumption,  $y(\eta) = y^0 + o(1)$ ,  $z(\eta) = z^0 + o(1)$  at  $\eta \to +\infty$ , and the functions  $\vartheta_i(\eta)$  (i = 1, 2) defined in (13), has a limit at  $\eta \to +\infty$ . Then  $y'(\eta)$  and  $z'(\eta)$  have a limit at  $\eta \to +\infty$ , and this limit is zero. Then,

$$\vartheta_{1}(\eta) = \left|\frac{dy}{d\eta} + a_{10}(\eta)y\right|^{p-2} \left(\frac{dy}{d\eta} + a_{10}(\eta)y\right) = \left|a_{10}^{0}y^{0}\right|^{p-2}a_{10}^{0}y^{0} + o(1),$$
$$\vartheta_{2}(\eta) = \left|\frac{dz}{d\eta} + a_{20}(\eta)z\right|^{p-2} \left(\frac{dz}{d\eta} + a_{20}(\eta)z\right) = \left|a_{20}^{0}z^{0}\right|^{p-2}a_{20}^{0}z^{0} + o(1).$$

at  $\eta \to +\infty$  and by (14), the derivative of functions  $\vartheta_i(\eta)$  (i = 1, 2) has a limit at  $\eta \to +\infty$ , which are obviously equal to zero.

Consequently, the following is necessary:

$$\lim_{\eta \to +\infty} \left( a_{11}(\eta)\vartheta_1(\eta) + a_{12}(\eta)y^{-\gamma_1}\vartheta_1^{\frac{1}{p-1}}(\eta) + a_{13}(\eta)y^{q_1-\gamma_1}z^{q_2} + a_{14}(\eta)y^{1-\gamma_1} \right) = 0,$$
$$\lim_{\eta \to +\infty} \left( a_{21}(\eta)\vartheta_2(\eta) + a_{22}(\eta)z^{-\gamma_2}\vartheta_2^{\frac{1}{p-1}}(\eta) + a_{23}(\eta)z^{q_4-\gamma_2}y^{q_3} + a_{24}(\eta)z^{1-\gamma_2} \right) = 0.$$

From this expression, it is easy to see that the system (13) has a solution  $(y(\eta), z(\eta))$  with a finite non-zero limit, at  $\eta \to +\infty$ , necessary, for compliance with one of the conditions of Theorems 2, 3, 4, 5.

Consequently, by the transformations introduced by (3) and (9), self-similar solution of the system equation (1) has an asymptotic at  $|x| \rightarrow a^{\frac{p-1}{p+n}}(t+T)^{\gamma}$  of the following form:

$$u_{A}(t,x) = (T+t)^{-\alpha_{1}} \left( a - \left( \frac{|x|}{(t+T)^{\gamma}} \right)^{\frac{p+n}{p-1}} \right)_{+}^{\frac{p+1}{p+\gamma_{1}-2}} (y^{0} + o(1)),$$
$$v_{A}(t,x) = (T+t)^{-\alpha_{2}} \left( a - \left( \frac{|x|}{(t+T)^{\gamma}} \right)^{\frac{p+n}{p-1}} \right)_{+}^{\frac{p-1}{p+\gamma_{2}-2}} (z^{0} + o(1)).$$

The theorems are thus proved.

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# On a problem for the loaded degenerating mixed type equation involving integral-differential operators

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This work aims to study the existence and uniqueness of a solution for a problem of the loaded degenerating mixed type equation. We consider the loaded parabolic-hyperbolic equation involving the Caputo fractional derivative and Riemann-Liouville integrals. The uniqueness of solution is proved by using the method of integral energy applying an extremum principle. Based on the statement of equivalence between "The existence and uniqueness of solution" and "Solvability of the respectively Fredholm type integral equations", the existence of a solution was proved.

Keywords: loaded degenerating equation, parabolic-hyperbolic type, integral operators, Caputo fractional derivative, existence and uniqueness of solution, integral equations.

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#### 1. Introduction

The first, most general definitions of loaded equations and various loaded equations were classified in detail by A. M. Nakhushev [1].

Definition 1. An equation Au(x) = f(x) is called a loaded equation in n dimensional Euclidean domain  $\Omega$  if the operator A depends of the restriction of the unknown function to a closed subset of  $\overline{\Omega}$ , of measure strictly less than n.

To that end, some local and non-local problems were investigated for the loaded mixed type equation involving fractional order integral-differential operators (see [2, 3]). In the works [4–7] we can see significant development in the field of fractional differential equations in recent years. Various phenomena in physics, like diffusion in a disordered or fractal medium, or in image analysis, or in risk management have been modeled by means of fractional partial differential equations. In general, there exists no method that yields an exact solution for these equations. Indeed, we can find numerous applications in viscoelasticity, neurons, electrochemistry, control, porous media, electromagnetism, etc., (for details, see [8–11]). See Ref. [12] for deterministic fractional models in bioengineering and nanotechnology. Fractional calculus is widely applied to the investigation of partial differential equations of mixed type and hyperbolic type with degenerations (see [7,13,14]). In a series of papers (see [15–17]), the authors considered some classes of boundary value problems for mixed type non degenerating and degenerating differential equations involving Caputo and Riemann-Liouville fractional derivatives of order  $0 < \alpha \leq 1$ .

#### 2. Preliminaries

## 2.1. Riemann-Liouville and Caputo integral-differential operators

Definition 2. Let f(x) be an absolutely continuous function over (a, b). Then the left and right Riemann–Liouville fractional integrals order  $\alpha$  ( $\alpha \in \mathbb{R}^+$ ) (respectively) are (see [4], p. 69)

$$\left(I_{a+}^{\alpha}f\right)x = \frac{1}{\Gamma(\alpha)}\int_{a}^{x}f(t)(x-t)^{\alpha-1}dt, \quad x > a$$
(1)

$$\left(I_{-b}^{\alpha}f\right)x = \frac{1}{\Gamma(\alpha)}\int_{x}^{b}f(t)(t-x)^{\alpha-1}dt, \quad x < b.$$
<sup>(2)</sup>

Definition 3. The Riemann-Liouville fractional derivatives  $D_{ax}^{\alpha}f$  and  $D_{xb}^{\alpha}f$  of order  $\alpha(\alpha \in \mathbb{R}^+)$ , are defined by (see [4], p. 70):

$$(D_{ax}^{\alpha}f)x = \frac{1}{\Gamma(n-\alpha)} \left(\frac{d}{dx}\right)^n \int_a^x \frac{f(t)}{\left(x-t\right)^{\alpha-n+1}} dt, \ n = [\alpha] + 1, \quad x > a;$$
(3)

$$(D_{xb}^{\alpha}f)x = \frac{1}{\Gamma(n-\alpha)} \left(-\frac{d}{dx}\right)^n \int_x^b \frac{f(t)}{(t-x)^{\alpha-n+1}} dt, \quad n = [\alpha] + 1, \quad x < b;$$
(4)

respectively, where  $[\alpha]$  is the integer part of  $\alpha$ . In particular, for  $\alpha = N \cup \{0\}$  we have  $(D_{ax}^0 f) x = f(x)$ ,  $(D_{xb}^0 f) x = f(x)$ ,  $(D_{ax}^n f) x = f^{(n)}(x)$ ;  $(D_{xb}^n f) x = (-1)^n f^{(n)}(x)$ ,  $n \in \mathbb{N}$ , where  $f^{(n)}(x)$  is the usual derivative of f(x) of order n.

Definition 4. Caputo fractional derivatives  ${}_{C}D^{\alpha}_{ax}f$  and  ${}_{C}D^{\alpha}_{xb}f$  of order  $\alpha > 0$  ( $\alpha \notin \mathbb{N} \cup \{0\}$ ) are defined by (see [4], p. 92):

$$({}_{C}D^{\alpha}_{ax}f)x = \frac{1}{\Gamma(n-\alpha)}\int_{a}^{x} \frac{f^{(n)}(t)}{(x-t)^{\alpha-n+1}}dt, \quad n = [\alpha] + 1, \quad x > a;$$
(5)

$$({}_{C}D_{xb}^{\alpha}f)x = \frac{(-1)^{n}}{\Gamma(n-\alpha)}\int_{x}^{b}\frac{f^{(n)}(t)}{(t-x)^{\alpha-n+1}}dt, \quad n = [\alpha] + 1, \quad x < b;$$
(6)

respectively. From (3)–(6), as a conclusion we will have:  $k - 1 < \alpha \leq k, k \in \mathbb{N}$ ; consequently, while for  $\alpha \in \mathbb{N} \cup \{0\}$  we have

$$(_{C}D^{0}_{ax}f) x = f(x), \quad (_{C}D^{0}_{xb}f) x = f(x),$$
  
 $(_{C}D^{n}_{ax}f) x = f^{(n)}(x), \quad (_{C}D^{n}_{xb}f) x = (-1)^{n}f^{(n)}(x), n \in \mathbb{N}.$ 

#### 2.2. Gauss hypergeometric function

Gauss hypergeometric function F(a, b, c, z) is defined in the unit desk as the sum of the hypergeometric series (see [4], p. 27):

$$F(a, b, c, z) = \sum_{k=0}^{\infty} \frac{(a)_k (b)_k}{(c)_k} \frac{z^k}{k!},$$
(7)

where |z| < 1,  $a, b \in \mathbb{C}$ ,  $c \in \mathbb{C} \setminus Z_0^-$  and  $(a)_0 = 1$ ,  $(a)_n = a(a+1)...(a+n-1) = \frac{\Gamma(a)}{\Gamma(a+n)}$ , (n = 1, 2, ...).

One such analytic continuation is given by Euler integral representation:

$$F(a,b,c;z) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_{0}^{1} x^{b-1} (1-x)^{c-b-1} (1-zx)^{-a} dx,$$
(8)

 $0 < \operatorname{Re} b < \operatorname{Re} c$ ,  $|\operatorname{arg}(1-z)| < \pi$ . The Gauss hypergeometric function F(a, b, c, z) allows the following estimation:

$$F(a,b,c;z) \leq \begin{cases} c_1, & \text{if } c-a-b>0, \quad 0 \leq z \leq 1; \\ c_2(1-z)^{c-a-b}, & \text{if } c-a-b<0, \quad 0 < z < 1; \\ c_3\left(1+|\ln(1-z)|\right), & \text{if } c-a-b=0. \end{cases}$$
(9)

#### 2.3. Wright type functions

The elementary definition of the Wright type function at  $\alpha > \beta$ ,  $\alpha > 0$  and for all  $z \in \mathbb{C}$ , is [18]

$$e_{\alpha,\beta}^{\mu,\delta}(z) = \sum_{k=0}^{\infty} \frac{z^n}{\Gamma(\alpha n + \mu)\Gamma(\delta - \beta n)}.$$
(10)

If  $\alpha = \mu = 1$ , then from (10) we have:

$$e_{1,\beta}^{1,\delta}(z) = \sum_{k=0}^{\infty} \frac{z^n}{n! \Gamma(\delta - \beta n)}.$$
(11)

#### 3. Problem formulation and main functional relation

We consider equation:

$$0 = \begin{cases} u_{xx} - C D_{oy}^{\alpha} u + \sum_{k=1}^{n} p_k I_{0x}^{\beta_k} u(x, 0), & \text{at } y > 0; \\ (-y)^m u_{xx} - x^m u_{yy} + \sum_{k=1}^{n} q_k I_{0\eta}^{\gamma_k} u\left(\eta^{\frac{1}{m+2}}, 0\right), & \text{at } y < 0 \end{cases}$$
(12)

with operators (see (1) and (5)):

$${}_{C}D^{\alpha}_{oy}u = \frac{1}{\Gamma(1-\alpha)}\int_{0}^{y} (y-t)^{-\alpha}u_{t}(x,t)dt, \quad \left(I^{\beta}_{ax}u\right)(x,0) = \frac{1}{\Gamma(\beta)}\int_{a}^{x} (x-t)^{\beta-1}u(t,0)dt, \tag{13}$$

where  $0 < \alpha, \beta_k, \gamma_k < 1, \xi = x^{\frac{m+2}{2}} - (-y)^{\frac{m+2}{2}}, m, p_k, q_k = const, m > 0.$ We set the  $\Omega$  domain, bounded with segments:  $A_1A_2 = \{(x,y) : x = 1, 0 < y < h\}, B_1B_2 = \{(x,y) : x = 0, 0 < y < h\}, B_2A_2 = \{(x,y) : y = h, 0 < x < 1\}$  at the y > 0, and by the characteristics:  $A_1C : x^{\frac{m+2}{2}} + (-y)^{\frac{m+2}{2}} = 1; B_1C : x^{\frac{m+2}{2}} - (-y)^{\frac{m+2}{2}} = 0$  of equation (12) at y < 0, where  $A_1(1;0), A_2(1;h), B_1(0;0), B_2(0;h), C\left(2^{-\frac{2}{m+2}}; -2^{-\frac{2}{m+2}}\right)$ . Introduce designations:  $\Omega^+ = \Omega \cap (y > 0), \Omega^- = \Omega \cap (y < 0)$ .

For equation (12), we consider the following problem: find a solution u(x, y) of equation (12) from the following class of functions:

$$W = \left\{ u(x,y) : \ u(x,y) \in C(\bar{\Omega}) \cap C^{2}(\Omega^{-}), \quad u_{xx} \in C\left(\Omega^{+}\right), \quad {}_{C}D_{oy}^{\alpha}u \in C\left(\Omega^{+}\right) \right\}$$

satisfies boundary conditions:

$$u(x,y)\Big|_{A_1A_2} = \varphi(y), 0 \le y \le h,$$
 (14)

$$u(x,y)\Big|_{B_1B_2} = \psi(y), 0 \le y \le h,$$
(15)

$$|u(x,y)|_{B_1C} = h(x), \quad 0 \le x \le 2^{-\frac{2}{m+2}}.$$
 (16)

and gluing conditions:

$$\lim_{y \to +0} y^{1-\alpha} u_y(x,y) = \lambda u_y(x,-0), \quad (x,0) \in A_1 B_1,$$
(17)

where  $\varphi(y)$ ,  $\psi(y)$ , h(x) are given functions and  $\lambda = const$  ( $\lambda \in \mathbb{R}^+$ ). In order to solve the above problem we need the following Riemann function.

Its known [19] that the Riemann function for equation (12) at y < 0 on the characteristics coordinate  $\xi = x^{\frac{m+2}{2}} - (-y)^{\frac{m+2}{2}}$  and  $\eta = x^{\frac{m+2}{2}} + (-y)^{\frac{m+2}{2}}$  defined with the Gauss hypergeometric function

$$R(\xi_0, \eta_0; \xi, \eta) = \frac{(\eta^2 - \xi^2)^{2\delta}}{(\eta^2 - \xi_0^2)^{\delta} (\eta_0^2 - \xi^2)^{\delta}} F\left(\delta, \delta, 1; \frac{(\xi_0^2 - \xi^2) (\eta^2 - \eta_0^2)}{(\eta^2 - \xi_0^2) (\eta_0^2 - \xi^2)}\right),$$
(18)

where  $\delta = \frac{m}{2(m+2)}$ . In fact, that a solution of the Cauchy problem for equation (12) in the domain  $\Omega^-$  with initial dates

$$u(x,0) = \tau(x), \quad 0 \le x \le 1;$$
  

$$u_y(x,-0) = \nu^-(x), \quad 0 < x < 1,$$
(19)

will be given by formula:

$$u(x,y) = k_1 \int_{\xi}^{\eta} (t^2 - \xi^2)^{-\delta} (\eta^2 - t^2)^{-\delta} \nu^{-} (t^{1-2\delta}) dt - k_2 \int_{\xi}^{\eta} (\eta^2 - \xi^2)^{1-2\delta} (t^2 - \xi^2)^{\delta-1} (\eta^2 - t^2)^{\delta-1} t\tau^{-} (t^{1-2\delta}) dt + \sum_{k=1}^{n} \int_{\xi}^{\eta} q_k I_{0t^2}^{\gamma_k} \tau(t^{1-2\delta}) dt \int_{t}^{\eta} \frac{(\eta^2 - \xi^2)^{2\delta}}{(\eta^2 - t^2)^{\delta} (z^2 - \xi^2)^{\delta}} F\left(\delta, \delta, 1; \frac{(t^2 - \xi^2)(\eta^2 - z^2)}{(\eta^2 - t^2)(z^2 - \xi^2)}\right) dz,$$
(20)

where

$$k_1 = \frac{\Gamma(2\delta)}{\Gamma^2(\delta)}, \quad k_2 = \frac{\Gamma(1-2\delta)}{2^{1-2\delta}\Gamma^2(1-\delta)} \left(\frac{m+2}{2}\right)^{-2\delta}$$

Let us find the relation between  $\tau^{-}(x)$  and  $\nu^{-}(x)$  transferred from the hyperbolic part  $\Omega^{-}$  to the line y = 0. By using condition (16) and taking (13) into account, from (20) we obtain:

$$\begin{split} \tilde{\nu}^{-}\left(\eta^{1-2\delta}\right) &= \frac{k_{2}\Gamma(1-\delta)}{k_{1}\Gamma(\delta)}\eta D_{0\,\eta^{2}}^{1-2\delta}\tilde{\tau}\left(\eta^{1-2\delta}\right) - \frac{2\Gamma(1-\delta)}{k_{1}}\eta^{2\delta}D_{0\,\eta^{2}}^{1-\delta}\int_{0}^{\eta}\sum_{k=1}^{n}\frac{q_{k}}{\Gamma(\gamma_{k})}dt\int_{0}^{t^{2}}(t^{2}-s)^{\gamma_{k}-1}\tilde{\tau}(s^{1/2-\delta})ds \times \\ &\int_{t}^{\eta}\frac{\left(\eta^{2}\right)^{2\delta}}{\left(\eta^{2}-t^{2}\right)^{\delta}(z^{2})^{\delta}}F\left(\delta,\delta,1;\frac{t^{2}\left(\eta^{2}-z^{2}\right)}{z^{2}\left(\eta^{2}-t^{2}\right)}\right)dz + \frac{2\Gamma(1-\delta)}{k_{1}}\eta^{2\delta}D_{0\,\eta^{2}}^{1-\delta}h\left[\left(\frac{\eta}{4}\right)^{\frac{2}{m+2}}\right]. \end{split}$$

Moreover, replacing  $\eta^2 \sim \eta_1$ ,  $t^2 \sim t$ ,  $z^2 \sim z$  we have:

$$\tilde{\nu}^{-}(\eta) = \frac{k_{2}\Gamma(1-\delta)}{k_{1}\Gamma(\delta)} \eta_{1}^{1/2} D_{0\eta_{1}}^{1-2\delta} \tilde{\tau}(\eta) - \frac{\Gamma(1-\delta)}{2k_{1}} \eta_{1}^{\delta} D_{0\eta_{1}}^{1-\delta} \int_{0}^{\eta_{1}} \sum_{k=1}^{n} \frac{q_{k} t^{1/2}}{\Gamma(\gamma_{k})} dt \int_{0}^{t} (t-s)^{\gamma_{k}-1} \tilde{\tau}(s) ds \times \int_{t}^{\eta_{1}} \frac{\eta_{1}^{2\delta}}{(\eta_{1}-t)^{\delta} z^{\delta+1/2}} F\left(\delta, \delta, 1; \frac{t(\eta_{1}-z)}{z(\eta_{1}-t)}\right) dz + \frac{2\Gamma(1-\delta)}{k_{1}} \eta_{1}^{\delta} D_{0\eta_{1}}^{1-\delta} h\left[\left(\frac{\eta_{1}}{4}\right)^{\frac{1}{m+2}}\right]$$
(21)  
$$\tilde{\nu}^{-}(\eta) = \nu^{-}\left(\eta^{1-2\delta}\right) = \nu^{-}\left(\eta_{1}^{1/2-\delta}\right),$$

were

$$\tilde{\tau}^{-}(\eta) = \nu^{-}(\eta^{1-2\delta}) = \nu^{-}(\eta^{1/2-\delta}),$$
$$\tilde{\tau}(\eta) = \tau(\eta^{1-2\delta}) = \tau(\eta^{1/2-\delta}).$$

Considering designations (19) and  $\lim_{y \to +0} y^{1-\alpha} u_y(x,y) = \nu^+(x), 0 < x < 1$  from gluing condition (17), we have

$$\nu^+(x) = \lambda \nu^-(x). \tag{22}$$

For further consideration, from Eq. (12) at  $y \rightarrow +0$  considering (13), (22) and

$$\lim_{y \to 0} D_{0y}^{\alpha - 1} f(y) = \Gamma(\alpha) \lim_{y \to 0} y^{1 - \alpha} f(y)$$

we obtain:

$$\tau''(x) - \Gamma(\alpha)\nu^{+}(x) + \sum_{k=1}^{n} p_k I_{0x}^{-\beta_k} \tau(x) = 0.$$
(23)

### 4. Uniqueness of the solution

*Theorem 1.* If satisfy conditions  $\lambda > 0$  and

$$0 < \alpha, \ \beta_k, \ \gamma_k < 1, \quad p_k < 0, \quad q_k < 0, \quad k = 1, 2, ..., n$$
 (24)

are satisfied, then, the solution is unique.

*Proof.* Now, we consider the corresponding homogeneous problem  $[\varphi(y) \equiv \psi(y) \equiv 0]$ . Let us estimate the integral  $J = \int_{0}^{1} \tau(x)\nu^{+}(x)dx$ .

We multiply to  $\tau(x)$  equation (23) and integrate from 0 to 1:

$$\Gamma(\alpha) \int_{0}^{1} \tau(x)\nu^{+}(x)dx = \int_{0}^{1} \tau''(x)\tau(x)dx + \int_{0}^{1} \tau(x)\sum_{k=1}^{n} p_{k}I_{0x}^{-\beta_{k}}\tau(x)dx.$$
(25)

Integrating by parts and using the relations  $\tau(0) = \tau(1) = 0$ , we obtain

$$J \equiv \int_{0}^{1} \tau(x)\nu^{+}(x)dx = -\int_{0}^{1} (\tau'(x))^{2}dx + \sum_{k=1}^{n} \frac{p_{k}}{\Gamma(\beta_{k})} \int_{0}^{1} \tau(x)dx \int_{0}^{x} (x-t)^{\beta_{k}-1}\tau(t)dt.$$

By using the formula (see [8], p. 188):

$$|x-t|^{-\gamma} = \frac{1}{\Gamma(\gamma)\cos\frac{\pi\gamma}{2}} \int_{0}^{\infty} z^{\gamma-1}\cos\left[z\left(x-t\right)\right] dz, \quad 0 < \gamma < 1,$$

after some simplifications, we will obtain (see [3]):

$$\sum_{k=1}^{n} \frac{1}{\Gamma(\beta_k)} \int_{0}^{1} \tau(x) dx \int_{0}^{x} (x-t)^{\beta_k - 1} \tau(t) dt \ge 0,$$

consequently by virtue (24), we will conclude that

$$\int_{0}^{1} \tau(x)\nu^{+}(x)dx \le 0.$$
(26)

Let us show that  $\int_{0}^{1} \tau(x)\nu^{-}(x)dx \ge 0$  for the hyperbolic domain  $\Omega^{-}$ . For this aim we investigate the integral (see (21)):

$$A(\eta) \equiv \eta^{\delta} D_{0\,\eta}^{1-\delta} \int_{0}^{\eta} \sum_{k=1}^{n} \frac{q_k t^{1/2}}{\Gamma(\gamma_k)} dt \int_{0}^{t} \frac{\tilde{\tau}(s) ds}{(t-s)^{1-\gamma_k}} \times \int_{t}^{\eta} \frac{\eta^{2\delta}}{(\eta-t)^{\delta} z^{\delta+1/2}} F\left(\delta, \delta, 1; \frac{t(\eta-z)}{z(\eta-t)}\right) dz$$

Entering replacement  $\frac{t(\eta - z)}{z(\eta - t)} = \sigma$  and after some simplifications we have:

$$\begin{split} A(\eta) &\equiv \sum_{k=1}^{n} \frac{q_{k}}{\Gamma(\gamma_{k})\Gamma(\delta)} \eta^{\delta} \frac{d}{d\eta} \int_{0}^{\eta} (\eta - \mu)^{\delta - 1} d\mu \int_{0}^{\mu} t^{1/2} dt \int_{0}^{t} (t - s)^{\gamma_{k} - 1} \tilde{\tau}(s) ds \times \\ &\int_{0}^{1} \frac{\mu^{\delta + 1/2} [\sigma(\mu - t) + t]^{\delta - 3/2}}{(\mu - t)^{\delta - 1} t^{\delta - 1/2}} F\left(\delta, \delta, 1; \sigma\right) d\sigma = \\ &\sum_{k=1}^{n} \frac{q_{k}}{\Gamma(\gamma_{k})\Gamma(\delta)} \eta^{\delta} \frac{d}{d\eta} \eta^{2 + \delta} \int_{0}^{1} \frac{\tilde{\mu}^{\delta + 1/2} d\tilde{\mu}}{(1 - \tilde{\mu})^{1 - \delta}} \int_{0}^{\tilde{\mu}} \frac{\tilde{t}^{1 - \delta}}{(\tilde{\mu} - \tilde{t})^{\delta - 1}} d\tilde{t} \int_{0}^{\tilde{t}\eta} \frac{\tilde{\tau}(s) ds}{(\tilde{t}\eta - s)^{\gamma_{k} - 1}} \times \\ &\int_{0}^{1} \left[ \sigma(\tilde{\mu} - \tilde{t}) + \tilde{t} \right]^{\delta - 3/2} F\left(\delta, \delta, 1; \sigma\right) d\sigma, \end{split}$$

where

$$ilde{\mu}=\mu/\eta, \quad ilde{t}=t/\eta.$$

Further, taking  $\tau(0) = \varphi(0)$  into account and integrating by parts on third integral we will obtain:

$$A(\eta) \equiv \varphi(0) \sum_{k=1}^{n} \frac{q_{k}(2+\delta+\gamma_{k})}{\Gamma(\gamma_{k}+1)\Gamma(\delta)} \eta^{1+2\delta+\gamma_{k}} \int_{0}^{1} \frac{\tilde{\mu}^{\delta+1/2} d\tilde{\mu}}{(1-\tilde{\mu})^{1-\delta}} \int_{0}^{\tilde{\mu}} \frac{\tilde{t}^{1+\gamma_{k}-\delta}}{(\tilde{\mu}-\tilde{t})^{\delta-1}} d\tilde{t} \times \int_{0}^{1} \left[\sigma(\tilde{\mu}-\tilde{t})+\tilde{t}\right]^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + \sum_{k=1}^{n} \frac{q_{k}(2+\delta)}{\Gamma(\gamma_{k}+1)\Gamma(\delta)} \eta^{1+2\delta} \int_{0}^{1} \frac{\tilde{\mu}^{\delta+1/2} d\tilde{\mu}}{(1-\tilde{\mu})^{1-\delta}} \int_{0}^{\tilde{\mu}} \frac{\tilde{t}^{1-\delta}}{(\tilde{\mu}-\tilde{t})^{\delta-1}} d\tilde{t} \int_{0}^{\tilde{t}\eta} (\tilde{t}\eta-s)^{\gamma_{k}} \tilde{\tau}'(s) ds \times \int_{0}^{1} \left[\sigma(\tilde{\mu}-\tilde{t})+\tilde{t}\right]^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + \sum_{k=1}^{n} \frac{q_{k}}{\Gamma(\gamma_{k})\Gamma(\delta)} \eta^{2+\delta} \int_{0}^{1} \frac{\tilde{\mu}^{\delta+1/2} d\tilde{\mu}}{(1-\tilde{\mu})^{1-\delta}} \int_{0}^{\tilde{\mu}} \tilde{t}^{2-\delta} (\tilde{\mu}-\tilde{t})^{1-\delta} d\tilde{t} \int_{0}^{\tilde{t}\eta} (\tilde{t}\eta-s)^{\gamma_{k}-1} \tilde{\tau}'(s) ds \times \int_{0}^{1} \left[\sigma(\tilde{\mu}-\tilde{t})+\tilde{t}\right]^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + C(\tilde{t})^{1-\delta} d\tilde{t} \int_{0}^{\tilde{t}\eta} \tilde{t}^{2-\delta} (\tilde{\mu}-\tilde{t})^{1-\delta} d\tilde{t} \int_{0}^{\tilde{t}\eta} (\tilde{t}\eta-s)^{\gamma_{k}-1} \tilde{\tau}'(s) ds \times \int_{0}^{1} \left[\sigma(\tilde{\mu}-\tilde{t})+\tilde{t}\right]^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + C(\tilde{t})^{1-\delta} d\tilde{t} \int_{0}^{\tilde{t}\eta} \tilde{t}^{2-\delta} (\tilde{\mu}-\tilde{t})^{1-\delta} d\tilde{t} \int_{0}^{\tilde{t}\eta} \tilde{t}^{2-\delta} (\tilde{t}\eta-s)^{\gamma_{k}-1} \tilde{\tau}'(s) ds + C(\tilde{t})^{1-\delta} \tilde{t}^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + C(\tilde{t})^{1-\delta} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + C(\tilde{t})^{1-\delta} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + C(\tilde{t})^{1-\delta} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + C(\tilde{t})^{1-\delta} \tilde{t}^{\delta-3/2} \tilde{t}^{\delta-3/2}$$

By changing the order of integration in the last two terms in (27), we obtain:

$$\begin{split} A(\eta) &\equiv \varphi(0) \sum_{k=1}^{n} \frac{q_{k}(2+\delta+\gamma_{k})}{\Gamma(\gamma_{k}+1)\Gamma(\delta)} \eta^{1+2\delta+\gamma_{k}} \int_{0}^{1} \frac{\tilde{\mu}^{\delta+1/2} d\tilde{\mu}}{(1-\tilde{\mu})^{1-\delta}} \int_{0}^{\mu} \frac{\tilde{t}^{1+\gamma_{k}-\delta} d\tilde{t}}{(\tilde{\mu}-\tilde{t})^{\delta-1}} \times \int_{0}^{1} \left[\sigma(\tilde{\mu}-\tilde{t})+\tilde{t}\right]^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + \\ \sum_{k=1}^{n} \frac{q_{k}(2+\delta)}{\Gamma(\gamma_{k}+1)\Gamma(\delta)} \eta^{1+2\delta} \int_{0}^{\eta} \tilde{\tau}'(s) ds \int_{s/\eta}^{1} \frac{\tilde{\mu}^{\delta+1/2} d\tilde{\mu}}{(1-\tilde{\mu})^{1-\delta}} \int_{s/\eta}^{\mu} \frac{\tilde{t}^{1-\delta}(\tilde{t}\eta-s)^{\gamma_{k}} d\tilde{t}}{(\tilde{\mu}-\tilde{t})^{\delta-1}} \times \int_{0}^{1} \left[\sigma(\tilde{\mu}-\tilde{t})+\tilde{t}\right]^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma + \\ \sum_{k=1}^{n} \frac{q_{k}}{\Gamma(\gamma_{k})\Gamma(\delta)} \eta^{2+2\delta} \int_{0}^{\eta} \tilde{\tau}'(s) ds \int_{s/\eta}^{1} \frac{\tilde{\mu}^{\delta+1/2} d\tilde{\mu}}{(1-\tilde{\mu})^{1-\delta}} \int_{s/\eta}^{\mu} \tilde{t}^{2-\delta}(\tilde{\mu}-\tilde{t})^{1-\delta}(\tilde{t}\eta-s)^{\gamma_{k}-1} d\tilde{t} \times \\ \int_{0}^{1} \left[\sigma(\tilde{\mu}-\tilde{t})+\tilde{t}\right]^{\delta-3/2} F\left(\delta,\delta,1;\sigma\right) d\sigma. \end{split}$$

Consequently, using inverse replacements  $\mu = \tilde{\mu}\eta$  and  $t = \tilde{t}\eta$ , we obtain:

$$A(\eta) \equiv \varphi(0) \sum_{k=1}^{n} \frac{q_{k}(2+\delta+\gamma_{k})}{\Gamma(\gamma_{k}+1)\Gamma(\delta)} \eta^{\delta-1} \int_{0}^{\eta} \frac{\mu^{\delta+1/2} d\mu}{(\eta-\mu)^{1-\delta}} \int_{0}^{\mu} \frac{t^{1+\gamma_{k}-\delta} dt}{(\mu-t)^{\delta-1}} \times \int_{0}^{1} [\sigma(\mu-t)+t]^{\delta-3/2} F(\delta,\delta,1;\sigma) \, d\sigma + \sum_{k=1}^{n} \frac{q_{k}(2+\delta)}{\Gamma(\gamma_{k}+1)\Gamma(\delta)} \eta^{\delta-1} \int_{0}^{\eta} \tilde{\tau}'(s) ds \int_{s}^{\eta} \frac{\mu^{\delta+1/2} d\mu}{(\eta-\mu)^{1-\delta}} \int_{s}^{\mu} \frac{t^{1-\delta}(t-s)^{\gamma_{k}} dt}{(\mu-t)^{\delta-1}} \times \int_{0}^{1} [\sigma(\mu-t)+t]^{\delta-3/2} F(\delta,\delta,1;\sigma) \, d\sigma + \sum_{k=1}^{n} \frac{q_{k}}{\Gamma(\gamma_{k})\Gamma(\delta)} \eta^{\delta-1} \int_{0}^{\eta} \tilde{\tau}'(s) ds \int_{s}^{\eta} \frac{\mu^{\delta+1/2} d\mu}{(\eta-\mu)^{1-\delta}} \int_{s}^{\mu} \frac{t^{2-\delta}(t-s)^{\gamma_{k}-1}}{(\mu-t)^{\delta-1}} dt \times \int_{0}^{1} [\sigma(\mu-t)+t]^{\delta-3/2} F(\delta,\delta,1;\sigma) \, d\sigma.$$
(28)

There, the following preliminary assertion holds.

