CONFERENCE ABSTRACTS

International Student Conference

“Science and Progress”

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St. Petersburg — Peterhof
November, 9–11
2021

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International Student Conference “Science and Progress” —
SPb.: SBORKA, 2021-224 p.p.
ISBN 978-5-85263-109-1

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A. Chemistry

Supramolecular Assemblies Analysis Using Machine Learning Image Processing

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Supramolecular self-assembly is a potential tool for trapping systems of active components [1]. Supramolecular chemistry is based on the formation of large clusters linked by non-covalent bonds.

Thus, two supramolecular self-assemblies' melamine cyanurate and melamine barbiturate are binary assemblies linked by hydrogen bonds into spatial structures [2].

These supramolecular self-assemblies can capture and store active organic molecules, including organic dyes [3].

It is not necessary to use only UV-Visible spectroscopy to analyze how efficiently a staining component or fluorophore is encapsulated into a supramolecular assembly. So, based on data from an optical fluorescence microscope, we get a database of images.

So, capsules of supramolecular self-assemblies, depending on the amount of the introduced fluorophore, have different sizes and luminescence intensity.

Using machine learning methods, we can characterize even samples with particles that are difficult to separate by the eye. We have created a database for more than four low concentrations (below 10pM) of the injected component with a fluorophore, reaching an accuracy of more than 82%.

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Simulation of the Li-Ion Battery Overcharge Protected by Voltage-Switchable Resistive Polymer Layer

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Recently, a new approach to overcharge protection of Li-ion batteries by voltage-switchable resistive polymer layer, placed between the cathode active mass and the current collector, was reported [1]. The unique feature of the layer under consideration is the ability to increase the electrode resistance when the cathode potential exceeds operating limits, preventing cell overcharge and degradation.

Here we simulate different overcharging modes applicable to system under consideration by extending the full-order Newman model of a lithium-ion battery cell by adding a description of the novel type of overcharge protection layer. The extended model was used to simulate Constant Current, Constant Voltage, and Constant Power charging modes as well as thermal effects and was implemented in Multiphysics (MP) software (COMSOL Inc., Palo Alto, CA). Comparison of electrochemical responses in the simulated modes demonstrated that the cell protected by the voltage-switchable resistive polymer layer has advantages when operating at any mode. Therefore, this simulation study proves the usefulness of the protective layer with switchable resistance. Moreover, this model is a powerful tool for material design and engineering tasks in LIB and other metal-ion batteries development as it allows fast and simple estimation of resistance and other parameters' values that meet a given safety standard.

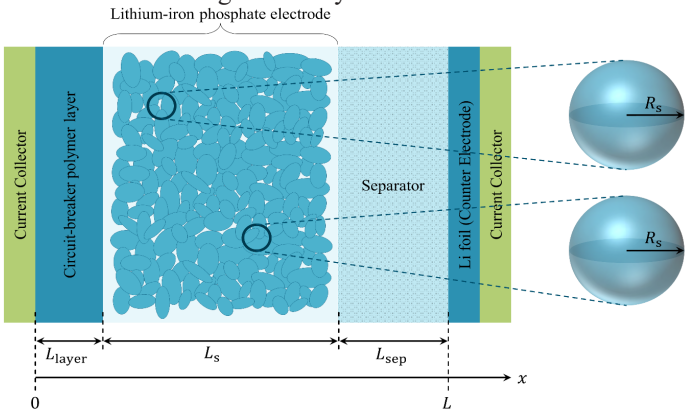

Fig. 1. Schematic of the half-cell configuration.

Acknowledgments: This work was supported by RSF. The authors are grateful to Saint-Petersburg State University Research Park.

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Local Delivery of Antibiotics in the Surgical Treatment of Bone Infections

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Currently, the number of surgeries for endoprosthesis of large joints and metal osteosynthesis is growing, as a result of which there an increase in complications are associated with the formation of bone tissue defects. When treating such defects, it is necessary to have biomaterials that can degrade in the environment of the human body and, as they are resorbed, be replaced by new natural bone tissue [1].

At the present stage of the development of surgery and dentistry, materials based on calcium phosphates are widely used to restore human bone tissue. There is a need to improve their physicochemical (mechanical, optical, sorption) and biochemical properties. It is believed that ideal calcium phosphate implants, ceramics, and dental cement should have a structure, composition, and morphology identical to human bone [2]. Also, a potential problem that arises during treatment is the risk of developing infectious complications due to bactericidal infections, therefore, an important advantage of biomaterials is antimicrobial properties to fight infections. The antimicrobial activity of biomaterials can be ensured by introducing substances into the composition that exhibit antimicrobial activity, for example, as tetracycline and gentamicin.

The purpose of this work was the development of hydroxyapatite, which has an antibacterial effect, and the study of its properties.

For materials used in regenerative medicine and bone implantology, an important property is the resorption of hydroxyapatite in saline. The rate of the resorption will be directly related to the microstructure and physicochemical characteristics of composite materials. Therefore, studies were carried out to identify the phase content of the materials fabricated via the diffusion method in agar matrix in a presence of antibiotics at 25°C. The concentration of calcium in saline was determined by titrimetry using Trilon B and Eriochrome Black T.

As a result, a system based on hydroxyapatite was developed, which has an antibacterial effect, and the amount of calcium ions Ca^{2+} passed into the solution was calculated.

Acknowledgments: Authors acknowledge RSF grant no.19-79-10244 for the financial support.

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Microplasma-assisted Synthesis of Iron Oxide for Battery Application

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Lithium-ion batteries have attracted widespread attentions because of their high storage capacities, stable cycling and high safety. However, the low theoretical capacity of conventional graphite anode material (372 mAh/g) has inhibited the further application for next-generation high-energy batteries. Iron oxides are attractive anode materials due to their natural abundance, high capacity, eco-friendly and low cost. However, they exhibit rapid capacity degradation and inferior cycling stability. One of the most effective methods, which has been employed to surmount the above issues, is to minimize the particles size down to the nanoscale.

In recent years, plasma in contact with liquid has attracted much attention for synthesis of nanoparticles with different morphology. In this research, we applied plasma in contact with liquid to synthesize amorphous iron oxide (Fe_xO_y) and to investigate it as a promising anode material. Some results are presented in Fig. 1. SEM analysis of Fe_xO_y showed that nanoparticles had "spiky" structure with a 20 nm diameter. The spike thickness was about 1-3 nm. Material demonstrated a good cycling stability at 0.3 A/g. The capacity decline was observed before 30 cycle, that could be related to the solid electrolyte formation. After 30 cycle capacity rapidly increased to 632 mAh/g at 550th cycle.

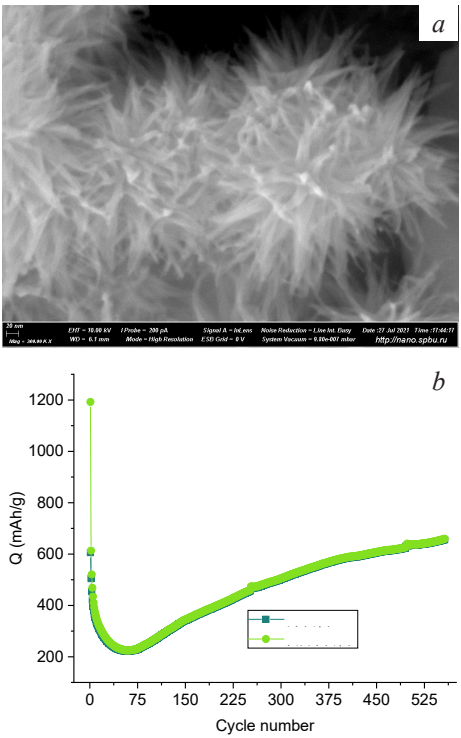

Fig. 1. SEM image of Fe_xO_y (a); cycling stability at 0.3 A/g, 0.01 – 2.85 V (b)/

Acknowledgments: This research was funded by RFBR, grant number 20-53-04010 and by BRFFR, grant number F21RM-104. The authors are grateful to Saint-Petersburg State University Research Park.

High-performance Liquid Chromatography (HPLC) as a Reference Method for Antibiotic Detection

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Currently, antibiotics are widely used in animal husbandry for the treatment of livestock, as growth stimulants, or as feed additives. Despite the advantages of their use, an increased concentration of antibiotics can also be observed in the final products consumed by humans: for example, in meat or milk. The presence of an antibiotic in food can cause serious risks for consumer's health including toxic lesions of the liver, kidneys, hematopoietic organs, neuritis of the auditory nerve, allergies, tendon ruptures, and in combination with certain medications lead to the development of severe cardiac arrhythmias. Of course, the concentration of any antibiotic in a particular product should not exceed the established threshold value. In our other works, we use potentiometric methods, for example, the method of cyclic voltammetry to determine the residual concentration of antibiotics. However, they are not accurate enough, so another method, such as high-performance liquid chromatography (HPLC), must be used as the reference method.

The essence of this method is the extraction of antibiotics from the product sample, purification of the extract, and determine the residual amount of antibiotics in the extract by HPLC coupled with DAD mass spectrometry. Chromatographic separation of the preparations on an X-ray column was achieved using a mobile phase containing an aqueous phase and an organic phase. After that, the HPLC-DAD method was in-house validated for the determination of the tetracyclines by evaluating the following parameters: selectivity, linear range, linearity, sensitivity, intra- and inter-assay precision, accuracy.

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Laser-Induced Deposition of Periodic Structures from Silver Nanoparticles for SERS Applications

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In recent years, much attention has been focused to the formation of noble metal nanostructures. This is mainly due to the possibility of using them as plasmonic platforms and nanosensors [1]. Periodic structures of silver NPs are promising for SERS, where Raman spectra can be enhanced by several orders of magnitude due to several mechanisms.

As an approach for obtaining periodic arrays of Ag nanoparticles, the method of laser-induced deposition (LID) from the $C_7H_5AgO_2$ metal-organic complex was chosen, and an Nd:YAG laser with a wavelength of 266 nm and a power of 40 mW was used as a laser radiation source. Periodic arrays were obtained as a result of LID with interference patterns of laser beams. As an analyte, alcohol solutions of Riboflavin was used. A wide concentration range was studied from 10^{-9} M/L to 10^{-6} M/L.

Scanning electron microscopy showed the spatial distribution of nanoparticles (Fig. 1, a). The average size of nanoparticles is 60-80 nm. The grating period is 2 μm. The obtained substrates with homogeneously distributed Ag NPs and their periodic arrays demonstrated SERS of the Riboflavin solutions (Fig. 1, b).

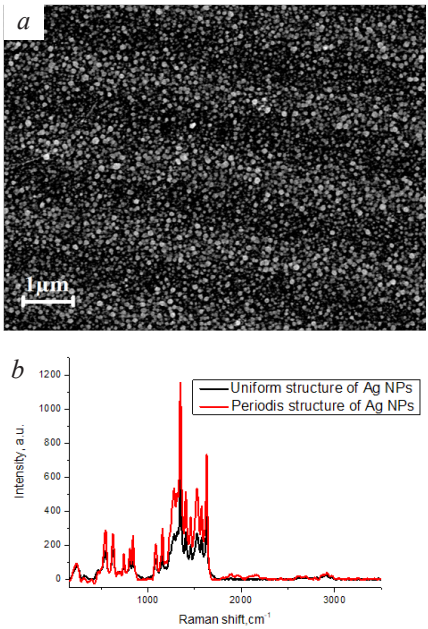

Fig.1. a) SEM image of the grating; b) Raman spectra demonstrated SERS of the Riboflavin solutions.

Acknowledgments: This work was supported by RFBR-DFG (RFBR project № 20-58-12015). Optical measurements were carried out using the equipment of the resource center «Optical and laser methods for studying matter», morphology and composition studied at the Interdisciplinary Resource Center in the direction «Nanotechnology» SPBU.

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Synthesis of Luminescent $NaYF_4:Sm^{3+}$, $NaYF_4:Yb^{3+}$, Ho^{3+}, $NaYF_4:Tb^{3+}$ Small-Sized Particles

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The photoluminescence is emission in the optical range of the visible, ultraviolet, or infrared light by the substance resulted from the light absorption. The luminescent compounds, so-called phosphors, are used almost everywhere in modern life. In medicine, nanosized luminescent materials are used as bioimaging probes in numerous cancer studies. It is known that fluorinated compounds of rare earth metals have pronounced luminescent properties. In this work, we studied the properties of small-sized particles based on $NaYF_4$ doped by Sm^{3+}, Ho^{3+}, Yb^{3+}, and Tb^{3+} ions.

The following materials were synthesized by hydrothermal method at 180°C: $NaY_{(1-x)}Sm_xF_4$, $NaY_{(0.8-x)}Ho_xYb_{0,2}F_4$, $NaY_{(1-x)}Tb_xF_4$. The morphology of the particles was studied using scanning electronic microscopy (SEM). The particles in the samples are hexagonal prisms with a diameter of 550-850 nm. An increase in the concentration of samarium, ytterbium, and terbium ions leads to a decrease in particle sizes. X-ray diffraction analysis demonstrated that all samples have a crystal phase of β-$NaYF_4$. An increase in the concentration of samarium, ytterbium, and terbium leads to an increase in the unit cell.

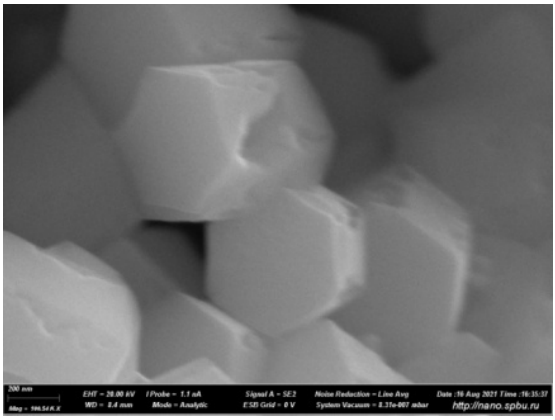

Fig. 1. SEM image of the sample $NaY_{0,98}Sm_{0,02}F_4$.

The samples doped by samarium and terbium ions demonstrate down-conversion red and green emission, respectively, upon UV excitation. The samples co-doped by ytterbium and holmium ions demonstrate up-conversion red emission upon IR excitation. The optimal concentration of dopant ions corresponding the brightest emission was determined in this work.

Acknowledgments: The authors are grateful to Saint-Petersburg State University Research Park.

Topology of an Electron Density and Electrostatic Potential Distribution Along the Bond Path for Evaluation of Halogen Bond's Strength

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Halogen bond (XB) belongs to the class of so-called σ-hole interactions. In Bader's QTAIM approach (Quantum Theory of Atoms in Molecules [1]) the topological analysis of XB's electron density (ED) yields bond path which follows the maximal gradient of ED between two interacting atoms through the (3; –1) critical point. Along the bond path both ED and total electrostatic potential (ESP) go through minima. In work [2] it was shown that the ED minimum is located closer to the electrophile halogen atom, while ESP minimum – to the electron-donating nucleophile atom. (Fig. 1).

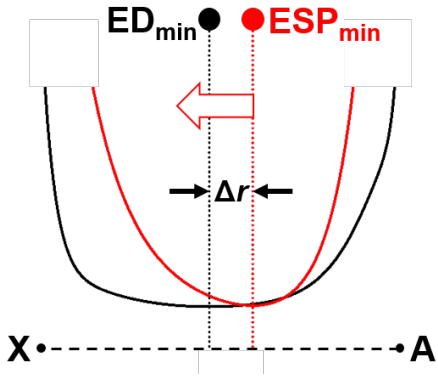

Fig. 1. Schematic representation of a possible relative position of ED and ESP minima for X···A halogen bond. Δr is a distance between two minima. The red arrow points to the electrophilic site provider.

In this computational work (M06-2X/def2-TZVPPD) we investigated how the distance between ED and ESP minima – Δr – changes upon strengthening of a XB. As model systems we considered a set of 116 complexes RX···$OPMe_3$ (where RX – various halogen donors in organic and inorganic molecules) and analyze electronic distribution along the XB.

Acknowledgments: This work was supported by RSF grant number 18-13-00050.

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Novel High-Performance Blend Hydroxyethyl Cellulose/ Sodium Alginate Membranes with Fullerenol for Enhanced Pervaporation Dehydration

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Nowadays, the development of membrane technologies as sustainable processes is necessary for various industrial fields to solve environmental problems. One of the perspective membrane methods for separation of liquid mixtures of low molecular weight substances is pervaporation. It may be an alternative to traditional separation methods, especially for the separation of azeotropic mixtures and dehydration. The development of highly efficient pervaporation membranes based on biopolymers with tailored properties is the most important task for pervaporation, in connection with the strengthening of control over the impact of production on the environment.

In this work biopolymers - hydroxyethyl cellulose (HEC) and sodium alginate (SA) were chosen as membrane materials to develop green high-performance blend membranes for pervaporation dehydration. To obtain membranes with improved properties, various methods were used: (1) the selection of the optimal composition of biopolymers in the membrane, (2) the selection of the optimal cross-linking method, and (3) the bulk modification by introducing of fullerenol nanoparticles into the blend membrane matrix. Structure of the membranes was investigated by spectroscopic (FTIR) and microscopic (SEM and AFM) methods. The physico-chemical properties were studied by measurements of contact angle and swelling degree. Transport properties of developed HEC/SA membranes were evaluated in pervaporation dehydration of isopropanol in a wide concentration range. It was demonstrated that a cross-linked supported membrane based on HEC/SA/fullerenol (5%) composite possessed the improved transport characteristics.

Acknowledgments: This work was supported by Russian Science Foundation [project No 20-79-10064]. The experimental work of this study was facilitated by the equipment from the Resource Centre of Geomodel, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Methods, Magnetic Resonance Research Centre, Centre for Innovative Technologies of Compo-site Nanomaterials, Nanophotonics Centre, Cryogenic department, Thermo-gravimetric and Calorimetric Research Centre and the Interdisciplinary Re-source Centre for Nanotechnology at the St. Petersburg State University.

Computational Study of Synthetic Routes Towards $PH_2BH_2EH_2$ (E = C, Si, Ge, Sn) Complexes

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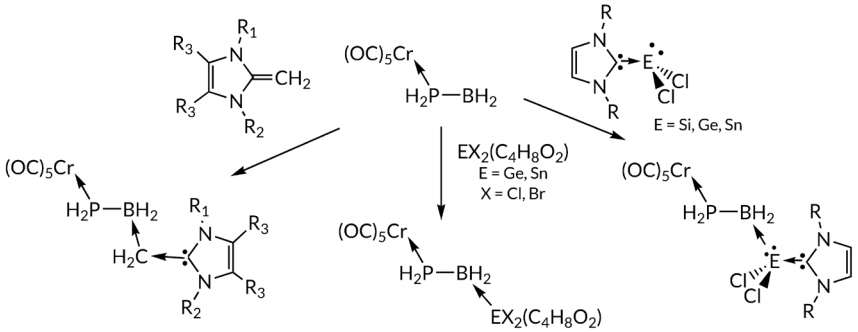
The compounds with combination of group 13/14/15 elements in a chain and only hydrogen substituents (parent compounds) are of high interest due to their potential use as single-source precursors for ternary materials for small band gap optical devices [1] and in construction of inorganic polymers – alternatives to the established organic-based polymers [2]. In contrast to parent compounds of group 13/15 and 14/15 elements, which complexes with Lewis acids and Lewis bases were synthesized, complexes of $E^{(15)}H_2E^{(13)}H_2E^{(14)}H_2$ are unknown up to now.

In order to define the optimal reagents for syntheses of $PH_2BH_2EH_2$ (E – group 14 element) complexes the computational study of three synthetic routes was carried out at B3LYP-D3/def2-TZVP level of theory (Scheme 1).



Scheme 1.

Almost all considered reactions (besides the reaction with $SnCl_2{\cdot}C_4H_8O_2$) are thermodynamically more favorable than the side processes of $Cr(CO)_5{\cdot}PH_2BH_2$ di- and trimerization with H_2 elimination in the gas phase. We propose three N-heterocyclic olefins (^{Me}IDippCH$_2$, Im(Me)(*i*-Pr)CH$_2$, Im(*i*-Pr)$_2$CH$_2$) for the synthesis of $PH_2BH_2CH_2$ complex, and $SiCl_2{\cdot}$IDipp and $GeCl_2{\cdot}$IDipp for the first step in the syntheses of $PH_2BH_2SiH_2$ and $PH_2BH_2GeH_2$ complexes.

Acknowledgments: This work was supported by the joint grant of RSF and DFG (RSF project No 21-43-04404). The use of the equipment of the Resource Center "Computer Center SPbU" is gratefully acknowledged.

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Features of the Dependence of Retention Indices on the Content of Methanol in an Eluent in Reversed Phase HPLC

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One of the important problems of contemporary instrumental analytical chemistry is the formation of hydrates of organic compounds in aqueous solutions (1), e.g., in conditions of reverse phase (RP) HPLC. However, the direct detecting the formation of hydrates by chromatographic or mass spectrometric methods seems to be impossible due to the instability of most of them.

$$X + nH_2O \leftrightarrows X{\times}nH_2O \quad (1)$$

In a previous study to solve this problem, an indirect approach was used to confirm the formation of hydrates; it is a recurrent approximation of retention parameters of analytes [1]. Besides that, important additional information can be obtained by using the concept of retention indices (RI) in RP HPLC measured in the scale of reference *n*-alkyl phenyl ketones $C_6H_5COC_nH_{2n+1}$:

$$RI_x = RI_n + (RI_{n+1} - RI_n)\,[\log t'_{R(x)} - \log t'_{R(n)}] / [\log t'_{R(n+1)} - \log t'_{R(n)}] \quad (2)$$

However, the RI values themselves do not provide any information indicating the formation of hydrates in an eluent, but the dependence of RIs on concentrations of organic component in an eluent (3) seems to be more informative:

$$RI = aC + b \quad (3)$$

The coefficients a and b are calculated by LSM, a = dRI/dC.

If we use methanol as the organic component of an eluent, the following regularity was revealed. The coefficients a = dRI/dC for hydrophobic analytes usually have large positive values, while these values for more hydrophylic analytes may be close to zero, or negative, as it is illustrated by table:

Table.1. Parameters of linear regression (3) for some hydrophobic and hydrophilic organic compounds.

Compound	Formation of hydrate	Mol. wt.	a = dRI/dC	b = RI at (C=0)	R
Toluene	No	92	4.0 ± 0.1	851 ± 8	0.99
o-Xylene	No	106	4.6 ± 0.3	911 ± 20	0.98
Phthalimide	Possible	137	-0.2 ± 0.0	708 ± 3	-0.95
Diethyl-*m*-toluamide	Possible	191	-2.0 ± 0.1	1050 ± 6	-0.99

The dependence of retention indices of analytes *vs* concentration of organic component of an eluent (3), we used as indirect method to confirm the forma- tion of hydrates of organic compounds in RP HPLC conditions.

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Development and Study of Novel Blend Hydroxyethyl Cellulose (HEC)/Polyvinyl Alcohol (PVA) Membranes Modified with Fullerene Derivatives for Pervaporation Dehydration

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The introduction of membrane processes in various fields of industry, in particular, pervaporation for the dehydration of alcohols, requires the development of novel membrane materials with the tailored properties. Pervaporation is one of the most perspective membrane processes actively applied for the separation of low molecular weight components, including isomer and azeotropic mixtures. Active development of pervaporation for the dehydration of alcohols is due to their active use as a promising alternative fuel, in cosmetics, fluids for cars, cleaning and disinfectants, etc. One of the promising ways to obtain a membrane material with improved properties is the development of the mixed-matrix membranes (MMMs): blending of well-known polymers and modification with nanoparticles to combine the advantages of polymers and a modifier.

In this work novel blend membranes based on hydroxyethyl cellulose (HEC)/polyvinyl alcohol (PVA) modified with water-soluble fullerene derivatives (polyhydroxylated fullerene (fullerenol), fullerene derivative with L-arginine and carboxyfullerene) were developed for enhanced pervaporation dehydration of alcohols. The structural features and physicochemical properties of HEC/PVA and HEC/PVA/fullerene derivative membranes were investigated by FTIR spectroscopy, scanning electron (SEM) and atomic force (AFM) microscopies, thermogravimetric analysis (TGA), measurements of contact angle and swelling degree. The obtained membranes were tested in pervaporation dehydration of isopropanol. It was demonstrated that the introduction of fullerene derivatives into the HEC/PVA matrix led to significant improvement in transport properties of membranes.

Acknowledgments: This work was supported by the Russian Science Foundation [grant № 20-79-10064]. The experimental work of this study was facilitated by the equipment from the Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Methods, Nanophotonics Centre, Cryogenic department, Thermogravimetric and Calorimetric Research Centre and the Interdisciplinary Resource Centre for Nanotechnology at the St. Petersburg State University.

Nanostructuring of Screen-Printed Electrodes by Prussian Blue and Polyelectrolytes Layers for Biosensoring

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Prussian blue (ferric ferrocyanide) is the part of an important group of inorganic compounds used in electrode modification. Prussian blue is used as an electronic transfer mediator and allows for an electrochemical reaction in the kinetic region of the electrode even when applying several layers of polyelectrolytes, which allows the use of such an electrode in any solutions.

Prussian blue is known as an artificial peroxidase, and it is a promising candidate for the catalysis of H_2O_2. Electrochemical sensors for H_2O_2 detection are developed by adding electroactive materials (metals, metal oxides, enzymes) on the surface of electrodes. Hydrogen peroxide is a mediator found in many biological reactions [1].

Carbon-based electrodes, such as screen-printed carbon electrodes (SPCEs), are the most common working electrodes used for the electrochemical sensing of various biological substances. Their success is mainly due to the minimum necessary overpotential required for the estimation of for these substances and the possibilities of mediator modification.

The screen-printed carbon electrode is modified with water-soluble polymers (polyethelimine and poly(sodium-4-styrensulfonate)), previously used for the determination of zinc in human biological fluids [2], by layer-by-layer method. Polyelectrolytes contribute to the immobilization of biologically active substances on a carbon electrode, that allows to prevent their leakage into the analyzed solution.

The paper studies the possibility of varying the content of Prussian blue and polyelectrolytes layers to obtain the optimal samples of electrochemical sensors for further using in biosensoring. The variation of the layers is carried out by changing the concentration of the initial solutions of Prussian blue and polyelectrolytes and the settings of the potentiostat during the modification of the electrode.

This method provides an opportunity to create unique biosensors in medicine to detect pathogens of infectious diseases and monitor human health

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Electrochemical Sensor for Detection of Staphylococcus Aureus

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The main advantage of rapid detection of the disease is its timely treatment and the ability to avoid serious consequences. Staphylococcus aureus is one of those bacteria that causes many diseases that can harm both the skin and spread in the human body and be detected already at late stages.

The basis for detection is a sample received from a person and its processing in real time on a miniature device, for constant monitoring.

In electrochemical sensors, the analytical signal is the formation of a complex with a system polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS) converted into an electrical signal, such as an electric current or a potential difference.

Fibrous materials are widely used in the field of electrochemistry and composite materials because of their carrier mobility, electrical conductivity, environmental stability, excellent mechanical properties, low weight, and high-temperature resistance, as well as the possibility [1]

We have developed a sensor with high accuracy and low detection limit of Staphylococcus aureus. This development is necessary to control and reduce the incidence of people. The main feature is the ability to make this development streaming, as it has a low cost.

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Study of Photocatalytic Activity of Butylamine-intercalated Perovskite-like Layered Oxide $H_2La_2Ti_3O_{10}$

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Layered perovskite-like oxides are complex oxides that consist of alternating perovskite blocks and blocks of different structure. They are attractive research objects due to the peculiarities of their structure and several unique properties, particularly the ability to intercalate molecules into the interlayer space, ion-exchange reactions, and delamination into the nanolayers. These properties not only determine the high photocatalytic activity of some representatives of this class of compounds but also open up many possibilities for their modification, for example, for the creation of hybrid and composite photocatalysts.[1, 2]

The present work is devoted to study of the photocatalytic activity of the triple-layered perovskite-like titanate $H_2La_2Ti_3O_{10}$ intercalated with n-butylamine in the reaction of hydrogen production from an aqueous methanol solution under UV light. Effects of alcohol concentration, catalyst amount, platinum loading, pH of suspension and temperature on the photocatalytic efficiency were investigated. It was shown, that the reaction rate gradually increases almost 10 times when the solution pH is changed from basic (pH = 12) to acidic (pH = 2). The dependence of the hydrogen evolution rate on the concentration of methanol, the loading of platinum and the amount of catalyst all demonstrate a maximum, while the change of temperature has almost no effect on the reaction rate. An apparent quantum efficiency of 44% was observed under optimal conditions.

Acknowledgments: This work was supported by the Russian Science Foundation (project No 19-13-00184). Authors are also grateful to Saint Petersburg State University Research Park: Center for X-ray Diffraction Studies, Center for Thermal Analysis and Calorimetry, Center for Chemical Analysis and Materials Research, Interdisciplinary Center for Nanotechnology, Magnetic Resonance Research Centre.

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Synthesis and Structures of $SnCl_4$ Complexes with 4,4'-bipyridine

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$SnCl_4$ forms donor-acceptor complexes with nitrogen-containing ligands due to its ability to accept a lone pair [1, 2]. Unlike complexes of tin tetrachloride with pyrazine [3], complexes with 4,4'-bipyridine (bipy) are unknown. In the present work we report syntheses and characterization of complexes in $SnCl_4$ - 4,4'-bipy system.

Since $SnCl_4$ is unstable on air, all operations were carried out in evacuated systems. The valve containing components was kept at 106-141 °C for a week and after that excess of tetrachloride was removed under vacuum. The $SnCl_4$:bipy ratio was 1.35:1. Single crystals of the complex were grown by sublimation in vacuum at 235-255 °C for two weeks. Structural characteristics were determined by the X-ray structural analysis. The complex is a 1:1 linear polymer $(SnCl_4 \cdot 4,4'\text{-bipy})_\infty$ (Fig. 1).

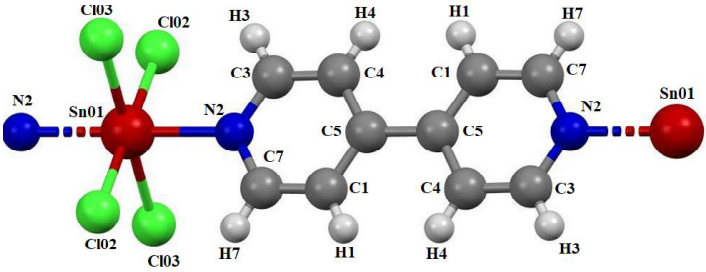

Fig. 1. The structure of the $[SnCl_4 \cdot bipy]_\infty$ *in the crystal.*

The complex was additionally characterized by IR spectroscopy and mass spectrometry. After keeping the complex at circa 260 °C for six weeks, single crystals of several new compounds were discovered and structures of $[H_2bipy][SnCl_4]$, $[H_2bipy]_2[SnCl_4][SnCl_6]$, $[(H_2bipy)_3Sn_{4.5}Cl_9]Cl_6$ and $SnCl_2(bipy\text{-}H)_2$ were determined. Formation of such complexes indicates reduction of $SnCl_4$ upon thermolysis.

Acknowledgments: This work was supported by the RSF grant 18-13-00196. The authors are grateful to SPSU Research Park and to Michael Seidl, University of Regensburg, for performing X-ray structural analysis.