Lemma 1. If a function  $\tau(x)$  has a positive maximum (respectively a negative minimum) at the point  $x = x_0 \in (0,1)$ , then  $\nu^-(x_0) > 0$  (respectively  $\nu^-(x_0) < 0$ ) at  $q_k < 0$ ,  $(k = \overline{1, n})$ .

*Proof.* Let function  $\tau(x)$  have a positive maximum at the point  $x = x_0 \in (0, 1)$  and  $\varphi(y) \equiv 0$ , then, from (28), we have:

$$\begin{split} A(x_0) &= \sum_{k=1}^n \frac{q_k(2+\delta)}{\Gamma(\gamma_k+1)\Gamma(\delta)} x_0^{\delta-1} \int_0^{x_0} \tilde{\tau}'(s) ds \int_s^{x_0} \frac{\mu^{\delta+1/2} d\mu}{(x_0-\mu)^{1-\delta}} \int_s^{\mu} \frac{t^{1-\delta}(t-s)^{\gamma_k}}{(\mu-t)^{\delta-1}} dt \times \\ &\int_0^1 \left[ \sigma(\mu-t) + t \right]^{\delta-3/2} F\left(\delta, \delta, 1; \sigma\right) d\sigma + \\ &\sum_{k=1}^n \frac{q_k}{\Gamma(\gamma_k)\Gamma(\delta)} x_0^{\delta-1} \int_0^{x_0} \tilde{\tau}'(s) ds \int_s^{x_0} \frac{\mu^{\delta+1/2} d\mu}{(x_0-\mu)^{1-\delta}} \int_s^{\mu} \frac{t^{2-\delta}(t-s)^{\gamma_k-1} dt}{(\mu-t)^{\delta-1}} \times \\ &\int_0^1 \left[ \sigma(\mu-t) + t \right]^{\delta-3/2} F\left(\delta, \delta, 1; \sigma\right) d\sigma. \end{split}$$

From here, due to  $\Gamma(\gamma_k) > 0$ ,  $\Gamma(\delta) > 0$ ,  $q_k < 0$ ,  $(k = \overline{1, n})$ ,  $F(\delta, \delta, 1; \sigma) > 0$  and

$$\int_{0}^{x_{0}} \tilde{\tau}'(s) ds = \int_{0}^{x_{0}} \lim_{x_{0} \to s} \frac{\tilde{\tau}(x_{0}) - \tilde{\tau}(s)}{x_{0} - s} ds > 0$$

we deduce that  $A(x_0) < 0$ .

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In fact, if  $\tau(x)$  has a positive maximum at the point  $x = x_0$  then  $D_{0x_0}^{1-2\delta}\tilde{\tau}(x_0) > 0$  (see [19]). Thus, owing to  $k_1, k_2 > 0$  from (21) at  $h(x) \equiv 0$  on the point of positive maximum, we will also deduce:

$$\tilde{\nu}^{-}(x_{0}) = \frac{k_{2}\Gamma(1-\delta)}{k_{1}\Gamma(\delta)} x_{0}^{1/2} D_{0\,x_{0}}^{1-2\delta} \tilde{\tau}(x_{0}) - \frac{\Gamma(1-\delta)}{2k_{1}} A(x_{0}) > 0.$$

Similarly, we can prove that on the point of negative minimum  $\tilde{\nu}^{-}(x_0) < 0$ . The lemma is proved.

Hence, based on the Lemma, we will deduce that

$$\int_{0}^{1} \tau(x)\nu^{-}(x)dx \ge 0.$$
(29)

Thus, due to conditions of the Theorem 1 from (29) and (26) we infer that  $\tau(x) \equiv 0$ . Consequently, from (21), we will obtain  $\nu^{-}(x) \equiv 0$ .

As a conclusion, based on the solution of the first boundary problem for the Eq.(12), [15], [20] owing to account (14) and (15) we will get  $u(x, y) \equiv 0$  in  $\overline{\Omega}^+$ , similarly, based on the solution (20) we obtain  $u(x, y) \equiv 0$  in closed domain  $\overline{\Omega}^-$ .

### 5. The existence of solution

Theorem 2. If all conditions of Theorem 1 are satisfied and

$$\varphi(y), \ \psi(y) \in C\left(\overline{I_2}\right) \cap C^1\left(I_2\right); \quad h(x) \in C^1\left(\overline{I_1}\right) \cap C^2\left(I_1\right)$$
(30)

then the solution of the investigating problem is exist.

Proof. Taking (22) into account from Eq.(23) we will obtain

$$\tau''(x) = f(x) \tag{31}$$

where

$$f(x) = \lambda \Gamma(\alpha) \nu^{-}(x) - \varphi(0) \sum_{k=1}^{n} \frac{x^{\beta_k} p_k}{\Gamma(\beta_k)} - \sum_{k=1}^{n} \frac{p_k}{\Gamma(\beta_k)} \int_{0}^{x} (x-t)^{\beta_k} \tau'(t) dt.$$
(32)

Solution of equation (31) together with conditions  $\tau(0) = \psi(0)$ ,  $\tau(1) = \varphi(0)$  has the form:

$$\tau(x) = \int_{0}^{x} (x-t)f(t)dt - x \int_{0}^{1} (1-t)f(t)dt + \varphi(0)(1-x) + x\psi(0)$$

consequently, we can find:

$$\tau'(x) = \int_{0}^{x} f(t)dt - \int_{0}^{1} (1-t)f(t)dt + \psi(0) - \varphi(0).$$
(33)

Taking (13) and (28) into account from (21) we will obtain:

$$\begin{split} \nu^{-}\left(x\right) &= \tilde{k} \cdot x^{\omega/2} \int_{0}^{\bar{}} \left(x^{\omega} - t^{\omega}\right)^{2\delta - 1} \tau'\left(t\right) dt - \\ \sum_{k=1}^{n} q_{k}^{1} x^{\frac{\delta - 1}{1 - 2\delta}} \int_{0}^{x} \tau'(s) ds \int_{s}^{x} \left(x^{\omega} - \mu^{\omega}\right)^{\delta - 1} \mu^{\frac{6\delta + 1}{2(1 - 2\delta)}} d\mu \int_{s}^{\mu} t^{\frac{1 + \delta}{1 - 2\delta}} (\mu^{\omega} - t^{\omega})^{1 - \delta} \times \\ &\left(t^{\omega} - s^{\omega}\right)^{\gamma_{k}} dt \int_{0}^{1} \left[\sigma \left(\mu^{\omega} - t^{\omega}\right) + t^{\omega}\right]^{\delta - 3/2} F\left(\delta, \delta, 1; \sigma\right) d\sigma - \\ &\sum_{k=1}^{n} q_{k}^{2} x^{\frac{\delta - 1}{1 - 2\delta}} \int_{0}^{x} \tau'(s) ds \int_{s}^{x} \left(x^{\frac{1}{1 - 2\delta}} - \mu^{\frac{1}{1 - 2\delta}}\right)^{\delta - 1} \mu^{\frac{6\delta + 1}{2(1 - 2\delta)}} d\mu \times \end{split}$$

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$$\int_{s}^{\mu} t^{\frac{2+\delta}{1-2\delta}} (\mu^{\omega} - t^{\omega})^{1-\delta} (t^{\omega} - s^{\omega})^{\gamma_{k}-1} dt \int_{0}^{1} [\sigma (\mu^{\omega} - t^{\omega}) + t^{\omega}]^{\delta-3/2} F(\delta, \delta, 1; \sigma) d\sigma - \sum_{k=1}^{n} q_{k}^{3} x^{\frac{\delta-1}{1-2\delta}} \int_{0}^{x} (x^{\omega} - \mu^{\omega})^{\delta-1} \mu^{\frac{6\delta+1}{2(1-2\delta)}} d\mu \int_{0}^{\mu} t^{\frac{1+\gamma_{k}+\delta}{1-2\delta}} (\mu^{\omega} - t^{\omega})^{\delta-1} dt \times \int_{0}^{1} [\sigma (\mu^{\omega} - t^{\omega}) + t^{\omega}]^{\delta-3/2} F(\delta, \delta, 1; \sigma) d\sigma + \frac{k_{2}\Gamma(1-\delta)}{k_{1}\Gamma(\delta)\Gamma(2\delta)} x^{\frac{4\delta-1}{2(1-2\delta)}} \varphi(0),$$
(34)

where

$$\begin{split} \omega &= \frac{1}{1 - 2\delta}, \quad \tilde{k} = \frac{\omega k_2 \Gamma(1 - \delta)}{k_1 \Gamma(\delta) \Gamma(2\delta)}, \quad q_k^1 = \frac{(2 + \delta) \Gamma(1 - \delta) q_k \omega^3}{2k_1 \Gamma(\gamma_k + 1) \Gamma(\delta)}, \\ q_k^2 &= \frac{\Gamma(1 - \delta) q_k \omega^3}{2k_1 \Gamma(\gamma_k) \Gamma(\delta)}, \quad q_k^3 = \frac{\Gamma(1 - \delta) (2 + \delta + \gamma_k) q_k \omega^2}{2k_1 \Gamma(\delta) \Gamma(\gamma_k + 1)} \varphi(0). \end{split}$$

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Further, considering (32) from (33), after some simplifications we will obtain:

$$\tau'(x) = \lambda \Gamma(\alpha) \int_{0}^{x} \nu^{-}(t) dt - \lambda \Gamma(\alpha) \int_{0}^{1} (1-t) \nu^{-}(t) dt - \sum_{k=1}^{n} \frac{p_{k}}{\Gamma(\beta_{k})} \int_{0}^{x} dt \int_{0}^{t} (t-s)^{\beta_{k}} \tau'(s) ds + \sum_{k=1}^{n} \frac{p_{k}}{\Gamma(\beta_{k})} \int_{0}^{1} (1-t) dt \int_{0}^{t} (t-s)^{\beta_{k}} \tau'(s) ds - \varphi(0) \sum_{k=1}^{n} \frac{x^{\beta_{k}+1} p_{k}}{(\beta_{k}+1)\Gamma(\beta_{k})} + \varphi(0) \sum_{k=1}^{n} \frac{p_{k}}{(\beta_{k}+1)(\beta_{k}+2)\Gamma(\beta_{k})} + \psi(0) - \varphi(0).$$
(35)

Substituting (34) into (35), we have:

$$\tau'(x) = \tilde{k}\lambda\Gamma(\alpha) \cdot \int_{0}^{x} t^{\frac{3-4\delta}{2(1-2\delta)}} dt \int_{0}^{t} (t^{\omega} - s^{\omega})^{2\delta-1} \tau'(s) \, ds - \tilde{k}\lambda\Gamma(\alpha) \cdot \int_{0}^{1} (1-t)t^{\frac{1}{2(1-2\delta)}} dt \int_{0}^{t} (t^{\omega} - s^{\omega})^{2\delta-1} \tau'(s) \, ds - \tilde{k}\lambda\Gamma(\alpha) \sum_{k=1}^{n} q_{k}^{1} \int_{0}^{1} (1-t)t^{\frac{1}{2(1-2\delta)}} dt \int_{0}^{t} \tau'(s)A(s,t) \, ds - \lambda\Gamma(\alpha) \sum_{k=1}^{n} q_{k}^{1} \int_{0}^{1} (1-t)t^{\frac{\delta-1}{1-2\delta}} dt \int_{0}^{t} \tau'(s)A(s,t) \, ds - \lambda\Gamma(\alpha) \sum_{k=1}^{n} q_{k}^{2} \int_{0}^{1} t^{\frac{-\delta}{1-2\delta}} dt \int_{0}^{t} \tau'(s)B(s,t) \, ds + \lambda\Gamma(\alpha) \sum_{k=1}^{n} q_{k}^{2} \int_{0}^{1} (1-t)t^{\frac{\delta-1}{1-2\delta}} dt \int_{0}^{t} \tau'(s)B(s,t) \, ds - \sum_{k=1}^{n} \frac{p_{k}}{\Gamma(\beta_{k})} \int_{0}^{s} dt \int_{0}^{t} (t-s)^{\beta_{k}} \tau'(s) \, ds + \sum_{k=1}^{n} \frac{p_{k}}{\Gamma(\beta_{k})} \int_{0}^{1} (1-t) dt \int_{0}^{t} (t-s)^{\beta_{k}} \tau'(s) \, ds + F(x),$$
(36)

where

$$F(x) = \varphi(0) \sum_{k=1}^{n} \left( \frac{p_k}{(\beta_k+1)(\beta_k+2)\Gamma(\beta_k)} - \frac{x^{\beta_k+1}p_k}{(\beta_k+1)\Gamma(\beta_k)} \right) - \lambda\Gamma(\alpha) \sum_{k=1}^{n} q_k^3 \int_0^x t^{\frac{\delta-1}{1-2\delta}} C(t)dt + \lambda\Gamma(\alpha) \sum_{k=1}^{n} q_k^3 \int_0^1 (1-t)t^{\frac{\delta-1}{1-2\delta}} C(t)dt - \frac{k_2\lambda\Gamma(\alpha)\Gamma(1-\delta)}{k_1\Gamma(\delta)\Gamma(2\delta)}\varphi(0) \int_0^1 (1-t)t^{\frac{4\delta-1}{2(1-2\delta)}}dt + \frac{2(1-2\delta)k_2\lambda\Gamma(\alpha)\Gamma(1-\delta)}{k_1\Gamma(\delta)\Gamma(2\delta)}\varphi(0)x^{\frac{\omega}{2}} - \psi(0) - \varphi(0),$$

$$A(s,t) = \int_s^t (t^\omega - \mu^\omega)^{\delta-1}\mu^{\frac{6\delta+1}{2(1-2\delta)}}d\mu \int_s^\mu z^{\frac{1+\delta}{1-2\delta}}(\mu^\omega - z^\omega)^{1-\delta} \times$$
(37)

On a problem for the loaded degenerating mixed type equation ...

$$(z^{\omega} - s^{\omega})^{\gamma_k} dz \int_0^1 \left[ \sigma \left( \mu^{\omega} - z^{\omega} \right) + z^{\omega} \right]^{\delta - 3/2} F\left( \delta, \delta, 1; \sigma \right) d\sigma,$$
(38)

$$B(s,t) = \int_{s}^{t} (t^{\omega} - \mu^{\omega})^{\delta - 1} \mu^{\frac{6\delta + 1}{2(1 - 2\delta)}} d\mu \int_{s}^{\mu} z^{\frac{2 + \delta}{1 - 2\delta}} (\mu^{\omega} - z^{\omega})^{1 - \delta} (z^{\omega} - s^{\omega})^{\gamma_{k} - 1} dz \times \int_{0}^{1} [\sigma (\mu^{\omega} - z^{\omega}) + z^{\omega}]^{\delta - 3/2} F(\delta, \delta, 1; \sigma) d\sigma,$$
(39)

$$C(t) = \int_{0}^{t} (t^{\omega} - \mu^{\omega})^{\delta - 1} \mu^{\frac{6\delta + 1}{2(1 - 2\delta)}} d\mu \int_{0}^{\mu} z^{\frac{1 + \gamma_{k} + \delta}{1 - 2\delta}} (\mu^{\omega} - z^{\omega})^{\delta - 1} dz \times \int_{0}^{1} [\sigma (\mu^{\omega} - z^{\omega}) + z^{\omega}]^{\delta - 3/2} F(\delta, \delta, 1; \sigma) d\sigma.$$
(40)

Changing the order of integration in (36), in total, we have integral equation:

$$\tau'(x) = \int_{0}^{1} K(x,s)\tau'(s)ds + F(x).$$
(41)

Here

$$K(x,s) = \begin{cases} K_1(x,s); & 0 \le s \le x; \\ K_2(x,s); & x \le s \le 1, \end{cases}$$
(42)

$$K_{1}(x,s) = \lambda \Gamma(\alpha) \int_{s}^{1} (1-t)t^{\frac{\delta-1}{1-2\delta}} \left[ \sum_{k=1}^{n} q_{k}^{1}A(s,t) + \sum_{k=1}^{n} q_{k}^{2}B(s,t) \right] dt + \lambda \tilde{k} \Gamma(\alpha) \left[ \int_{s}^{x} t^{\frac{3-4\delta}{2-4\delta}} (t^{\omega} - s^{\omega})^{2\delta-1} dt - \int_{x}^{1} (1-t)t^{\frac{1}{2-4\delta}} (t^{\omega} - s^{\omega})^{2\delta-1} dt \right] - \lambda \Gamma(\alpha) \int_{s}^{x} t^{\frac{-\delta}{1-2\delta}} \left[ \sum_{k=1}^{n} q_{k}^{1}A(s,t) + \sum_{k=1}^{n} q_{k}^{2}B(s,t) \right] dt + \sum_{k=1}^{n} \frac{p_{k}}{\Gamma(\beta_{k})} \left[ \int_{s}^{1} (1-t)(t-s)^{\beta_{k}} dt + \frac{(x-s)^{\beta_{k}+1}}{\beta_{k}+1} \right],$$

$$K_{2}(x,s) = \lambda \Gamma(\alpha) \int_{s}^{1} (1-t)t^{\frac{\delta-1}{1-2\delta}} \left[ \sum_{k=1}^{n} q_{k}^{1}A(s,t) + \sum_{k=1}^{n} q_{k}^{2}B(s,t) \right] dt - \lambda \tilde{k} \Gamma(\alpha) \int_{s}^{1} (1-t)t^{\frac{1}{2-4\delta}} (t^{\omega} - s^{\omega})^{2\delta-1} dt + \sum_{k=1}^{n} \frac{p_{k}}{\Gamma(\beta_{k})} \int_{s}^{1} (1-t)(t-s)^{\beta_{k}} dt.$$

$$(44)$$

In fact, the estimates of functions A(s,t), B(s,t) and C(t) play an important roles for estimating K(x,s). Now, we estimate |A(s,t)|. Due to properties of the hypergeometric function (9) from (38), we obtain:

$$|A(s,t)| \le \left| \int_{s}^{t} (t^{\rho} - \mu^{\rho})^{\delta - 1} \mu^{\frac{4\delta}{2(1 - 2\delta)}} d\mu \int_{s}^{\mu} z^{\frac{1 + \delta}{1 - 2\delta}} \frac{(z^{\rho} - s^{\rho})^{\gamma_{k}}}{(\mu^{\rho} - z^{\rho})^{\delta}} \left| z^{1/2} - \mu^{1/2} \right| dz \right|.$$

Introducing the change of variables  $z^{\rho} = s^{\rho} + (\mu^{\rho} - s^{\rho}) z_1$  and due to (8), we get

$$|A(s,t)| \le \left|t^{1/2} - s^{1/2}\right| s^{\frac{1}{2-4\delta}} \left| \int_{s}^{t} \frac{(\mu^{\rho} - s^{\rho})^{1-\delta+\gamma_{k}}}{(t^{\rho} - \mu^{\rho})^{1-\delta}} \mu^{\frac{4\delta}{1-2\delta}} F\left(-\frac{1}{2}, 1+\gamma_{k}, 2+\gamma_{k}-\delta; \frac{s-\mu}{s}\right) d\mu \right|.$$

In the sequel, due to

$$2 + \gamma_k - \delta - 1 - \gamma_k + \frac{1}{2} = \frac{3}{2} - \delta > 0,$$
$$\left| \frac{s - \mu}{s} \right| \le 1,$$

we have (see (9))

$$F\left(-\frac{1}{2}, 1+\gamma_k, 2+\gamma_k-\delta; \frac{s-\mu}{s}\right) \le const$$

consequently, changing of variables  $\mu^{\rho} = s^{\rho} + (t^{\rho} - s^{\rho}) \mu_1$  and by virtue formula (8), after some evaluation finally, we get

$$|A(s,t)| \le \left(t^{1/2} - s^{1/2}\right) s^{\frac{1+4\delta}{2-4\delta}} (t-s)^{1+\gamma_k} \le const.$$
(45)

Similarly, by estimating B(s,t) and C(t) (see (39) and (40)), we can get

$$|B(s,t)| \le \left(t^{1/2} - s^{1/2}\right) s^{\frac{3+4\delta}{2-4\delta}} (t-s)^{\gamma_k} \le const, \quad C(t) \le const.$$
(46)

Hence, due to class of given functions (see (30)) and (45), (46) considering (43) and (44) from (37) and (42) respectively we deduce  $|K(x,s)| \le const$ , for all  $0 \le x$ ,  $s \le 1$ ,  $|F(x)| \le const$ ,  $0 \le x \le 1$ . Since kernel K(x,s) is continuous and function in right-side F(x) is continuously differentiable, for the solution of integral equation (41) we can write via resolvent-kernel:

$$\tau'(x) = F(x) - \int_{0}^{1} \Re(x, s) F(s) ds,$$
(47)

where  $\Re(x, s)$  is the resolvent-kernel of K(x, s). Unknown functions  $\nu^{-}(x)$  we will find from (34). Solution of the Problem I in the domain  $\Omega^{+}$  we write as follows [15,20]:

$$\begin{split} u(x,y) &= \int_{0}^{y} G_{\xi}(x,y,0,\eta)\psi(\eta)d\eta - \int_{0}^{y} G_{\xi}(x,y,1,\eta)\varphi(\eta)d\eta + \int_{0}^{1} G_{0}(x-\xi,y)\tau(\xi)d\xi - \\ &\int_{0}^{y} \int_{0}^{1} G(x,y,0,\eta)\sum_{k=1}^{n} p_{k}I_{0\xi}^{\beta_{k}}\tau(\xi)d\xi d\eta. \end{split}$$

Here

$$G_0(x-\xi,y) = \frac{1}{\Gamma(1-\alpha)} \int_0^y \eta^{-\alpha} G(x,y,\xi,\eta) d\eta,$$

$$G(x, y, \xi, \eta) = \frac{(y-\eta)^{\alpha/2-1}}{2} \sum_{n=-\infty}^{\infty} \left[ e_{1,\alpha/2}^{1,\alpha/2} \left( -\frac{|x-\xi+2n|}{(y-\eta)^{\alpha/2}} \right) - e_{1,\alpha/2}^{1,\alpha/2} \left( -\frac{|x+\xi+2n|}{(y-\eta)^{\alpha/2}} \right) \right]$$

is the Green's function of the first boundary problem Eq. (12) in the domain  $\Omega^+$  with the Riemann-Liouville fractional differential operator instead of the Caputo ones [20],

$$e_{1,\delta}^{1,\delta}(z) = \sum_{n=0}^{\infty} \frac{z^n}{n!\Gamma(\delta - \delta n)}$$

is the Wright type function [18]. Solution of the Problem I in the domain  $\Omega^-$  will be found by the formula (20). Hence, the Theorem 2 is proved.

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# Interaction of fast and slow varying electromagnetic waves propagating in paraelectric or ferroelectric material

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Once, a referee asked how one can write an oscillator model for a ferroelectric and the total Maxwell equation for a rapidly varying electric field. From what is known about polarization, it is a slow function of time and coordinates, but the optical wave is a fast function. However, there are examples for the interaction of high frequency and low frequency waves in nonlinear wave theory. This means that similar equations can be written for ferroelectric polarization and electromagnetic waves.

Keywords: Maxwell equation, electromagnetic waves, Duffing oscillator model, ferroelectric.

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#### 1. Introduction

The pulse propagation of electromagnetic radiation in different media having a long-range order is an attractive problem of electrodynamics. There are dielectrics having a permanent polarization in the absence of an external electric field, which are similar to magneto-ordered media. This simple class of media is ferroelectric. Another class is the magnetoelectric, where both permanent polarization and permanent magnetization exist, even though the electromagnetic field is absent. A common feature of these media is their highly nonlinear response to the incident electromagnetic wave. Nonlinear optical phenomena in the ferroelectric have been considered. The self-focusing of the few-cycle pulses in ferroelectric [1], the self-interaction processes [2–8], the soliton generation [9–12], the second harmonic generation [13–15] have been investigated in the last ten-fifteen years.

It is important to note that the order parameter of the ferroelectric (i.e., the polarization) in many cases is due to lattice dynamics. The result is a slow varying of the polarization in the optical frequency scale. Thus, electromagnetic wave propagation gives rise to an interaction of the rapidly and slowly varying waves. The aim of this paper to demonstrate that the Ginzburg–Landau–Devonshir model can be adapted for description of the rapidly and slowly varying electromagnetic waves in a ferroelectric medium.