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Synthesis and Electrocatalytic Activity of Nitrogen- and Transition Metal-doped Carbon-based Materials

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The development of active and efficient catalytic materials for electrochemical oxygen reduction reaction (ORR) is an important and challenging task. Among existing, Pt-based catalysts are the most efficient, however they are expensive and suffer from low stability. One of possible replacements of noble-metal catalysts are mixed materials, based on carbon and impregnated with nitrogen and transition metals. These materials are inexpensive and exhibit high efficiency in ORR [1, 2].

This work comprises description of synthesis, structure characterization and study of electrochemical efficiency in ORR of several obtained compounds. Suggested catalytic materials are prepared via hydrothermal synthesis of initial composition with subsequent pyrolysis. Initial composition consists of polyacrylonitrile, transition metal (Co or Cu) salt and organic ligand. This method allows to obtain homogenous and high-porous solid substances that contain carbon-nitrogen-metal (C-N-M) complexes, which have been shown to exhibit good performance in ORR catalysis.

Acknowledgments: This research was funded by the Russian Foundation for Basic Research, grant number 20-03-00746 a. Scientific research was partially performed at the Research park of St. Petersburg State University: Thermogravimetric and Calorimetric Research Centre, Centre for Physical Methods of Surface Investigation, Interdisciplinary Resource Centre for Nanotechnology, Cryogenic department.

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Enhancement of the Electrochemical Performance of δ-MnO_2 Electrodes by Introducing Conducting Polymer

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In recent years aqueous zinc-ion batteries (AZIBs) have attracted special attention because of high abundance of zinc, low oxidation potential (0.76 V vs SHE) and high theoretical capacity. The development of novel high-capacitive and stable cathode materials for AZIBs is on the top of research. Among different types of cathode materials manganese dioxide MnO_2 has been regarded as a promising cathode material for AZIBs, due to its environmental friendliness, abundant resources, high theoretical capacity, and relatively wide working voltage. Layered-type manganese oxide δ-MnO_2 is perspective cathode material because of large interlayer distance ((near 7 Å) which would facilitate Zn^{2+} ions intercalation and improve the cycling performance [1]. Nevertheless, the electronic conductivity of MnO_2 is low (near 10^{-6} $S \cdot cm^{-1}$).

To overcome this drawback and enhance the electrochemical performance of δ-MnO_2-based cathode materials, different types of conductive additives were used like carbon-based materials [2] or conducting polymers [3].

In this work, we used two ways for creation δ-MnO_2-based electrodes with conducting polymer: i) introducing the chemically obtained poly(3,4-ethylenedioxythiophene) (PEDOT) in the electrode composition and ii) coating of MnO_2 powder by aqueous dispersion of PEDOT with polystyrene sulfonate (PEDOT:PSS). To evaluate the electrochemical properties, cyclic voltammetry and galvanostatic charge/discharge techniques were applied.

We obtain that both composite electrodes with conducting polymer additive demonstrate higher capacity values than pristine δ-MnO_2 cathodes in a wide current range. At low current densities a continuous increasing of current is observed which associated with formation of electroactive ε-MnO_2 layer on the electrode surface. Stability during long cycling is also higher for modified δ-MnO_2 electrodes.

Acknowledgments: This work was supported by RFBR (#21-53-53012). The authors would like to thank the Center for X-ray Diffraction Methods and the Interdisciplinary Center for Nanotechnology of Research Park of Saint Petersburg State University.

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Crystal-chemical Design of Gold(I) Complexes with Isocyanide Ligands

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The work studied monoisocyanide complexes of gold(I) with halogen-substituted arylisocyanide ligands (Fig. 1). The choice of halogen-substituted arylisocyanides is due to the fact that in the solid phase compounds can aggregate to form a combination of aurophilic interactions and halogen bonds [1]; in this case, the type and energy of halogen bonds will act as a structure-determining factor that sets the general packing motif and thereby determines the parameters of aggregate-induced luminescence.

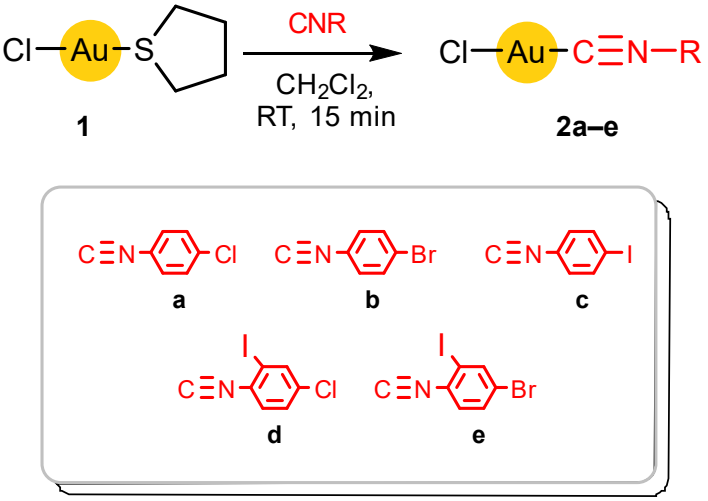

Fig. 1. Scheme of the synthesis of gold(I) halide complexes with isocyanide ligands.

The study of gold(I) complexes with halogen-substituted aryl isocyanide ligands showed that in the solid phase they can aggregate to form a combination of aurophilic interactions and/or halogen bonds. All synthesized compounds exhibit photoluminescence in the range of 400–500 nm, which corresponds to the spectrum blue.

Acknowledgments: This work was supported by the Russian Science Foundation (project No 21-73-10083). Measurements were performed at the Center for Magnetic Resonance, the Center for X-ray Diffraction Studies, the Center for Chemical Analysis and Materials Research, and the Chemistry Educational Centre (all belonging to Saint Petersburg State University).

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Synthesis of 1,3-Di(trifluoromethyl)indanes and α-(Trifluoromethyl)styrenes via Superelectrophilic Activation of (α-Me_3SiO-trifluoropropyl)(het)arenes

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Today fluorinated organic molecules play important role in various fields of science and technology. In organic synthesis ones of the versatile building blocks are α-(trifluoromethyl)styrenes, widely applied to construct more complex fluorinated compounds via C-F activation [1]. At the same time, 1-(trifluoromethyl)indanes, being good ligands for cannabinoid receptors CB1 and CB2 types, are target molecules in drug discovery [2]. The development of new synthetic approaches to fluorinated styrenes and the construction of new fluorinated indane systems are current issues of organic synthesis.

We have found that (α-Me_3SiO-trifluoropropyl)(het)arenes (or corresponding alcohols) under action of trifluoromethanesulfonic acid (TfOH) can be converted both into initially forming α-(trifluoromethyl)styrenes and products of their electrophilic «dimerization» - 1,3-di(trifluoromethyl)indanes in reasonable to excellent yields (Fig. 1).

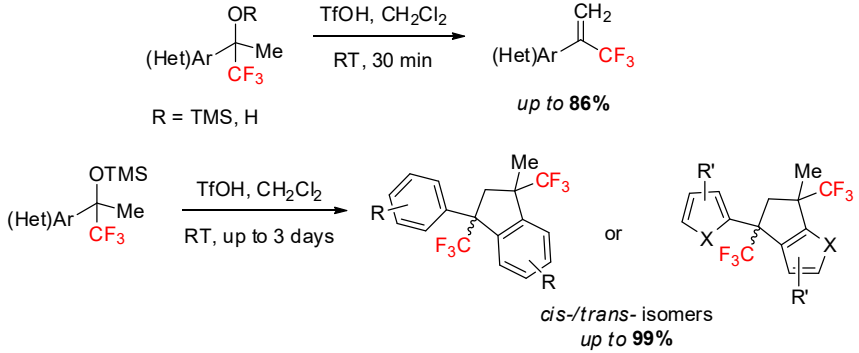

Fig. 1. Synthesis of trifluoromethyl substituted indanes and styrenes.

Acknowledgments: This work was supported by Russian Scientific Foundation (grant no. 21-13-00006).

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Organo-inorganic Derivatives of Layered Perovskite-Like Oxide $HB_2Nb_3O_{10}$ (B = Ca, Sr) with Amino Alcohols

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The products of intercalation of organic compounds into the interlayer space of layered perovskite-like oxides are of interest both in themselves and because of the possibility of their use in the synthesis of hybrid materials modified by covalently bound organic groups (grafting), potentially having many practical applications [1, 2].

This work is devoted to the development of methods and optimization of synthesis conditions, as well as the complex characterization of the obtained hybrid organo-inorganic derivatives based on layered perovskite-like niobates $HB_2Nb_3O_{10}$ (B = Ca, Sr) with monoethanolamine and dimethylaminoethanol. The development of the synthesis procedure was carried out under the conditions of a standard laboratory experiment with varying temperature (25, 60, 90, 150°C), time (1, 3, 7, 14 days) and concentration of an aqueous solution of amino alcohol (10, 50, 70, 90, 100%), as well as using microwave and hydrothermal synthesis methods. The obtained objects were studied using a complex of complementary modern methods of physico-chemical analysis, which made it possible to obtain reliable information about the structure, thermal stability, as well as to establish the quantitative composition.

During the research, for the first time a number of organo-inorganic derivatives of layered niobates $HB_2Nb_3O_{10}$ with intercalated amino alcohols was successfully synthesized. These derivatives contain from 0.5 to 0.9 molecules of monoethanolamine and dimethylaminoethanol per formula unit. In addition, a grafted derivative was obtained with monoethanolamine by partial thermal degradation of intercalated samples, that is, by thermolysis.

Acknowledgments: The research was carried out using the equipment of the Science Park of St. The authors thank the RC "X-ray diffraction research methods", RC "Thermogravimetric and calorimetric research methods", RC "Methods of analysis of the composition of matter", RC "Magnetic resonance research methods". The study was supported by the Russian Foundation for Basic Research (Grant No. 20-73-00027).

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«Green» Extraction Technique for the Determination of Formaldehyde in Milk

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In the modern world, much attention is paid to «green» extraction solvents. From this point of view, thymol as a natural terpenoid is of interest. Previously, this substance was not used as an individual extractant.

In this regard, a simple and environmentally friendly scheme for the fluorometric determination of formaldehyde in milk with the use of thymol as extraction solvent was developed. Formaldehyde is a carcinogen, but it is often added to milk as a preservative to increase the shelf life of the product and keep it odorless [1]. Therefore, the determination of the formaldehyde content in milk is an urgent analytical task.

The proposed scheme assumes the air-assisted dispersive liquid-liquid microextraction of the formaldehyde derivative into the molten thymol coupled with fluorometric analysis. The formation of derivative and extraction process are carried out by heating and stirring with air provided by thermostat and peristaltic pump, respectively. After extraction the liquid organic phase with the derivative is placed on a black paper template. Fluorometric measurements are performed by spectrofluorometer equipped with the solid sample holder.

The scheme proposed was applied for the determination of formaldehyde in three milk samples. The correctness of the results obtained was confirmed by the "add-found" method.

Acknowledgments: This project was financially supported by the Russian Science Foundation (project no. № 21-13-00020, https://rscf.ru/project/21-13-00020/). The authors are also grateful to «Chemical Analysis and Materials Research Centre» of Saint Petersburg State University Research Park.

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Luminescent Micro- and Nanocrystalline Europium(III) Terephthalates as Luminescent Probes for Heavy Metal Ions

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Rare-earth-based luminescent metal-organic frameworks are used in various fields of science and technology as luminescent sensors, probes for bioimaging, luminescent thermometers, and components of light-emitting devices. In current work, we synthesized the small-sized luminescent MOF, $Eu_2bdc_3 \cdot 4H_2O$ by ultrasonic-assisted method. Sodium terephthalate was added to the solution of europium chloride accompanied by ultrasonication. Small particles were formed in solution. We found that the particle size is determined by the reagent concentration and ultrasonication conditions. Coarse-, micro- and nanocrystalline europium(III) terephthalate tetrahydrate MOFs were obtained in this work. The particles of coarse-crystalline material are dendrimer-like microparticle assemblies with the average particle size of 120±30 μm. The europium(III) terephthalate microparticles are 7 μm long leaf-like plates. The average size of the $Eu_2bdc_3 \cdot 4H_2O$ nanoparticles is equal to about 8±2 nm.

The synthesized materials demonstrate red emission due to the $^5D_0 - ^7F_J$ (J= 0-4) transitions of Eu^{3+} ion upon 250 nm excitation into 1ππ* state of the terephthalate ion. Size reduction results in broadened emission bands, an increase in the non-radiative rate constants and a decrease in both the quantum efficiency of the $^5D_0$ level and Eu^{3+} and the luminescence quantum yields. Cu^{2+}, Cr^{3+}, and Fe^{3+} ions efficiently and selectively quench the luminescence of nanocrystalline europium (III) terephthalate. Therefore, nanoparticles can be used as efficient luminescent sensors for heavy metal ions in waste and drinking water.

Evolution of Arsinic Acids Hydrogen-Bonded Complexes Properties in Media with Different Dielectric Permittivity

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It is well known that acids described by general formula R_2XOOH (X = P, As) can participate in hydrogen bonding both as donors (by XOH moiety) and acceptors (by X=O moiety). Hydrogen-bonded self-associates and hetero-complexes of phosphinic RR'POOH acids are explored in gases, solutions and condensed matter by experimental spectral techniques as well as by quantum chemistry methods [1–3].

Arsinic acids R_2AsOOH synthesis aspects and self-associate formation was recently studied by our research group [4]. In this work, we studied completely unexplored topic – properties of hydrogen-bonded of arsinic acids R2AsOOH with various proton donating (Fig. 1a) and proton accepting (Fig. 1b) species in isotropic polarized media (with ε=1–80) by means of quantum chemistry (MP2/def2-TZVP). The main goal of this work was to evaluate the changes in geometric, energetic and spectral parameters of investigated complexes upon polarity change of a media.

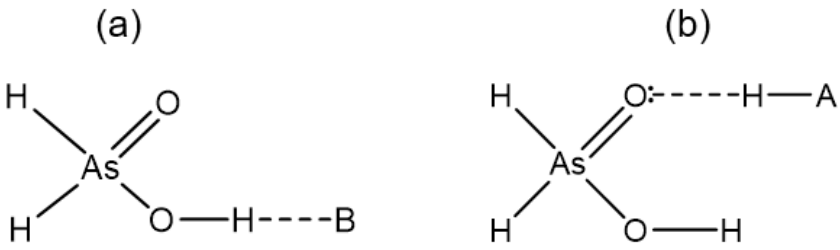

Fig. 1. Schemes of studied complexes: (a) H_2AsOOH as a H-bond donor, (b) as a H-bond acceptor; B = base; HA = acid.

Acknowledgments: This work was supported by RFBR grant 20-03-00231.

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Histidine Containing Polypeptide Nanoparticles for SiRNA Delivery

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Polymeric nanoparticles have attained considerable attention in the field of biomedicine over the past decades. The particles can enhance drug stability and efficacy, reduce side effects and allow the control of drug release. However, the cornerstone in their application is a low transfection efficiency. A great number of studies have been focused on developing of novel synthetic drug carriers with successful cell penetration and intracellular drug release [1, 2].

Gene therapy through the use of siRNA is becoming an efficient therapeutic option for the treatment of widespread illnesses. To prevent siRNA from rapid blood clearance and cytosolic degradation, nanoparticles are used as drug carriers [3]. Cationic polymers are perspective in this regard since they can condense negatively charged RNA molecules into compact forms that are resistant to serum proteins. pH-sensitivity of a polymer can provide enhanced endosomal escape of these polyplexes into cytosol due to the "proton-sponge effect".

The aim of this research work was the creation of positively charged biocompatible polypeptide nanoparticles. The target copolymers were synthesized via ring-opening polymerization of N-carboxyanhydrides of α-amino acid derivatives. The samples were modified with histidine and their transfection efficiency was compared as well as cytotoxicity and stability.

The morphology, size and size distribution of the nanoparticles obtained were investigated via nanoparticle tracking analysis, dynamic light-scattering and transmission electron microscopy. Cytotoxicity of the particles was evaluated using several cell lines (ARPE, SIRC, and MDA-MB231). The experiment of intracellular delivery of siRNA encapsulated in polymer nanoparticles was carried out and the gene silencing was successful.

Acknowledgments: This work was supported by Russian Foundation for Basic Research (project No 20-33-90181).

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Organic Modification of Layered Perovskite-Like Titanates $HLnTiO_4$ (Ln = La, Nd) as an Efficient Approach to the Enhancement of Their Photocatalytic Performance towards Hydrogen Production

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Overcoming many global environmental problems, caused by rapid industrial growth and the active use of traditional fuels in the XX–XXI centuries, is associated with the development of waste-free technologies and alternative energy sources including hydrogen fuel. With this regard, photocatalytic oxidation of bioalcohols and related biomass processing products is considered as an effective and environmentally friendly approach to the hydrogen production.

One of the classes of promising heterogeneous photocatalysts being actively explored is represented by layered perovskite-like oxides. The improvement of their photocatalytic activity can be carried out via cationic and anionic substitution, the creation of composites with metal co-catalysts, sensitization with dyes as well as exfoliation into perovskite nanosheets [1].

The present research focuses on a poorly studied approach to increasing photocatalytic activity of layered perovskite-like oxides – modification of their interlayer space with organic components. In particular, we have synthesized for the first time two series *n*-alkylamine and *n*-alkoxy derivatives of titanates $HLnTiO_4$ and investigated the kinetics of light-driven hydrogen generation from the model aqueous solution of methanol over the hybrid samples obtained. It has been established that the organic modification of the interlayer space of the titanates is an efficient way to improve their photocatalytic activity. The rate of increase in the activity turns out to be up to 70 times compared to that of the initial unmodified titanates and up to 17 times in comparison with the «classic» photocatalyst TiO_2 P25 Degussa. Thus, the interlayer organic modification proves to be an effective strategy to manage photocatalytic activity of layered perovskites, which may be applied to other photocatalytically active materials.

Acknowledgments: The study was conducted using the equipment of the Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Research, Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Interdisciplinary Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials. The study was supported by the grant of Russian Scientific Foundation (19-13-00184).

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Stability of Hybrid Inorganic-Organic Photocatalysts Based on the Layered Perovskite-Like Titanate $H_2La_2Ti_3O_{10}$ in the Reaction of Hydrogen Generation from Aqueous Methanol

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In light of the depletion of fossil fuels and the tightening of international environmental legislation, creation of new efficient photocatalysts for hydrogen production from aqueous bioalcohols and other biomass processing products proves to be one of the topical areas of chemistry and materials science.

The present research focuses on the stability of *n*-alkylamine and *n*-alkoxy derivatives of the layered perovskite-like titanate $H_2La_2Ti_3O_{10}$ as promising photocatalysts for hydrogen production. These hybrid inorganic-organic compounds have been found to demonstrate superior photocatalytic activity exceeding that of the initial protonated titanate up to 117 times and of titanium dioxide TiO_2 P25 Degussa – up to 51 times. Moreover, additional platinization of the samples' surface allows achieving apparent quantum efficiency in the reaction of hydrogen formation from aqueous methanol of more than 40% and, having said so, the hydrogen generation rate stable preserves throughout the whole measurement time. However, the inorganic-organic derivatives undergo partial decomposition of the interlayer organic modifiers under the operation conditions, which does not result in the photocatalytic activity reduction. Apparently, the inserted organic modifiers facilitate the penetration of the reactants (methanol and water) into the interlayer space, considered a separate reaction zone [1]. These transport channels, probably, continue functioning even after partial or even complete degradation of the organic modifiers, which explains the stable photocatalytic reaction rate. In addition, the enhanced photocatalytic activity of the inorganic-organic derivatives may be associated with the selective platinum reduction in the interlayer space and other areas of the samples where it does not occur in the absence of organic modifiers. However, this issue requires further investigation.

Acknowledgments: The study was conducted using the equipment of the Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Research, Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Interdisciplinary Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials. The study was supported by grants of Russian Scientific Foundation (20-73-00027) and President of Russian Federation (MK-480.2020.3).

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Structure and Electrokinetic Potential of Nanoporous Glasses Doped with Silver Halides

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The development of modern technologies sets the task of developing practically significant high-performance materials with functional properties. One of the classes of such materials are light-sensitive silver-containing vitreous nanocomposites used for optical instrumentation. In this work, micro- (MIP, average pore radius is 1.5 nm, porosity is 25 %) and macroporous (MAP, average pore radius is 17 - 21 nm, porosity is 50 - 59 %) high-silica glasses were used as matrices, which were impregnated in two stages with $AgNO_3$ solutions, and then with KHal (Hal = Cl, Br, I) solutions [1]. It is known that the properties of nanostructured materials and their functional characteristics are primarily determined by the structural parameters and the state of their surface [2]. In connection with this, the work investigated the structure and electrokinetic potential of silicate porous glasses (MIP and MAP) and glasses modified with silver halides (MIP-AgCl, MAP-AgCl, MIP-AgBr, MAP-AgBr, MIP-AgI, MAP-AgI) in 0.01 M solutions of indifferent $NaNO_3$ electrolyte and $AgNO_3$ solutions containing potential-determining Ag^+ ions. The content of Ag_2O found by X-ray fluorescence analysis was (wt. %): MIP-AgCl 0.322, MAP-AgCl 1.122, MIP-AgBr 0.322, MAP-AgBr 1.992, MIP-AgI 0.239, MAP-AgI 0.801. The presence of phases of Ag_2O and AgHal was proved by X-ray phase analysis of silver-containing porous glasses. The electrokinetic potential (ζ) of porous glass particles was found by laser Doppler electrophoresis. It was found that the modification of porous silicate glass leads to an increase in the $|\zeta|$ values.

Acknowledgments: This study was supported by the Russian Foundation for Basic Research (project no. 20-03-00544a). The part of the study related to the synthesis of the studied materials was carried out as part of a state assignment of the Institute of Silicate Chemistry, Russian Academy of Sciences (IChS RAS) with the support of the Ministry of Education and Science of Russia (project AAAA-A19-119022290087-1). The measurements were performed at the Research Park of St. Petersburg State University (Interdisciplinary Resource Centre for Nanotechnology, Centre for X-ray Diffraction Studies and Center for Chemical Analysis and Materials Research).

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Molecular Thermometers Based on Europium(III) Complexes

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Nanoscale temperature measurement concerns the determination of temperature or temperature differences at the sub-micron scale. Applications include microelectronics, optics, microfluidics, chemical reaction, and biochemical processes, such as living cells and nanomedicine [1-3].

Lanthanide complexes are widely and successfully used for bioimaging due to several benefits such as sharp transitions with a large Stokes shift located in the visible spectral range, insensitivity to oxygen, sensitivity to the local environment, and long excited-state lifetime. It allows eliminating short-time autofluorescence of the cells from the signal of complex in vivo [2]. At the same time it is necessary to make a barrier between the environment and complexes to make thermometers irresponsive to the local changes. Hence, we synthesized latex nanoparticles with our complexes (Fig. 1). All the compounds were characterized using NMR spectroscopy, ESI mass-spectrometry, photophysical properties were carefully measured in solution.

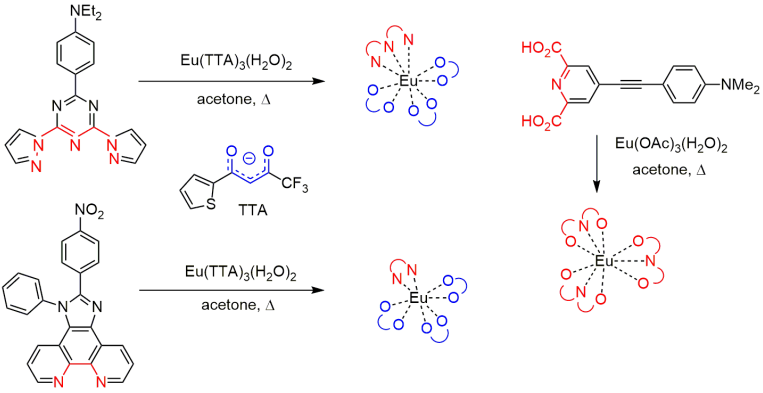

Fig. 1. Scheme of synthesis of europium(III) complexes.

Acknowledgements: This work was supported by the Russian Science Foundation (project No 19-13-00132). The authors are grateful to Saint-Petersburg State University Research Park.

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Soft Hydrogel Actuator for Machine-Learning-Assisted Bacteria Detection

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Currently, various methods are used to count the number of viable bacteria, which have certain drawbacks. However, until now, methods for determining the viability of mature bacteria are limited, and methods of microscopic counting, plate counting, and turbidity methods are commonly used [1–4]. Therefore, it is so important to develop a sensitive, fast, non-toxic, inexpensive, and easy-to-use method for determining the viability and counting bacteria.

We propose using of the current-voltage (I−V) characteristics at the interface between the eutectic gallium-indium alloy (eGaIn) electrode and the hydrogel (Fig. 1) to detect Streptococcus thermophilus and Bacillus coagulans bacterial concentrations in the range from 10^4 to 10^8 CFU/mL. The collected volt-ampere data was used for machine learning. The multilayer perceptron model showed the best result, demonstrated 94% accuracy and recognized all concentrations of bacteria in the culture medium. Thus, the developed principle of the platform has a great prospect of being used as a more convenient method for the quantitative detection of bacteria.

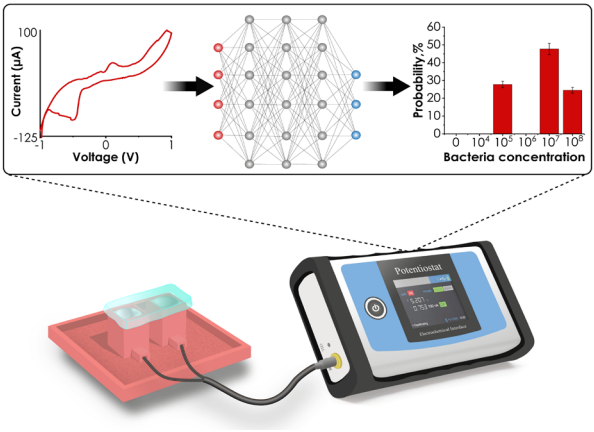

Fig. 1. Scheme and principle of operation of the electrochemical system.

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Synthesis of Diastereomerically Pure 3-Cyanoazetidin-2-ones via Thermally Promoted Tandem Wolff Rearrangement–Staudinger [2+2] Cycloaddition

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β-Lactams are privileged scaffolds that found broad application in the design of antibacterial drugs. The most common approach to β-lactam core is the Staudinger [2+2] cycloaddition of imines and ketenes, the latter being generated *in situ* via the Rh(II)-catalyzed Wolff rearrangement of α-diazocarbonyl compounds. Though this approach is well-explored, it has a main drawback such as the use of expensive Rh(II)-catalysts so as to generate carbenes. Furthermore, still there is an issue with the diversity of functional groups that can be introduced into the β-lactam ring.

In the present work, we developed the first transition metal-free diastereoselective synthesis of cyano β-lactams from imines and surprisingly insufficiently explored α-diazo-β-ketonitriles based on tandem of thermally initiated Wolff rearrangement, occurring in refluxing toluene, and Staudinger cycloaddition (Fig. 1). Furthermore, the synthesis represents the first example of cyano ketenes generation from diazoketonitriles. The reaction developed tolerates substrates with various substituents, even bulky ones, and delivers rare polysubstituted cyano β-lactams with excellent diastereoselectivity and generally high yields. The relative stereochemistry of products was assigned by the single-crystal X-ray crystallography. In addition, we investigated limitations of our approach and possible transformations of substituents in the lactam ring.

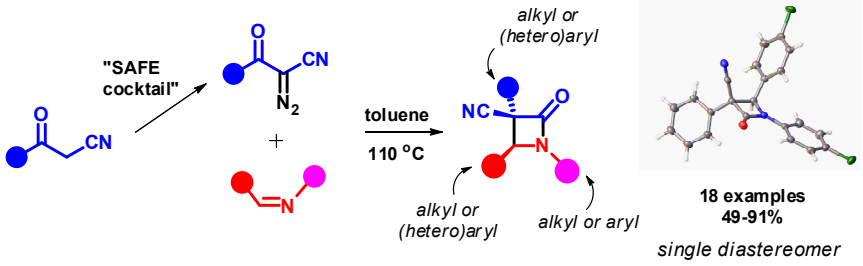

Fig. 1.Synthesis of cyano β-lactams.

Acknowledgments: This work was supported by RFBR (project № 20-03-00922). The authors are grateful to Saint-Petersburg State University Research Park.

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Development and Study of Novel Pervaporation Membranes Based on Polyphenylene Oxide Modified with Graphene Oxide

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Membrane separation methods are the most promising field of sustainable processes due to their beneficial characteristics, namely, waste-free, environmentally friendly, low-energy and compact equipment. Therefore, the development of membrane processes is one of the most urgent and important directions for industry. Pervaporation is a membrane method that actively used for the separation of azeotropic mixtures, isomer, close-boiling and thermally unstable low molecular weight substances. The rapid development of pervaporation requires the research of new highly effective membranes with tailored properties. One of the most perspective ways to improve characteristics of polymer membranes is the introduction of carbon nanoparticles into a well-known polymer matrix. In this work the most permeable glassy polymer polyphenylene oxide (PPO) was used as the polymer network, and graphene oxide (GO) was used as modifier due to various oxygenated functional groups.

The aim of work was to create novel high-performance pervaporation membranes based on PPO modified with GO. The optimal conditions for preparation of these membranes were developed. The structural characteristics of obtained composites and membranes were studied by spectroscopic (FTIR) and microscopic (SEM and AFM) methods. Transport characteristics of membranes were investigated in pervaporation for the recovery of industrially significant substance - ethylene glycol from water and methanol. The improvement of the developed membrane properties was achieved due to the functionalization of the membrane surface and changes in free volume during the modification process.

Acknowledgments: This work was supported by Russian Science Foundation [project No 21-73-00043]. The experimental work was facilitated by equipment from the Resource Centers for Nanotechnology, Chemical Analysis and Materials Research Centre, Cryogenic Department and Centre “Nanofabrication of Photoactive Materials (Nanophotonics)” at the St. Petersburg State University.

Novel Membrane Based on Polyacrylonitrile Modified by Titanium Dioxide for Water/Oil Separation

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Ultrafiltration is a membrane separation process carried out by filtering a liquid; the driving force of which is the pressure difference on both sides of the membrane. Ultrafiltration is the most used membrane process in the industry (in the food, chemical and microbiological industries for purification from proteins, viruses, bacteria and etc.). The pore size of ultrafiltration membranes ranges from 0.01 to 0.1 micrometers.

Polyacrylonitrile is a polymer that is often used in the manufacture of ultrafiltration membranes. The widespread use of PAN is associated with a number of advantages, such as high thermal and chemical stability, resistance in non-polar and low-polarity organic solvents, as well as low cost. The main disadvantage of PAN-based membranes is a decrease in the productivity of the filtration process due to the membrane fouling. In the present research, to solve this problem, photocatalytic membranes based on PAN modified with titanium oxide have been developed. Titanium dioxide (TiO_2) has chemical and thermal stability, good yield on decomposition of organic pollutants, high recyclability and low cost, which makes it often used as a semiconductor for photocatalytic membranes. In this work, ultrafiltration membranes based on PAN modified with titanium oxide have been obtained. Three types of membrane modification using nano-sized and micro-sized TiO_2 have been developed: solid-phase method, dynamic deposition and solution method. The developed membranes were analyzed by scanning electron microscopy, contact angle, atomic force microscopy and porosity. Their transport properties were investigated in the process of ultrafiltration separation of the cutting fluid and bovine serum albumin (BSA). It was found that modification with titanium dioxide improves the transport and antifouling properties of PAN-based membranes.