#### 2. Base equations

General equations for the description of electromagnetic waves in a ferroelectric material can be written by using the phenomenological equation:

$$\tau_0^2 \frac{\partial^2 \mathbf{P}}{\partial t^2} + \gamma^{-1} \frac{\partial \mathbf{P}}{\partial t} = -\frac{\delta \Phi}{\delta \mathbf{P}}$$

where  $\Phi = \Phi[\mathbf{P}, \mathbf{E}]$  is Ginzburg–Landau–Devonshir free energy functional [16–20]:

$$\Phi = \int dz \left\{ \frac{1}{2} A \mathbf{P}^2 + \frac{1}{4} B \mathbf{P}^4 + \frac{1}{6} C \mathbf{P}^6 - g \mathbf{E} \cdot \mathbf{P} \right\}.$$
 (1)

This equation must be added to the wave equation for the electric field strength  $\mathbf{E}$  [21]:

$$\nabla \times \nabla \times \mathbf{E} - \frac{\mu}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{4\pi\mu}{c^2} \frac{\partial^2 \mathbf{P}}{\partial t^2}.$$
(2)

In the one dimensional case and at C = 0, these equations can be rewritten as:

$$c^{2}E_{zz} - E_{tt} = 4\pi P_{tt},$$
(3)  
 $\tau_{0}^{2}P_{tt} + \gamma^{-1}P_{t} + AP + BP^{3} = gE.$ 
(4)

Here,  $g = \omega_p^2/4\pi$  – coupling constant

Let us assume that electromagnetic wave consists of a quasi- harmonic wave and an electromagnetic spike (wave without carry wave). This means the spectra of these wave parts are not enveloped. Furthermore, let the following relations be right:

$$E(z,t) = E_s(z,t) + E_f(z,t), P(z,t) = P_s(z,t) + P_f(z,t),$$
(5)

for a high frequency (HF)  $E_f$ ,  $P_f$  and for a low frequency (LF)  $E_s$ ,  $P_s$  components electric field and polarization, where:

$$E_f(z,t) = (E^+ e^{ik_1 z} + E^- e^{-ik_1 z}) e^{-i\omega_1 t} + c.c.,$$
  

$$P_f(z,t) = (P^+ e^{ik_1 z} + P^- e^{-ik_1 z}) e^{-i\omega_1 t} + c.c.$$

For the nonlinear terms in (4) one can write:

$$P^3 = P_s^3 + 3P_s^2 P_f + 3P_s P_f^2 + P_f^3.$$

The third term in this sum can be represented as:

$$P_{f}^{2} = (P^{+}e^{ik_{1}z} + P^{-}e^{-ik_{1}z})^{2}e^{-i2\omega_{1}t} + (P^{+*}e^{-ik_{1}z} + P^{-*}e^{ik_{1}z})^{2}e^{i2\omega_{1}t} + 2(P^{+}e^{ik_{1}z} + P^{-}e^{-ik_{1}z})(P^{+*}e^{-ik_{1}z} + P^{-*}e^{ik_{1}z}).$$
 (6)

Hence, this term describes the second harmonic generation (SHG) and the constant field generation. Some part of this expression takes account in LF part of polarization. The phase mismatch is necessary to get effective SHG, otherwise that can be neglected.

The next term can be represented as:

$$P_{f}^{3} = (P^{+}e^{ik_{1}z} + P^{-}e^{-ik_{1}z})^{3}e^{-i3\omega_{1}t} + (P^{+*}e^{-ik_{1}z} + P^{-*}e^{ik_{1}z})^{3}e^{i3\omega_{1}t} + 3(P^{+}e^{ik_{1}z} + P^{-}e^{-ik_{1}z})^{2}(P^{+*}e^{-ik_{1}z} + P^{-*}e^{ik_{1}z})e^{-i\omega_{1}t} + 3(P^{+}e^{ik_{1}z} + P^{-}e^{-ik_{1}z})(P^{+*}e^{-ik_{1}z} + P^{-*}e^{ik_{1}z})^{2}e^{i\omega_{1}t}.$$
 (7)

Some of these terms are corresponded with third harmonic generation and some of them describe the selfinteraction. The third harmonic generation will be neglected as well.

#### 3. Reduction of wave equations

The wave equation (3) can be transformed to Fourier form:

$$\left(-k^2 + \frac{\omega^2}{c^2}\right)E(k,\omega) = -\frac{4\pi\omega^2}{c^2}P(k,\omega).$$

Due to spectra  $E_s(k,\omega)$ ,  $E_f(k,\omega)$  and  $P_s(k,\omega)$ ,  $P_f(k,\omega)$  not being enveloped, the wave equation can be separated into two parts:

$$\left(-k^2 + \frac{\omega^2}{c^2}\right) E_s(k,\omega) = -\frac{4\pi\omega^2}{c^2} P_s(k,\omega),$$
$$\left(-k^2 + \frac{\omega^2}{c^2}\right) E_f(k,\omega) = -\frac{4\pi\omega^2}{c^2} P_f(k,\omega).$$

In the first equation, the frequencies and wave numbers lie near zero, as all functions  $E_s(k,\omega)$  and  $P_s(k,\omega)$ are localized near zero variables. In the second equation, the functions  $E_f(k,\omega)$  and  $P_f(k,\omega)$  are localized near  $(\omega_1, k_1), (-\omega_1, k_1), (\omega_1, -k_1)$  and  $(-\omega_1, -k_1)$ . Considering the slowly varying envelopes of electric fields and polarizations near the pair of points  $(\omega_1, k_1)$  and  $(\omega_1, -k_1)$ , one can write the following equation:

$$\left(-(k\pm k_1) + \frac{(\omega_1+\omega)^2}{c^2}\right)E^{\pm}(k,\omega) = -\frac{4\pi(\omega_1+\omega)^2}{c^2}P^{\pm}(k,\omega),$$

where  $\omega \ll \omega_1$ ,  $k \ll k_1$ . This is due to narrow wave pocket of quasiharmonic waves. Taking  $k_1 = \omega_1/c$  in to account, this equation can be approximated as:

$$\left(\mp 2kk_1 + \frac{2\omega_1\omega}{c^2}\right)E^{\pm}(k,\omega) \approx -\frac{4\pi\omega_1^2}{c^2}P^{\pm}(k,\omega),$$
$$\left(\mp k + \frac{\omega}{c}\right)E^{\pm}(k,\omega) \approx -4\pi k_1 P^{\pm}(k,\omega).$$

or

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This relation (the dispersion relation) corresponds to following equation:

$$\pm \frac{\partial E^{\pm}}{\partial z} + \frac{1}{c} \frac{\partial E^{\pm}}{\partial t} = 2i\pi k_1 P^{\pm}.$$
(8)

This is the base equation for the slowly varying envelopes of the HF electric fields  $E^{\pm}(z,t)$ . For LF field  $E_s(z,t)$  the wave equation is used:

$$\frac{\partial^2 E_s}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E_s}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P_s}{\partial t^2}.$$
(9)

These equations are coupled through polarizations.

#### 4. Reduction of polarization equations

In both wave equations (8) and (9) the different polarizations presente. The equation for  $P_s$  can be written in following form:

$$\tau_0^2 \frac{\partial^2 P_s}{\partial t^2} + \gamma^{-1} \frac{\partial P_s}{\partial t} + AP_s + B[P^3]_s = gE_s, \tag{10}$$

where  $[P^3]_s$  is mark of slowly varying part of  $P^3$ . This part must be extracted from (6) and (7), but there are no low frequency terms among (7). Then, taking into account (6), we can write:

$$P_f^2]_s = 2\left(P^+P^{+*} + P^-P^{-*}\right) = 2\left(|P^+|^2 + |P^-|^2\right)$$

Thus,

$$[P^3]_s = P_s^3 + 2\left(|P^+|^2 + |P^-|^2\right)$$

Now, we can present the evolution equation for the LF-part of polarization:

$$\tau_0^2 \frac{\partial^2 P_s}{\partial t^2} + \gamma^{-1} \frac{\partial P_s}{\partial t} + AP_s + BP_s^3 = gE_s - 6BP_s \left( |P^+|^2 + |P^-|^2 \right).$$
(11)

It is worth noting that the slowly varying polarization evolves under both external electric field  $E_s$ , and the rapidly varying part of the polarization  $P^{\pm}$ .

To find equation for slowly varying envelopes of fast part of the polarization, it is necessary for one to take Fourier transformation of the base equation for polarization (4). This leads to:

$$(-\tau_0^2\omega^2 - i\gamma^{-1}\omega + A)P(\omega) + B\mathcal{F}[P^3](\omega) = gE(\omega).$$

The symbol  $\mathcal{F}[P^3](\omega)$  denotes Fourier image of polarization in cube. The relative variables in this equation are localized near the points  $(\omega_1, k_1)$  and  $(\omega_1, -k_1)$  due to narrow wave pockets  $E(\omega)$  and  $P(\omega)$ . This leads to:

$$\left(-\tau_0^2(\omega+\omega)^2 - i\gamma^{-1}(\omega_1+\omega) + A\right)P^{\pm}(\omega) + B\mathcal{F}[P^3]^{\pm}(\omega) = gE^{\pm}(\omega).$$

In the general case (the Fourier transformation is linear one), we get:

$$\mathcal{F}[P^3] = \mathcal{F}[P_s^3] + 3\mathcal{F}[P_s^2 P_f] + 3\mathcal{F}[P_s P_f^2] + \mathcal{F}[P_f^3].$$

The first term is not zero only near  $\omega = 0$ , hence this term is not the HF-term. The second term can be written approximately as:

$$3\mathcal{F}[P_s^2 P_f] \approx 3P_s^2 \mathcal{F}[P_f].$$

The third term  $\mathcal{F}[P_s P_f^2]$  is approximately  $P_s \mathcal{F}[P_f^2]$ . This term is localized near  $\omega = \pm \omega_1$  and  $\omega = 0$ . Hence, this term is irrelevant. The SHG is not under consideration. The term  $\mathcal{F}[P_f^3]$  contents the parts localized near  $\pm 3\omega$  and  $\pm \omega$ . Among the all terms in  $P_f^3$  relevant ones are following

$$P_f^3 = 3\left[|P^+|^2P^+ + 2|P^-|^2P^+\right]e^{-i\omega_1t + ik_1z} + 3\left[|P^-|^2P^- + 2|P^+|^2P^-\right]e^{-i\omega_1t - ik_1z} + c.c. + \dots$$

where dots indicate terms, containing  $e^{i\omega_1 \pm i3k_1 z}$ .

Thus, the equation is:

$$\left[-\tau_0^2(\omega+\omega)^2 - i\gamma^{-1}(\omega_1+\omega) + A\right] P^{\pm}(\omega) + 3BP_s^2 P^{\pm}(\omega) + 3B\left(|P^{\pm}(\omega)|^2 + 2|P^{\mp}(\omega)|^2\right) P^{\pm}(\omega) = gE^{\pm}(\omega).$$

Taking into account  $\omega \ll \omega_1$  this equation can be reduced to:

$$(\gamma^{-1} - i2\tau_0^2\omega_1)(-i\omega)P^{\pm}(\omega) + (A - \tau_0^2\omega_1^2 - i\gamma\omega_1)P^{\pm}(\omega) + 3BP_s^2P^{\pm}(\omega) + 3B\left(|P^{\pm}(\omega)|^2 + 2|P^{\mp}(\omega)|^2\right)P^{\pm}(\omega) = gE^{\pm}(\omega)$$
  
Inverse Fourier transformation for this expression results in the equation:

$$\left(\gamma^{-1} - i2\tau_0^2\omega_1\right)\frac{\partial P^{\perp}}{\partial t} + \left(A - \tau_0^2\omega_1^2 - i\gamma\omega_1\right)P^{\pm} + 3BP_s^2P^{\pm} + 3B\left(|P^{\pm}|^2 + 2|P^{\mp}|^2\right)P^{\pm} = gE^{\pm}.$$
Interaction of the electromagnetic waves in ferroelectric material

If introduce new parameters: the renormalized relaxation time  $\tau_1 = 2\tau_0^2\omega_1 - i\gamma^{-1}$  and the renormalized Landau parameter  $A_1 = A - \tau_0^2\omega_1^2 - i\omega_1\gamma^{-1}$ , then the equation for slowly varying part of polarization takes the form:

$$-i\tau_1 \frac{\partial P^{\pm}}{\partial t} + A_1 P^{\pm} + 3BP_s^2 P^{\pm} + 3B\left(|P^{\pm}|^2 + 2|P^{\mp}|^2\right) P^{\pm} = gE^{\pm}.$$
 (12)

The equations (8) and (12) describe the forward  $(E^+, P^+)$  and backward  $(E^-, P^-)$  waves propagation, which are coupled by nonlinear interaction.

#### 5. Unidirectional approximation

Above, the total Maxwell equation was used for description of two waves propagating in both directions along the z-axis. Frequently, propagation in one direction may be considered. In this case, let us denote  $E^+ = \tilde{E}$ ,  $P^+ = \tilde{P}$ . The system of equations is:

$$\frac{\partial E_s}{\partial z} + \frac{1}{c} \frac{\partial E_s}{\partial t} = \frac{2\pi}{c} \frac{\partial P_s}{\partial t},\tag{13}$$

$$\tau_0^2 \frac{\partial^2 P_s}{\partial t^2} + \gamma^{-1} \frac{\partial P_s}{\partial t} + AP_s + BP_s^3 = gE_s - 6BP_s |\tilde{P}|^2, \tag{14}$$

$$\frac{\partial \tilde{E}}{\partial z} + \frac{1}{c} \frac{\partial \tilde{E}}{\partial t} = 2i\pi k_1 \tilde{P},\tag{15}$$

$$-i\tau_1\frac{\partial\tilde{P}}{\partial t} + (A_1 + 3BP_s^2)\tilde{P} + 3B|\tilde{P}|^2\tilde{P} = g\tilde{E}.$$
(16)

The equations (13) and (14) are the generation of the Maxwell–Duffing system. The extra term in right hand side of (14) represents the coupling between HF and LF waves.

It should be noted that if one put  $\tilde{P} = 0$ ,  $\tilde{E} = 0$  and  $\gamma^{-1} = 0$ , the system of equations (13) and (14) will be reduced to model equations, which are used in [2,3,8].

#### 6. Conclusion

In this paper, the simplest model of the electromagnetic wave propagation in a one-dimensional ferroelectric medium is considered. The nonlinear properties of the medium leads to coupling between the high frequency and low frequency components for electric field and polarization. In the general case, a high frequency incident optical wave generates both HF and LF responses in the medium. Thus, the interaction of the rapidly and slowly varying electromagnetic waves will take place. The extremely short electromagnetic pulse or the few-cycle pulses generate both high and low frequency components of the polarization in a ferroelectric medium. This results in HF radiation. If this radiation is not taken into consideration, the Maxwell–Duffing model [1,2,9] can be used for describing the extremely short electromagnetic pulse propagation in a one-dimensional ferroelectric medium.

In the 2D epitaxial ferroelectric islands and in the thin films, the size effects on domain configuration and polarization play a large role in the electromagnetic response [25, 26]. These effects can be accounted for in the model under consideration.

Here, the parametric processes, for example second harmonic generation, are not considered. However, this can be done with no problem.

The one-dimensional model is considered. Usually, ferroelectric materials are anisotropic crystals. Taking into account of this anisotropy will result in the cumbersome system of equations. It is of interest to investigate nonlinear wave propagation in the framework of these models. The formation of the spatial structures, e.g. the spatial solitons, the light bullets and needles, is expected.

It has been known that in certain substances the ferroelectricity can be of a purely electronic nature [22–24]. The study of nonlinear wave propagation in such media is very attractive because speed of the electron response can be comparable to electromagnetic field variation.

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#### Chiral characteristics of metasurface based on gammadion cross in THz frequency range

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The chiral properties of a metasurface made of 2-D array of twisted gammadion crosses was studied at frequencies ranging from 0.1-0.12 THz. The influences of unit cell design on the optical activity and the ellipticity of the metasurface were revealed. The maximal values of ellipticity and polarization azimuth rotation angle were obtained for the gammadion crosses with petals in the form of the truncated circles. The changing of the semi axes' relation of gammadion cross ellipses allows tuning of the operational frequency and creation of a multiband polarizer.

Keywords: metasurface, metamaterials, chiral structure, terahertz frequency.

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#### 1. Introduction

Recently, metamaterials have become increasingly interesting for scientists, due to their smart properties and capability for extraordinary manipulation of electromagnetic waves: blocking, absorbing, enhancing, bending and polarization changing. Metasurfaces, or planar metamaterials (consisting of one or more layers of flat structures) has attracted a special interest due to their capacity for strong electromagnetic wave manipulation and small losses compared to bulk metamaterials. They can be easy fabricated by lithography or laser engraving [1]. Of particular interest is the development of chiral metasurfaces for wave polarization control [2]. Chirality is the geometric property of spatial particles, namely it is an asymmetry and distinction of an object from its mirror image. Chiral metamaterials can demonstrate some interesting properties, such as optical activity and circular dichroism [3] as well as negative index of refraction [2]. There is a large number of chiral unit cell designs (crosses [4], hammadions [5], U-shaped resonators [6] and others). The design and mutual arrangement of chiral unit cells strongly influence its ability for wave polarization. It would be particularly interesting to know the optical properties of such metasurfaces in the terahertz (THz) frequency range, which is safe for humans and sensitive to chemical changes in biomolecules, due to the deficit of polarizing components in this frequency range [7]. THz chiral metasurfaces may be used for time-domain spectroscopic polarimetry of biological objects to develop new diagnostic methods for common diseases such as cancer and diabetes. In this paper, we studied the influence of unit cell form on the metasurface's chiral properties.

#### 2. Description of the structure

The chiral metasurface under study consists of a 2-D chiral unit cell array of twisted gammadion crosses with size of  $< \lambda/4$ . This size permitted us to use the effective medium theory. Two designs of crosses were considered to control of chiral effects. The first gammadion cross has "petals" in the form of the truncated circles. This was taken as a basic chiral element. The scheme of this design is shown in Fig. 1-a. The chiral element made of perfect electric conductor which is placed on a silicone (this material allowed control of the metasurface's spectral characteristics by changing its optical properties under the photoexcitation, for example) with permittivity  $\varepsilon = 11.56$ , substrate with thickness of  $b = 150 \ \mu m$  (less than  $\lambda/10$ ) and side of  $a = 450 \ \mu m$ . The second cross design has "petals" in the form of the truncated ellipses with semi-axes ratio 2.2:1 (Fig. 1-b).

#### 3. Numerical simulation

In simulations, the commercial software CST Microwave Studio was used to obtain the total scattering matrix, which relates the incident waves to the scattered waves. The Finite Difference Time Domain method was chosen from other numerical methods [8,9] due to its simplicity and versatility. The radiation source was linearly polarized electromagnetic wave for frequencies ranging from 0.1–0.12 THz. The scheme of this simulation experiment is shown in Fig. 2. A linearly polarized wave passing through the metasurface had its polarization changed to an elliptical one. An additional linear polarizer was used to determine the wave polarization ellipse. The polarizer consists of an array of perfect electric conductor strips, placed on a silicone substrate with periodic boundary



FIG. 1. a) Illustration of the basic structure. Outer radius  $R_1 = 150 \ \mu$ m, inner radius  $R_2 = 123.3 \ \mu$ m. b) The difference between basic structure (black gammadion cross) and elliptical one (gray gammadion cross)

conditions. The wave polarization was changed to linear after passing through this polarizer. Thus, it is possible to obtain the ellipse of polarization turning the polarizer. As a result, the spectra of transmission coefficients for TE and TM polarized waves were found for two linear polarizer positions.



FIG. 2. The scheme of experiment for A) TE-wave, B) TM-wave

#### 4. Results

Using the spectra of transmission coefficients, it is possible to calculate optical activity and circular dichroism of the structure. The polarization azimuth rotation angle  $\theta$  and ellipticity  $\eta$  were used to measure optical activity and the degree of circular dichroism correspondingly. The spectra of the polarization azimuth rotation angle and ellipticity were calculated using formulas (1) and (2) [3]:

$$\theta = [\arg(T_{++}) - \arg(T_{--})], \qquad (1)$$

$$\eta = \frac{1}{2} \sin^{-1} \left[ \frac{|T_{++}|^2 - |T_{--}|^2}{|T_{++}|^2 + |T_{--}|^2} \right],\tag{2}$$

where  $T_{++}$  is the transmission spectrum of right-handed circularly polarized wave,  $T_{--}$  is the transmission spectrum of left-handed circularly polarized one, which can be found using the following formulas simplified for bi-isotropic chiral structures:

$$T_{++} = T_{xx} + iT_{xy},\tag{3}$$

$$T_{--} = T_{xx} - iT_{xy}.$$
 (4)

The transmission coefficients in (3) and (4) for linearly polarized waves can be obtained from numerical simulation results, where the first and second indices indicate the output and input wave polarizations, respectively, e.g.:  $T_{xx} = E_x^o/E_x^i$  and  $T_{xy} = E_x^o/E_y^i$ ,  $(E_x^o$  is the output x-polarized field,  $E_x^i$  is the input x-polarized field,  $E_y^i$  is the input y-polarized field).

From the numerical simulation results, the spectra of polarization azimuth rotation angle and ellipticity coefficient were found for each chiral structure design. The results are shown in Fig. 3.

As seen from Fig. 3, the changing of ellipse semi axes relation of gammadion cross allows tuning of the polarization azimuth rotation angle and ellipticity values as well as the operational frequency range. The basic



FIG. 3. Spectra of ellipticity and optical activity for the basic structure (thin gray line) and elliptical structure (bold black lines)

structure shows better chiral properties than the elliptical one, particularly, it changes the polarization of the electromagnetic wave from a linear to an elliptical one with maximum ellipticity of  $|\eta| = 44.9^{\circ}$  ( $|\eta| = 45^{\circ}$  corresponds to circularly polarized wave) as well as it is rotated the plane of wave polarization on maximum angle of  $\theta = 82^{\circ}$  vat a frequency of 0.106 THz. The structure with elliptical gammadion crosses also demonstrates chiral effects but they are not as pronounced as in the basic structure. However, it should be noted that the ellipticity and the optical activity of the second metasurface have two extreme values of  $|\eta| = 43.6^{\circ}$  at 0.113 THz and  $|\eta| = 28.6^{\circ}$  with  $\theta = 5.1^{\circ}$  at 0.115 THz, which allows its use as a polarizer at two frequencies.

#### 5. Conclusions

Therefore, the impact of gammadion cross design on the metasurface's chiral characteristics was investigated at frequencies ranging from 0.1–0.12 THz. The gammadion cross with "petals" in the form of the truncated circles was shown to have better extreme values for the ellipticity and polarization azimuth rotation angle in comparison with the elliptical design. Also, it was shown that the changing of relation of ellipse semi axes of cross allows tuning of the polarizer's operating frequency. Additionally, the elliptical metasurface design may be used for the development of a dual band polarizer.

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#### Optically controlled terahertz filter based on graphene and cross-like metasurface

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We propose a theoretical model for the optically controlled terahertz filter based on hybrid graphene/metasurface structure. Such a device has a high accuracy for the frequency adjustment by the different intensities of the optical pumping in the infrared spectral range, fast response time and polarization independence. The tuning by optical pumping of the spectral characteristics of the filter in term of resonant frequency and Q-factor was shown.

Keywords: terahertz filter, graphene, metamaterial.

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# 1. Introduction

Currently, devices that can generate, control and receive the radiation in the terahertz (THz) frequency range have been widely spread since the first sources and receivers of such radiation were created. Radiation in this frequency range is nonionizing in nature and easily passes through the majority of dielectrics, but is strongly absorbed by conductors and some dielectrics. These properties allow the use THz radiation in spectroscopy [1], near-field microscopy [2], scanning security systems, and also in medicine (for example, in the tomography which can visualize layers of the body up to several cm in depth) and in communications systems. A huge incentive for the creation of devices to control THz radiation is that doing so would allow the application of this radiation in many directions, including the field of the THz communications [3].

Graphene is a promising material for use as the basis of THz devices. Graphene is a two-dimensional allotropic modification of carbon in which its atoms are arranged in a planar hexagonal lattice. Due to its exceptional electronic and optical properties and high resistance to deformation [4], graphene may become a key component in solar cells, light emitting diodes, flexible touch screens, ultrafast lasers and frequency converters [5]. The frequency of graphene plasma waves lies in the terahertz range [6], making graphene appealing for controllable terahertz devices such as modulators and filters, where the resonant frequency can be tuned by an external electric field or optical pumping. In recent research, various hybrid structures based on graphene/metamaterial were proposed, and their optical parameters were controlled by application of a bias voltage between metamaterial and graphene [7–11] or by optical pumping in the infrared frequency range [12]. The central resonant frequency for such devices depended on the geometrical parameters of unit cell and the conductivity of graphene [8].

In this article, we propose and demonstrate an optically tunable THz filter based on hybrid system consisting of graphene and a metasurface with cross-like elements that provides polarization invariance for the structure. This geometry is commonly used because the resonant frequency of the structure is uniquely defined by only few parameters of the unit cell. Additionally, it is also relatively simple to manufacture such a structure. This filter has a very high accuracy for frequency adjustment by varying the intensity of the infrared radiation, and it also has a fast response time. Control via optical pumping instead of the electric field allows one to avoid such difficulties as the coating of the composite structure by the microelectrodes and usage of the electronic circuits to control the characteristics of the filter. In accordance with these advantages, such a device may find application in THz communications systems.

#### 2. Optical pumping of graphene

The surface conductivity model is used to describe the properties of graphene as its numerical value can be measured across a wide frequency range [13].

The gapless band structure of graphene leads to unusual behavior for its conductivity. So, for the terahertz frequency range, the dependence of graphene's conductivity upon the frequency of the incident radiation is observed. Under the influence of optical pumping in the visible and infrared frequency range, the photogeneration of

electron-hole pairs with an efficiency of 2.3 % is observed. Immediately after pumping the electron-hole pairs are tend to transformed into the lower-energy state.

Optical generation of the electron-hole pairs in graphene is described by the quasi-Fermi level  $\mu$  (the chemical potential), which for the nonexcited state of graphene, is located at the intersection of the valence band and conduction band, and its energy is equal to zero.

The theoretical value of the surface conductivity for graphene can be calculated using the Kubo formula [14], which gives the expressions for the complex conductivity for the graphene monolayer, which takes into account both the intraband  $\hat{\sigma}_{intra}$  and the interband  $\hat{\sigma}_{inter}$  transitions, depending on the frequency  $\omega$ :

$$\hat{\sigma}_{\text{intra}}\left(\omega\right) = \frac{2e^2k_BT\tau}{\pi\hbar^2\left(1-i\omega\tau\right)} \left[\ln\left(\exp\left(\frac{\mu}{k_BT}\right) + 1\right) - \frac{\mu}{2k_BT}\right],\tag{1}$$

$$\hat{\sigma}_{\text{inter}}\left(\omega\right) = \frac{e^2}{4\hbar} \left[\frac{1}{2} + \frac{1}{\pi} \operatorname{atan}\left(\frac{\hbar\omega - 2\mu}{2k_BT}\right) - i\frac{1}{\pi} \ln\left(\frac{\hbar\omega + 2\mu}{\hbar\omega - 2\mu}\right)\right],\tag{2}$$

where e is the elementary charge,  $k_B$  is the Boltzmann constant,  $\tau \approx 1$  ps is the relaxation time of carriers,  $\hbar$  is the Dirac constant, T is the temperature, i is the imaginary unit.

At the same time, the surface conductivity of the graphene monolayer is defined by the sum of the intraband and the interband transitions:

$$\hat{\sigma} = \hat{\sigma}_{\text{intra}} + \hat{\sigma}_{\text{inter}}.$$
(3)

The value of the chemical potential under the influence of optical pumping with the frequency  $\nu_{\text{pump}} = \Omega/2\pi$ and the energy which is more than  $k_B T$ , is defined as [15]:

$$\mu = \hbar \nu_F \sqrt{\frac{2\pi \alpha \tau_R I_\Omega}{\hbar \Omega}},\tag{4}$$

where  $\nu_F = 106$  m/s is the Fermi velocity of charge carriers in graphene,  $\alpha = 1/137$  is the fine structure constant,  $\tau_R \approx 1$  ns is the time of a recombination of the electron-hole pairs,  $I_{\Omega}$  is the graphene pumping intensity.

The dependences of the normalized surface conduction of graphene on the frequency  $\omega$  with or without optical pumping and a wavelength of 1.5  $\mu$ m and intensity  $I_{\Omega} = 3$  W/mm<sup>2</sup>, which are calculated using the expressions (1) – (4) are shown in Fig. 1. The tuning of graphene's chemical potential under the influence of optical pumping was shown to change the real and imaginary parts of the conductivity.



FIG. 1. The dispersion of the real and imaginary parts of the normalized conductivity of graphene at a temperature T = 293 K: 1 – without pumping, 2 – under the optical pumping with wavelength of 1.5  $\mu$ m and intensity  $I_{\Omega} = 3$  W/mm<sup>2</sup> (the solid lines represents the imaginary part of the conductivity, dashed lines – real part of conductivity)

The real part of surface conductivity is known to be responsible for the absorption in the material, while the imaginary part of the surface conductivity allows one to calculate the phase difference between the electric field in the material and the excitation field, i.e., the delay in propagating through the material of the electromagnetic field. Information about the phase delay has a significant importance in the design of composite structures based on graphene and metamaterial, as the addition of graphene into the structure of metamaterial-based subwavelength resonator significantly shifts its resonant frequency.

As can be seen from Fig. 1, the largest difference between the imaginary part of surface conductivity with and without pumping is observed at a frequency of 0.18 THz, however, at that same frequency, significant losses are present. For this reason, the resonant frequency of the developed metamaterial was chosen in the higher frequency region of the spectrum, where the losses are minimal and the difference between the value  $\text{Im}(\sigma)$  with and without pumping is still significant. Frequencies near 0.4 THz satisfy this condition. In addition, there are several radiation sources which operate at a frequency close to 0.4 THz [16], that can be useful for experimental verification of the calculations.

#### 3. Optically tunable bandpass filter and method of calculation

In this work, we studied hybrid structure based on the cross-like metasurface and optically pumped graphene in the terahertz frequency range. To describe all the effects occurring in such a composite structure, the usage of analytical methods is difficult, therefore, to address these issues, we applied a numerical approach.