Acknowledgments: The reported study was funded by RFBR, Sirius University of Science and Technology, JSC Russian Railways and Educational Fund "Talent and success", project number 20-38-51022. The experimental work of this study was facilitated by the equipment from the, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Methods, Magnetic Resonance Research Centre, Centre for Innovative Technologies of Composite Nanomaterials, Nanophotonics Centre, Cryogenic department, Thermogravimetric and Calorimetric Research Centre and the Interdisciplinary Resource Centre for Nanotechnology at the St. Petersburg State University.

Novel Self-Cleaning Ultrafiltration Membranes Based on Poly(m-phenylene isophtalamide) Modified by TiO_2

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Due to the growing ecological concerns, purification of water has become a matter of great significance. Membrane technologies, especially ultrafiltration, have proven their efficiency in separating water from oil, which is the main pollutant. However, porous membranes used in ultrafiltration can be contaminated. This problem can be solved by the addition of specific particles with antibacterial and photocatalytic properties, such as titanium oxide (TiO_2), to the membrane matrix. As a membrane material was chosen poly(m-phenylene isophthalamide) (PA) for ultrafilration membrane preparation due to its good chemical and thermal resistance. The insertion of titanium oxide into a poly(m-phenylene isophthalamide) (PA) membrane matrix could improve its separation performance for a vast array of industrial applications, including water purification.

In this study, the modified membranes were prepared by non-solvent-induced phase separation, and characterized by measurements of water contact angle and porosity, scanning electron and atomic force microscopy. The analysis of transport characteristics was conducted by ultrafiltration of industrially relevant samples such as coolant lubricant emulsion in water and bovine serum albumin (BSA) solution. Prolonged ultrafiltration using BSA solution and reversible fouling under UV radiation was used to investigate the self-cleaning ability of the best performing modified membrane.

Acknowledgments: The reported study was funded by RFBR, Sirius University of Science and Technology, JSC Russian Railways and Educational Fund “Talent and success”, project number 20-38-51022. The experimental work of this study was facilitated by the equipment from the Resource Centre of Geomodel, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Methods, Magnetic Resonance Research Centre, Centre for Innovative Technologies of Composite Nanomaterials, Nanophotonics Centre, Cryogenic department, Thermogravimetric and Calorimetric Research Centre and the Interdisciplinary Resource Centre for Nanotechnology at the St. Petersburg State University.

Novel Organogold Stilbene Photoswitchers: Synthesis and Photochromic Properties

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Photoswitches capable of changing their configuration under the influence of light are finding more and more applications, for example, used in optical memories, logic gates, photoswitchable electronics [1]. At the same time, the modification of such systems with organometallic moieties could change their photochemical, and in particular, photophysical properties, which makes such organometallic systems attractive for development research.

It is known that the inclusion of an Au(I) organometallic moeity is often leads to a change in electronic, photophysical properties of the resulting object due to mixing of their electronic orbitals.

In the present work, we report the synthesis, characterization and investigation of photophysical and photochromic characteristics of the series of light-triggered stilbene-organogold(I) compounds (Fig. 1) capable of reversible *cis-trans* photoisomerization.

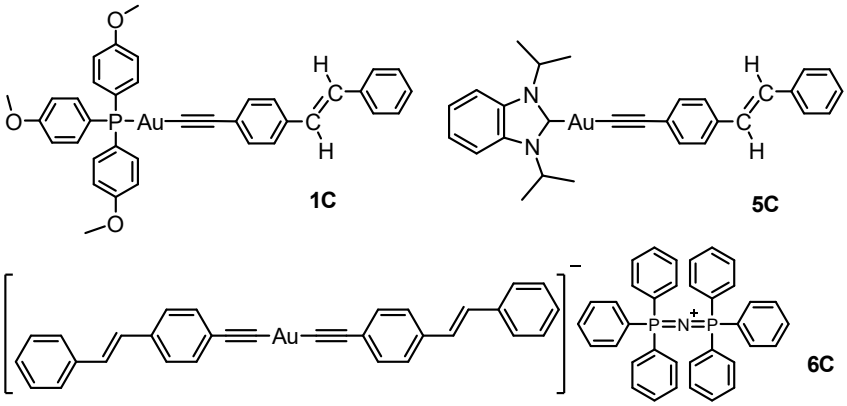

Fig. 1. Organogold(I) complexes bearing stilbene photochromic moieties.

Acknowledgments: This work was supported by the Russian Science Foundation, project 21-13-00052. The studies were performed using the equipment of Centres for Magnetic Resonance, for Chemical Analysis and Materials Research (Research Park of St Petersburg University).

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Express Extraction-Photometric Determination of Boron in Aqueous and Organic Phases

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Boron compounds are widely used in nuclear power, medicine, metallurgy and other industries. There are many methods of boron analysis, though for some of its species the measurement is rather elaborate and labor-consuming. Nowadays photometric determination of boron as tetrafluoroborate ion with use of organic dyes is most perspective. In particular, work [1] describes the technique of extraction-photometric determination of tetrafluoroborate using thionin derivatives as dyes. However, available technique require time and consumption of large amounts of organic solvent [2]. The aim of the work was to develop a convenient and express extraction-photometric method of tetrafluoroborate ion (BF_4^-) analysis in aqueous and organic environments, as a complex with Methylene Blue (MB) extracted in dichloroethane (*Equation 1*).

$$(BF_4^-)_{aq/org} + (MB^+)_{aq} = (BF_4^- \cdot MB^+)_{org} \quad (1)$$

The influence of MB concentration, H_2SO_4 concentration and Na_2SO_4 attendance on the analytic signal was investigated. Optimal conditions for extraction-photometric determination were selected and the linear relationship between attenuation of dyed solution and BF_4^- concentration was obtained in the concentration gap from 10^{-4} M to 10^{-3} M with Pearson's *r* value 0,999 (Fig. 1). The method allows to determine BF_4^- concentration in both aqueous and organic phases with detection limit 10^{-4} M (1 μg/ml of boron) and error less than 10%.

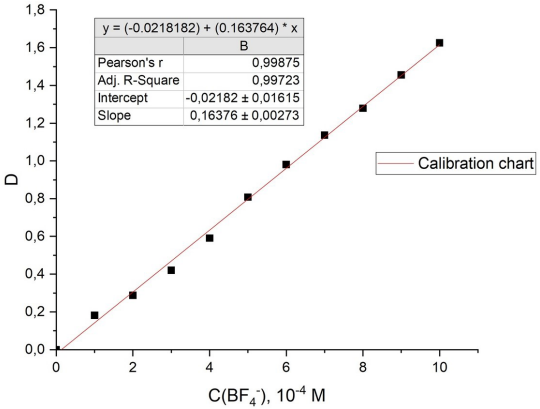

Fig. 1. Calibration dependence.

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Correlation Between Structural Parameters and Photoluminescent Characteristics of Eu-Doped Boehmite Nanoparticles

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Photoluminescent markers are a well-promising tool for bio-imaging and chemical analysis, helping to locate specific compounds in vivo or for optimizing sample preparation and analysis procedures. Various doped oxide nanoparticles are a promising material for this purpose because of low toxicity and enhanced stability. Europium is one of the most popular dopants for this purpose as it is accessible and well-studied. Host need to be high-crystalline to provide high quantum yield of photoluminescence (PL), but that is hard to combine with dopant intercalation. We assume that PL intensity can depend on dopant position in crystal lattice, which can lead to PL quenching in case of high dopant concentrations.

The aim of this work is to develop the synthetic procedure to obtain boehmite nanoparticles – a highly crystalline non-toxic host – doped with Europium, and to study the PL characteristics of obtained nanoparticles, which could be produced in at least two different shapes.

Eu-doped boehmite nanoparticles were synthesized under hydrothermal conditions at different pH values and Eu amounts ranging from 1 to 10 mol.%. Nanoparticles were characterized with XRD, FTIR, TEM, SSA and XPS. Alkaline conditions, pH 9, caused an extra phase, as well as pH 7 with 10 mol.% Eu. Other samples demonstrated two different morphologies depending on the pH of the initial solution: 35 nm in width and 200 nm in length rods at pH 4 and 20 and 55 nm plates at pH 7 respectively. According to TGA-DSC data, temperature of the transition into aluminum oxide does not depend on the particle size and the concentration of the dopant.

PL study of as-prepared nanoparticles in pellet and in suspension showed that concentration of quenching for rod-like particles emission at 618 nm was 1 mol.%, while for plate-like it was 5 mol.% respectively. By performing quantum-chemical calculations, it was established that quenching concentration depends on the dopant position in the host crystal structure. Also the PL peak at 700 nm was examined and related to oxygen vacancies PL in boehmite. As a result, we have established correlation between morphology of nanoparticles and quenching concentration, through changing of the position of the dopant.

Acknowledgments: Investigation was accomplished with help of Centre for Optical and Laser Materials Research, Research Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre and Centre for Innovative Technologies of Composite Nanomaterials of Saint Petersburg.

Spectrophotometric Method for the Determination of Urea in Milk Based on Microextraction in Deep Eutectic Solvent

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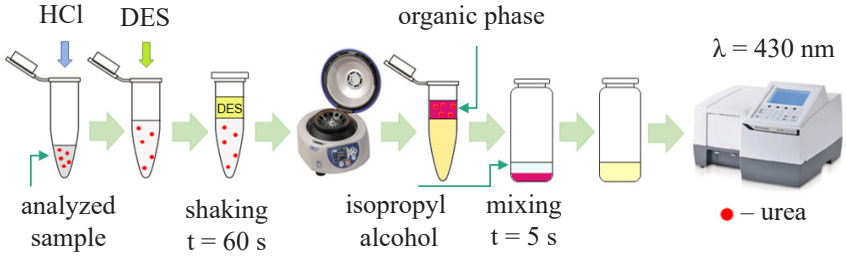
Nowadays, milk is the most likely food item being at risk of adulteration. Urea being a nitrogenous compound is added in milk to increase the apparent protein content. The concentration of urea beyond the upper limit (700 mg/L) is extremely hazardous to human health.

Deep eutectic solvents (DES) have recently become increasingly popular as ecological effective extractants due to their properties as high thermal stability, low volatility, tunable polarity, non-toxicity and biodegradability. A DES is generally composed of two or three cheap and safe components which are capable of associating with each other, through hydrogen bond interactions, to form an eutectic mixture. The resulting DES is characterized by a melting point lower than that of each individual component.

In the current study, an efficient and rapid method, which is based on a colorimetric reaction between urea and 4-dimethylaminobenzaldehyde, for the quantification of urea in milk is presented. A novel deep eutectic solvent obtained by thymol and 4-dimethylaminobenzaldehyde (1:1, mol/mol) was used as an effective extractant for urea determination in milk. Under optimal conditions, the limit of detection for urea in milk were 10 mg kg^{-1}. Low limit of detection and the use of deep eutectic solvent instead of organic solvents make it possible to use this



method for food quality control.

Fig. 1. Scheme of spectrophotometric method for the determination of urea in milk based on microextraction in deep eutectic solvent.

Acknowledgments: The work was supported by a grant from the President of the Russian Federation MK-1154.2020.3. The authors are grateful to Saint Petersburg State University Research Park.

Calixarene-Modified Heavy-Metal Ion Selective Screen-Printed Electrodes

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Screen-printing is a promising approach towards the simple, rapid, and inexpensive production of (bio)sensors. Sensors based on screen printed electrodes (SPEs), including microelectrodes and modified electrodes, have expanded the potential in detection and quantitation of a number of transition metal ions such as Zn(II), Cu(II), Fe(III) including cyclic voltammetry (CVA) and impedance spectroscopy techniques. As working electrodes (WEs), carbon, Cu, Bi, and glassy carbon modified with Hg salts are employed. Despite the advantages of precipitation of heavy metals into the amalgam, this method is undesirable due to mercury toxicity. Alternatively, less toxic water-soluble polyelectrolytes could immobilize heavy metals salts on the surface of a WE and scale the electrode modification process [1].

Calixarene scaffold is particularly interesting for surface modification of WEs of SPE and electrochemical determination of heavy metal ions as it is an effective and selective receptor towards ions and neutral molecules. These macrocycles possess strong complexation ability, which enables them to maintain their recognition behavior in confined space [2].

Commercially available SPEs usually provide good experimental results, but their high cost and limited service life require an alternative approach to electrode fabrication. Herein, we offer SPEs made with modified ink composition based on a suspension of graphite and acetyl cellulose in cyclohexane modified with thiacalix[4]arene.

Preliminary experiments showed high stability and satisfactory electrochemical characteristics of the calixarene-modified electrodes and suggest high potential of thiacalixarene receptors for recognition of ultralow quantities of toxic metal ions, which is currently under study.

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Gd-Doped Hydroxyapatite Nanoparticles as a Perspective MRI Contrast Agent: Synthesis, Characterization and First MR Study

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Magnetic resonance imaging (MRI) is a medical imaging technique used in radiology to form pictures of the anatomy and the physiological processes of the body. MRI contrast agents (CA) is using to improve the visibility of internal body structures. Gadolinium-based contrast agents are used in up to 35% of magnetic resonance imaging (MRI) examinations for T1 mode in clinical practice. Chelating complexes, such as Primovist® and Omniscan®, in the same cases can have a toxic effect on humans. Development of a new types of non-toxic and biocompatible contrast agents is still under discussion. Our approach is to introduce the gadolinium ions to non-toxic and biocompatible host to make it more applicable in medical practice. Hydroxyapatite (Hap) biocompatible nanoparticles was chosen as a host for a new contrast agent.-

The first stage of the work is dedicated to the development of the synthetic procedure to produce the Gd high doped Hap nanoparticles (NPs) with a different size and shape which are considered as a key factor impact on MRI signal. The NPs were synthesized by co-precipitation method followed by the thermal treatment under atmospheric and hydrothermal conditions with the using of low and high concentration of initial reagents. The regulation of this parameters can initiate an orientational attachment process which leads to interaction between initial particles. In this case, the parameters of the "initial" NPs depend on the concentration of the initial reagents in the reaction medium, and the "final" NPs - on the holding temperature. All samples were fully characterized by XRD, TEM, FTIR, AES. Synthesized particles were monocrystalline with a rod-like shape and a size from 11 to 32 nm and aspect ratio 1:3. The band gap values diminish after doping from 3,64 to 4,67 eV, the Gd amount is close to 2,5mol.% for all the samples.

At the second stage of the work the MRI date of nanoparticles embedded in agarose matrix were taking of T1 and T2 modes. The relaxation time in T1 mode depends on nanoparticles size from 352 to 2730 ms, and in T2 mode is constant and close to 25 ms, which is a good result and non-usual for T1 contrast agents. Thus, the possibility of using the Gadolinium doped hydroxyapatite nanoparticles as T1 contrast agents was successfully demonstrated for the first time.

Acknowledgments: Scientific research was performed using the equipment of the Research Park of St. Petersburg State University (Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Centre for Innovative Technologies of Composite Nanomaterials, Centre for Optical and Laser Materials Research, Centre for Magnetic Resonance).

Synthesis of Weakly-Agglomerated Oxide Phosphors for Non-Contact Thermometry

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To date, the production and study of nanothermometers is a popular research topic in the world scientific community [1]. The possibility of providing thermal sensing with high accuracy in non-contact regime makes luminescence nanothermometers extremely important in modern biotechnology. Also important factors for such nanostructures are their high chemical and physical stability and inertness. In this work, we took YVO_4 and $LaVO_4$ as crystalline hosts and rare earth ions (REI) as temperature-dependent active centers. Luminescence thermometry was performed via ratiometric approach.

YVO_4 and $LaVO_4$ powders doped with REI were synthesized with the synthesis method in molten salt. The results of the X-ray diffraction analysis (XRD), morphology (SEM) were obtained and analyzed. Samples with different amounts of doped REIs were obtained, concentration series for various REIs and their combinations were also studied.