Simulation of the electromagnetic fields in composite structure graphene/metamaterial was performed using the CST Microwave Studio software package with the frequency domain kernel which solves Maxwell's equations by the finite difference method. The boundary conditions were chosen along the x and y unit cell directions with the opened Floquet ports along the z axis. As a result of this simulation, it is possible to obtain S-parameters ( $S_{11}$ is the amplitude of the reflection coefficient,  $S_{12}$  is the amplitude of the transmission coefficient).

The graphene monolayer was defined as an infinitely thin sheet with surface impedance  $Z = 1/\sigma$ , where the conductivity  $\sigma$  is described by the equations (1) – (4).

The filter is an artificial resonant structure made of an aluminum film with a thickness of 0.5  $\mu$ m having crosslike slots. This film is covered by a graphene monolayer and located on the dielectric substrate with thickness of 65  $\mu$ m and permittivity  $\varepsilon = 3$ . The frequency spectrum of such a metasurface is determined by the width K and the length L of the cross-like slots, and also by the size G of the unit cell. This form of a slot provides the polarization independence of the structure relative to the incident radiation. For numerical modeling, geometric parameters of the cross-like metasurface were selected such that the resonant frequency of the composite structure was about 0.4 THz, and the Q-factor was no less than 1.5 with a transmission coefficient value of 45 % without optical pumping. The schematic of the proposed filter is presented in Fig. 2.



FIG. 2. Schematic of the elementary cell of the filter: 1 – graphene, 2 – aluminum, 3 – PET substrate

As a result of the simulation of the cross-like metasurface without graphene, we identified areas of the structure that make the largest contribution to the localization of the electromagnetic field. In accordance with this, we propose the structural unit cell, in which graphene covers the sections of the aluminum film, which are connect the end faces of the cross-like slots, as the electric field in these regions is maximized.

#### 4. Results and discussion

By optimizing the geometrical parameters of the cross-like resonator ( $K = 45 \ \mu m$ ,  $L = 180 \ \mu m$ ,  $G = 440 \ \mu m$ ), we have obtained the highest value for the quality factor Q = 1.9 with the amplitude of the transmission coefficient of 45 %.

The dependence of the transmission coefficient amplitude on frequency for various pumping intensity values is shown in Fig. 3.



FIG. 3. The frequency dependence of the transmission coefficient amplitude for several pumping intensity values  $(1 - 0 \text{ W/mm}^2, 2 - 2 \text{ W/mm}^2, 3 - 6 \text{ W/mm}^2, 4 - 10 \text{ W/mm}^2)$ 



FIG. 4. The dependence of the central resonance frequency position on the pumping intensity

FIG. 5. The dependence of the transmission coefficient value on the pumping intensity

Figure 3 shows the frequency dependence for the amplitude of the transmission coefficient of the transmitted wave and its relative change for different graphene conductivity values, which is changed when graphene is pumped by optical radiation with a wavelength of 1.5  $\mu$ m. The minimum value for the transmission coefficient is observed in the absence of optical pumping. Under optical pumping of the composite structure, the amplitude of the wave

passing through the filter gradually increases; additionally, the Q-factor also increases, while and the resonant frequency is shifted to the higher frequency region. Figs. 4 and 5 show the dependences of the central resonant frequency and amplitude of the transmission coefficient, respectively, on the pumping intensity.

Thus, by means of numerical simulations, we have demonstrated the possibility for optical control of a THz wave passing through the hybrid filter based on the metamaterial and graphene, as the conductivity of graphene can be controlled by optical radiation. At the same time, the proposed filter is polarization-invariant due to structural symmetry.

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# Generation of pure single-photon states in commercial photonic-crystal fibers on telecommunication frequencies

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We studied the theoretical possibility of generating single-photon states in fibers with active profile dispersion formed by spontaneous four-wave mixing (SFWM) using femtosecond laser pulses. The possibility of eliminating the spectral correlation for single-photon states generated in commercial fibers was assessed. To model the structure of photonic crystal fibers and the modes of SFWM generation, an optimization was performed on the parameters of the pump and the fiber structure.

Keywords: single photon, spontaneous four-wave mixing, photonic crystal fiber, quantum optics.

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### 1. Introduction

A single-photon source is an essential part of many quantum information devices. The specific characteristics of such sources determine possibilities for their application [1]. Currently, the most promising trends are the following: 1) quantum memory devices and quantum calculation algorithms for searching in unordered databases; 2) quantum repeaters for building scalable quantum networks with high security; 3) applications for quantum metrology and quantum informatics.

Spontaneous parametric down-conversion (SPDC) and spontaneous four-wave mixing (SFWM) are currently the most promising and advanced methods to generate single photons. In fact, SPDC and SFWM methods imply that there is the possibility of obtaining a two-photon state of light. The main advantages of these methods include the following: high stability of obtained states in time; the potential to generate spectrally limited pulses at room temperature; the possibility to adjust optical wavelength and spectrum width as well as the minute influence of multi-photon states. Basic disadvantages of the methods include the random nature of single-photon generation, which leads to the probability of obtaining a two-photon state, and a correlation between signal and idler photons. The correlation is caused by idiosyncracies of the two-photon generation process. Thus, mixed single-photon states are obtained for SPDS and SFWM methods. This means that there is a spatial, polarization and spectral correlation between the pair of photons. The elimination of all these types of correlation is necessary to obtain a "clean" single-photon state. A fundamental difficulty is the elimination of the spectral correlation between the signal and idler photons. This can be overcome by the proper selection of parameters for the nonlinear medium and the laser's pump, such that the special matching conditions for the pump photon, signal and idler photons can be obtained. That is the essence of the problem for creating a single-photon source.

Single-mode structures have several advantages over other media: generation in single spatial mode; suppression of lateral spatial modes; and high consistency with fiber-optical networks. Photonic crystal fibers (PCF) have the potential to provide the conditions with spectrally limited laser pulses [1,2]. It should also be noted that the efficiency of single-photon states is strongly dependent upon the parameters of the nonlinear medium and pump pulses.

This article provides the analysis of clean single-photon generation based on the SFWM method and femtosecond spectrally scanning laser for the commercial PCFs.

#### 2. PCF model development

In order to determine spectrum and correlation characteristics for the SFWM photon fields, it is necessary to determine exact values for the index of refraction and dispersion of PCFs at its length, which takes part in the parametric processes. Usually it is not possible to obtain an analytical solution for the complex internal structure of PCFs to determine its characteristics and its fundamental modes. This is why computations of the effective

refraction index, dispersion and other characteristics of PCF are provided by means of numerical solution of Maxwell's equations. In this study, simulations were performed using Comsol Multiphysics software.

The obtained model of PCF hexagonal structure (core diameter  $2.4 \pm 0.1 \mu$ m; distance between holes  $2.9 \pm 0.1 \mu$ m; hollow region diameter  $27 \pm 0.5 \mu$ m) corresponds to commercial fibers with zero dispersion at 800 nm.

The diameter of holes d, the distance between them p as well as core diameter are defined in the process PCF design. The type and applicability of the PCF determines the geometry of its microstructure. For example, fibers with high level of nonlinearity are promising for the generation of photon pairs and characterized by hexagonal structure with small sized core diameter. The core material for the model fibers is silica; holes are filled with air under atmospheric pressure. Searching for fundamental modes in the fiber core with distribution close to that of a Gaussian one is carried out for each wavelength within the modelling process. By changing the wavelength within certain range, it is possible to analyze the character of the following desired values: effective refraction index, path loss, dispersion and c.

Calculations for the effective index of refraction and dispersion as a function of wavelength are shown in Fig. 1 and Fig. 2. The effective index of refraction for a nonlinear medium decreases with increasing of wavelength and the ratio of holes diameter to distance between holes. Increasing the air filling ratio forms a fundamental mode that occurs in the fiber core. Monitoring the parameters of fiber cladding and its microstructure, in general, allows one to form an emission into the fiber core without significant losses. For the model of the fibers, dispersion attains a negative value over the range 600 - 800 nm, equals zero from 800 - 900 nm and has positive values for higher wavelengths. Evaluation of dispersion curves allows one to determine wavelength range with zero dispersion as well as the generation and propagation conditions for the signal and idler photons.



FIG. 1. Effective refraction index  $n_{eff}$  as a function wavelength

FIG. 2. Dispersion of PCF model

#### 3. Evaluation of SFWM modes

The process of spontaneous four-wave mixing (SFWM) at the quantum level can be represented as the virtual absorption of two pump photons (p) with the further generation of pair of photons known as signal (s) and idler (i) photons [1]. Because of the negligibly small response time for Kerr nonlinearity  $\chi^{(3)}$ , it is possible to detect one photon in the pair in order to notify of the presence of the second one. The signal and idler wavelengths in the SFWM mode for the desired fiber structure and specific laser source pump are determined by the conditions of phase matching and conservation of the energy, see equations (1) and (4):

$$2w_p = w_s + w_i. \tag{1}$$

Nonlinear interaction occurs in the solid silica core of PCFs used for SFWM generation of photon pairs, and the cladding has periodical structure, that consists of air-filled holes.

Two-photon state, caused by four-wave mixing in the optical fiber of the length L can be described by the following expression [3,4]:

$$|\Psi\rangle = |0\rangle_s |0\rangle_i + \kappa \iint dw_s dw_i F(w_s, w_i) |w_s\rangle_s |w_i\rangle, \tag{2}$$

where  $\kappa$  is a constant, which determines the efficiency of generation. This constant has a linear dependence on the fiber's length, the amplitude of electrical field for each of the pump fields and depends on relative polarization pump fields and generated photon pairs.  $F(w_s, w_i)$  is the function of spectral amplitude of the biphoton (signal and idler photon), which describes spectral and correlation properties of the generated photon pair. The joint spectral amplitude function can be described as follows:

$$F(w_s, w_i) = \int dw' \alpha_1(w') \alpha_2(w_s + w_i - w') \times \sin c \left[ \frac{L}{2} \Delta k(w', w_s, w_i) \right] \exp \left[ i \frac{L}{2} \Delta k(w', w_s, w_i) \right], \tag{3}$$

where  $\alpha_{1,2}(w)$  is spectral pump amplitudes;  $\Delta k(w', w_s, w_i)$  is the function of phase matching, that for the case of two-photon pump and one polarization for signal and idler fields, is given by the equation:

$$\Delta k(w_p, w_s, w_i) = k(w_p) + k(w_s + w_i - w_p) - k(w_s) - k(w_i) - (\gamma_1 P_1 + \gamma_2 P_2), \tag{4}$$

$$k_q = \frac{\omega_q n^{eff}(\omega_q)}{c}, \quad q = p, s, i,$$
(5)

where  $\gamma_1 P_1 + \gamma_2 P_2$  is the self-cross phase modulation for two pumps with peak powers  $P_1$  and  $P_2$  and corresponds to the nonlinearity coefficients  $\gamma_1$  and  $\gamma_2$ , which in their turn depend on the fitted fiber and pump wavelength, and is taken into account [6,7]. Limitations of energy conservation are determined by the second term of phase detuning in equation (3). The factorable state is the state, where  $F(w_s, w_i)$  is the result of multiplication of two functions: eigen-functions of signal,  $S(w_s)$ , and idler,  $I(w_i)$ , photons.

The results of numerical simulations for the effective index of refraction and PCF dispersion allowed us to obtain the matching conditions and the joint spectral amplitude for the signal and idler photons. The objective of the simulation is to find the modes of generation of photon pairs with minimum spectral correlation and wavelengths commonly used for the telecommunications applications. Calculations of the joint spectral amplitudes at different wavelengths, based on the commercial PCFs models and laboratory femtosecond facilities, were performed. In this sense, the most promising type of PCF was found (Fig. 2). The joint spectral amplitude of eigen-function for the PCF is shown in Fig. 3 and it demonstrates the probability for the generation of signal (X-axis) and idler (Y-axis) photons.



FIG. 3. Joint spectral amplitude for the signal and idler photons (a) and Schmidt decomposition for PCF (800 nm zero dispersion) with 734 nm pump wavelength (b)

In order to determine the purity of single-photon states, a method for the decomposition of the spectral amplitude function of two-photon states F into Schmidt modes was developed [7]. Assume that initial state vector can be described as follows:

$$|\psi\rangle = |0\rangle + \iint F(\omega_i, \omega_s) a^+(\omega_i) a^+(\omega_s) d\omega_i d\omega_s.$$
(6)

Therefore, Schmidt decomposition is given by:

$$F(\omega_i, \omega_s) = \sum_n \sqrt{\lambda_n} \alpha_n(\omega_i) \beta_n(\omega_s), \qquad \sum_n \lambda_n = 1,$$
(7)

where  $\alpha_n(\omega_i)$  and  $\beta_n(\omega_i)$  are Schmidt functions (modes), and  $\lambda_n$  are decomposition coefficients by Schmidt modes [7]. For the case of pure (factorable) states in the Schmidt decomposition, there is only one mode, wherein the Schmidt number equals 1. Therefore, evaluation of the Schmidt number for SFWM generation mode provides the estimation of purity for single-photon state. Conducted optimization using the parameters of laser pump allowed us to find the most promising mode to generate photons with small spectral correlation, when Schmidt number equals 1.0451, at 734 nm pump for wavelengths of 1550 and 480 nm.

#### 4. Conclusion

This study includes results from the analysis of PCF structures similar to commercial PCFs in order to generate correlated photon pairs within the process of spontaneous four-wave mixing with minimum spectrum correlation at frequently used telecommunications wavelengths. Numerical simulation of these structures was performed and the dependence of effective index of refraction and dispersion of wavelength was found. Based on the obtained results, promising modes were found to generate single photons with small spectrum correlation for the following conditions: hexagonal structure (Fig. 1), zero dispersion wavelength 800 nm, 734 nm pump, Schmidt number of 1.0451 and wavelength of 1550 nm.

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## Ce:YAG transparent ceramics based on nanopowders produced by laser ablation method: Fabrication, optical and scintillation properties

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Transparent Ce:YAG ceramics were fabricated by the solid-state reaction method with an additional round of pre-calcining using nanopowders of Ce<sub>2x</sub>Y<sub>2-2x</sub>O<sub>3</sub> (x = 0.001, 0.01, 0.03 and 0.05) and Al<sub>2</sub>O<sub>3</sub> synthesized by laser ablation. Additional pre-calcining of the nanopowder mixture in air was used to partially transform the oxides into the YAG phase before sintering. The transmittance of the obtained 2-mm-thick Ce:YAG ceramics was over 81 % in the wavelength range of 500–900 nm. The average volumes of the scattering centers in the obtained ceramics were evaluated by direct count method to be 34, 74, 53, 50 ppm for 0.1, 1, 3 and 5 % Ce doping concentration, respectively. The absolute light yields, energy resolutions under 662 keV gamma ray, and decay curves of scintillations of the fabricated Ce:YAG samples were measured and compared to those of Ce:YAG and CsI:Tl single crystals.

Keywords: Laser ablation, nanopowder, yttrium aluminium garnet, cerium, scintillator, transparent ceramics, transmittance.

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#### 1. Introduction

Most of the scintillation materials used in ionizing radiation detectors have been obtained in a single crystalline form. It is well known that growing high melting point scintillation crystals is time-consuming and expensive. For this application, one of the most promising approaches is to replace single crystals by ceramic materials. For example, to date, several scintillation ceramics have been successfully used in medical imaging devices (General Electric's premium X-ray CT) [1,2].

The important factors that influence the scintillation properties include a high optical quality of material, effective atomic number, decay time of scintillations, and uniformity distribution of activator ions in the host lattice. Growing high-quality large-sized single crystals with a homogeneous dopant distribution is difficult due to doping gradients in the melt. Ceramic technology offers the possibility for fabricating highly transparent and large-sized garnet materials at lower temperatures and with a homogeneous or controlled gradient activator ion distribution [3,4].

One of the most famous and most modern ceramic scintillators is a well-known scintillator based on Ce<sup>3+</sup>doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (Ce:YAG) with a garnet structure [5]. YAG is a promising candidate for scintillator applications because of its excellent optical and thermomechanical properties, high electron conversion efficiency, good energy resolution, reasonably fast decay time, mechanical ruggedness and durability, good thermal conductivity, and vacuum compatibility [6]. Ce-doped YAG single crystals and ceramic materials are widely used in medical imaging devices [1,7], white LED applications [8–10], white high-power LEDs [11], electron microscopes,  $\beta$ -, soft  $\gamma$ - or X-ray counters and spectrometers, and electron- or X-ray image screens [12].

Additionally, polycrystalline laser ceramics are extremely attractive materials due to their ease of fabrication, low cost, unlimited dimensions, high doping concentration of activator ions and multifunctional composite structure. To fabricate highly transparent ceramics, it is necessary to obtain thin grain boundaries ( $\sim 1$  nm) and a pore-free structure. There are two main methods for meeting these requirements. In the first approach, referred to as the solid state reaction method (SSR) [13] or the reactive sintering method [14], commercial oxide powders are mixed together, then the mixture is dried, pressed and sintered to transparency. Thus, the phase transformations of  $Y_2O_3$ and  $Al_2O_3$  into  $Y_3Al_5O_{12}$  occur at the vacuum sintering.

According to the second approach [15, 16], ceramics are synthesized from YAG nanopowder. Chemical coprecipitation route [15, 16], citrate gel [17] and gel combustion methods [18, 19] are used to produce this type of nanopowder.

However, the optical quality of YAG-based ceramics obtained from nanopowders produced by the laser ablation method is better when phase transformation into YAG partially occurs before vacuum sintering [20].

In this paper, we fabricate transparent Ce:YAG ceramic samples with different  $Ce^{3+}$  concentrations and report on the microstructural, optical, radioluminescence and scintillation properties of the obtained ceramics. We believe that the synthesis of nanopowders for transparent ceramics is a key parameter to simultaneously achieve a high doping level and uniform activator ion distribution in bulk ceramic scintillators. In this regard, a laser ablation technique used for the synthesis of raw materials is a very attractive method to produce particles with a complex chemical composition because the required components could be properly and homogeneously mixed at the atomic scale in vapors during the process of evaporation and condensation.

#### 2. Experimental

The pulse-periodic CO<sub>2</sub> laser LAERT ( $\lambda = 10.6 \ \mu m$ ) [21] was used to produce nanopowders. The main laser parameters at the synthesis of nanopowders were as follows: average power P = 600-800 W, peak power  $P_p = 10-11$  kW, half-height duration  $\tau_l = 200 \ \mu s$ , pulse repetition rate f = 500 Hz.

In the present study, coarse  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (> 99.99 %, 150 nm, Sumitomo chemical Co., Ltd., Tokyo, Japan), Y<sub>2</sub>O<sub>3</sub> (> 99.99 %, 1–20  $\mu$ m, Lanhit, Moscow, Russia) and Nd<sub>2</sub>O<sub>3</sub> (> 99.99 %, 1–15  $\mu$ m, Lanhit, Moscow, Russia) were used as initial powders. Yttrium and neodymium oxides were mixed together for 24 h in a rotary mixer with inclined axis of rotation to prepare Ce<sub>2x</sub>Y<sub>2–2x</sub>O<sub>3</sub> (x = 0.001, 0.01, 0.03, and 0.05) laser target. Furthermore, the mixture of coarse powders (or Al<sub>2</sub>O<sub>3</sub> powder) was compacted with a uniaxial static press at the pressure of 10 MPa. Subsequently, the targets were sintered at 1300 °C for 5 h in air so that prepared targets would not be destroyed under the action of laser radiation during the synthesis of nanopowders. After sintering, the laser targets were 60 mm in diameter and 19 mm in thickness.

The  $Ce^{3+}$ :Y<sub>2</sub>O<sub>3</sub> nanopowder was produced at evaporation of 0.1, 1, 3, 5 at.%  $Ce^{3+}$ :Y<sub>2</sub>O<sub>3</sub> target material with eventual condensation of vapor in air flow. Particles are weakly agglomerated and have a weakly faceted near-spherical shape. Fig. 1(c) shows the size distribution of  $Ce^{3+}$ :Y<sub>2</sub>O<sub>3</sub> nanopowder (Fig. 1(a)) after sedimentation. Sedimentation of nanopowder after laser evaporation was used for removal of splinters of a target and drops of material. The distribution peak is realized at 13 nm, the average particle size being 13 nm. According to the BET analysis (TriStar 3000), the specific surface area of the  $Ce^{3+}$ :Y<sub>2</sub>O<sub>3</sub> particles was 51.23 m<sup>2</sup>/g.

X-ray diffraction analysis (XRD) on D8 Discover diffractometer has shown that the particles of the Ce<sup>3+</sup>:Y<sub>2</sub>O<sub>3</sub> nanopowder have a monoclinic  $\gamma$ -Y<sub>2</sub>O<sub>3</sub> phase. The transformation of metastable monoclinic phase in a main cubic is accompanied by substantial growth of elementary cell volume (a = 12.011 Å). Therefore, in order to avoid



FIG. 1. Transmission electron microscopy (TEM) images of (a)  $Ce:Y_2O_3$  and (b)  $Al_2O_3$  nanopowders produced by the laser ablation method. (c) Size distribution of the nanopowders

destruction of ceramic sample during sintering, this phase transformation was performed in advance by annealing of  $Ce^{3+}$ :Y<sub>2</sub>O<sub>3</sub> nanopowder at 1000 °C for 30 min. XRD analysis of annealed nanopowder on D8 Discover diffractometer has shown that content of the cubic phase at these annealing conditions is equal to 100 %. According to the BET analysis, the specific surface area of the  $Ce^{3+}$ :Y<sub>2</sub>O<sub>3</sub> particles after annealing was 18.12 m<sup>2</sup>/g, thus showing that the average particle size increased from 11 to 71 nm.

The laser method also was used for producing of Al<sub>2</sub>O<sub>3</sub> nanopowder. Fig. 1(c) shows the size distribution of Al<sub>2</sub>O<sub>3</sub> nanopowder (Fig. 1(b)) after sedimentation. Particles are weakly agglomerated and have a weakly faceted near-spherical shape. The distribution peak is realized at 13 nm, the average particle sizes 13 nm. According to the BET analysis, the specific surface area of Al<sub>2</sub>O<sub>3</sub> nanopowder was 82.96 m<sup>2</sup>/g. XRD analysis on D8 Discover diffractometer showed that the content of main  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystalline phase is 90 wt.%. Also, there is a low-temperature  $\delta$ -Al<sub>2</sub>O<sub>3</sub> phase with a content of 10 wt.%. Al<sub>2</sub>O<sub>3</sub> nanopowder on D8 Discover diffractometer has shown that content of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase at these annealed nanopowder on D8 Discover diffractometer has analysis the specific surface area of the Ce<sup>3+</sup>:Y<sub>2</sub>O<sub>3</sub> particles after annealing was 10.05 m<sup>2</sup>/g.

Nanopowders (annealed  $Al_2O_3$  and  $Ce:Y_2O_3$ ) were weighed according to the chemical stoichiometry composition of 0.1, 1, 3, 5 at.%  $Ce^{3+}:YAG$  ((Ce + Y) : Al = 3 : 5) and mixed with ethyl alcohol and 0.5 mas.% sintering aid tetraethyl orthosilicate (TEOS). The mass ratio of nanopowder, balls and ethanol was 1 : 4 : 8, respectively. Then, the mixed slurry was ball milled in a plastic bottle with YSZ balls for 48 h. After ball milling the slurry was dried using the vacuum rotary evaporator and then annealed at 600 °C for 3 h to remove organic impurities.

The compact was prepared from the powders with  $Ce^{3+}$ :YAG crystal structure. For preparation of  $Ce^{3+}$ :YAG powder, the mixture was compacted into pellets with relative density of 20 %. Then, the pellets were annealed in air at 1200 °C for 3 h. XRD analysis on D8 Discover diffractometer showed that the content of YAG phase in the pellets was 96–98 %. Additionally, the pellets were ball milled in ethyl alcohol with YSZ balls for 48 h. The received powder was uniaxially pressed into disks with a diameter of 15 mm and a thickness of 2–4 mm at 200 MPa. The density of green body was 2.2 g/cm<sup>3</sup> (relative density of 48 %).

Then compact was annealed in air at 800 °C for 3 h to remove the organic impurities. The compacts were sintered at 1780 °C for 20 h in a high temperature vacuum furnace under  $3 \cdot 10^{-5}$  mbar vacuum during holding and then annealed at 1300 °C for 5 h in air. The as-synthesized samples of transparent Ce:YAG were 10 mm in diameter and 2 mm in thickness and are presented in Fig. 2.



FIG. 2. Photograph of as-synthesized Ce:YAG ceramics ( $\emptyset 10 \times 2 \text{ mm}$ )

The microstructural properties of ceramic Ce:YAG samples were measured using optical microscope OLYM-PUS BX51TRF-5.

The optical transmittance and absorption spectra of the obtained Ce:YAG ceramics were measured using a Shimadzu UV-2450 spectrophotometer in the 200–900 nm wavelength range. The X-ray luminescence (XRL) spectra and decay curves were measured using a setup ASNI-ROSTT (experimental physics department, UrFU) on the basis of an MDR-2 monochromator. The XRL channel is equipped by an URS-1 X-ray source (40 kV, 10 mA, W-anode) and a Hamamatsu R928 photomultiplier (180–900 nm). The measurements of decay curves were carried out using a pulse electron gun (pulse duration 15 ns, energy 150 keV), FEU-39 photomultiplier and Tektronix TDS5034B oscilloscope with a 50 Ohm load.

The scintillation properties of ceramic Ce:YAG samples were measured using a "Spectr-1" certified setup equipped by an FEU-130 photomultiplier, spectrometer and spectrometric amplifier "Aspect". The <sup>137</sup>Cs and <sup>239</sup>Pu were used as  $\gamma$ - and  $\alpha$ -source. A CsI-Tl single crystal with  $\emptyset 10 \times 2$  mm size was used as a reference scintillator.

#### 3. Results and discussion

Figure 2 shows the photograph of the sintered ceramics obtained after annealing and polishing. The samples appear transparent for all doping concentrations and have a yellow color which is conventional for such material.

Figure 3 shows the photograph of surfaces of a double polished Ce:YAG ceramics samples after annealing at 1350 °C for 5 h and thermal etching. The average grain size is not dependent upon the Ce<sup>3+</sup> dopant concentration and is 17  $\mu$ m. There is scattering centers of various sizes.



FIG. 3. The photograph of surfaces of a double polished Ce<sup>3+</sup>:YAG ceramics samples

The distribution of the scattering centers at various depths throughout the sample was calculated using optical microscope OLYMPUS. The central area of the samples was scanned at intervals of 50  $\mu$ m with the volume of a sample under analysis being 577 × 433 × 50  $\mu$ m<sup>3</sup>. We failed to separate pores from secondary phases, so they were summarized.

The scattering centers were conditionally divided into large – more than 2  $\mu$ m and small – less than 2  $\mu$ m. The dimensions of large formations were calculated specifically for each one. As the small scattering centers were usually spherical, therefore for calculation of porosity the average volume of such centers was multiplied by quantity.

The distribution of scattering centers was comparably homogeneous. In some layers, there were large scattering centers with a diameter of more than 10  $\mu$ m that led to significant differences between the concentrations of scattering centers for two nearby layers.

The content of the secondary phases and concentration of pores was 34, 74, 53, 50 ppm for 0.1, 1, 3 and 5 % of  $Ce^{3+}$ , respectively.

The transmission spectra of 2-mm-thick Ce:YAG ceramics are shown in Fig. 4. As can be seen from the figure the highest transmittance of over 81 % in the range of 500–900 nm has the sample with the lowest doping level of Ce<sup>3+</sup> (0.1 at.%). The optical transmittance of samples depends on the Ce<sup>3+</sup> dopant concentration and is equal to 72 and 77 % for 1 % and for 3 % and 5 % of Ce<sup>3+</sup>, respectively. In the transmission and absorption spectra  $4f \rightarrow 5d^1$  and  $4f \rightarrow 5d^2$  absorption bands of trivalent cerium are observed at 337 and 457 nm. With an increase in the Ce<sup>3+</sup> content, the absorption bands become stronger and the edge of the transparent region near 500 nm is shifted to the right side. The change of the edge position leads to a color modification of samples (Fig. 3). The bands located below 340 nm with the maxima at 225, 258 and 301 nm can be attributed to absorption transitions in Ce<sup>4+</sup>-centers. A similar fine structure of absorption bands in Ce:LuAG and a description of Ce<sup>4+</sup>-centers formation in a garnet host was reported in [22].

The XRL measurements of the fabricated ceramic samples show that the bright d-f luminescence of Ce<sup>3+</sup> is observed in the 425–700 nm region with a maximum at 527–545 nm. The XRL spectra consist of two luminescence bands attributed to  ${}^{2}D \rightarrow {}^{2}F_{7/2}$ , and  ${}^{2}D \rightarrow {}^{2}F_{5/2}$  transitions in Ce<sup>3+</sup> ions [23]. The maximum intensity of luminescence has the sample with 1 at.% of Ce. An increase in the cerium concentration from 1 to 3 and 5 at.% leads to concentration quenching of luminescence and the intensity of XRL is reduced (Fig. 5). For various Ce concentrations, the positions of maxima are changed due to the variation of the absorption edge near 470–520 nm (Fig. 4).

Besides the Ce<sup>3+</sup> luminescence bands, the luminescence of self-trapped excision (STE) in YAG [24] is observed in the 250–450 nm region (Fig. 5). The shape of the STE band is due to the shape of Ce<sup>3+</sup> absorption bands (see Fig. 4(b)). The intensity of the STE band decreases with an increase in dopant concentration. The STE band is almost completely absent in samples doped with 3 and 5 % of Ce. The observed narrow band at 312 nm (Fig. 5) is attributed to a well-known f-f transition in uncontrolled Gd<sup>3+</sup> impurity ions.