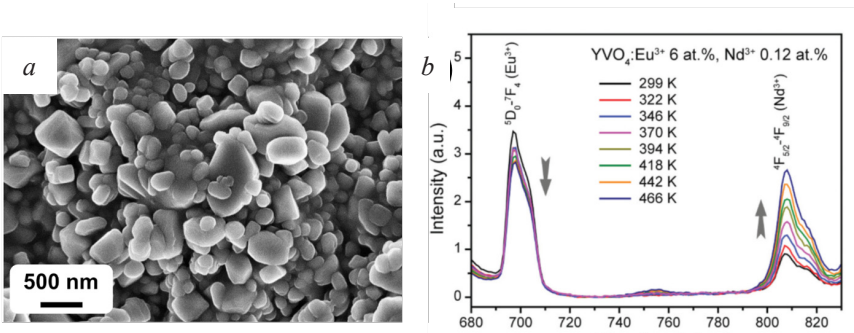

Fig. 1. a) SEM picture of YVO_4: Nd^{3+} 0.03 at.%, Er^{3+} 1.5 at.%, Tm^{3+} 0.2 at.%; b) emission spectrum of co-doped YVO_4: Eu^{3+} 6 at.%, Nd^{3+} 0.12 at.% at various temperatures.

Acknowledgments: The research has been partially funded by the Russian Science Foundation № 21-79-10018. The authors are also grateful to "Centre for Optical and Laser Materials Research", "Research Centre for X-ray Diffraction Studies" and "Interdisciplinary Resource Centre for Nanotechnology" of Saint Petersburg State University Research Park.

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Microextraction of Sulfonamides from Food Samples in Deep Eutectic Solvent

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Determination of antibiotics from food samples is important topic for researches. Antibiotics' metabolites are often found in food samples, which may be caused by misuse of antibiotics for treatment, and these residues can enter the human body and cause many risks to consumer health.

Sulfonamides (SAs) are antibiotics widely used in medicine and veterinary to treat infection disease. Mostly used method for the determination of sulfonamides is HPLC. However, this determination method needs sample pretreatment procedure, containing elimination of matrix effect and concentration stage. Recently, deep eutectic solvents (DESs) have attracted increasing attention for sample pretreatment. DESs are mixture of two or more precursors with a melting temperature lower than that of the individual components of DESs.

In this paper, new DES (vanillin:thymol) was investigated for selective extraction of SAs based on reaction between SAs and vanillin with formation of colored Schiff bases (Fig. 1).

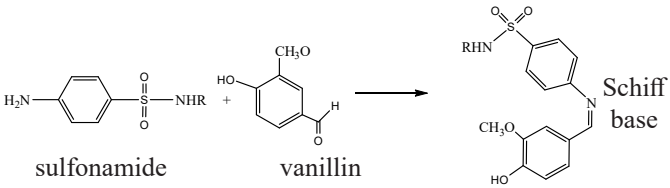

Fig. 1. Schiff base reaction between sulfonamide and vanillin

An effective and fast liquid-liquid microextraction procedure based on the use of hydrophobic deep eutectic solvent was developed. DES containing vanillin and thymol (1:1, mol/mol) was chosen for separation and preconcentration of sulfonamides. The approach (Fig . 2) was applied for the HPLC-UV determination of sulfapyridine, sulfathiazole, sulfacetamide and sulfadiazine in food samples. The extraction conditions were optimized. Under the optimum conditions, good linearity in the range of 0.5-50 mg L^{-1} was obtained. The limit of detection was 0.05 mg L^{-1}.

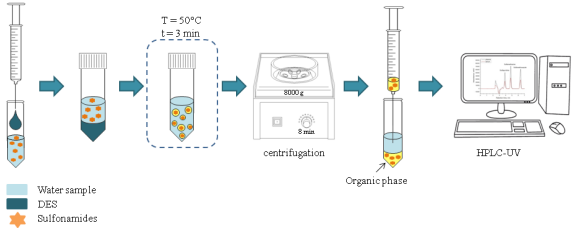

Fig. 2. Schematic representation of the pretreatment procedure.

Acknowledgments: This work was supported by the Russian Foundation (project No 20-73-00043).

The Investigation of The Liquid-Liquid Equilibria in the System Acetic Acid – *N*-amyl Alcohol – *N*-amyl Acetate – Water at Polythermal Conditions

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The esterification reaction is known to be an important industrial and laboratory method for synthesis of a number of esters, in particular amyl acetate which is used as a solvent, flavoring and extractive agent in pulp industry, food and cosmetic industry etc. At the same time the system acetic acid – amyl alcohol – amyl acetate – water belongs to such kind of mixtures where, along with the possible chemical reaction, the splitting phenomenon can be observed. In this regard the design of amyl acetate industrial synthesis requires both the chemical equilibria data and the information about the phase equilibria.

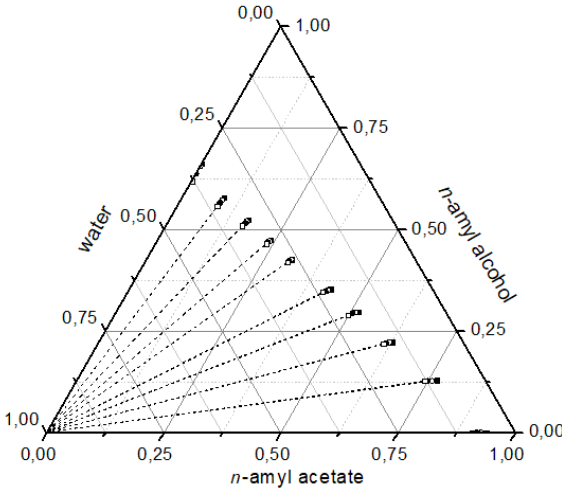

Fig. 1. The diagram of LLE of amyl alcohol – amyl acetate – water system at 293.15K (■)*, 303.15K* (○)*, 313K* (●) *and 323.15K* (□).

In this work the compositions of coexisting phases for the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water and its ternary and binary subsystems were determined using gas chromatography method. The data were obtained for temperature range 293.15 – 323.15 K at atmospheric pressure (Fig. 1). The results were compared with solubility data, presented in literature [1, 2]. The UNIFAC and NRTL models were applied for data correlation.

Acknowledgments: The authors are grateful to Russian Science Foundation (grant 21-13-00038) for the financial support in study of LLE in ternary systems and correlation of these data and to Russian Foundation for Basic Research (project 19-03-00375) for the support in experimental study of quaternary mixtures.

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Electrochemical Stability of Aqueous System Containing Lithium and Cesium Acetates.

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In modern research, the problem of «green chemistry» comes to the fore. An important role in this direction is occupied by the development and creation of liquid crystal systems with good electrical conductivity for further use in the creation of non-toxic, highly efficient conductor systems with good electrochemical properties, low freezing point and high solubility. Water-in-salt (WIS) systems turned out to be promising in this regard, which make it possible to achieve electrochemical stability windows close in size to non-aqueous electrolytes. A water system containing lithium and potassium acetates was previously investigated [1]. This study showed an extended window of electrochemical stability and compatibility with traditional electrode materials of lithium-ion batteries (Fig. 1). In our research the electrochemical stability in LiOAc – CsOAc – H2O system was measured at different component ratios. The cesium salt was chosen as an additive to lithium acetate because firstly the cesium ion has a strong destructive effect on water, which leads to an increase in the mobility of ions in solutions and a decrease in their viscosity. Secondly, cesium acetate has an extremely high solubility in water, which makes it possible to obtain highly concentrated systems. The densities of tested solutions were also measured in this work. Analysis of the obtained results of electrochemical measurements and comparison with the literature data in the studied system containing potassium acetate is carried out.

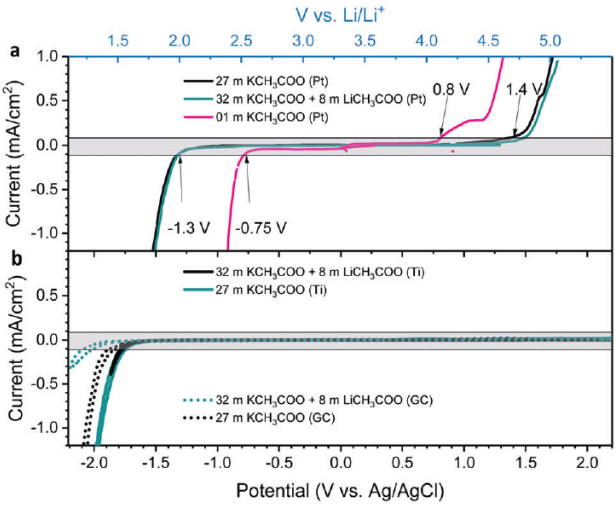

Fig. 1. Voltamogram image for LiOAc-KOAc-H_2O system.

Acknowledgments: The authors are grateful to Saint-Petersburg State University Research Park.

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Novel Pervaporation and Ultrafiltration Membranes Based on Polyphenylenesulfone Modified by Titanium Dioxide

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Ultrafiltration (UF) is one of most popular filtration processes that is used in pharmaceutical, chemical, food, textile and many other industries for refining macromolecular fluids. Pervaporation (PV) is other popular membrane process that is used for separation of low molecular weight ingredients, including thermally unstable mixtures, azeotropic mixtures and isomer mixtures. It is possible to improve the transport qualities of the membrane by developing of the mixed - matrix membranes (MMMs), which consist of a modification the polymer matrix by introduction an inorganic compound that leads to getting tailoring properties.

In the present reseach two types of membranes: porous membrane for ultrafiltration and non-porous (dense) membrane for pervaporation were developed. Polyphenylenesulphone (PPSU) was chosen as the polymer material due to its thermal and chemical resistance and high tensile strength; titanium dioxide (TiO_2) was chosen as a modifier due to its low cost, high reusability and chemical stability. Physical and chemical properties of PPSU/TiO_2 membranes were studied by atomic force microscopy, scanning electron microscopy, Fourier-transform infrared spectroscopy, nuclear magnetic resonance, X-ray diffraction analysis, swelling experiments, thermogravimetric analysis and contact angle. The transport properties of UF membranes were investigated in separation of the bovine serum albumin (BSA) and cutting fluid. Transport properties of PV membranes were investigated by separation of several industrially significant mixtures: isopropanol/water and ethyl acetate/water mixtures. It was found that introduction of TiO_2 leads to significant improvements of filtration properties of membranes based on PPSU.

Acknowledgments: The reported study was funded by RFBR, Sirius University of Science and Technology, JSC Russian Railways and Educational Fund "Talent and success", project number 20-38-51022. The experimental work of this study was facilitated by the equipment from the Resource Centre of Geomodel, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Methods, Magnetic Resonance Research Centre, Centre for Innovative Technologies of Composite Nanomaterials, Nanophotonics Centre, Cryogenic department, Thermogravimetric and Calorimetric Research Centre and the Interdisciplinary Resource Centre for Nanotechnology at the St. Petersburg State University.

Supramolecular Structure for Creating Functional Materials

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A bottom-up construction of functional materials based on supramolecular self-assembly has been a subject of fundamental interest for the past years. The main purpose to study the properties of supramolecular association, as well as modification of the initial components or using additives to obtain materials with different properties.

In our research, melamine and barbituric acid were chosen as objects of investigation. Barbituric acid is closed analog of cyanuric acid, and it is known that melamine and cyanuric acid are canonical recognition pair, undergo a hydrogen-bonding driven molecular self-assembly [1]. Barbituric acid has in the structure an active methylene group located at the C-5 position in the molecule. This position is a reaction center and can be easily involved in condensation reactions with aldehydes or ketones that do not contain an α-hydrogen. This general type of reaction is known as the Knoevenagel condensation reaction. Knoevenagel condensation is an important and widely used method for the formation of carbon-carbon bonds in organic synthesis with numerous applications in the synthesis of carbocyclic and heterocyclic compounds [2]. Initially we used vanillin as an aldehyde since it is human friendly material. After that we was interested in another aldehydes, whose chemical formula is similar to vanillin. We created a correlation between the addition of functional groups in modify barbituric acid and properties of them in luminescence.

We have considered how various substituents in the modification of barbituric acid by R-substituted benzaldehydes affect the luminescence not only for modification of barbituric acid, but also of the supramolecular assembly. In the future, it is also planned to consider other structures. Since the luminescence of these assemblies can help in the subsequent detection of various substances that can be included in this supramolecular assembly, as for example in the works of our university [3], where various dyes were included in the melamine barbiturate, as an indicative model of the possibility of capturing large organic molecules by supramolecular assemblies.

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Microextraction of Melamine from Dairy Products in Deep Eutectic Solvent Prior to HPLC-UV Analysis

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Melamine ($C_3H_6N_6$) is a heterocyclic nitrogen compound which is used in the synthesis of melamine-formaldehyde resins. But because of its high percentage of nitrogen and low price melamine was illegally added to dairy products, infant formulas, chocolates, etc in order to increase the protein content. Melamine itself has a low toxicity, but in the presence of cyanuric acid, melamine precipitates in the kidneys in the form of melamine cyanurate crystals, which can lead to kidney failure. The need of monitoring melamine required the development of new analytical methods with higher sensitivity and rapidness. Due to the complex matrix of the dairy products, the preparatory stages are necessary for its subsequent analysis. Deep eutectic solvents have recently become increasingly popular as an ecological effective extractants. These eutectic solvents are compounds formed by a donor and an acceptor of hydrogen bond, the formation of this bond significantly lowers the melting point of the eutectic solvent. Deep eutectic solvents can be made from environmentally friendly natural compounds such as thymol, menthol and fatty acids. In current work, natural deep eutectic solvents were firstly used for separation and concentration of melamine from milk and dairy products for subsequent HPLC-UV analysis. DESs based on natural terpenes (thymol and menthol) and fatty acids were considered as eutectic solvents. In current work was shown that DES that consist of thymol and carboxylic acids show the highest extraction efficiency at the level of 95% in a wide pH range. It was also optimized the conditions for the melamine extraction. Optimal conditions allow to use this method to determine the melamine at the level of 1 μg/kg, which allows to use this method for food quality control.

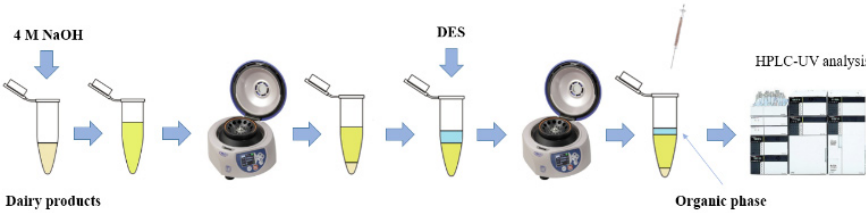

Fig. 1. Scheme of microextraction of melamine from a powdered milk using DES prior to HPLC-UV analysis.

Acknowledgments: The work was supported by a grant from the President of the Russian Federation MK-1154.2020.3. The authors are grateful to Saint Petersburg State University Research Park.

Study of Mass and Charge Transfer at Low Temperatures in Salen Type Nickel Polymer Complexes

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Chemical power sources are used in portable electronics and electric vehicles, energy storage and power systems. In particular, the use of low-temperature batteries and supercapacitors in devices designed for cold climates or space is of great interest. The main disadvantage is a significant decrease in capacity and rapid discharge at low temperatures. As a rule, the operating temperature range of such systems is from -20 to + 60 °C, however, their effectiveness is greatly reduced bellow 0 °C. Due to a decrease in temperatures, the kinetics of electrode processes in chemical current sources slows down. In this case, an increase in viscosity of electrolyte occurs, which leads to a decrease in conductivity and diffusion limitation of charge transfer.

Manufacturers are doing their best to increase the density of energy storage, thereby increasing the battery life of devices. One of the ways to solve this problem is to create an effective cathode material capable of showing the best characteristics at low temperatures in comparison with those currently used ones. Polymer complexes of nickel with ligands of the Salen type are a promising material for use in energy-intensive sources due to a more flexible structure and a highly developed surface, which has a significant effect on both the capacity and stability of such complexes.