FIG. 4. The optical transmittance (a) and absorption (b) spectra of ceramic Ce:YAG samples



FIG. 5. The XRL spectra of ceramic Ce:YAG samples

For a detailed study of energy relaxation processes in Ce:YAG ceramics, the decay curves (Fig. 6) under a pulse electron beam were measured. The decay parameters (Table 1) were measured in the 545 nm band (for 0.1 % Ce also in 390 nm) and identified through the fitting procedure which was performed using the expression with the sum of two exponents,  $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_{21}}$ , where  $A_i$  – intensity of component,  $\tau_i$  – decay constant of the decay curve.

The decay curve measured in the STE band at 390 nm had fast and slow components (Fig. 6, the decay parameters for the STE band are presented in Table 1). The fast component was attributed to a relaxation of a convenient STE which was localized at Al-sites. The slow component can be attributed to the relaxation of the defect-bound exciton (DBE). The  $Y^{3+}Al$  antisite defects are likely possible defects for the DBE creation in the YAG host [24].

The decay curve measured in the  $Ce^{3+}$  band at 545 nm also had two components (Fig. 6). Table 1 shows that with an increase in the  $Ce^{3+}$  concentration, the decay constants decreased from 110 to 26 ns for the fast component



FIG. 6. The decay curves of ceramic Ce:YAG samples under pulse cathode beam collected at 545 nm wavelength

TABLE 1.	The decay	parameters	of ceramic	Ce:YAG	pulse	cathode	luminescence
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Sample	$\tau_1$ , ns	$A_1, \%$	$\tau_2$ , ns	$A_2, \%$	Reduced Chi-Sqr	Adj. R-Square
0.1 % Ce (390 nm)	45.9	87	541	13	$1.61 \cdot 10^{-5}$	0.99823
0.1 % Ce (545 nm)	110	85	562	15	$5.53 \cdot 10^{-6}$	0.99972
1 % Ce	99	96	526	4	$3.04 \cdot 10^{-6}$	0.9998
3 % Ce	72	99.5	489	0.5	$9.65 \cdot 10^{-6}$	0.99958
5 % Ce	26	99.0	338	1.0	$1.26 \cdot 10^{-5}$	0.99915

and from 562 to 338 ns for the slow component. The relative intensity ( $A_1$  in Table 1) of the fast component increases with an increase in the Ce<sup>3+</sup> concentration. However, the intensity of the slow component in the decay curve of highly doped (3 and 5 %) samples was negligible and practically the entire part of the Ce<sup>3+</sup> luminescence had a fast decay time.

The fast component of the decay curve for the sample doped with 5 % of  $Ce^{3+}$  is 26 ns. A similar value of decay time (~ 28 ns) was reported for the luminescence decay of YAG nanoparticles doped with 4 at.% of Ce [25]. The short decay time for the luminescence of  $Ce^{3+}$  ions in YAG host is unusually low and can be connected with a concentration quenching effect. The decay time variation of the luminescence for the  $Ce^{3+}$  band in YAG for various dopant concentrations was also presented in [26].

The slow decay component of  $Ce^{3+}$  luminescence is usually connected with the involvement in the relaxation processes of point defects such as oxygen vacancies, which can be shallow traps for charge carriers. The presence of such shallow traps significantly increases the decay time of luminescence due to the absorption and reabsorption of charge carriers. The decrease of decay time and the intensity of the slow component with an increase in the  $Ce^{3+}$  concentration indicates the reduction of or/and transformation of point defects in the YAG lattice. This explanation also seems plausible since the decay curves of the samples doped with 0.1, 1 and 3 at.% of  $Ce^{3+}$ have a region of increase (see inset in Fig. 6). The durations of this increased region in the decay curves decrease with an increase in Ce concentration. The presence of the region of increase in the luminescence decay curve usually indicates the intermediate localization of the charge carriers in the shallow traps and reflects the migration processes of electronic excitations in the crystal lattice. However, for the sample doped with 5 at.% of  $Ce^{3+}$ , the region of increase for the decay curve is absent (Fig. 6). Conversely, the observed behavior of the decay parameters of the  $Ce^{3+}$ -center luminescence (for the fast and slow components) appears to be an influence of the concentration quenching effect on relaxation processes. In addition, the content of  $Ce^{4+}$ -ions in the YAG lattice can affect the efficiency of non-radiative relaxation by the  $Ce^{3+} \rightarrow Ce^{4+}$  interaction channel. The origin of the very fast luminescence decay of  $Ce^{3+}$  in highly doped YAG needs further study. In order to determine the scintillation properties of the obtained Ce:YAG ceramics, the pulse-height spectra (PHS) were measured under  $\alpha$ - and  $\gamma$ -source excitations. The pulse height spectra are presented in Figs. 7 and 8. The main parameters of ceramic Ce:YAG samples are presented in Table 2. The data for YAG ceramic and single crystal is also presented for comparison. A commercial CsI:Tl scintillator with the same sizes is used as a reference sample. ALY was calculated using a CsI:Tl single crystal. As can be seen from Table 2, YAG doped with 1 at.% of Ce<sup>3+</sup> has a the highest absolute light yield and the lowest  $\alpha/\gamma$  ratio among the other investigated Ce:YAG samples. Energy resolutions of the fabricated ceramic scintillator are not high (10–15 %) due to a low effective atomic number. The resolution can be increased using thicker samples.



FIG. 7. gamma-ray pulse-height spectra of  $^{137}$ Cs measured using the ceramic Ce:YAG samples with varied concentration of Ce in comparison with standard CsI:Tl scintillator ( $\emptyset 10 \times 2$  mm)



FIG. 8. The alpha particles pulse-height spectra of  $^{239}$ Pu measured using the ceramic Ce:YAG samples with varied concentration of Ce in comparison with standard CsI:Tl scintillator ( $\emptyset 10 \times 2 \text{ mm}$ )

Sample	$\gamma$ -ray ( <sup>137</sup> C	Cs, 662 keV)	$\alpha$ -particles ( <sup>239</sup> Pu, 5.15 MeV)	$\alpha/\gamma$ ratio
	Relative light Absolute light		Relative light	
	yield, %	yield, ph/MeV	yield, %	
CsI:Tl	100	65000	100	—
0.1 % Ce	7.6*	4940*	3.2	0.055
1 % Ce	32	20800	7.8	0.032
3 % Ce	29.2	18980	8.0	0.036
5 % Ce	27.6	17940	8.1	0.038
0.27 % Ce:YAG		19802	_	_
single crystal [27]		19002		
0.5 % Ce:YAG	37	_	_	_
ceramic [28]				

TABLE 2. The scintillation properties of ceramic Ce:YAG samples

\*Parameter is obtained from the evaluation due to the absence of photopeak.

#### 4. Conclusions

Nanopowders of  $Ce_{2x}Y_{2-2x}O_3$  (x = 0.001, 0.01, 0.03, and 0.05) and  $Al_2O_3$  synthesized by laser ablation were used to fabricate transparent Ce:YAG ceramics via a solid-state reaction method with an additional round of pre-calcining. The microstructural, optical, radioluminescence and scintillation properties of the obtained ceramics were investigated. The content of the secondary phases and pore concentration in most transparent (81 % in the range of 500–900 nm) Ce:YAG ceramic sample with 0.1 % of Ce<sup>3+</sup> was 34 ppm. The average grain size did not depend on the Ce<sup>3+</sup> dopant concentration and was 17  $\mu$ m. The Ce:YAG ceramic sample with 1 % of Ce<sup>3+</sup> gave the most intense luminescence and highest absolute and relative light yields under  $\alpha$  and  $\gamma$  ionizing radiation. However, the Ce:YAG ceramic sample doped with 5 % of Ce<sup>3+</sup> gave the best kinetic characteristics. The 5 % Ce:YAG has the main fast component with a 26 ns decay time and a negligible weak slow component with a decay time of 338 ns. Herewith, the ALY was slightly less than that of 1 % Ce:YAG.

A ceramic Ce:YAG scintillator can be attractive for positron emission tomography (PET) and similar devices owing to the applicability for any system with photodiode registration and short decay times.

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# Distribution of supercritical nucleation centers during the crystallization process in the presence of a flow as illustrated by the example of boron carbide-reinforced aluminum

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The distribution of heavily post-critical nucleation centers in the nucleation kinetics subject to the macroscopic flow effect has been successfully obtained. Examples of rotary and convective motions during the centrifugal casting are considered. The obtained distribution has been confirmed by an experimental investigation of the composite material AK12 (boron carbide  $(B_4C)$ ) crystallization.

Keywords: First-order phase transition, Distribution of supercritical nucleation centers, Crystallization in the presence of flow effect.

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#### 1. Introduction

In the first-order phase transition, e.g., crystallization, two steps are identified. The first one [1] is the formation of critically sized nucleation centers in the metastable system, i.e. the size of nucleation centers is such that the system does not return to the initial one-phase state. The second step [2] is the evolution of post-critical big nucleation centers of a new phase. It is such quickly growing nucleation centers that accumulate, integrate, and absorb the metastable phase with small-sized nucleation centers.

This paper focuses on the second step, using the example of crystallization. The theory of this step of the nucleation process without the macroscopic flow effect in the metastable material is well known, but this theory is constructed using the example of vapor condensation (see, for example, review [3]). In recent years, the size distribution of supercritical nucleation centers and its time evolution were obtained within the framework of this theory [4,5].

In connection with the use of centrifugal casting technologies with a high rotary speed of lingots, a problem arose when predicting the influence of the flow, first of all, rotation, will have on crystallization and, in a broader sense, on first order phase transitions. Certainly, flow effects of different kinds occur during the material treatment. For example, during extra-high-power energy flux application, different mechanisms of convection excitation are revealed [6]. However, it is the influence of rotation that seems to be of special interest.

The investigation of rotations influence is important for developing technologies for gradient spatiallyinhomogeneous composite material production. Due to spatial inhomogeneity, for example, surface hardening, such materials could potentially be used for manufacturing structures operating under extremely difficult conditions.

Centrifugal casting is a well-known practice of producing composite materials, in particular, aluminum-based ones [7]. Alternatively, additional reinforcing materials allow one to perform microscopic investigation of sections of solid castings, which indicate the state of melt precisely on the second step of nucleation.

In this work, the distribution of supercritical nucleation centers in the presence of flow effect, which was obtained theoretically, will be confirmed experimentally using the example of a composite produced by centrifugal casting from the aluminum alloy AK12 and boron carbide particles.

#### 2. Distribution of supercritical nucleation centers in the presence of flow effect

Let us consider the mixture of the main material (in this experiment, it will be aluminum alloy AK12) and additional material (in this experiment, it will consist of boron carbide particles). Nucleation [4] occurs mainly at

#### Distribution of supercritical nucleation centers

condensation centers around the particles of the additional material. At the post-critical step, when no macroscopic flow effects exist, the function of nucleation centers distribution [5] may be written as a Gaussian distribution:

$$G = \Theta(t) \frac{1}{\sqrt{Dt}} \exp\left(-\frac{(d-d_0)^2}{4Dt}\right). \tag{1}$$

Here, D is the coefficient of small nucleation centers diffusion, actually, the coefficient of molecular diffusion in liquid melt; t is the time from the beginning of the process;  $d - d_0$  is the degree of post criticality, which determines the deviation of the large nucleation center size d from the critical nucleation center size  $d_0$  under conditions displaying a high degree of post criticality,  $d \gg d_0$ . The value  $\Theta$  – is the amplitude, which does not depend on the nucleation center size.

From the nucleation pattern, it is obvious that the probability of a small nucleation centers being absorbed by a big one is proportional to the coefficient D. On the other hand, from the dimension considerations, it follows that  $D \sim vS/R \approx C_1 vR$ , where S is the surface area and R is the size of the big nucleation center. The order of magnitude of the constant  $C_1$  is one. Most importantly,  $D \sim v$  rms velocity of small nucleation centers.

In the presence of a flow effect in the liquid melt, it is the flow velocity that becomes the main part of relative motion velocity of nucleation centers.

In the case of convective motion excitation, the flow velocity is proportional to the square root of overcriticality, the amount by which the number determining convection exceeds the critical value at which convection is excited [6].

During rotation, a large nucleation center tends to proceed in straight-line motion, but the viscous friction force prevents it. It is easy to find out that in this case the velocity caused by rotation with the angular speed  $\omega$  of small nucleation centers located at the distance r from the rotation axis will be:

$$v = \omega r \exp\left(-\frac{9\eta t}{2\rho R^2}\right),\tag{2}$$

where  $\eta$  and  $\rho$  are viscosity and liquid density correspondingly. This directly follows from the law of motion of a particle in a rotating melt by the action of Stokes force  $6\pi\eta vR$ . Certainly, it is proposed here that a small nucleation center is originally a sphere. Another form of nucleation center may correspond to a somewhat different numerical coefficient in exponent, but qualitatively, the result will not change.

Thus, in the function of large nucleation centers size distribution (spectrum) in the presence of rotation the diffusion coefficient should be replaced with the following value:

$$D = C_2 \omega r \exp\left(-\frac{9\eta t}{2\rho R^2}\right),\tag{3}$$

Here,  $C_2$  is another constant, but it is as well as  $C_1$ , has the same order of magnitude.

These results will be experimentally confirmed in the next section.

It may be considered that it is the boron carbide particles that are the nucleation centers and their distribution on the material sample after crystallization (Fig. 1) reflects the distribution of supercritical nucleation centers before the phase transition. During the phase transition, the nucleation centers accrete and their growth is limited only by the size of melt. During rapid rotation, centrifugal forces support the growth mainly from the axis of rotation to the lingot. Hence, it follows that the size of the nucleation center d turns into the distance between the nucleation center position and the external boundary of the melt.

The distribution (1) is Green's function of the kinetic equation determining the growth of supercritical nucleation centers [4, 5]. To obtain the distribution D of boron carbide in the sample, it is necessary to put in it the time of phase transition  $t_f$ , which is much less than the typical fall time  $2\rho R^2/9\eta$ , and put in (1) the value of D, which is determined by the flow in accordance with formula (3) for supercritical nucleation centers before the phase transition.

Let us note the supercritical nucleation centers distribution before the phase transition as a function of distance x measured from the external wall of the sample or, which is the same, from the lingot. We have:

$$P(x) = A \exp\left(-\frac{x^2}{4\sigma^2}\right).$$
(4)

Here, A is the amplitude, which has the form:

$$A = \frac{B}{\sqrt{\omega r R t_f}} \exp\left(-\frac{9\eta t_f}{8\rho R^2}\right).$$
(5)

This value contains the parameter B which depends upon the buoyancy forces.



FIG. 1. Typical microstructure of a sample of composite of alloy AK12 with addition of 10 %  $B_4C$ . Regions encircled with dark ovals are the reinforcing additional material. The distance from the external wall is indicated (in mm) from right to left

The standard deviation in distribution

$$\sigma = \sqrt{\omega r R t_f} \exp\left(-\frac{9\eta t_f}{8\rho R^2}\right),\tag{6}$$

may be considered to be independent of the buoyancy force. The value  $C_2$  from (3) is included in value  $t_f$ , defined the most roughly. The derived above relation  $D \sim vR$  was used for obtaining of expressions (4) – (6).

#### 3. Design of the material produced by centrifugal casting method from AK12 and boron carbide particles

As previously mentioned, aluminum alloy AK12 with density in the liquid state  $\rho_a \approx 2.67$  g/cm<sup>3</sup> was used as the primary material. Particles of boron carbide with the density of powder  $\rho_b \approx 2.5$  g/cm<sup>3</sup> were used as the additional material. These particles had the shape of a sphere with the diameter  $\leq 60 \ \mu$ m and accounted for 10% of the mixture weight.

Samples shaped as bushings with  $r_{\min} \le r \le 93 \text{ mm} = r_{\max}$  were produced using the centrifugal casting method with the angular speed  $\omega = 40\pi$  rad/s. The bushings were slit by element and were investigated by the Leica microscope. The results are presented in Fig. 1.

Recalculation in the distribution of boron carbide particles in layers on three levels of casting height (60– 90 mm) is presented in Figs. 2–4.

The casting conditions were the same for all samples: the heating temperature was  $210 \pm 10$  °C for the lingot and 750  $\pm$  10 °C for the melt.

#### 4. Discussion

Experimental data were processed according to the ideas developed in Sect. 2. Continuous lines are drawn in Figs. 2–4 using formulae (4) in the least-squares technique. The curves have the following parameters: line in Fig. 2, corresponding to the top of the sample, has the amplitude  $A = A_1 = 30$  % and the standard deviation  $\sigma = \sigma_1 = 0.88$  mm; line in Fig. 3, corresponding to the centre (middle) of the sample, has the amplitude A = 19.6 % and  $4\sigma^2 = 9.6$  mm<sup>2</sup>; line in Fig. 4, corresponding to the bottom of the sample, has the amplitude A = 20.6 % and  $4\sigma^2 = 7.4$  mm<sup>2</sup>. As can be seen from Fig. 1, the reinforcing particles are concentrated in the middle and bottom of the sample, therefore lines on Figs. 3, 4, corresponding to the middle and the bottom, sharply differ from the line for the top part (Fig. 2) and slightly differ from each other. For simplicity, these two lines will be considered as one with the parameters  $A = A_2 = 20$  % and  $\sigma = \sigma_2 = 1.46$  mm.

It is important that the phase transition time for supercritical nucleation centers calculated by formula (6) is much less than the characteristic fall time at  $\eta \approx 0.0032$  Pa·s and  $R \gg 60 \ \mu m$ ,

$$8\rho_a R^2/9\eta \ge 1$$
 s.



FIG. 2. Typical distribution of boron carbide particles in samples of the same material as in Fig. 1 in the top part of the bushing. The continuous line is the distribution function



The distributions presented in Figs. 2–4 are in good agreement with the experimental results obtained by processing first-hand observation data in Fig. 1, if the nucleation center size achieves the crystallization region size, which is approximately equal to the sample thickness  $R \approx 10$  mm, in a phase transition time, which is approximately several milliseconds. More precisely: in the top of the bushing, where there is less reinforcing material, this time is  $t_f \approx 3$  ms, but in the middle and the bottom parts, where there is more reinforcing material, it is  $t_f \approx 2$  ms.

Now, it is easy to determine from (5) the parameter B depending on buoyancy forces. We find:  $B_1 = 4.2$  mm;  $B_2 = 3.4$  mm. Certainly, all the determined values are no more than qualitative (order-of-magnitude) estimates which may depend on many neglected factors, for example, viscosity increases abruptly at the time of phase transition [8]. Tribological properties also depend upon the contact surface properties of the structures which correspond to different nucleation centers [9]. However, these estimates will certainly help choose the quantity and quality of the reinforcing material necessary for producing the material with tailored properties.

### 5. Conclusion

It was proved that the distribution (spectrum) of large supercritical nucleation centers during nucleation, at least, during crystallization, with the flow effect may be obtained from the distribution determined as a result of solution of the kinetic equation [5] without macroscopic flow effects. For this purpose, the value replacing the diffusion coefficient and determined by the macroscopic flow velocity should be included in the distribution of supercritical nucleation centers. The phase transition time was estimated here at about several milliseconds. As expected, the presence of reinforcing particles, which are the primary critical nucleation centers, accelerates the phase transition.

It has been demonstrated that additional material  $B_4C$  can increase the hardness of near-surface layers using the centrifugal casting method and, consequently, this method can be used for designing materials with tailored structural properties.



FIG. 4. Typical distribution of boron carbide particles in samples of the same material as in Fig. 1 in the bottom part of the bushing. The continuous line is the distribution function

As it was postulated, success was achieved in creating surface layers with a higher concentration of the reinforcing (additional) phase. All this suggests that a gradient composite material can be created (designed) using centrifugal casting methods with a high rotation velocity.

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# Multidimensional light bullets in Fermi liquid in the presence of magnetic field and AdS/CFT correspondence

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We consider the evolution of a light bullet in a fermi-liquid while considering the presence of a magnetic field. The energy spectrum for the Fermi liquid was calculated in the framework of AdS/CFT correspondence. The influence of a magnetic field's amplitude and its period on light bullet evolution was obtained. The stable character of the light bullet propagation in the Fermi liquid in the presence of a magnetic field was confirmed.

Keywords: light bullets, AdS/CFT correspondence, magnetic field.

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#### 1. Introduction

A theory for normal Fermi liquids was constructed by L.D. Landau in 1956 [1], based on the representation of the perturbation energy as a functional of the distribution function. This theory was further developed for finite Fermi systems by A.B. Migdal [2]. A Fermi liquid is a quantum fluid in which elementary excitations (quasiparticles) have a half-integral spin and obey Fermi–Dirac statistics (for example, conduction electrons in a metal).

The Fermi liquid theory continues to develop rapidly and it is used to solve modern problems in various fields of science. For example, in Ref. [3], based on the relativistic version of the Fermi liquid theory, an equation of state for the dense substance of a neutron star in the presence of a strong quantizing magnetic field was obtained. Another interesting research area is the study of non-Fermi and holographic Fermi liquids [4]. These schemes are based on charged black holes asymptotically inserted in Anti de Sitter (AdS) spaces. According to the AdS/CFT correspondence, quantum gravity on this background is holographically dual to certain field theories in flat space. When we add spinor fields to the gravitational theory, it is possible to realize holographic Fermi surfaces with a variety of Fermi liquid and non-Fermi liquid spectral functions [5].

In this paper, we investigate the influence of a Fermi liquid on light bullet propagation in the presence of a magnetic field. The dispersion law for the Fermi liquid is calculated based on the idea of AdS/CFT correspondence [6], which has recently found wide applications in solid state physics. This approach allowed us to obtain the Green's function [7,8], and to calculate the energy spectrum for the Fermi liquid.

Note, this approach has been well-proved and has already been used by researchers to study the evolution of extremely short optical pulses in a marginal Fermi liquid [9], which demonstrated the stable nature for the propagation of the one- and two-dimensional pulses due to the balance of the dispersion and the nonlinearity of the medium [9].

At the same time, the problem associated with the external magnetic field, remains unsolved.

#### 2. Basic equations

We begin our investigation of the light bullet (LB) dynamics with well-known dispersion relation E(p) for quasiparticles. At the construction of the LB propagation model, we describe the electromagnetic field of the pulse based on the Maxwell equations, in the Coulomb gauge [10]  $\mathbf{E} = -\partial \mathbf{A}/c\partial t$ . A vector-potential has a form:  $\mathbf{A} = (0, 0, A_z)$ . In the two-dimensional (a) and three-dimensional case (b) we have (here the light velocity c = 1):

$$\frac{\partial^2 \mathbf{A}}{\partial x^2} + \frac{\partial^2 \mathbf{A}}{\partial y^2} - \frac{\partial^2 \mathbf{A}}{\partial t^2} + 4\pi j = 0, \tag{1}$$

$$\frac{\partial^2 \mathbf{A}}{\partial t^2} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial A}{\partial r} \right) + \frac{\partial^2 \mathbf{A}}{\partial x^2} + \frac{1}{r^2} \frac{\partial^2 \mathbf{A}}{\partial \varphi^2} + 4\pi j = 0, \tag{2}$$

where *j* is the electric current that appears due to the action of the electric field of the pulse on quasiparticles. Here, in the two-dimensional case, we neglect with the light bullet diffraction scattering in the direction perpendicular to the propagation axis. Since for the non-Fermi liquids, there is a region with a large lifetime of quasiparticles, the quasiparticles ensemble at typical time for the dynamics problems of the light bullets (order  $10^{-14}$  s) can be described in the framework of the collisionless kinetic Boltzmann equation [11]:

$$\frac{\partial f}{\partial t} - \frac{q}{c} \sum_{\alpha} \frac{\partial A_{\alpha}}{\partial t} \frac{\partial f}{\partial p_{\alpha}} = 0, \tag{3}$$

where  $f = f(p_{\alpha}, s, t)$  is the distribution function, which implicitly depends on the coordinate. The distribution function f at the initial time coincides with the equilibrium function of the Fermi distribution  $F_0$ :

$$F_0 = \frac{1}{1 + \exp\{E(\mathbf{p})/k_b T\}}$$

where T is the temperature,  $k_b$  is the Boltzmann constant. For the current density  $\mathbf{j} = (0, 0, j_z)$  we can write:

$$j_z = q \int d^3 p v_z f,\tag{4}$$

here, we introduce the group velocity  $v_z = \partial E(\mathbf{p})/\partial p_z$ . Solving the equation (3) by the method of characteristics, one can obtain:

$$j_{z} = q \int_{-q_{0}}^{q_{0}} \int_{-q_{0}}^{q_{0}} \int_{-q_{0}}^{q_{0}} d^{3} p v_{z} \left[ p - \frac{q}{c} A_{z} \left( t \right) \right] F_{0} \left( \mathbf{p} \right).$$
(5)

The integration in Eq. (5) is carried out over the first Brillouin zone,  $q_0$  corresponds to the layer near the Fermi surface. The dependence of the basic quantities on  $q_0$  has a logarithmic nature, which allows us to arbitrarily choose it.

#### 3. The excitation dispersion law and AdS/CFT correspondence

We begin with the dispersion law (here k is measured from the Fermi level):

$$\varepsilon = \varepsilon \left( |k| \right), \ |k| = \left( k_z^2 + k_\perp^2 \right)^{0.5}.$$
(6)

It is more convenient to present in the following form:

$$\varepsilon = \varepsilon \left( k_z, k_\perp^2 \right). \tag{7}$$

Let us write the expression for the current density. It can be found, for example, in the Ref. [12]:

$$j = n_0 \int dk \, v_x \left( k_z - A, k_\perp^2 \right) f\left( k_z, k_\perp^2 \right),\tag{8}$$

Here, f is the distribution Fermi function,  $v_x = \frac{\partial \varepsilon \left(k_z, k_{\perp}^2\right)}{\partial k_x}$ .

For the low-temperature case, we can change f on 1 in the layer near the Fermi surface. The layer thickness is defined with the conservation of the number of particles:

$$\int_{-\Delta}^{\Delta} dk = \int_{ZB} dk f$$

Then:

$$j = n_0 \int_{-\Delta}^{\Delta} dk_z \int_{0}^{\sqrt{2\Delta}} k_{\perp} dk_{\perp} \int_{0}^{2\pi} dk_{\phi} \frac{\partial \varepsilon \left(k_z - A, k_{\perp}^2\right)}{\partial k_x} = \pi n_0 \int_{0}^{2\Delta^2} dx \left(\varepsilon \left(\Delta - A, x\right) - \varepsilon \left(-\Delta - A, x\right)\right).$$
(9)

Let us specify the dispersion law  $\varepsilon = \varepsilon(k_z, k_\perp^2)$  using AdS/CFT correspondence ideas and following the work [13].

Let us consider two- and one-dimensional boundary theories, corresponding to a gravity theory in asymptotically  $AdS_4$ . The Lagrangian can be chosen in standard type for both gravitational field and gauge field with U(1) symmetry [13]:

$$L = \frac{1}{2g^2} \left( R + \frac{6}{\Lambda^2} \right) - \frac{1}{4e^2} F_{\mu\nu} F^{\mu\nu},$$
(10)

where g is gravitational interaction constant, e is a charge,  $F_{\mu\nu}$  is stress tensor for the gauge field. The given choice of the Lagrangian is in accordance with the solution as the Reissner-Nordstrom-AdS black hole:

$$ds^{2} = \frac{\Lambda^{2}}{r^{2}} \left( -f(r)dt^{2} + \frac{dr^{2}}{f(r)} + dx^{2} + dy^{2} \right),$$

$$A_{0} = \mu \left( 1 - \frac{r}{r_{+}} \right)$$
(11)

here  $\mu$  corresponds to chemical potential as usual,  $r_+$  is according to event horizon.

There are the following expressions:

$$f(r) = 1 - \left(1 + \frac{r_{+}^{2}\mu^{2}}{2\gamma^{2}}\right) \left(\frac{r}{r_{+}}\right)^{3} + \frac{r_{+}^{2}\mu^{2}}{2\gamma^{2}} \left(\frac{r}{r_{+}}\right)^{4},$$
  

$$T = \frac{1}{4\pi r_{+}} \left(3 - \frac{r_{+}^{2}\mu^{2}}{2\gamma^{2}}\right),$$
  

$$\gamma = e\Lambda/g,$$
(12)

here T is temperature. Selecting the Lagrangian for sample fermions in the following form:

$$L = \bar{\psi}\Gamma^{\mu} \left(\partial_{\mu} + \frac{1}{4}\omega^{ab}_{\mu}\Gamma_{ab} + iA_{\mu}\right)\psi - m\bar{\psi}\psi, \qquad (13)$$

where m is mass,  $\frac{1}{4}\omega_{\mu}^{ab}\Gamma_{ab}$  corresponds to spin interaction. Then, we define the Green's function for fermionic operator  $O_{\psi}$  as follows:

$$G_R(t,\bar{x}) = i\theta(t) \left\langle \left\{ O_{\psi}(t,\bar{x}), O_{\psi}^+(0) \right\} \right\rangle$$

where  $\theta(t)$  is the Heaviside step function, angle brackets signify averaging, curved brackets signify anticommutator. As it is shown in [13] the Green's function has the form:

$$G_R(w, \bar{k}) = \frac{h}{k - k_F - w/v_F - \Sigma(w, k_F)}$$
(14)

where  $k = |\bar{k}|$ ,  $k_F$  is Fermi momentum,  $v_F$  is Fermi velocity. The main difference of the given Green's function, whose poles determine the dispersion law of quasiparticles lies in the fact that the quasiparticles' dissipation highly depends on parameter:  $\nu_k = \frac{1}{\sqrt{6}} \sqrt{m^2 L^2 + \frac{3k^2}{\mu^2} - \gamma^2}$ . Note,  $\nu$  is closely related to the critical exponent.

At low temperatures, the dispersion law can be written using AdS/CFT corrspondence:

$$\varepsilon(k) = c \left(k_z^2 + k_\perp^2\right)^{\nu/2}.$$
(15)

Taking into account the magnetic field, which we assume is spatially modulated for the problem generality:  $H = Q \cdot \sin(\alpha \cdot y)$ , we can write the current density in its explicit form:

$$j(A) = \frac{\pi n_0 c}{0.5\nu + 1} \left( (\Delta + A)^{\delta_1} - (\Delta - A)^{\delta_1} + \left( (\Delta - A)^2 + 2\Delta^2 \right)^{\delta_2} - \left( (\Delta + A)^2 + 2\Delta^2 \right)^{\delta_2} \right), \quad (16)$$
$$\delta_1 = \nu + 2 + H, \quad \delta_2 = 0.5\nu + 1 + H.$$

The relation between the parameter  $\nu$  and the magnetic field is given by formula [14]:

$$v_k = \sqrt{\frac{k^2 + m^2}{6} - \frac{q_{eff}^2}{12}}, \quad q_{eff} = q\sqrt{1 - \frac{h^2}{3}}, \tag{17}$$

where q is the fermion charge,  $q_{eff}$  is the effective charge, h is the magnetic field, m is the fermion mass.

#### 4. Dynamics of light bullets with a plane wave front

Further, we consider two-dimensional light bullets with the initial conditions:

$$A(x, y, 0) = B \cdot \exp\left(-x^2/\gamma_x^2\right) \cdot \exp\left(-y^2/\gamma_y^2\right),$$
  
$$\frac{dA(x, y, 0)}{dt} = B \cdot \frac{2u}{\gamma_x^2} \cdot \exp\left(-x^2/\gamma_x^2\right) \cdot \exp\left(-y^2/\gamma_y^2\right),$$
(18)

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where is the pulse amplitude, u is the initial velocity of the pulse along the x axis,  $\gamma_x$ ,  $\gamma_y$  define the pulse width. Equations (1, 14) were solved numerically with a direct difference scheme of the cross type [15]. The time and coordinate steps were determined from the standard stability conditions.

The influence of the magnetic field amplitude on two-dimensional light bullets is presented in Fig. 1.



FIG. 1. The intensity of 2D electromagnetic pulse  $I(x, y, t) = E^2(x, y, t)$  for the Fermi liquid  $(t = 1 \cdot 10^{-13} \text{ s}, \alpha = 0.01)$ : a) Q = 0.1; b) Q = 0.2; c) Q = 0.4. Units along the x and y axis correspond to 20 nm

It should be noted that the magnetic field amplitude practically has little effect on the shape and amplitude of the main pulse. We have only changes in the "tail" after the main pulse. Moreover, the larger Q value, the greater part of the energy is pumped to the "tail".

The influence of the period of modulation of the magnetic field on a two-dimensional ultimately short pulse is demonstrated in Fig. 2.



FIG. 2. The intensity of 2D electromagnetic pulse  $I(x, y, t) = E^2(x, y, t)$  for the Fermi liquid  $(t = 1 \cdot 10^{-13} \text{ s}, Q = 0.2)$ : a)  $\alpha = 0.01$ ; b)  $\alpha = 0.05$ ; c)  $\alpha = 0.1$ . Units along the x and y axis correspond to 20 nm

As in the case of different amplitude values for the magnetic field, we observe a change in the shape of the "tail" following the main pulse, which is not affected by the period of the magnetic field.

A picture of the light bullet propagation in the Fermi liquid in the three-dimensional case can be seen in Fig. 3 and Fig. 4. The initial condition in the three-dimensional case was chosen in the form:

$$A(x,r,0) = R \cdot \exp\left(-\frac{(x-x_0)^2}{\gamma_x^2}\right) \exp\left(-\frac{r^2}{\gamma_r^2}\right),$$

$$\frac{dA(x,r,0)}{dt} = 2R\nu_x \frac{(x-x_0)}{\gamma_x^2} \exp\left(-\frac{(x-x_0)^2}{\gamma_x^2}\right) \exp\left(-\frac{r^2}{\gamma_r^2}\right),$$
(19)

where r is the radius, R is the amplitude,  $\gamma_x$ ,  $\gamma_r$  define the pulse width,  $x_0$  is the initial displacement of the pulse center,  $\nu_z$  is the initial velocity of the pulse along the x axis. Note that as in the 2D case, time is the evolution variable.



FIG. 3. The intensity of 3D electromagnetic pulse  $I(x, r, t) = E^2(x, r, t)$  for the Fermi liquid  $(t = 1 \cdot 10^{-13} \text{ s}, \alpha = 0.01)$ : a) Q = 0.1; b) Q = 0.2; c) Q = 0.4. Unity along the *r*-axis corresponds to 30 nm, along the x - 20 nm



FIG. 4. The intensity of 3D electromagnetic pulse  $I(x, y, t) = E^2(x, y, t)$  for the Fermi liquid  $(t = 1 \cdot 10^{-13} \text{ s}, Q = 0.2)$ : a)  $\alpha = 0.01$ ; b)  $\alpha = 0.05$ ; c)  $\alpha = 0.1$ . Unity along the *r*-axis corresponds to 30 nm, along the x - 20 nm

Here, we observe an analog of the two-dimensional pulse behavior. And, accordingly, the change in the amplitude and period of the magnetic field causes only a change in the "tail" shape.

Thus, it is shown that the light bullet in the Fermi liquid propagates stably when the main parameters of the modulated magnetic field (amplitude and period) change.

#### 5. Conclusions

Based on the obtained results, we can conclude the following:

- 1. The model, which describes the dynamics of ultra-short 2D and 3D laser pulses in a Fermi liquid in the frameworks of AdS/CFT correspondence while taking into account the magnetic field, is proposed.
- 2. The numerical calculations show that in the 2D and 3D cases, there are stable nonlinear waves, light pulses that are localized in two or three directions.
- **3.** Regarding the light bullet propagation in the Fermi liquid, its dispersion in the transverse direction is rather weak, and the energy is mainly concentrated in the central region of the pulse.

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# Phase composition and magnetic properties of $Ni_{1-x}Co_xFe_2O_4$ nanocrystals with spinel structure, synthesized by Co-precipitation

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Nanopowders of nickel ferrite doped with cobalt were synthesized by co-precipitation using a 3 % KOH solution as a precipitant. The effects of different annealing regimes on the composition and particle size of  $Ni_{1-x}Co_xFe_2O_4$  were studied. It was established that with annealing at t = 1000 °C for 2 h single-phase products were formed with a crystallite size of 30–50 nm. The saturation magnetization and the coercive force increased as the content of the dopant increased from 50.3 emu/g and 51.94 Oe for NiFe<sub>2</sub>O<sub>4</sub> to 80.45 emu/g and 848.32 Oe for CoFe<sub>2</sub>O<sub>4</sub>.

Keywords: ferrites, spinel, nanocrystals, co-precipitation, magnetic properties.

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#### 1. Introduction

Among magnetic materials, nanocrystalline ferrites with a spinel structure of type  $MFe_2O_4$  (M = Co, Ni, Zn, Mn) are distinguished by high permeability, saturation magnetization and are used to produce new multifunctional materials, such as high-frequency devices, due to the decreased Foucault currents and increased duration of their functioning [1–5]. In addition, ferrites with a spinel structure are cheaper and more stable (in terms of time and temperature) compared to metals and alloys.

The magnetic and electrical characteristics of these ferrites depend on their chemical composition, cation location, particle size, dopant content and the synthesis method [1–9].  $CoFe_2O_4$  is hard magnetic ferrite with a high coercive force  $H_c > 1500$  Oe, with an average saturation magnetization of  $M_s \sim 40$  emu/g [10]. NiFe<sub>2</sub>O<sub>4</sub> is a soft magnetic material characterized by small values of coercive force, saturation magnetization and excessive magnetization ( $H_c = 46.46$  Oe,  $M_s = 8.8$  emu/g,  $M_r = 0.2$  emu/g) [1–3]. Different magnetic properties of ferrites are required for different applications and can be achieved in several ways: either by controlling the particle size, or by changing the concentrations of hard and soft magnetic phases in the material by introduction of another element (dopant) or by the formation of coatings on SiO<sub>2</sub> [11–14].

Sol-gel processes, including the formation of complexes with the addition of surfactants are promising for the synthesis of ferromagnetic oxide nanomaterials  $MFe_2O_4$  (M = Co, Ni). An important advantage of such complexes is the lower annealing temperature in comparison to solid-phase synthesis, leading to decreased size of the obtained particles [2–5, 10, 11]. However, the formation of a single-phase product synthesized by the sol-gel method is affected by many factors, such as the annealing temperature and time, the gel formation temperature, the stoichiometry of the surfactant/metal ions, pH value, and others.

In previous studies [1,12], MFe<sub>2</sub>O<sub>4</sub> nanocrystals (M = Co, Ni) were obtained by co-precipitation of  $M^{2+}$  and Fe<sup>3+</sup> cations at room temperature with the addition of an aqueous ammonia at pH = 11. However, at pH = 11, Co(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> are dissolved with the formation of complexes with ammonia in accordance with the following equation:

$$M(OH)_2 \downarrow +6NH_3 \rightarrow [M(NH_3)_6](OH)_2,$$

therefore, it is impossible to completely precipitate cobalt and nickel hydroxides with an aqueous solution of ammonia, which makes the achievement of the molar ratio  $M^{2+}$ :  $Fe^{3+} = 1 : 2$  in the composition of precipitation complicated.

In this study, we investigated conditions for the formation of nanocrystals with the spinel structure  $Ni_{1-x}Co_xFe_2O_4$  (x = 0; 0.2; 0.4; 0.6; 0.8; 1) by co-precipitation during the hydrolysis of M(II) and Fe(III) cations in boiling water, followed by cooling and addition of 3% aqueous KOH as a precipitant, as well as the phase composition and magnetic properties of the formed compounds. Hydrolysis of M(II) and Fe(III) cations in

boiling water leads to the formation of a stable precipitate and decreased particle size compared to co-precipitation of the hydroxide ions at room temperature. Some nanosystems of  $LnFeO_3$  (Ln = La, Y) type were obtained by this co-precipitation method [15, 16].

#### 2. Materials and methods

#### 2.1. Initial substances

The precursors for these syntheses were aqueous solutions of nickel (II), cobalt (II) and iron (III) nitrates (all – chemically pure) with a molar ratio of Ni<sup>2+</sup> : Co<sup>2+</sup> : Fe<sup>3+</sup> = (1 - x) : x : 2. The precipitant was an aqueous solution of potassium hydroxide (3 %).

#### **2.2.** The synthesis of $Ni_{1-x}Co_xFe_2O_4$ nanoparticles

 $Ni_{1-x}Co_xFe_2O_4$  nanoparticles were synthesized by adding 50 mL of a mixture containing Ni(NO<sub>3</sub>)<sub>2</sub> 0.1 M,  $Co(NO_3)_2$  0.1 M and  $Fe(NO_3)_3$  0.2 M into 500 mL of boiling water with magnetic stirring. The obtained colloidal system was cooled to room temperature. The system acquired a reddish-brown color which it retained upon cooling. Then, 3 % aqueous solution of potassium hydroxide in the amount required for complete precipitation of the cations (until the disappearance of the phenolphthalein color) was added with magnetic stirring.

The precipitated hydroxides were stirred for 30–40 min with magnetic stirring. The obtained precipitate was separated using a vacuum filter, washed several times with distilled water and dried at room temperature to a constant weight.

#### 2.3. Methods of investigation

The obtained samples were finely ground into a powder and subjected to complex thermal analysis using thermal analyzer Labsys Evo (TG-DSC 1600 °C, France), including thermogravimetric analysis (TGA) and differential-scanning calorimetry (DSC). The thermal analysis was carried out in the dry air. The heating rate was 10 °/min; the maximum heating temperature was 1100 °C.

The phase compositions of the samples were determined by X-ray phase analysis (XPA, diffractometer SIEMEN D – 5000 Brucker, Germany), CuK<sub> $\alpha$ </sub>-radiation,  $\lambda = 0.15406$  nm,  $2\theta = 10-80$ °, measurement interval 0.02°/sec. The obtained diffractograms were analyzed using the JCPDS database.

The average crystal size according to XPA data and the constant parameter of the spinel cubic lattice  $Ni_{1-x}Co_xFe_2O_4$  were calculated by following equations:

$$d = \frac{0.89 \cdot \lambda}{\beta \cos \theta},\tag{1}$$

$$a = \frac{\lambda}{2\sin\theta}\sqrt{h^2 + k^2 + l^2},\tag{2}$$

where d – average crystal size, Å;  $\lambda$  – X-ray tube wavelength (for the copper tube used in this recording,  $\lambda = 0.15406$  nm);  $2\theta$  – is the position of the maximum of the peak, deg;  $\beta$  – is the true physical broadening of the diffraction maximum, rad.; h, k, l – Miller indices, correspond to the peaks with the highest intensity.

The sizes and morphologies of the nanoparticles were determined by transmission electron microscopy (TEM– JEOL 1400, Japan).

Magnetic characteristics of  $Ni_{1-x}Co_xFe_2O_4$  nanopowders were studied using a Microsene EV11 (Japan) vibration magnetometer at room temperature.

#### 2.4. Results and discussion

The results of complex thermal analysis of the obtained precipitate for  $Ni_{0.6}Co_{0.4}Fe_2O_4$  nanopowder before annealing, shown in Fig. 1, demonstrated that mass loss of the sample during all heat treatment processes from room temperature to 1100 °C was 16.61 % (TGA curve). The mass loss of the sample heated from 65 °C to 320 °C occurs rapidly, as indicated by the slope of TGA curve. Two peaks of endothelial effects at 200 °C and 27 °C, characteristic for desorption, evaporation and decomposition of nickel (II), cobalt (II) and iron (III) hydroxides were detected on DSC curve.

After that, the mass loss of the sample is slower, terminating at  $\sim 650$  °C due to the continuation of decomposition of hydroxides with formation of NiO, CoO and Fe<sub>2</sub>O<sub>3</sub>. At this point, a large peak corresponding to heat release at 500–650 °C appeared.

Subsequently, in accordance with the thermal analysis data of  $Ni_{0.6}Co_{0.4}Fe_2O_4$ , thermal treatment was carried out at 700, 800 and 1000°C for 2 h in order to establish the conditions for the formation of single-phase  $Ni_{1-x}Co_xFe_2O_4$  products.
Phase composition and magnetic properties of  $Ni_{1-x}Co_xFe_2O_4$  nanocrystals...



FIG. 1. DSC and TGA curves of precipitate sample for production of  $Ni_{0.6}Co_{0.4}Fe_2O_4$  before annealing

The diffractograms of undoped NiFe<sub>2</sub>O<sub>4</sub> (Fig. 2) after annealing at 700, 800 and 1000 °C showed that the background of lines of diffractograms are stable, the intensities of the peaks increase and their widths decrease at higher temperatures. Consequently, when the annealing temperature increased from 700 °C to 1000 °C, the degree of crystallization of the samples increased with decreasing average crystal size. The presence of only one phase of NiFe<sub>2</sub>O<sub>4</sub> spinel with a cubic structure belonging to Fd3m spatial group (JCPDS 00-010-0325) was detected in the diffractograms of all samples.



FIG. 2. Diffractograms of NiFe $_2O_4$  samples, obtained by the co-precipitation method after annealing at 700, 800 and 1000 °C for 2 h

In diffractograms of  $CoFe_2O_4$  samples after annealing at 700, 800 and 1000 °C (Fig. 3), peaks corresponding to only one phase –  $CoFe_2O_4$  with a cubic structure belonging to the spatial Fd3m group (JCPDS 00-022-1086) were also present.

Later, in accordance with the XPA data of MFe<sub>2</sub>O<sub>4</sub> samples (M = Ni, Co), the following annealing modes were selected for the formation of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.2, 0.4, 0.6 and 0.8): temperature 800 and 1000 °C, time - 2 h.

X-ray phase analysis (Figs. 4, 5) of the synthesized nanopowders demonstrated the formation of solid solutions between NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> [12,13], peaks with different x values coincided with each other and with standard



FIG. 3. Diffractograms of  $CoFe_2O_4$  samples, obtained by the co-precipitation method after annealing at 700, 800 and 1000 °C for 2 h

diffractograms of JCPDS base. However, the slow scanning of the peak angles with the highest intensity (2 $\theta$  was from 34.5 to 35.5 deg., Miller's indices (311)) (Fig. 4) showed the shift of X-ray diffraction lines to the left (decrease of 2 $\theta$ ) as x values increased (Fig. 5). This fact proves the substitution of nickel by cobalt in Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> spinel [14]. The average size of crystals of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> spinel after annealing at 800 and 1000 °C for 2 h, calculated by formula (1), was from 19 to 50 nm and it gradually increased with an increase in the degree of doping from x = 0 to x = 0.6, and then decreased. The parameter of the crystalline cubic lattice (a) of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> nanocrystals, calculated from formula (2), increased with increased annealing temperatures and cobalt content in the samples (Tables 1 and 2). The last trend can be explained by the fact that the ionic radius of Ni<sup>2+</sup> (0.72 Å) is lower than that of Co<sup>2+</sup> (0.74 Å) [11]. Similar results were obtained in studies [11, 12, 14].



FIG. 4. Diffractograms of  $Ni_{1-x}Co_xFe_2O_4$  samples obtained by the co-precipitation method after annealing at 1000 °C for 2 h



FIG. 5. Displacement of X-ray diffraction lines of  $Ni_{1-x}Co_xFe_2O_4$  samples after annealing at 1000 °C for 2 h

TABLE 1. Parameters of crystalline structure of  $Ni_{1-x}Co_xFe_2O_4$  samples, synthesized by the co-precipitation method after annealing at 800 °C for 2 h

x	0	0.2	0.4	0.6	0.8	1
$2\theta_{\max}$ , deg	35.6714	35.6293	35.5707	35.5636	35.5244	35.4663
FWHM, rad.	0.311	0.276	0.223	0.192	0.378	0.432
D, nm	26.540	33.202	38.195	42.969	22.187	19.092
<i>a</i> , Å	8.311	8.351	8.364	8.366	8.375	8.387

TABLE 2. Parameters of crystalline structure of  $Ni_{1-x}Co_xFe_2O_4$  samples synthesized by the co-precipitation method after annealing at 1000 °C for 2 h

x	0	0.2	0.4	0.6	0.8	1
$2\theta_{\max}$ , deg	35.6756	35.6058	35.5881	35.5292	35.4835	35.4499
FWHM, rad.	0.251	0.221	0.195	0.168	0.314	0.382
D, nm	32.880	39.139	42.311	49.113	26.204	21.590
<i>a</i> , Å	8.340	8.356	8.366	8.373	8.384	8.392

TEM images of NiFe<sub>2</sub>O<sub>4</sub>, Ni<sub>0.6</sub>Co<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> samples after annealing at 800  $^{\circ}$ C for 2 h (Fig. 6) showed that the size of the synthesized particles was 30–50 nm.

The magnetization curves of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> samples, measured at room temperature are shown in Fig. 7, while their magnetic characteristics are shown in Table 3. Analysis of the obtained results shows that saturation magnetization  $(M_s)$ , excess magnetization  $(M_r)$ , and coercive force  $(H_c)$  of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> samples increase with increased cobalt content in NiFe<sub>2</sub>O<sub>4</sub> lattice. The increase in  $M_r$  and  $H_c$  values was due to an increase in the size of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> crystals as the cobalt content increased (see Table 2). The increase in saturation magnetization  $(M_s)$  is explained by the fact that the magnetic moment of Co<sup>2+</sup> cation  $(\mu = 3\mu_B)$  is higher than the magnetic moment of Ni<sup>2+</sup>ion  $(\mu = 2\mu_B)$  [17].

Excess magnetization values of the samples ( $M_r = 7.58-38.45 \text{ emu/g}$ ) obtained in this study were not different from data published earlier [10–12], but coercive force value ( $H_c = 51.94-838.42$  Oe) decreased 2–3-fold depending on the value of x. The saturation magnetization ( $M_s = 50.3-80.45 \text{ emu/g}$ ) was not only higher than the saturation magnetization of CoFe<sub>2</sub>O<sub>4</sub> spinel, but also much higher than the saturation magnetization of NiFe<sub>2</sub>O<sub>4</sub> spinel [3, 4, 10, 17]. In addition, the saturation magnetization value of CoFe<sub>2</sub>O<sub>4</sub> nanocrystals synthesized in this study, after annealing at 1000 °C for 2 h ( $M_s = 80.45 \text{ emu/g}$ ) was higher than the standard saturation magnetization value of CoFe<sub>2</sub>O<sub>4</sub> multidimensional materials ( $M_s = 80 \text{ emu/g}$ ) [18].

Thus,  $Ni_{1-x}Co_xFe_2O_4$  nanocrystals, synthesized by simple co-precipitation method, take precedence over  $CoFe_2O_4$  nanocrystals by  $H_c$  value and over  $NiFe_2O_4$  – by the value of  $M_s$ .



FIG. 6. TEM-images of Ni<sub>1-x</sub>Co<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> powders after annealing at 800 °C during 2 h



FIG. 7. Field dependence of magnetization of  $Ni_{1-x}Co_xFe_2O_4$ , nanocrystals synthesized by the co-precipitation method after annealing at 1000 °C for 2 h

TABLE 3. Magnetic characteristics of  $Ni_{1-x}Co_xFe_2O_4$  nanocrystals synthesized by the coprecipitation method after annealing at 1000 °C for 2 h

Ni <sub>1-x</sub> Co <sub>x</sub> Fe <sub>2</sub> O <sub>4</sub>	$M_s$ , emu/g	$M_r$ , emu/g	$H_c$ , Oe
x = 0	50.3	7.58	51.94
<i>x</i> = 0.2	57.57	9.93	70.49
<i>x</i> = 0.4	66.07	10.26	73.41
<i>x</i> = 0.6	71.44	26.41	547.89
x = 0.8	78.16	30.96	706.26
x = 1	80.45	38.45	848.32

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#### 3. Conclusions

 $Ni_{1-x}Co_xFe_2O_4$  nanopowders (x = 0; 0.2; 0.4; 0.6; 0.8; 1) with a spinel structure were synthesized by a simple co-precipitation method using a 3 % aqueous solution of KOH as a precipitant. Single-phase samples were formed by annealing the precipitates at 700, 800 and 1000 °C for 2 h. The obtained  $Ni_{1-x}Co_xFe_2O_4$  nanocrystals had a particle size of about 30–50 nm. The size of their crystals, the cubic lattice, and the magnetic characteristics ( $H_c$ ,  $M_r$  and  $M_s$ ) increased with the increase of cobalt content in NiFe<sub>2</sub>O<sub>4</sub> spinel.

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## The microstructure of the surface of thin PbS films deposited from the coordination compounds diacetatodi(thiourea)lead

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This paper presents the results from a study of the microstructure of the surface of lead sulfide films deposited via the pyrolysis of aqueous  $[Pb(N_2H_4CS)_2(CH_3COO)_2]$  aerosols. The influences of temperature and the concentration of thiourea on the synthesized films' surface topography were investigated. A change in the type of conductivity with increasing temperature was observed.

Keywords: method of aerosol pyrolysis, pyrolytic films, coordination compounds, surface microstructure, type of conductivity.

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#### 1. Introduction

Nanoscale objects and systems have a number of specific properties in comparison to their corresponding bulk materials, primarily, this is due to the manifestation of size effects in physico-chemical, optical and electronic properties, allowing an expansion in the range of applications for semiconductors. Additionally, the requirements for surface properties, e.g. roughness of the surface, its purity, uniformity of impurity distribution, etc. over quite large areas are crucial.

The method of scanning probe microscopy is widely used to study a surface with a spatial resolution up to atomic resolution. One of the important modern methods of probe microscopy is atomic force microscopy for the study of microrelief and local surface properties [1].

Along with oxide systems [2, 3], an important place among semiconductor materials with interesting optical, electrical, photoelectric and luminescent properties belongs to metal sulfides and solid solutions based on them. This provides a wide choice of starting materials for the manufacture of infrared detectors, chemical sensors, light-emitting diodes, phototransistors, photopotentiometers, semiconductor lasers [4–6].

A special place among photosensitive materials is occupied by narrow-gap thin layers of lead sulfide, which are widely used in optoelectronics [7].

Traditionally, high-temperature methods of production and vacuum installations which require complex and expensive equipment have been used for the deposition of PbS layers. Therefore, the actual problem is the development of a simple and inexpensive method for spraying solutions of thiourea complexes onto a heated substrate (pulverization method) based on the thermal destruction (pyrolysis) of complex compounds for the synthesis of metal sulfide thin films, thus also permitting the synthesis of materials with controlled properties [8].

Earlier [9–11], we studied lead sulfide films deposited from solutions of  $[Pb(N_2H_4CS)_2Cl_2]$  coordination compounds at different temperatures and starting material concentrations.

The purpose of this work is to reveal the relationship between the synthesis conditions and surface properties of lead sulfide films, the deposited layers of di(thiourea) lead(II) acetate, to study the change in the type of conductivity with increasing temperature.

#### 2. Materials and methods

Synthesis of PbS films was carried out by pyrolysis of aerosolized aqueous solutions of thiourea coordination compounds (TCC) [Pb(N<sub>2</sub>H<sub>4</sub>CS)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>] formed by the interaction of lead acetate ( $C_{Pb}^{2+} = 0.1 \text{ mol/l}$ ) and thiourea ( $C_{TH} = 0.1-0.5 \text{ mol/l}$ ). To obtain the samples used, "chemically-pure" grades of Pb(CH<sub>3</sub>COO)<sub>2</sub> and N<sub>2</sub>H<sub>4</sub>CS (TH) were used.

The temperature (T) of the sital and quartz substrates was varied from 200 to 450  $^{\circ}$ C. The deposition time of the PbS film was 2 min.

Investigation of the surface morphology for the obtained samples and the construction of histograms of the distribution of surface heights were performed via atomic force microscopy (AFM) SOLVER P47. The thickness of the obtained films was measured by scanning electron microscopy (SEM) using a Jeol JSM-6510LV instrument. Determination of the conductivity of the samples was done using the hot probe method.



FIG. 1. AFM – surface scans in the phase contrast mode (a, c, e) and a histogram of the distribution density for surface heights (b, d, f) of PbS films synthesized at 200 °C (a, b), 350 °C (c, d) and 450 °C (e, f) ( $C_{Pb}^{2+}$ :  $C_{TH}$ = 1:2)

#### 3. Results and discussion

Figure 1 shows the surface scans obtained by the method of displaying the phase and the histogram of the density distribution of the surface heights of PbS films precipitated from di(thiourea) lead(II) acetate synthesized at T = 200 °C, 350 °C and 450 °C in the ratio of the components of the initial solution of lead acetate and thiourea 1:2. The scanning area was 5 × 5  $\mu$ m<sup>2</sup>.

The AFM results showed that the microstructure of the surface of the films is formed from round-shaped grains that uniformly cover the surface of the substrate. The average size of the elements is 30-40 nm at temperatures of 200-350 °C and 15-20 nm at 400-450 °C.

From the analysis of microphotographs and parameters, it follows that at low temperatures, the formed grains do not have time to form smoother layers with close grain packing, an increase in temperature from 200 °C to 450 °C leads to the formation of films characterized by a more developed relief and a nanostructured surface.

In the concentration range of the initial components  $C_{Pb}^{2+}$ : STM from 1:1 to 1:4, the height difference value within the scanning region ( $\Delta$ ) and the roughness value (Ra) increase, followed by a decrease for 1:5 (Fig. 2, 3). All these data indicate that an increase in the concentration of the sulfur source (TH) leads to the appearance in the solution of unbound thiourea, which interferes with the thermal destruction process and does not participate in the formation of PbS, as a result of which, layers with less developed relief are deposited. The ratio of  $C_{Pb}^{2+}$ :  $C_{TH}$  1:2 and 1:3 is the most optimal for obtaining qualitative films according to these parameters.

Analysis of SEM images showed that the surfaces of the synthesized samples are dense and homogeneous, with films synthesized at low temperatures being characterized by a more wavy relief, in comparison to those films obtained at higher temperatures. The thickness of the obtained samples varied from 400–500 nm (Fig. 4).



FIG. 2. Dependence of the relief height difference within the scan area at 250 °C (1) and 300 °C (2) on the thiourea concentration in the solution ( $C_{TH}$ )

FIG. 3. Dependence of the roughness value at a temperature of 250  $^{\circ}$ C (1) and 300  $^{\circ}$ C (2) on the concentration of thiourea in solution (C<sub>TH</sub>)



FIG. 4. Electron microscopic images of the surface of PbS films synthesized at a temperature of 250 °C (a = 1:2) and 300 °C (b = 1:1, c = 1:5)

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The results of determining the type of conductivity of the samples showed that films obtained at low temperatures up to 300 °C have hole-type conductivity. This can be explained by the fact that under the given conditions, the decomposition of the  $[Pb(N_2H_4CS)_2(CH_3COO)_2]$  complex does not take place completely and as a result, fragments of -S-Pb-S- are formed, which creates an excess of sulfur atoms relative to the stoichiometry of the lead sulfide, which Is characteristic of a p-type semiconductor.