Herein, the energy storage characteristics of cathodes based on Salen type materials at low temperatures were determined. The polymer nickel complexes with ligands of the Salen type were synthesized by electrochemical polymerization. The electrochemical properties, as well as the kinetics of charge transfer, were investigated by the method of cyclic voltammetry. Mass transfer parameters of the polymer film in the different electrolytes were determined by electrochemical quartz microbalance. The study was carried out in anhydrous solutions based on acetonitrile with the addition of various salts of electrolytes, whose anions differ in size and mobility.

Acknowledgments: Scientific research was partially performed at the Research park of St. Petersburg State University: Thermogravimetric and Calorimetric Research Centre, Centre for Physical Methods of Surface Investigation, Interdisciplinary Resource Centre for Nanotechnology, Cryogenic department. This research was funded by the Russian Foundation for Basic Research, grant number 20-03-00746 a.

Influence of the Microelements on Anticancer Metabolites Biosynthesis in Basidiomycetes

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Mushrooms and their extracts have long been used in folk medicine and food due to their low calorific value and pleasant taste and are also reported to have beneficial biological activities, thus now found applications in nutraceutical and pharmaceutical products. They are filamentous fungi with fruiting bodies packed with beneficial nutrients such as carbohydrates, fibers, proteins, vitamins, and minerals [1]. Mushrooms with medicinal value are defined as "mushroom nutraceuticals" and are consumed in capsule or tablet form as dietary supplements. Simultaneously, interest in mushrooms as a potential source of bioactive compounds has increased, and much research on the bioactivity of these compounds has been conducted in the last two decades. The secondary metabolites derived from mushrooms have demonstrated diverse biological properties such as anticancer, antidiabetic, immunomodulatory, antimicrobial, anti-inflammatory, antiviral, antiallergic, and antioxidative activities [2].

Basidiomycetes, which were used for the project, were cultivated with the microelements for enrichment. Enrichment basidiomycetes can be used as a dietary supplement in meat products. Microelements that were used are zinc, selenium, and magnesium. For this work anticancer metabolite, ergosterol was chosen to estimate its quantity in dry powder depending on the content of the microelements.

The method of the extraction was chosen and optimized based on the number of dry powder samples. Gas chromatography coupled with mass spectrometry of electron beam was chosen as a standard method for the detection of sterols. Correlation between quantitative content of microelements and quantitative content of ergosterol was founded.

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Pyridyl-functionalized Phosphinine as a Ligand for Novel Cu(I) Complexes

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In modern coordination chemistry, the search for novel ligands is one of the aims of principal importance. Pyridyl-functionalized phosphinines [1] can be an example of new potentially applicable ligand class. Herein, we examine the reactivity of chelating phosphinine towards copper(I).

Two novel phosphinine-containing copper(I) complexes and their isostructural diimine analogues were synthetized and characterized. The photophysical behavior of these systems strongly depends on the properties of the chelating ligand. Low-temperature solid-state emission spectra reveal the thermally activated delayed fluorescent nature of the emission state.

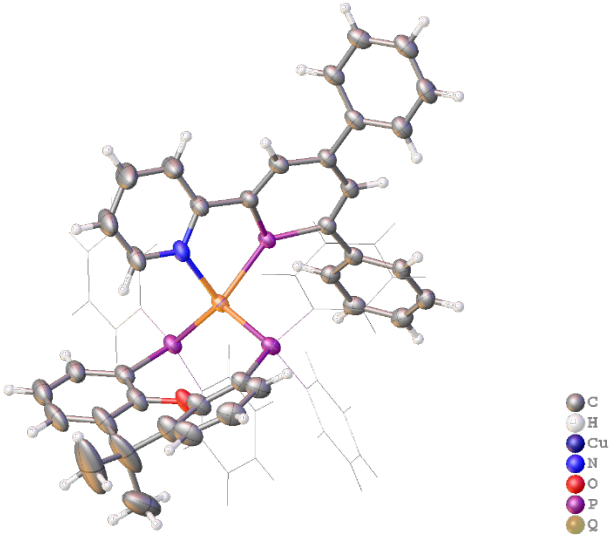

Fig. 1. Molecular structure of phosphinine-containing copper(I) complex

Acknowledgments: This work is supported by the German-Russian Interdisciplinary Science Center (G-RISC) funded by the German Federal Foreign Office via the German Academic Exchange Service (DAAD). The authors are grateful to St Petersburg University Research Park.

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Diastereoselective Synthesis of δ-Lactams *via* Two-component Castagnoli-Cushman Reaction of Imines and Glutaric Acid Derivatives

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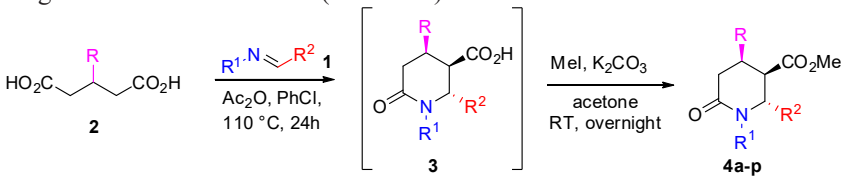
Multicomponent reactions are a powerful tool for synthesizing diverse libraries of compounds with periphery's variations. One of such reactions is Castagnoli-Cushman reaction (CCR) between anhydrides and imines (prepared in a separated step or generated *in situ* from amines and aldehydes). CCR is a stereoselective and convenient approach leading to saturated (high F_{sp3}) skeletally diverse lactams with several stereogenic centers. Such molecules are known as "lead-like" compounds and are of great interest for medicinal chemistry applications. In particular, 2-piperidone moiety is presence in such natural products as anticancer piperlongumine, antinociceptic alkaloid allomatrin and others [1-2]. Thus, investigation of the range of possible substrates for CCR is a privileged goal for synthetic organic and medicinal chemists.

Previously in our research group saturated δ-lactams could be only synthesized *via* reduction of their unsaturated analogs [3]. Moreover, such method led to formation of only two stereogenic centers in positions 2- and 4- of lactam's ring in *cis*-configuration.

In this study we accomplished a two-component format of CCR of imines **1** and glutaric acid derivatives **2** (Scheme 1).



*Scheme 1. Preparation of δ-lactams **4a-p**.*

Except for several examples, in most cases, it was problematic to isolate pure compounds **3**. So, we conducted methylation of **3** with further purification by flash column chromatography. Such strategy led us to a set of saturated δ-lactams with *trans*-configuration of substituents in the 2- and 4-positions of the heterocyclic ring.

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Synthesis of NHC-Stabilized Triphosphanylborane

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Binary and composite 13/15 materials are widely applied in micro- and optoelectronics and semiconducting materials. The chemistry of 13/15 group element hydrides is a rapidly developing area, since such compounds can be used as single-source precursors for composite materials [1, 2]. In contrast to compounds containing organic substituents, hydrides do not contaminate the product with carbon. However, phosphanylboranes require an additional stabilization, because they can polymerize due to the donor-acceptor interactions. Development of precursors for CVD, which contain both 13 and 15 group elements at different ratios in one molecule is of particular interest.

In this work the IDipp-stabilized triphosphanylborane was synthesized from IDipp·BBr_3 complex and $LiPH_2$·DME (IDipp = 1,3-Bis-(2,6-diisopropylphenyl)-imidazolin-2-yliden, DME = 1,2-dimethoxyethane). The solid $LiPH_2$·DME was added to the suspension of IDipp·BBr_3 in THF, cooled to -80 °C, stirred for 2 hours in a cooling bath, than removed from the cooling bath and left to reach the room temperature. After that the THF was removed, product extracted with toluene, than dried under vacuum and washed with hexane. Purification of the target product is difficult due to the similar solubility of the starting IDipp·BBr_3 complex and IDipp·$B(PH_2)_3$ in THF, toluene or hexane. According to the ^{11}B and ^{31}P NMR-spectra the product is formed, but only a minor amount of starting materials was converted. Further work will be related to the search of another precursor instead of IDipp·BBr_3.

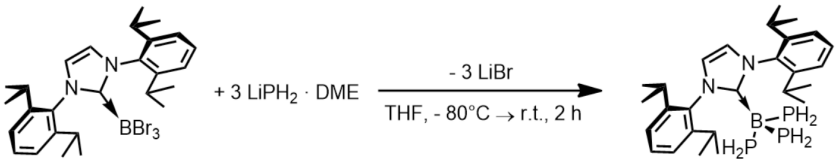

Fig. 1. Synthetic route to triphosphanylborane.

Acknowledgments: This work was supported by joint RSF-DFG grant № 21-43-04404. Authors are grateful to NMR department of the University of Regensburg.

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Hydrophobic Deep Eutectic Solvents for the Separation of Zearalenone from Bread Followed by Liquid Chromatographic Determination

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Deep eutectic solvents (DES), having similar properties to ionic liquids, are increasingly used in various fields of analytical chemistry. They have been proven to be an environmentally safe alternative to commonly used toxic organic extractants such as chlorinated organic solvents. DES is a mixture of two or more precursors with a melting point lower than that of the individual components. The composition of DES can be easily varied, which allows tuning its properties for selective and efficient extraction of the target compound. In this study, hydrophobic DESs based on menthol and long-chain alcohols, stable in aqueous medium, were studied for the separation of zearalenone from bread for the first time.

The main problems of food analysis are low concentrations of analytes and the complexity of matrices, that contain many interfering components, so the analyte should be extracted and preconcentrated prior to its determination. To solve this analytical task, an effective, fast and sensitive dispersive liquid-liquid microextraction method based on the hydrophobic deep eutectic solvents was developed in this work. The suggested sample preparation procedure (Fig. 1) was coupled to high-performance liquid chromatography with fluorometric detection and allowed zearalenone quantification in food at trace level.

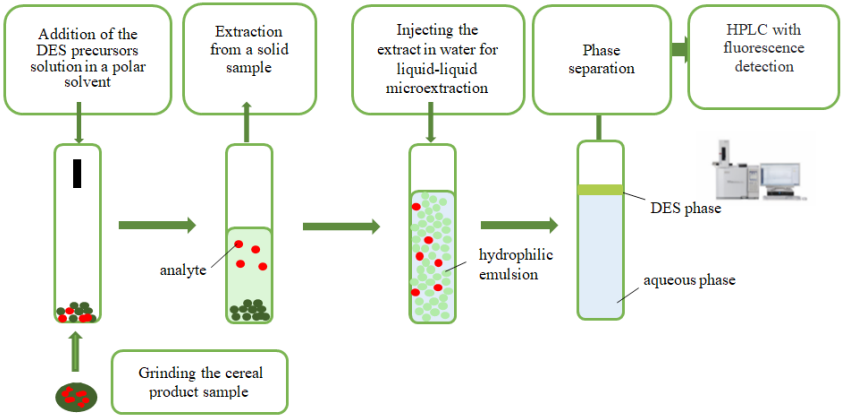

Fig. 1. Sample preparation procedure.

Acknowledgments: This work was supported by the Russian Science Foundation (project No 21-13-00020, https://rscf.ru/project/21-13-00020/).

Polyelectrolyte Multilayers for Robust Carbon Fiber-Based Potentiometric Ion Sensing and Correlation between Elemental Constituent in Blood and Urine

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Nowadays, there are many methods of detection of various bioelements for monitoring human health. Most of them are required special equipment, high expenses, and a long time to obtain results. In this work, we report on using polyelectrolyte multilayers for robust carbon fiber-based potentiometric sensing to determine ion concentration in human biofluids.

The electrochemical detection is realized using miniaturized ion-selective electrodes modified with polyelectrolytes. In this investigation, polyelectrolytes are applied as a modifier of the working surface by layer-by-layer (LbL) deposition to improve sensor electrochemical characteristics. This approach based on the sequential deposition of oppositely charged molecules due to electrostatic interactions allows formatting of ultrathin molecular films with wide functional possibility.

The electrode application is demonstrated to measure detectable ions, such as potassium and sodium, in urine and blood samples from patients with COVID-19. The level these analytes in the human organism is an essential indicator of human health and a deviation from the normal content can be a signal of the presence of a disease. It was detected that potassium content is below normal and sodium content is above normal in the studied samples. It is found that an imbalance in the content of potassium and sodium in urine and blood is related to changes in the content of zinc in patients with coronavirus which was studied previously.

In the future the sensor system based on miniature ion-selective electrodes and combined with software of digital device will enable to collect of large data to early diagnosis and rapid monitoring.

Acknowledgments: The authors acknowledge RSF grant No 19-73-00315 for financial support.

New Thermo- and Potentioresistive Organometallic Polymers

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Overcharging of lithium-ion cells is one of the causes of serious safety problems. Despite many efforts to prevent these problems by using battery management systems, chemical protection remains the most reliable solution [1].

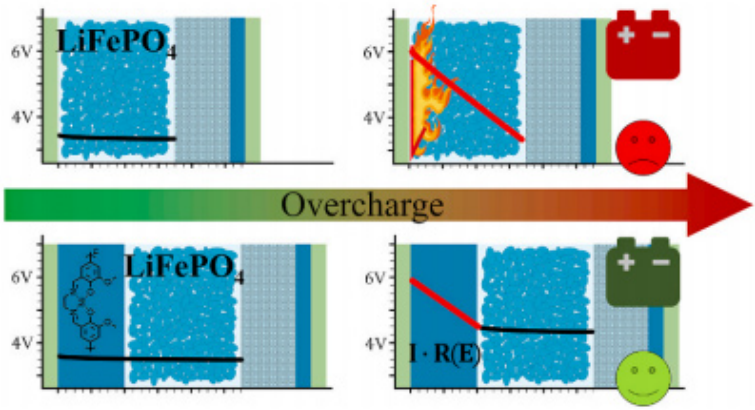

Fig. 1. Application of overcharge protection of lithium-ion cells

The aim of this work is to develop a new approach to overcharge protection of lithium-ion cells, which is provided by the use of an electrically conductive polymer that changes the electrical conductivity from conductive to insulating state depending on the battery operation status.

To achieve this aim, Salen type ligands can be used and their properties can be regulated by increasing the length of alkoxy chains at the 3-position of Salen ligand.

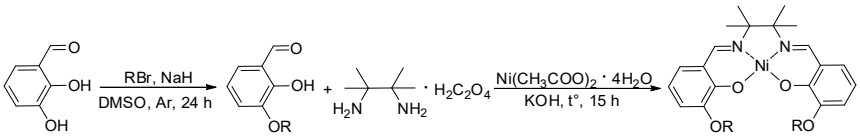

Fig. 2. Scheme of the synthesis of the monomer complex.

Then, the target polymer layers were obtained by electrochemical polymerization and their thermo- and potentioresistive properties were investigated.

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Rational Design of Ni-doped SnO_2 Nanoparticles for Organic Dyes and Bacterial Water Remediation: Synthesis and Photocatalytic Procedure

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The significance of the ocean pollution caused by industrial waste and the reuse of wastewater requires new effective treatment systems based on the use of sunlight for removing toxic organic pollutants and hazardous living microorganisms. The present research aims to provide an approach for the regulation of photocatalytic activity using doped wide band gap semiconductor nanoparticles under ultraviolet (UV) and visible-light irradiation. In order to clarify this aspect, we synthesized Ni-doped SnO_2 nanospheres by precipitation method with dopant concentrations 11 mol% and 33 mol%. The influence of crystallite size (regulation is achieved due to the initiation of slow and fast processes of NP formation) on photocatalytic activity is also under discussion.