With an increase in temperature (350-450 °C), a transition to the electronic type of conductivity occurs, which is due to the fact that the decomposition of the coordination compound occurs more fully, resulting in the formation of -Pb-S- fragments, which participate in lead sulfide formation. At high temperatures, the activity of oxygen increases and it enters the PbS lattice, occupying the sulfur vacancies, and thus, a lack of sulfur ions is created against stoichiometry, which is typical for an n-type semiconductor.

#### 4. Conclusion

The microstructure of the surface of lead sulfide films precipitated from diacetatodi(thiourea)lead at temperatures ranging from 200 to 450 °C was investigated. It is established that as the temperature increases, the film formation was characterized by a more developed relief. With an increase in the concentration of thiourea in the sprayed solution, layers with less developed relief are deposited. In the transition from low to high temperatures, the type of conductivity changes from that of the hole to the electron.

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#### Synchronization signal distortion in quantum communication systems

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An important problem in the practical implementation of fiber optical quantum communication systems is to synchronize the sender and receiver modules using a separate optical channel. The signal visibility in the quantum channel, which contributes to quantum bit error rate, is influenced by the synchronization signal delay. In this work, we investigate the dependence of the synchronization signal parameters on the dispersive effects in the fiber for a subcarrier wave quantum communication system (SCWQC), which is promising for quantum networking applications. The ITU-T G.652D standard single mode optical fiber was used for modeling. The maximum calculated phase mismatch of the synchronization signal for the system operating at 100 km fiber length corresponds to 1.7 ps signal time delay. The results show that dispersion causes significant signal distortion, therefore additional phase adjustment at least every 2.3 hours is required for stable system operation.

Keywords: quantum communications, clock synchronization, temperature dependence of the signal, chromatic dispersion.

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#### 1. Introduction

The development of quantum technologies is opening up new potential applications in the use of quantum algorithms, creation and modeling of complex physical, biological systems, new physical methods of sending, receiving and processing information. To continue progress in these areas we need to evaluate the possibility of integrating quantum technologies and especially quantum communication (QC) with existing communication networks [1,2].

A common approach to establishing long-distance links in QC is based on using optical signals transmitted through fibers. In this paper, we consider a subcarrier wave quantum communication system (SCWQC), important for practical applications [3]. One of the key features of the practical QC systems is the signal transmitted through a separate channel which synchronizes its transmitter and receiver modules. For errorless operation of the system, compensation mechanisms against negative effects of signal distortion should be considered [4, 5].

The synchronization signal time delay may occur as a result of external influences, and one of these main effects is temperature [6]. A temperature model of an optical cable was created earlier to consider real-life environment operating conditions of the SCWQC system [7]. Using it, in [7] we discussed refractive index dependence on temperature, which led to the signal delay, and the results showed that phase adjustment is required every 158 ms for stable system operation.

This paper investigates another signal factor which can contribute to synchronizing signal delay in optical fiber: using created temperature model –s distortion dependence of dispersion effects. We estimated the influence of daily temperature on signal temporal delay due to chromatic dispersion and apply the calculations for system improvement.

#### 2. Process modeling

In a subcarrier wave quantum communication system phase matching between the transmitter and the receiver is defined by clock signals from respective voltage controlled oscillators. Thereby, the problem of system synchronization is reduced to fine tuning of the transmitter and receiver oscillators. Detailed descriptions of phase modulating in a SCWQC system are provided in [8,9].

The main characteristics of the QC systems are determined by the QBER. This is defined as the ratio between the erroneous bits and the total number of received quantum bits [1]. Two main factors contribute to the QBER value: the signal visibility in the quantum channel and the dark count of the detector. Since the visibility value represents the probability of photon out-of-phase detection, it depends on the quality of optical phase matching of the transmitter and receiver phase modulators used for encoding qubits. For modern practical QC systems, the desired visibility value is usually around 98–99 %. As shown in [7], the minimum acceptable visibility value in SCWQC system is corresponding to maximum modulating signal phase mismatch  $\Delta \phi = 0.043$ .

The relation between the phase and time delays  $\Delta t$  of a signal with frequency  $\Omega$  is given by:

$$\Delta t = \frac{\Delta \phi}{\Omega}$$

The  $\Omega$  value is typically several gigahertz for SCWQC systems [3,8]; we used a value of 4 GHz in our calculations. Therefore, the maximum tolerable synchronization signal time delay is 1.7 ps.

The temperature model developed in [7] is intended to account for the effect of cable heating on the occurrence optical signal delay. This model was created considering a typical daily temperature profile and parameters of a conventional optical cable, with ITU-T. G.652D standard single mode optical fibers deployed inside. The heat equation with new boundary conditions were solved to account for wind speed.

The two-dimensional heat equation for the cable is:

$$c\rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right), \tag{1}$$

where  $\lambda$  is thermal conductivity,  $\rho$  represents density and c is heat capacity. New boundaries conditions are:

$$\lambda \left. \frac{\partial T}{\partial r} \right|_{r=R} = \alpha(t)(Ta(t) - T|_{r=R}),$$

where r and R are the radial coordinate and radius of the cable. The coefficient of convective heat exchange  $\alpha$  depends on Nusselt number Nu and cable diameter D [10]:

$$\alpha = \lambda \cdot Nu/D,$$

Nusselt number depends on experimental coefficients C and m and Reynolds number Re:

$$Nu = C \cdot \mathrm{Re}^m$$
.

The Reynolds number is calculated on wind speed V and kinematic viscosity  $\eta$ :

$$\operatorname{Re} = DV/\eta$$

The wind speed changes periodically depending on time  $V = V_0 + V \cos(\omega t)$ .

For fibers in the cable, the temperature change will decay with increasing distance from the cable outer jacket into the core of the fibers [11]:

$$T = T_0 + \delta T \exp\left(-\frac{a\tau}{h^2}\right) \cos(at),$$

where  $T_0$  is the average daily temperature,  $\delta T$  is the temperature variation, h is the distance between cable outer jacket and the fiber core, a is thermal diffusivity,  $\tau$  is the time in seconds. The initial (mean) environmental temperature T is chosen to be 15 degrees, with  $\delta T = 10$  degrees oscillation amplitude over a 24 hour period.

In the following section, we find the temperature dependence of synchronization signal phase using the created temperature model and numerically solve equations to find the dispersion contribution to synchronization signal delay.

#### 3. Chromatic dispersion temperature dependence

To analyze the effect of the dispersion on the synchronization signal we consider total chromatic dispersion described by the third-order Sellmeier equation [12]. For the chosen optical fiber it can be modeled as:

$$D(\lambda) = \frac{S_0}{4} \left( \lambda - \frac{\lambda_0^4}{\lambda^3} \right),\tag{2}$$

where  $\lambda_0$  is the zero dispersion wavelength,  $S_0$  is the chromatic dispersion slope at  $\lambda$ . Assuming both parameters depend on temperature, we then take the derivative the equation (2) with respect to temperature:

$$\frac{dD}{dT} = \frac{1}{4} \left( \lambda - \frac{\lambda_0^4}{\lambda^3} \right) \frac{dS_0}{dT} - \frac{S_0 \lambda_0^3}{\lambda^3} \frac{d\lambda_0}{dT}.$$

Both  $\frac{dS_0}{dT}$  and  $\frac{d\lambda_0}{dT}$  contribute significantly to  $\frac{dD}{dT}$  at a given wavelength. This component affects the signal distribution and may lead to incorrect operation of the QC system. To prevent this, it is necessary to take this effect into account. Fiber standard dispersion coefficient  $D(T_0)$  is already accounted for in system operation. However, deviation from the standard value due to temperature can strongly affect the signal delay. Thus the second component should be considered as well.

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The total signal delay due to temperature effect is:

$$\Delta t = \frac{dD}{dT}(T - T_0)\Delta\lambda L,\tag{3}$$

where L is the length of the cable,  $\Delta \lambda$  is the spectral width.

#### 4. Results and discussion

We implemented temperature model used previously to determine the synchronization signal temporal delay due to chromatic dispersion in the SCWQC system with a cable length of 100 km. The created model takes into account the size and thermal conductivity of the different cable elements and fibers location. For calculations we chose the fiber located closest to the cable surface to account for critical effects. The index difference between the core and cladding was kept constant, while the temperature changed. The coefficients values of the cable described are the following [13]:

$$\frac{dS_0}{dT} = -0.4 \cdot 10^{-6} \frac{\text{ps}}{\text{nm}^2 \cdot \text{km} \cdot \text{K}},$$
$$\frac{d\lambda_0}{dT} = 0.026 \frac{\text{nm}}{\text{K}}.$$

Equation (1) was solved for the chosen conditions and time delay was calculated. Since the time delay and temperature changes are linearly dependent, the signal delay in time can be found. Fig. 1 shows the dependence of the synchronization signal temporal delay induced by cable heating due to daily temperature oscillations As can be seen the temperature which induces the maximum tolerable time delay of 1.7 ps accumulates every 2.3 hours. Therefore, for SCWQC systems an additional modulation signal adjustment must be performed to avoid the influence of the discussed dispersion factor.



FIG. 1. Dependence of the signal delay time upon cable heating

#### 5. Conclusion

We modeled the temperature dependence of the synchronization signal delay in optical fiber cables due to chromatic dispersion effects. The temperature dependence of zero dispersion wavelength and chromatic dispersion slope were considered. The temperature model was used to determine the necessary phase adjustment interval for the SCWQC synchronization system operating with a standard optical cable. It has been shown that the temperature effects cause the maximum tolerable signal delay of 1.7 ps due to dispersion effects every 2.3 hours. Therefore, additional phase adjustment is required to compensate for this effect.

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#### Indirect interaction of impurity spins on the surface of topological insulators

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In this work, a mathematical model to study the indirect interaction in topological insulators was constructed. Analysis of the model was carried out numerically. We have calculated the indirect exchange interaction in the film of a topological insulator, for example Bi<sub>2</sub>Te<sub>3</sub>, within the s–d model. The calculations showed that the magnetic ordering of the impurity spins varies periodically with increasing distance between atoms, asymptotically decreasing to zero.  $\lambda$  is a parameter associated with hexagonal distortion and is a component of the dispersion relation. The dependence of the constants of the effective exchange interaction upon the  $\lambda$  parameter is shown; this parameter characterizes the crystal lattice geometry for a topological insulator.

Keywords: topological insulators, impurity spin, indirect exchange, s-d model.

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#### 1. Introduction

Currently, scientists are increasingly interested in the study of topological insulators [1], and questions about the interaction of topological insulators with different kinds of impurities that could exist in a thin film of this material.

Different applications perspective of spintronics, based, in particular, on the effects of spin-spin interactions, has been confirmed theoretically and experimentally [2–4]. This focused on the main mechanism of the interaction of spins because it is an indirect mechanism (e.g. RKKY, through the conduction electrons)) in the cases of such potentially useful substances such as graphene, bigraphene, systems of quantum dots, in article [5–7].

All of the above makes the task of consideration of collective effects related to the interaction of impurities with the electrons of a thin film of a topological insulator, i.e., indirect exchange interaction [8,9], highly relevant.

Particularly strong "spin-orbit coupling" (tight coupling between the spin orientation and the direction of its movement) in the atoms of heavy elements such as bismuth may generate topological invariants that lead to the most radical consequences for the material properties. In fact, inside the semiconductor and the insulator becomes "metallic" on the surface of the conductor. At the same time, due to the spin-orbit interaction and its consequences, the material properties are very attractive from the point of view of practical applications. Researchers have long been trying to create a radically new direction in electronics – spintronic devices that are optimal for the storage and transmission of information would use the spin of electrons rather than their displacement. The fragile nature of quantum effects is difficult to manage and is very strongly inhibits the development of practical devices, well, in fact the nature of the phenomenon of spin TI promises prospects for progress.

#### 2. Basic equations

We consider a film of a topological insulator within the framework of the model described in [10]. We will choose the Hamiltonian system as the standard form for the s–d exchange models [11]:

$$H = H_0 + H_{int},\tag{1}$$

$$H_0 = \sum_{k,\sigma} \varepsilon_k a_{k\sigma}^+ a_{k\sigma}, \quad H_{int} = \sum_{nn'} J(\mathbf{q}) \sum_{\sigma\sigma'} S_q \sigma_{\sigma\sigma'} a_{n\sigma}^+ a_{n'\sigma'},$$

where  $S_q = \sum_R S_R \exp(i\mathbf{q}\mathbf{R})$ ;  $\mathbf{q} = \mathbf{n} - \mathbf{n}'$ ;  $J(\mathbf{q})$  – Fourier transform of interaction potential d-impurities with the electrons in the conduction band;  $\sigma_{\sigma\sigma\prime}$  – the Pauli matrices;  $S_R$  – is the spin vector of the impurity, located at the point R;  $a_{k\sigma}^+$ ,  $a_{k\sigma}$  – the creation operators and annihilation of electrons with spins  $\sigma$  and with wave vectors k.

#### Indirect interaction of impurity spins on the surface of topological insulators

Next, we considered a thin film of a topological insulator, we chose the Hamiltonian for this in the long-wave approximation [12]:

$$H_{0} = \left(p_{x}^{2} + p_{y}^{2}\right)/2m + v_{F}\left(p_{x}\sigma_{y} - p_{y}\sigma_{x}\right) + \frac{\lambda}{2}\left(p_{+}^{3} + p_{-}^{3}\right),$$

$$p_{\pm} = p_{x} \pm ip_{y}.$$
(2)

The derivation of the effective Hamiltonian (2) for a thin film starting from the Hamiltonian for a bulk sample is presented in a number of papers, of which, we only mention [14].

In expression (2),  $p_x, p_y$  – components of the electron momentum, m is the effective electron mass,  $v_F$  – the Fermi velocity,  $\lambda$  is a parameter associated with hexagonal distortion and is a component of the dispersion relation. Typical values of the Hamiltonian parameters, for example for Bi<sub>2</sub>Te<sub>3</sub>, is [13]:  $m \propto 35 \text{ eV}^{-1}\text{\AA}^{-2}$ ,  $v_f \propto 5 \cdot 10^{-4} \text{ eV}^{-1}\text{\AA}$ .

The Hamiltonian (2) is easily diagonalized and sets the range of the electrons:

$$\varepsilon(p_x, p_y) = \left(p_x^2 + p_y^2\right) / 2m + \sqrt{v_f^2 \left(p_x^2 + p_y^2\right) + \frac{\lambda^2 p_x}{2} \left(p_x^2 - 3p_y^2\right)}.$$
(3)

Thus, expression (2) can be inserted in (1).

The Frohlich method of calculating indirect interactions [14] is based on the assumption that for the operators of the matrix elements, the following inequality  $|H_{int}| \ll |H_0|$  holds, and consists of two stages. The first is the transition from the form (1) to a new form with the help of the unitary transformation,  $U = \exp(-L)$ , where L – is anti-Hermitian operator satisfying the condition:

$$H_{int} + [H_0, L] = 0. (4)$$

In the new view, the Hamiltonian H takes the form of:

$$H \to \tilde{H} = H_0 + \frac{1}{2} [H_{int}, L] + O(H_{int}^3).$$
 (5)

A solution of the operator equation (4) will take the following expression [13]:

$$L = \frac{1}{i\hbar} \lim_{\varepsilon \to 0} \int_{-\infty}^{0} e^{\varepsilon t} H_{int}(t) dt, \quad H_{int}(t) = \exp\left(\frac{iH_0t}{\hbar}\right) H_{int} \exp\left(-\frac{iH_0t}{\hbar}\right).$$

The second stage consists of averaging the expression (4) for the transformed Hamiltonian H on the condition of the interactions of the field-vector: in averaging with the equilibrium density matrix for the electronic subsystem. Thus, the 2-nd order term in perturbation theory  $H_{ss} = \frac{1}{2} \langle [H_{int}, L] \rangle$ , where angular brackets denote the average value with the equilibrium density matrix for the electronic subsystems in the expansion (5) cease depending on the creation operators and annihilation of electrons, but maintains the dependence on the spin operators of different impurity atoms and, therefore, has meaning for the indirect interaction operator.

After calculation of the respective switches, the operator L has the form:

$$L = \sum_{pp'} J(\mathbf{q}) \sum_{\sigma} \left\{ \frac{\left(S_q^x - iS_q^y\right) a_{p,\sigma}^+ a_{p',-\sigma}}{\varepsilon_{p'} - \varepsilon_p + \hbar\omega_0} + \frac{\left(S_q^x + iS_q^y\right) a_{p,-\sigma}^+ a_{p',\sigma}}{\varepsilon_{p'} - \varepsilon_p - \hbar\omega_0} \right\}.$$
(6)

Substituting (6) into (5) and thermo dynamical averaging gives:

$$H_{ss} = 2 \sum_{p_1 p_2 R_1 R_2} M \left( \exp\left(i(p_1 - p_2)(R_1 - R_2)\right) S_{R_1}^- S_{R_2}^- + \exp\left(i(p_2 - p_1)(R_1 - R_2)\right) S_{R_1}^- S_{R_2}^+ \right).$$

Where, we have introduced the following notation for constants of the exchange interaction:

$$M = \frac{1}{2} J_{p_1 - p_2} J_{p_2 - p_1} \left\{ \frac{\exp\left(-\beta \varepsilon_{p_1}\right) - \exp\left(-\beta \varepsilon_{p_2}\right)}{\varepsilon_{p_1} - \varepsilon_{p_2}} \right\},$$

where M is the meaningful constants indirect exchange interaction of the impurities' spins, carried out by crystallite conduction electrons.

We have considered the exchange interaction of localized impurities of the spins in the direct space; for that, we have applied the inverse Fourier transform (in reciprocal space, integration was carried out at the Brillouin zone):

$$J_{eff} = \int_{0}^{\frac{\pi}{3a}} dk_{x1} \int_{0}^{\frac{\sqrt{3}}{3}k_{x1}} dk_{y1} \int_{0}^{\frac{\pi}{3a}} dk_{x2} \int_{0}^{\frac{\sqrt{3}}{3}k_{x2}} 2M(k_{x1}, k_{y1}, k_{x2}, k_{y2}) \exp\left\{i\left(k_{x1} - k_{x2}\right)x\right\} \exp\left\{i\left(k_{y1} - k_{y2}\right)y\right\} dk_{y2}.$$

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We would like to note that the oscillating part is already contained implicitly in this dependence and by evaluating the integrals with the pass method, it is possible to show the existence of exponential decline, i.e. strong magnitude reduce of indirect interactions with increasing distances between the impurities. We would like to point out that this behavior is always typical for mechanism of indirect exchange through the conduction electrons and caused by the local character of the interaction of electrons with impurity atoms.

Exchange interaction depends on the distance and the direction, but we consider only the dependence on the distance. The dependence of the exchange interaction on the direction is in the Hamiltonian for electrons. This is lost after averaging over the electronic subsystem states.

#### 3. The results of numerical simulation

Due to a rather complicated dependence of the resulting operator of the indirect interaction from the task parameters, the found parameters were analyzed numerically. Thus, Fig. 1 shows a typical dependence of constants of the interaction exchange (having the meaning of system energy, depending only on the impurity spin orientation) between the components of the impurity spin from the distance for different values of parameter  $\lambda$ . This parameter characterizes the complexity of the studied system's geometry in contrast to the usual square lattice.



FIG. 1. The dependence of the indirect interaction constants on the distance for small  $\lambda$ . The distance between the localized spins is expressed in units of the lattice constant a = 2.49 Å

Figures 1 and 2 show the dependence of the exchange interaction constants on the parameter  $\lambda$ . As can be seen from the figures, the value of the exchange interaction constant is greater than in the case of large values of the parameter  $\lambda$ .

The obtained results confirm the possibility of formation of areas with ferromagnetic or antiferromagnetic type of ordering (change of the sign of the exchange interaction constant) the impurity atoms with variation geometry of the lattice, which is undoubtedly important for different applications.

#### 4. Conclusion

The peculiarity of the indirect interaction of the electron spins with the help of topological insulator films studied in this work is that the exchange interaction was considered, based on the long-wave approximation. This dispersion relation includes pulses of electrons near the Dirac points.

In conclusion, we will formulate the main inference of this work:



FIG. 2. The dependence of the constants of the indirect interaction on the distance for bigger  $\lambda$ . The distance between the localized spins is expressed in units of the lattice constant a = 2.49 Å

- 1. The increase of the constant  $\lambda$  leads to an increase in the constants' amplitude of the indirect interaction of the impurities, depending on the distance that could be associated with the configuration change of the crystal lattice
- The General nature of the indirect interaction has a form which is similar to other systems, the periodic dependence of the exchange interaction constants on the distance between the impurity spins, which decreases to zero asymptotically with increasing distance.

We use a monograph White "Quantum theory of magnetism" to compare our results with the results obtained in classical metallic systems. The spins of the conduction electrons created the oscillating polarization in classical metallic systems with the introduction into the metal localized moment. Spin density oscillations have the same shape as the Friedel charge density oscillations that occur, screening the charge impurity by electron gas. Indirect interaction in topological insulators and metal systems is similar, but the decrease of the interaction value of the distance in our study system is much faster. This fact, in our opinion, is due to the presence of a complex spin-orbit interaction in topological insulators.

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#### Biological effect of zirconium dioxide-based nanoparticles

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This work demonstrates the positive effects of zirconium dioxide nanoparticles on cells in vitro. This is supported by the absence of toxicity, stimulation of metabolic and proliferative activity. The nanoparticles of solid solution of europium oxide in europium dioxide do not exhibit an explicit biological effect. The potentially successful application of zirconium dioxide-based nanoparticles in pharmacology has been demonstrated.

Keywords: zirconium dioxide, europium oxide, nanoparticles, toxicity, metabolic activity, proliferative activity.

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#### 1. Introduction

Systematic studies of biological effects of nanoparticles of varying compositions, morphologies and dimensions have been performed by many authors [1–4]. This is due to both their potential medical application of nanoparticles [5–11] and danger for humans [12–15]. The promising future of biomedical application and the potential danger of nanoparticles are to a considerable extent predicated by their ability to penetrate through cell and intercellular membranes and, therefore, spread throughout the organism.

Previous research [16–22] has demonstrated the promising results for the application of nanoparticles of some metal dioxides and of solid solutions, which are composed so that they will have utility in biomedical applications. The additives, which provide certain functional properties to nanostructured materials, in particular, luminescent properties, are often used in the aforementioned nanoparticles as an admixture component. The luminescent properties of those nanoparticles that are intended for biomedical application can be useful when analysing the distribution of nanoparticles within living organisms.

One promising method for obtaining oxide nanoparticles is hydrothermal processing of the respective hydroxides. A significant advantage of hydrothermal synthesis, as compared to other methods, is that it makes it possible to obtain in some cases, as was shown in [23–27], almost completely non-agglomerated nanoparticles, which have a narrow size distribution range. Such properties of the nanopowders, which are formed under hydrothermal conditions, are the result of a fast nucleation process, as was shown in [28,29].

It is worth noting that though there are several studies [16-22] dedicated to the biological effects of the nanoparticles, which are based on metal dioxides such as TiO<sub>2</sub>, HfO<sub>2</sub>, CeO<sub>2</sub>, and solid solutions containing them, there is considerably less information about the biological effect of zirconium dioxide-based nanoparticles [30-32]. However, since zirconium dioxide based nanopowders, solid solutions, nanocomposites and other ZrO<sub>2</sub>-containing nanomaterials, have become widely spread in scientific research and technological applications [33-37], studying their biological effect is important.

The reasons listed above provide the motivation for us to study the impact that  $ZrO_2$ -based nanoparticles and solid solutions such as the luminescent  $ZrO_2(Eu_2O_3)$  have on biological objects.

#### 2. Experimental methods

#### 2.1. Synthesis of nanoparticles

Zirconium dioxide-based nanoparticles were obtained through hydrothermal processing of preliminarily coprecipitated zirconium and europium hydroxides at 225 °C and under a pressure of 10 MPa during 2 h in accordance with the methods described in the work [23]. The structural state and the size of the crystallites of the nanoparticles obtained were determined on the basis of X-ray diffractometry of the samples (diffractometer DRON-3, CuK $\alpha$ -radiation). The calculation of the ratio of monoclinic and cubic ZrO<sub>2</sub> modifications was performed using the formula given in [23]. The size of crystallites was calculated based on the data, which refers to the broadening of X-ray diffraction lines, using Scherrer's formula.

The size of particles was analyzed on the basis of transmission electron microscopy (microscope EM-125 with Uacc = 75 kV).

#### 2.2. Biological effect of nanoparticles (materials and methods)

The study of biological characteristics of  $ZrO_2$  and  $ZrO_2(Eu_2O_3 \ 1 \ mol.\%)$  nanoparticles was performed using preparations in the form of suspensions of nanoparticles of the said composition. The preparations under study were represented by the suspensions of nanoparticles of two types: highly diluted suspensions of nanocrystals and concentrated suspensions. Testing was carried out on the monolayer of the cell line L-41 (bone marrow cells from a leukemia patient) for all four types of preparations using a wide range of concentrations with nearly a hundred-fold variance. A full description of the procedures for cytotoxicity and biological activity analyses of  $ZrO_2$  and  $ZrO_2(Eu_2O_3)$  nanoparticles is given below.

The dispersions of  $ZrO_2$  and  $ZrO_2(1 \text{ mol.}\% \text{ Eu}_2O_3)$  nanoparticles were studied, which were taken in the form of two fractions – supernatant fluid and sediment. All the fractions were studied separately. The degree of dispersion dilution with water is given in Table 1. In total, 7 compositions of supernatant fluid and 6 compositions of sediment were studied.  $ZrO_2$  sediment was re-suspended in 3.0 ml of supernatant fluid.  $ZrO_2(1 \text{ mol.}\% \text{ EuO}_3)$  sediment was re-suspended in 2.0 ml.

	Supernatant fraction			Sediment		
No c		Volume of culture medium, mcl	Volume of studied compounds, mcl	No	Volume of culture medium, mcl	Volume of studied compounds, mcl
Mi	1	1.000	300	8	1.000	200
	2	2 1.000 200		9	1.000	100
	3	1.000	50	10	1.000	25
	4	1.000	1.000 (dilution 3)	11	1.000	1.000 (dilution 9)
ution	5 1.000		1.000 (dilution 4)	12	1,000	1.000 (dilution 10)
Dil	1.000 6 1.000		1.000 (dilution 5)	13	1.000	1.000 (dilution 11)
	7	1.000 1.000 (dilution 6)				

TABLE 1. Dilution of the fractions of sediment and supernatant dispersion of  $ZrO_2$  and  $ZrO_2(Eu_2O_3)$ 

Constant cell line L-41 was used as the cell model. The line was cultivated in MEM (MEM – Minimum Essential Medium) with addition of 7 % of ABS (Adult Bovine Serum for cell culture) (of Biolot company) (ABS = Adult Bovine Serum for cell culture 'Biolot') and gentamicin (100 U/ml).

The following characteristics were studied: cytotoxicity, proliferative activity and metabolic activity, determined by spectrophotometric analysis by means of MTT assay.

To determine cytotoxicity in lifetime condition, the cells were inoculated on 96-well plastic plates. The changes were registered visually during the period of 1–10 days by means of inverted microscope (Leitz, Germany). To prepare cytological preparations, the cells were inoculated on coverslips, then fixed with methanol (10 min) and stained in accordance with Romanovsky–Giemsa method. The substances under study were applied on the intraday monolayer of the cell line L-41 in the proper concentrations.

To determine proliferative activity, the cells, taken in the concentration 50,000 per ml, were inoculated into plastic flasks of 30 ml in volume where the studied substances had already been introduced into the culture medium. The quantity of control flasks was equal to 5; the quantity of flasks per each tested concentration was 3. The cells, in order for them to be counted, were removed on the fourth day of cultivation. The effect of the studied

compounds on cell proliferation was determined for the concentrations 6 and 7 (Table 1). Proliferation index was calculated as the ratio of the yield of experimental cells to the yield of control cells.

In order to study the metabolic activity, the cells were inoculated on 96-well plates and the fractions under study were introduced on the monolayer in supporting medium MEM without serum after a day.

The registration with the use of MTT-assay was performed at different points of cultivation timeline in the presence of fractions of the studied compounds.

#### 3. Results and discussion

The nanopowders that are based on  $ZrO_2$  and  $ZrO_2(1 \text{ mol.}\% \text{ Eu}_2O_3)$  were obtained under hydrothermal conditions. The analysis of the structure condition showed that the obtained nanocrystals are predominantly represented by tetragonal modification of zirconium dioxide (t-ZrO<sub>2</sub>). In zirconium dioxide-based samples, the ratio of tetragonal modification and monoclinic modification of zirconium dioxide (m-ZrO<sub>2</sub>) constitutes 80:20 mol.% (Fig. 1). Such ratio of structural types for zirconium dioxide nanoparticles, being formed under the conditions of hydrothermal processing, had also been noted earlier [23, 28, 29, 38]. The introduction of 1 mol.% Eu<sub>2</sub>O<sub>3</sub> under hydrothermal conditions leads to the formation of zirconium dioxide-based nanocrystals of only tetragonal modification (Fig. 1).



FIG. 1. X-ray diffractogram of ZrO2 and ZrO2 (1 mol.% Eu2O3) nanopowders

The average size of  $ZrO_2$  crystals having monoclinic and tetragonal modification, determined using the Xray diffraction line broadening values, were 15 and 22 nm, respectively. Analysis of the X-ray diffraction lines broadening for  $ZrO_2(1 \text{ mol.}\% \text{ Eu}_2O_3)$  sample, showed that the average size of  $ZrO_2(\text{Eu}_2O_3)$  crystals was 10 nm. Analysis of the nanopowders using transmission electron microscopy revealed that the average size of particles, of both  $ZrO_2$ , and  $ZrO_2(1 \text{ mol.}\% \text{ Eu}_2O_3)$ , in general ranged from 10 to 15 nm with quite a narrow range of distribution of particles by size (Fig. 2). That is the sizes of particles, within the error of methods, coincide with the size of crystals.

The studies of cytotoxicity (lifetime observation) undertaken within 10 days of culturing (5 experiments) showed the absence of explicit destructive and degenerative processes, both in the structure of confluent monolayer, and in the cells themselves, as well as under the influence of higher concentrations (Table 1, positions 1, 2, 8, 9). No apparent toxicosis, cell destruction and polymorphism were observed on cytological preparations in the concentrations 2 and 3 (supernatant fraction) and 9, 10 (sediment), i.e. at the highest concentrations. The presence of a clearly visible considerable quantity for the solid-phase fraction of the preparations under study on the cell monolayer was noted at concentrations 9 and 10. Nevertheless, in this case, no significant changes were observed in the main morphofunctional characteristics of the cells.

To evaluate the proliferative activity of the cells L-41, which were cultured in the presence of the studied supernatant fractions based on  $ZrO_2$  nanocrystals and supernatant based on  $ZrO_2(Eu_2O_3)$  nanocrystals, the index of proliferation was determined. The concentrations 6 and 7 (Table 2) were used.



FIG. 2. Microphotos of ZrO<sub>2</sub> and ZrO<sub>2</sub> (1 mol.% Eu<sub>2</sub>O<sub>3</sub>) nanopowders

ZrO <sub>2</sub> nanopa	articles	ZrO <sub>2</sub> (Eu <sub>2</sub> O <sub>3</sub> ) nanoparticles		
Substance concentrations Proliferation index		Substance concentrations	Proliferation index	
6	1.7	6	1.1	
7	1.26	7	0.95	
Control	1	Control	1	

TABLE 2. Results of determination of proliferative activity of nanoparticles

As it follows from the data presented in Table 2,  $ZrO_2$  nanoparticles render a stimulating influence on the proliferative activity of cells, in small (1,000:6.25, 1,000:3.12) concentrations. The values of Proliferation index applicable to the samples that are based on the solid solution of  $ZrO_2(Eu_2O_3)$  turned out to be comparable with the control values. Such difference can be attributed to the fact that a considerable portion of the europium oxide in  $ZrO_2(Eu_2O_3)$  nanoparticles can be concentrated on the surface of the nanoparticles, thus forming the structure of 'core-shell' type. The possibility for such structure to appear can be traced in the outcomes of the works [39], which show that the structures of 'core-shell' type are formed when a synthesis is taking place, under analogous conditions, of the nanoparticles, which are based on the solid solutions  $ZrO_2(Y_2O_3)$ ,  $ZrO_2(Gd_2O_3)$  that are similar in chemical nature to  $ZrO_2(Eu_2O_3)$ . Further confirmation was given by the results of the work [38], dedicated to the analysis of luminescent properties of  $ZrO_2(Eu_2O_3)$ , in which a conclusion is drawn about the partial localization of europium oxide on the surface of nanoparticles. In connection with the obtained data, it can be concluded that it is the surface molecules of zirconium dioxide that possess proliferative activity, and the surface, enriched with europium oxide is biologically inert in this respect.

Evaluation of metabolic activity was accomplished using the MTT assay (spectrophotometric analysis), which was carried out in 4 experiments on 96-well plates. The analysis of all the data obtained using MTT assay for each of 4 fractions of the studied samples showed that all the studied compositions did not inhibit the metabolic activity of L-41 cells over a wide range of concentrations (1,000:300 – 1,000:3.12), i.e. at the concentrations of disperse phase, which differ from each other nearly by 100-fold. The MTT assay, which was performed on the third day of cultivation of L-41 cells with each of 4 newly obtained fractions, showed that there were considerable stimulating properties for these fractions, especially of those taken in smaller concentrations. Thus, as it follows from the data of MTT assay, all the studied compositions not only do not inhibit the metabolic activity of L-41 cells, but, if taken in small concentrations, increase it 1.4-1.6 fold. In the course of storage of initial fractions these properties were lost, which may be explained by the change of the surface condition of nanoparticles with time and impairment of the fraction's sterility.

As a result of the cytotoxicity analysis for the studied compositions, the absence of the expressed cytotoxicity both in the structure of the confluent monolayer and in the cells themselves, as well as under the influence of large concentrations of nanoparticles (ratio of culture medium and the studied fraction constitutes 10:3), was determined. No changes of basic morphofunctional characteristics of cells were observed, even in the case of the presence of considerable quantity of disperse phase based on  $ZrO_2$  and  $ZrO_2(Eu_2O_3)$  nanoparticles on the cell monolayer.

#### Biological effect of zirconium dioxide-based nanoparticles

Thus, in order to generalize all the data obtained, it is possible to make a conclusion about the positive character of the influence of  $ZrO_2$  and  $ZrO_2(1 \text{ mol.}\% \text{ Eu}_2O_3)$  nanoparticles on cells in vitro. This is confirmed by the absence of toxicity and by the stimulation of metabolic and proliferative activity. The performed studies show that  $ZrO_2$  and  $ZrO_2(\text{Eu}_2O_3)$  nanoparticles have promising futures as the objects of further study with regard to their biological properties along with further possible application in pharmacology.

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# Cryometry data and excess thermodynamic functions in the binary system: water soluble bis-adduct of light fullerene $C_{70}$ with lysine. Assymmetrical thermodynamic model of virtual gibbs energy decomposition – VD-AS

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The temperature of water-ice crystallization initiation decreases ( $\Delta T$ ) were determined in the binary water solutions of water soluble derivative of light fullerene C<sub>70</sub> with amino-acid lysine at 272.99 – 273.15 K. Partial molar excess functions for H<sub>2</sub>O were calculated. For the thermodynamic description of our systems, we have elaborated an original semi-empirical model VD-AS (Virial Decomposition Asymmetric Model), based on the virial decomposition of the molar Gibbs energy of the component molar fractions in the solution. With the help of the VD-AS model, partial molar functions of nano-clusters were calculated. Excess and full average Gibbs energies for the solutions and miscibility gaps concentration regions (with the help of diffusional instability equations) were calculated. Thus, the VD-AS model excellently describes pre-delamination or micro-heterogeneous-structure formation in the considered solutions. These calculations were accordingly confirmed by dynamic light scattering data.

Keywords: cryometry, light fullerene C70, lysine, thermodynamic model.

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#### 1. Introduction

The article is a continuation of the investigations devoted to the synthesis, identification and investigation of physico-chemical properties of water soluble of light fullerene ( $C_{60}$  and  $C_{70}$ ) derivatives, such as: complex eithers of two-based carbonic acids (malonates, oxalates), poly-hydroxylated forms (fullerenols), amino-acid derivatives (argenine, alanine) some other derivatives [1–23]. In these works, in particular, the physico-chemical properties of aqueous light fullerene derivative solutions, depending on the solutions' concentrations, were investigated: poly-thermal solubility and crystal hydrate compositions; volume properties (density, average and partial component molar volumes); refractive indices, specific and molar refractions; conductivity and pH (apparent dissociation degrees and concentration dissociation constants); associates dimensions and electro-kinetic  $\xi$  – potentials, etc.

The investigation of such fullerenes derivatives is necessary for the following reasons:

First: The application of fullerenes considerably limited by their almost complete incompatibility with water and aqueous solutions, such as, for example: physiological solution, blood, lymph, gastric juice etc. Solubility of light fullerenes, for example, in pure water at 25°C is practically negligible  $(10^{-12}-10^{-14} \text{ g/dm}^3 \text{ for } C_{60} \text{ and } C_{70}, \text{ correspondingly}).$ 

Second: These fullerene derivatives, with amino-acids possess unique anti-oxidant, antibacterial, antiviral and antifungal properties, can absorb different type free radicals, UV photons etc. These facts determine high potential for its application in medicine, pharmacology, cosmetics, food and wine industry etc.

The investigation of the excess thermodynamic functions in such systems (activities, activity coefficients, excess (or mixing) Gibbs energies (enthalpies, entropies) etc.), to the best of our knowledge, until this time, has not been provided, except for two original works [24, 25]. In those articles, in the binary systems with the help of cryometry investigations, the authors determined the decrease in temperature for ice crystallization initiation

(liquidus temperatures), water activities, water activity coefficients, and then, solving numerically the Gibbs-Duhem equation – activities and activity coefficients of fullerene derivatives. No other data concerning the excess function in the considered systems, obtained, for example by the isopiestic method, have been found. Meanwhile, such data may be very scientifically interesting, because these aqueous solutions have very specific and rare consistent hierarchical type of association (see below).

#### 2. Cryometry data in the binary water solutions of water soluble light fullerene derivatives

The temperature of water-ice crystallization initiation decreases  $(\Delta T)$  were determined in binary aqueous solutions of water-soluble light fullerene derivative:  $C_{70}(C_6H_{13}N_2O_2)_2 - H_2O$  at 272.99 – 273.15 K. The temperature range corresponds to concentration range X (Molar fraction of  $C_{70}(C_6H_{13}N_2O_2)_2$  in the solution) = 0–1.38 · 10<sup>-4</sup> rel. un. or C (volume concentration)  $\approx 0$ –10 g/dm<sup>3</sup>. Such concentrations range for fullerene containing systems is wide enough and corresponds to the solubility of  $C_{70}(C_6H_{13}N_2O_2)_2$  in water at 273.15 K. Even at these concentrations, the solutions may lose the diffusive stability, i.e. pre-flake (see below).

Solution concentrations (in molar fractions) vary over a wide range  $x_{nano-cluster} = 1.1 \cdot 10^{-6} - 1.4 \cdot 10^{-4}$  rel.un. The liquidus temperatures were determined with the help of Beckman thermometer with the linear resolution of the device scale  $\Delta T/\Delta h \approx 0.01$  K/mm (h – height of Hg capillary raising). Cryometry data  $\Delta T(x_{nano-cluster})$  are shown in Fig. 1 and in Table 1.

TABLE 1. Cryometry data and excess thermodynamic functions for the bis-lysine adduct of  $C_{70}$  light fullerene –  $C_{70}(C_6H_{13}N_2O_2)_2$  –  $H_2O$  binary system at 272.99–273.15 K. Asymmetrical model of excess Gibbs energy decomposition model – VD-AS is used

Molar fraction of	Ice crystallization	$\ln a_{H2O}$	$\ln \gamma_{H2O}$	$\ln \gamma^{as}_{C70(C6H13N2O2)2}$
C <sub>70</sub> (C <sub>6</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	initiation	ln(water activity)	In (water activity	In (activity coefficient
in the solution	temperature	(rel.un.)	coefficient)	of
$X_{C70(C6H13N2O2)2}$	decrease		(rel.un.)	$C_{70}(C_6H_{13}N_2O_2)_2$
(rel.un.)	$\Delta T$ (K)			(rel.un.)
0.000	0.000	0.000	0.000	0.000
$1.083 \cdot 10^{-6}$	0.005	$-5.86 \cdot 10^{-5}$	$-5.75 \cdot 10^{-5}$	3.38
$2.166 \cdot 10^{-6}$	0.013	$-1.44 \cdot 10^{-4}$	$-1.42 \cdot 10^{-4}$	6.65
$4.332 \cdot 10^{-6}$	0.020	$-2.22 \cdot 10^{-4}$	$-2.18 \cdot 10^{-4}$	12.9
$8.66 \cdot 10^{-6}$	0.030	$3.33 \cdot 10^{-4}$	$-3.25 \cdot 10^{-4}$	24.3
$1.73 \cdot 10^{-5}$	0.050	$-5.49 \cdot 10^{-4}$	$-5.32 \cdot 10^{-4}$	42.2
$3.46 \cdot 10^{-5}$	0.075	$-8.22 \cdot 10^{-4}$	$-7.87 \cdot 10^{-4}$	66.0
$6.92 \cdot 10^{-5}$	0.11	-0.00122	-0.00116	72.5
$1.38 \cdot 10^{-4}$	0.16	-0.00178	-0.00164	73.1

Expanded uncertainties are:  $U(\Delta T) = \pm 0.002$  (dilute solutions) - 0.005 (concentrated solutions) K,  $U_r(\ln a_{H_2O}) = 0.5$  (concentrated solutions) - 5 (dilute solutions) rel. %,  $U_r(\ln \gamma_{H_2O}) = 0.5$  (concentrated solutions) - 5 (dilute solutions) rel. % and  $U_r(\ln \gamma_1^{ass}) = 2$  (dilute solutions) - 5 (concentrated solutions) rel.% (as the sum result of experimental errors and numerical approximation).

One can see, that all dependencies  $\Delta T(x_{nano-cluster})$  are sharply nonlinear, which prove very high positive deviations of the solutions from ideality for all solutions, even those which are very dilute. In Fig. 1, for comparison, the arrow represents the value  $\Delta T^{id}$  for the ideal non-electrolyte solution. We can see the experimental  $\Delta T$  exceeds  $\Delta T^{id}$  by 1–2 orders of magnitude (for comparable concentrated and dilute solutions, correspondingly). So, one should expect probably gigantic positive deviations of the solution from the ideality in a thermodynamic sense.



FIG. 1. Temperature of water-ice crystallization beginning (liquidus temperature) decrease ( $\Delta$ T) against molar fraction concentration in the binary solutions:  $C_{70}(C_6H_{13}N_2O_2)_2 - H_2O$  at 272.99 – 273.15 K. Arrow shows  $\Delta$ T-function for the ideal non-electrolyte solution

#### 3. Calculation of water excess functions

For calculating the water activity we have used the well-known equation obtained from the equality of chemical H<sub>2</sub>O potentials in pure solid ice and non-ideal liquid solution [34, 35]:

$$\left[-\Delta H_W^f \Delta T - \Delta C_P \Delta T^2\right] / \left[R\left(T_0^f - \Delta T\right)T_0^f\right] = \ln a_{H2O},\tag{1}$$

where  $\Delta H_W^f = 5990$  J/mole,  $\Delta C_P = -38.893$  J/mole·K,  $T_0^f = 273.15$  K heat, temperature of ice fusion and change of heat capacity in the process of ice fusion, correspondingly. Equation (1) was displayed in the symmetrical normalization scale for thermodynamic functions for both solution components:

$$a_{H2O}(x_{H2O} = 1) = \gamma_{H2O}(x_{H2O} = 1) = 1,$$
(2)

$$a_{nano-cluster} \left( x_{nano-cluster} = 1 \right) = \gamma_{nano-cluster} \left( x_{nano-cluster} = 1 \right) = 1, \tag{3}$$

where  $x_i$  and  $a_i$ ,  $\gamma_i$  – molar fraction, activity and activity coefficient of *i*-th component.

Calculated data for  $\ln[a_{H_{2O}}(x_{nano-cluster})]$  are represented in Fig. 2 and Table. 1.

Additional researchers [24, 25] calculated concentration dependencies  $\ln \gamma_{H2O}$ , derivatives  $d \ln \gamma_{H2O}/dx_{nano-cluster}$  (numerically). Then, other researchers [34, 35] calculated the dependencies  $d \ln \gamma_{nano-cluster}/dx_{nano-cluster}$ , (according to the classical Gibbs–Duhem differential equation) also numerically and at the end by numerical integration the dependencies  $\ln \gamma_{nano-cluster}(x_{nano-cluster})$  were calculated. As a result, as was previously expected, gigantic positive deviations of the solution from ideality for the functions  $\ln \gamma_{nano-cluster}$  were obtained  $\ln \gamma_{nano-cluster} \approx n(10^0 - 10^1)$  (see Table 1 and Fig. 4). Naturally, in all likelihood, no existing thermodynamic model can describe such nontrivial behavior of nano-cluster thermodynamic functions.

#### 4. Virial Decomposition Asymmetric Model - VD-AS

For the description of such nontrivial thermodynamic behavior of the considered aqueous solutions, we have elaborated semi-empirical model VD-AS (Virial Decomposition Asymmetric Model), based on the virial decomposition of excess molar Gibbs energy on the solution for the components molar fractions. This technique has often been used for the thermodynamic description of binary and multicomponent systems with different physico-chemical nature, such as: electrolyte solutions [26–29], non-electrolyte (semiconductor) melts [30–33], isovalent



FIG. 2. Logarithm of water activity  $(\ln a_{H2O})$  against molar fraction concentration in the binary solutions:  $C_{70}(C_6H_{13}N_2O_2)_2 - H_2O$  at 272.99 – 273.15 K

substitution solid solutions [34–36]. If one takes only one term in the decomposition for the binary system (corresponding to the invariant second virial coefficient), see later equation (4) well-known strictly regular solutions model – RSM, is realized. Under the assumption of temperature dependence for the only virial coefficient, a quasi-regular solution model – QRSM is realized. If one uses third virial coefficients for the decomposition, a sub-regular solution model – SRSM is realized. Finally, when one alsoconsiders the contribution of the electrostatic non-specific interactions (according to Debye–Huckel theory) Pitzer's model in different variants is realized.

So, we assume the following numeration: 1 - is the number of the dissolved component (nano-cluster in our case), 2 - is the number of the solvent (H<sub>2</sub>O). Let us propose the following expression:

$$G^{ex}/RT = (n_1 + n_2) \sum_{i=1} \sum_{j=1} X_1^i X_2^j \cdot \lambda_{ij} = \left( \sum_{i=1} \sum_{j=1} n_1^i n_2^j \cdot \lambda_{ij} \right) / (n_1 + n_2)^{i+j-1},$$
(4)

where  $G^{ex}$  – full molar excess solution Gibbs energy, R = 8.31 J/K, T – temperature (K),  $n_i$  and  $X_i$  – molar number and molar fraction of *i*-th component, correspondingly,  $\lambda_{ij} - ij$ -th virial coefficient in the decomposition of  $G^{ex}/RT$  on the component molar numbers. In other words,  $\lambda_{ij}$  are naturally identified as divided by RTspecific energy of interaction of *i* particles of the 1-st component and *j* particles of the 2-nd component. If one takes into account the huge ( $\sim$  two orders of magnitude) differences in the components' molar masses (1-st are heavy) and its linear dimensions (almost one order – nanoclusters, in our case, are hollow), it is quite clear, that if the upper limit of the summation, according to the 1-st component, may be more by one-two orders of magnitude.

Let us calculate excess thermodynamic functions of the components:  $\ln \gamma_i$ :

$$\ln \gamma_1 = \partial \left( G^{ex} / RT \right) / \partial n_1 = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ i - (i+j-1) X_1 \right] X_1^{i-1} X_2^j \cdot \lambda_{ij}, \tag{5}$$

$$\ln \gamma_2 = \partial \left( G^{ex} / RT \right) / \partial n_2 = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ j - (i+j-1) X_2 \right] X_1^i X_2^{j-1} \cdot \lambda_{ij}.$$
(6)

In our case, molar fractions of the components are incomparable:

$$X_2 \gg X_1, \quad X_2 > 0.999 \approx 1, \quad X_1 \ll 1.$$
 (7)

Cryometry data and excess thermodynamic functions in the binary system...

Thus, equations (5), (6) may be simplified:

$$\ln \gamma_1 \approx \sum_{i=1}^{j} i X_1^{i-1} \sum_{j=1}^{j} \lambda_{ij},\tag{8}$$

$$\ln \gamma_2 \approx \sum_{i=1}^{i} (1-i) X_1^i \sum_{j=1}^{i} \lambda_{ij} = \sum_{i=2}^{i} (1-i) X_1^i \sum_{j=1}^{i} \lambda_{ij}.$$
(9)

From the systems (5), (6) and (8), (9), one can see that, they agree in a thermodynamic sense, i.e. Gibbs–Duhem equation is valid at T, P = const:

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 = 0, (10)$$

or, for example, from the equations (7), (8) we can get identity:

$$X_1 \sum_{i=1}^{i} i(i-1) X_1^{i-2} \lambda_{ij} dX_1 + \sum_{i=1}^{i} (1-i) i X_1^{i-1} \lambda_{ij} dX_1 = 0.$$
(11)

Let us transfer system (8), (9), denoting as  $\Lambda_i$  summary virial coefficients:

$$\sum_{j=1} \lambda_{ij} = \Lambda_i \left( T \right), \tag{12}$$

so, in our conditions of consideration:

$$\ln \gamma_1 \approx \sum_{i=1} i \Lambda_i X_1^{i-1},\tag{13}$$

$$\ln \gamma_2 \approx \sum_{i=1} (1-i) \Lambda_i X_1^i = \sum_{i=2} (1-i) \Lambda_i X_1^i.$$
(14)

One can see that if  $\Lambda_1 \neq 0$ , then logarithms of the limit activity coefficients  $-\ln \gamma_i^0 = \lim_{X_1 \to 0} \ln \gamma_i$ , correspond to symmetrical method or normalization of the excess thermodynamic functions, namely:

$$\ln \gamma_1^0 = \Lambda_1 \neq 0, \quad \gamma_1 \left( X_1 \to 0 \right) = \gamma_1^0 \neq 1, \tag{15}$$

$$\ln \gamma_2^0 = 0, \quad \gamma_2 \left( X_1 \to 0 \right) = 1. \tag{16}$$

In our case, for the incomparable, it is more convenient to use the asymmetrical normalization scale (for this, one should only demand the performing of the single condition  $\Lambda_1 = 0$ ):

$$\ln \gamma_1^0 = 0, \quad \gamma_1 \left( X_1 \to 0 \right) = \gamma_1^0 = 1, \tag{17}$$

$$\ln \gamma_2^0 = 0, \quad \gamma_2 \left( X_1 \to 0 \right) = 1, \tag{18}$$

$$\ln \gamma_1^{ass} \approx \sum_{i=2} i \Lambda_i X_1^{i-1},\tag{19}$$

$$\ln \gamma_2^{ass} \approx \sum_{i=2} \left( 1 - i \right) \Lambda_i X_1^i.$$
<sup>(20)</sup>

This normalization scale will always be used by us as the default.

Let us introduce the function  $G^{mix}/RT$  (divided by RT molar Gibbs energy of mixing), the second isothermal – isobaric concentration derivative of which is equal to the full solution molar Gibbs energy:

$$G^{mix}/RT = X_1 \ln X_1 + X_2 \ln X_2 + X_1 \ln \gamma_1 + X_2 \ln \gamma_2,$$
(21)

 $\partial \left[ G^{mix} / RT \right] / \partial X_1 =$ 

$$1/X_1 + 1/X_2 - (\ln X_2 + 1) + \sum_{i=1}^{i} i^2 \Lambda_i X_1^{i-1} + \sum_{i=2}^{i} (1-i) \Lambda_i \left[ i (i-1) X_1^{i-2} - (i+1) X_1^{i-1} \right], \quad (22)$$

$$\partial^2 \left[ G^{mix-ass}/RT \right] / \partial X_1^2 \approx 1/X_1 + \sum_{i=2} i \left( i - 1 \right) \Lambda_i X_1^{i-2}.$$
 (23)

In a completely similar manner, we can calculate (divided by RT) first isothermal – isobaric concentration derivative of the chemical potential or logarithm of the activity of the 1-st component –  $\mu_1$  and  $\ln a_1$ , correspondingly:

$$1/RT \left( \partial \mu_1 / \partial X_1 \right) = \left( \partial \ln a_1 / \partial X_1 \right) \approx 1/X_1 + \sum_{i=2} i \left( i - 1 \right) \Lambda_i X_1^{i-2}.$$
 (24)

So, the equation of the diffusional (spinodal) stability loss will be the following:

$$G_{11}^{mix-ass} = \partial^2 \left[ G^{mix-ass} / RT \right] / \partial X_1^2 = (\partial \ln a_1 / \partial X_1) \approx 1 / X_1 + \sum_{i=2}^{i} i (i-1) \Lambda_i X_1^{i-2} = 0.$$
(25)

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## 5. Application of VD-AS model to the description water soluble derivatives of light fullerenes water solutions. Calculation of nanoclusters excess functions. Miscibility gaps

Preliminary calculations show, that the 3-term approximation in the VD-AS – model (i.e. i = 2, 3, 4) is sufficient for more or less successful for the excess thermodynamic functions calculation with the satisfactory accuracy:

$$\ln \gamma_1^{ass} \approx 2\Lambda_2 X_1 + 3\Lambda_3 X_1^2 + 4\Lambda_4 X_1^3, \tag{26}$$

$$\ln \gamma_2^{ass} \approx -\Lambda_2 X_1^2 - 2\Lambda_3 X_1^3 - 3\Lambda_4 X_1^4.$$
(27)

So, the equation of the diffusional (spinodal) stability loss will be the following:

$$12\Lambda_4 X_1^3 + 6\Lambda_3 X_1^2 + 2\Lambda_2 X_1 + 1 = 0, (28)$$

or is explicitly elementarily solved relative to  $X_1$  (according to Cardan formula) cubic equation.

All calculated parameters for the VD-AS – model are represented in Table 2.

In all considered binary systems, we calculated the concentration dependencies  $\ln \gamma_{H2O}$  (see Table 1):

$$\ln \gamma_2 = \ln \gamma_{H2O} = \ln a_{H2O} - \ln X_{H2O} = \ln a_{H2O} - \ln(1 - X_1), \tag{29}$$

and from these functions,  $\ln \gamma_2(X_1)$ , according to equation (27) and we determined parameters of VD-AS model:  $\Lambda_2$ ,  $\Lambda_3$ ,  $\Lambda_4$  (see Table. 2).

TABLE 2. Parameters of model VD-AS ( $\Lambda_2$ ,  $\Lambda_3$ ,  $\Lambda_4$ ) and concentration boards of diffusion instability regions ( $X^{diff-instab}$ ) in the binary system:  $C_{70}(C_6H_{13}N_2O_2)_2 - H_2O$  272.00–273.15 K

VD-AS model parameters (rel.un.)					
$\Lambda_2$ (relun.) $\Lambda_3$ (relun.) $\Lambda_4$ (relun.) $\approx X^{diff-instab}$ (rel.u.)					
$1.58 \cdot 10^{6}$	$-1.40 \cdot 10^{10}$	$4.15 \cdot 10^{13}$	$6.0 \cdot 10^{-5}$		

Formally, the huge values for the summary virial coefficients  $\Lambda_i$  in general are not surprising, if we remember that, according to the physical sense, they are the sums of the rows, consist of probably thousands terms, responsible for the energies of interactions of a few nano-clusters with a very large number of water molecules.

Then, according to the equation (26), we calculated the concentration dependencies  $\ln \gamma_1^{ass}(X_1)$  (See Table 1 and Fig. 3). From Fig. 3, one can see that some dependencies  $\ln \gamma_1^{ass}(X_1)$  will cross through the maximum at the values:  $X_1 \approx 1.5 \cdot 10^{-4}$  rel. un. (in our case it occurs slightly out of the investigated concentration range). The maximum state may be easily determined from equation (26), solving square equation:

$$1/2d\left(\ln\gamma_1^{ass}/dX_1\right) = \Lambda_2 + 3\Lambda_3 X_1 + 6\Lambda_4 X_1^2 = 0.$$
(30)

Then, according to the equation (28), we determined the boards of diffusional stability loss –  $X^{diff}$  (see Table 2 and Fig. 4), solving cubic equation:

$$F = 12\Lambda_4 X_1^3 + 6\Lambda_3 X_1^2 + 2\Lambda_2 X_1 + 1 = 0.$$
(31)

As one can see from Table 2, all cubic equations (28) for our considered systems have real positive roots in real concentration ranges, which correspond to the existence of liquid solutions of nano-clusters in water. From this fact, one can conclude that at some concentration range:  $X_1^{diff} \approx 6.0 \cdot 10^{-5}$  rel. un. the system begins to display flaking, or perhaps pre-flaking (see later). In Fig. 4, the concentration dependencies of the diffusional instability functions  $F^{diff-instab} = 12\Lambda_4 X_1^3 + 6\Lambda_3 X_1^2 + 2\Lambda_2 X_1 + 1$  are represented. From Fig. 4, we see that almost all functions  $F^{diff-instab}(X_1)$  have intersections with the abscissa axis, which corresponds to diffusional stability loss.



FIG. 3. Logarithm of light fullerene water soluble derivative activity coefficient  $(\ln \gamma_i)$  against molar fraction concentration in the binary solutions  $C_{70}(C_6H_{13}N_2O_2)_2 - H_2O$  at 272.99–273.15 K



FIG. 4. Instability board function F against molar fraction concentration in the binary solutions:  $C_{70}(C_6H_{13}N_2O_2)_2 - H_2O$  at 272.99–273.15 K

#### 6. Conclusions

- (1) The temperature of water-ice crystallization initiation decreases in the binary water solutions of water soluble derivative of light fullerene  $C_{70}$  with the amino-acid lysine were determined at 272.99–273.15 K.
- (2) Partial molar excess functions for  $H_2O$  were calculated.
- (3) For the thermodynamic description of our system, we have elaborated original semi-empirical model VD-AS, based on the virial decomposition of molar Gibbs energy of the component molar fractions in the solution.
- (4) With the help of VD-AS model partial molar functions of nano-clusters, excess and full average Gibbs energies for the solutions and miscibility gaps concentration regions were calculated.

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