As expected, XRD data demonstrated rutile SnO_2 peaks only (PDF 00-041-1445). According to TEM and SSA data, the nanosphere diameter do not exceed 4 nm. XPS data confirms the valence state of Ni and Sn atoms. In addition, the amount of structural defects and oxygen vacancies was determined using Raman spectroscopy and XPS, respectively. The band gap values were determined by UV-adsorption spectra. The band structure and density of states of the as-prepared NPs were calculated within the density functional theory approach. The photocatalytic activity of the samples was tested using colored methylene blue (MB), E. coli bacteria, UV, and 2 visible light sources of different intensity with predefined emission spectra under mechanical and gas bubble stirring. The "dark" adsorption of organic molecules on the surface of the samples has been studied.

The results obtained helped to establish that gas bubble stirring improved the photocatalytic degradation of MB from 73% (magnetic stirring) to 86% (aeration) for the sample with 33 mol% of dopant, which show that oxygen and air nanobubbles can act as environmentally friendly catalysts for boosting the performance of photocatalytic water treatment systems. Based on research, photocatalytic activity of Ni-doped SnO_2 is determined by structural parameter specified by the oxygen vacancy amount/defect amount ratio which can be easily adjusted/regulated by changing the synthesis parameters.

Acknowledgments: The authors are thankful for the financial support provided by the RFBR (no. 20-03-00762 A). Scientific research was performed using the equipment of the Research Park of St. Petersburg State University (Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Centre for Physical Methods of Surface Investigation, Centre for Optical and Laser Materials Research, Interdisciplinary Resource Centre for Nanotechnology).

Multielectrode Electrochemical System for Antibiotics Detection in Raw Milk

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The widespread use of antibiotics leads to the rapid spread of antibiotic resistance and poses a high risk to human health. The presence of antibiotics in the microbial system can lead to genetic mutations that allow bacteria to survive and then multiply as antibiotic resistant.

There are many ways to classify, but electrochemical biosensors have several advantages. They are portable, reliable, and highly sensitive.

We propose to use current-voltage characteristics (VAC) to detect various concentrations of antibiotics. This approach represents a new way of assessing the food industry. The use of machine learning methods in this work allowed us to obtain significant scientific results and new possibilities for analysis.

This electrochemical system demonstrates a new approach to the detection of different groups of antibiotics.

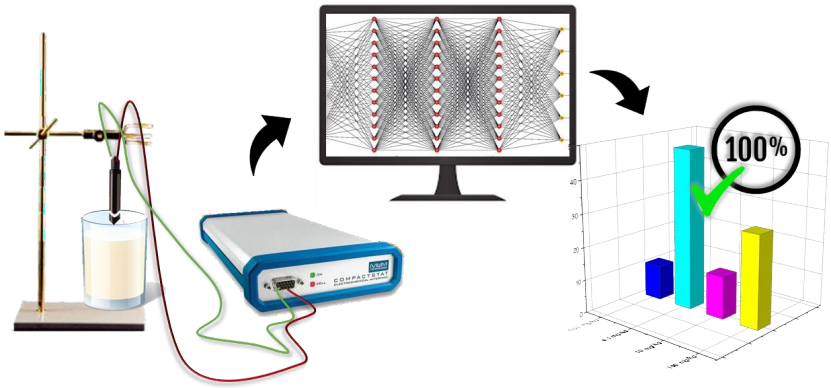

Fig.1. Scheme of the electrochemical system

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Polynuclear Metal Complexes Formed by Coupling of Azaheterocyclic Thiones with Coordinated Aryl Isocyanides

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In recent decades, transition metal complexes with aminocarbene ligands (NHC – N-heterocyclic carbenes, ADC – acyclic diaminocarbenes) took a special place in coordination and organometallic chemistry due to their wide application in various application areas such as catalysis, material design, and medical chemistry. One of the promising and easy in processing methods for generating of complexes with various types of aminocarbene ligands is metal-mediated addition of nucleophiles to coordinated isocyanides [1].

In this work, we have studied the Pd^{II} and Pt^{II}-mediated coupling of aryl isocyanides with azaheterocyclic thiones acting as ambident *S*,*N*-nucleophiles. The reaction of *bis*(arylisocyanide) complexes with thiones in the presence of one equivalent of base leads to the formation of mononuclear *C*,*S*-chelated aminocarbene complexes in which the carbene fragment is formed by the endocyclic nitrogen atom of the thione what is the first example of such interaction [2]. In the presence of excess base in the reaction with unsubstituted thiones yields the deprotonation of the formed complexes and allows obtaining polynuclear coordination macrocyclic compounds. These compounds can be converted to mononuclear species by the addition of triphenylphosphine.

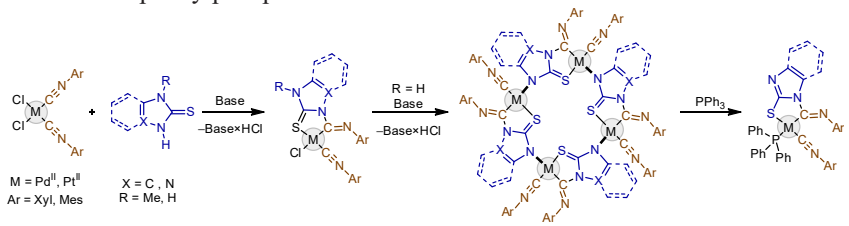

Fig. 1. Coupling of coordinated arylisocyanides with azaheterocyclic thiones.

Acknowledgments: This work was supported by the Russian Science Foundation (project No 19-13-00008). Physicochemical studies were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research (all belong to SPbU).

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Synthesis of Polythiophene Doped Sulfonated Polycatechol

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Functional additives can significantly improve the energy storage performance of poly(3,4-ethylenedioxythiophene) (PEDOT). For example, sulfonated polystyrene (PSS) increases conductivity of PEDOT, while polycatechol improves the capacity of material (Figs. 1, 2). Recently, we reported a novel SPVQ polymer, which combines the properties of both polymers. Herein we report the improved approaches for the synthesis of the PEDOT:SPVQ materials via electrochemical and chemical routes.

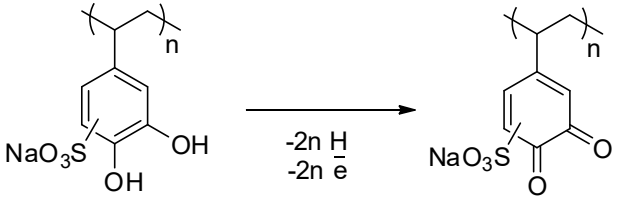

Fig. 1. The oxidation reaction of SPVQ.

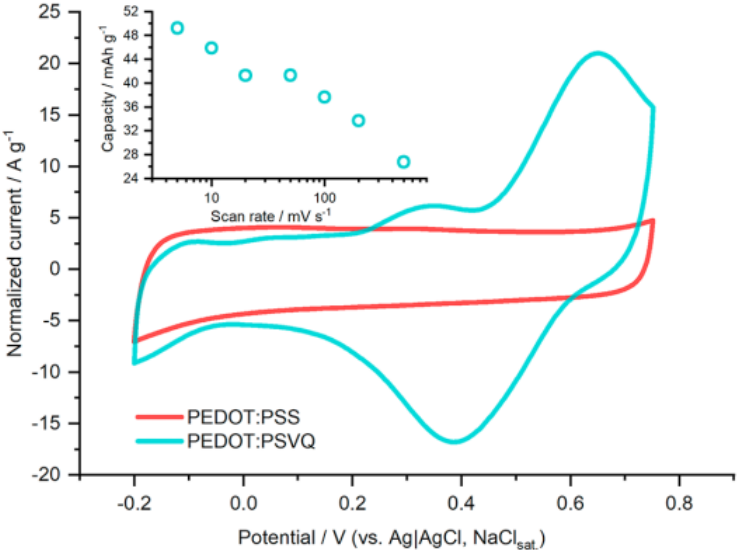

Fig. 2. Cyclic voltammograms curve of PEDOT:PSS and PEDOT:SPVQ films.

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Perovskite-like Oxide Doped into Polyetherimide Mixed Matrix Membranes for Liquid and Gas Separation

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In the last decades, many novel polymeric materials have been considered for preparing highly energy-efficient liquid and gas separation membranes. Considering the advantages of polymer membranes, the incorporation of inorganic nanoparticles into a polymer matrix can be an exciting solution for the development of materials with improved operational and transport properties. Layered perovskite-like oxides seem to be promising modifiers due to a combination of two factors: 1) the possibility of creating selective channels through the interlayer space of the perovskite structure; 2) the possibility of increasing the free volume in the membrane, which should increase the permeability of the membrane from solid particles, which will loosen the polymer chains.

The aim of this work was to develop and comprehensively study membranes with the addition of perovskite-like oxides in a polymer matrix. Special attention was paid to the study of the structure formation of hybrid membranes by SEM and AFM methods, which revealed different compositions of the upper and lower surfaces of perovskite-containing membranes. The influence of inorganic modifiers on thermal properties, hydrophilicity, and density is estimated.

The pervaporation performance of the membrane was evaluated for the methanol/cyclohexane mixture. Pervaporation experiments showed that incorporating perovskites is in favor of enhancing the membrane performance – high selectivity and increased permeability. The gas separation properties of the mixed matrix membranes are discussed and compared with the neat polymer. Pure gas permeation measurements show a drastic increase of separation effectiveness for all gases (H_2, He, O_2, N_2) compared to the neat polymer.

Acknowledgments: This work was supported by the Russian Foundation for Basic Research (project No 19-33-90048) and grant of the President RF [project No MK-1280.2020.3]. The authors are grateful to Saint-Petersburg State University Research Park.

Sonochemical Nanostructuring of Copper-Zinc Alloy

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Ultrasound treatment usage for fabrication of various materials finds application in medicine [1] in the industry [2] in catalysis [3] or green chemistry. With the cavitation effect, sonochemically modification allows the formation of a morphology gradient on the surface. Cu-Zn alloy is well-known as a high-effective catalyst. Free radical formed on the surface Cu-Zn alloy dramatically affected cell function. Release usually forced with the dissolution of the system were copper incorporated roughness affect. Ultrasound cavitation using for active surface construction, whereas bacteria themselves bring in the power and trigger the response. Interestingly synergy effect of combination sonochemical treatment and bacterial metabolism to the protection of biocompatible surfaces were studied. At present research, we wanted to design several phases of Cu-Zn alloy for testing a biocide activity. The hypothesis was to determine how different functional groups on the surface of the ultrasound structuring Cu-Zn alloy were affected by bacterial strains. The idea is that a significant role places copper ions releasing from the species.

In summary, we have successfully fabricated gradient materials of ultrasound treatment of Cu-Zn alloy. After the sonication, the alloy was easily separated at three different phases with different surface morphology and release activity of copper ions.

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Creation of Synthetic Hydroxyapatite in the Presence of Optically Active Substances

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At present, considerable attention is being paid to the study of the deposition of calcium phosphate minerals. Until now the mechanism of precipitation of calcium phosphates in human body is of interest.

It is known that calcium and phosphorus are the main inorganic components of bone tissue, are part of the mineral phase of hydroxyapatite. These chemical elements support the structural basis of the body.

The main functions of calcium are the protection of the musculoskeletal system and the regulation of muscle contraction. In addition, calcium is an important component of the blood clotting system.

Understanding the process of calcium phosphate precipitation is of great interest for various fields of science. Phosphates are formed in the presence of various dextrorotatory or levorotatory α-aminoacids, enzymes and hormones in living organisms [1-2].

The aim of the research was to create gradient materials and determine the properties of the obtained materials.

Samples with gradient precipitation of calcium phosphate in the volume of agar solution were selected. These samples were obtained by mixing 0.02 mol Na_2HPO_4, 0.4 wt. % agar solution, and active substance. In our research, such additives as L-ascorbic and L-glutamic acids were used in various concentrations. Precipitated calcium phosphate without additives was taken as a control sample.

The gradient concentration of calcium in obtained materials was checked using titration. Titration was performed using an ammonia buffer and black T eriochrome ground into powder in a mortar with sodium chloride.

Thus, the titration has determined that our model system allows to fabricate the materials with gradient concentration of calcium. The amount of calcium ions in such materials is varied from 0.2 mol/l·g to 0.05 mmol/l·g.

Acknowledgments: Authors acknowledge RSF grant no.19-79-10244 for the financial support.

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Features of the Complexes of $Al(C_6F_5)_3$ with Pyridine-type Ligands: Pyrazine, 2-Aminopyridine and 4,4'- Bipyridine

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The donor–acceptor complexes based on 13-15 group elements are prospective precursors for the chemical vapor deposition (CVD) of binary and composite nitride [1]. Bidentate N-donors such as pyrazine (pyz) and 4,4'-bipyridine (bipy) can form metal-organic frameworks (MOFs) with aluminium trihalides [2]. $Al(C_6F_5)_3$ is one of the strongest Lewis acids used in catalytic reactions [3].

In the present research the structures of the complexes $Al(C_6F_5)_3$ with pyz, 2-aminopyridine (aPy) and bipy were established by X-ray structural analysis for the first time (Fig. 1). The complex $Al(C_6F_5)_3$ with pyridine (Py) was reported earlier [4]. Despite of N atom of the pyridine ring is more basic than the amino-substituent, in complex with aPy aluminum atom coordinate the NH_2-group with simultaneous transfer of a proton to the N atom of the pyridine ring. It makes possible to achieve super short donor-acceptor Al–N bond lengths. Based on the values of the Al–N bond length in Å, the increase in the strength of the donor-acceptor interaction occurs in the following order: $Al(C_6F_5)_3 \cdot$aPy (1.885(1)) > $Al(C_6F_5)_3 \cdot$Py (1.959(2)) ≈ $Al(C_6F_5)_3 \cdot$bipy (1.962(2)) > $Al(C_6F_5)_3 \cdot$pyz (2.025(1)).

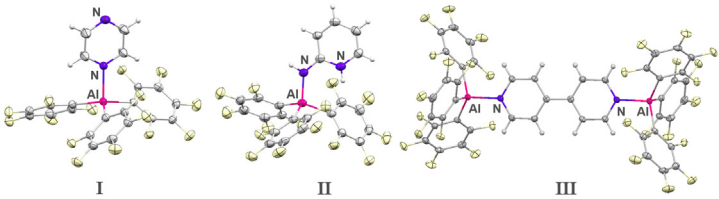

Fig. 1. Molecular structures of studied complexes in crystals. ***I*** *$Al(C_6F_5)_3 \cdot$pyz.* ***II*** *$Al(C_6F_5)_3 \cdot$aPy.* ***III*** *$Al(C_6F_5)_3 \cdot$bipy.*

Acknowledgments: This work was supported by the Russian Science Foundation (project № 18-13-00196). The authors are grateful to Saint-Petersburg State University Research Park and M.A. Kryukova for X-ray structure analysis.

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Synthesis of Indenes via the Reaction of Trihalomethyl-substituted Enones with Arenes in CF_3SO_3H

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Indenes are privileged structural motif in organic and organometallic chemistry. They are present in many biologically and pharmaceutically active compounds. Although a wide range of synthetic methods for indene ring formation have been reported, substituted indenes are still challenging to obtain, especially from cheap and accessible reactants [1].

Superelectrophilic activation of unsaturated compounds is an important and efficient tool for synthesis of various organic molecules, and the attempts to develop suitable methodology for substituted indenes and indanes were fruitful [2]. We found that trihalomethyl-substituted enone **1** readily reacted with various arenes to obtain enones **2a-f**. Reactions with some arenes yielded an intermediary product **3a-b**.

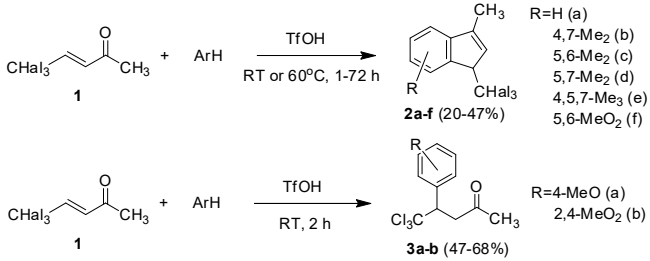

*Fig. 1. Reactions of enone **1** with different arenes.*

Plausible reaction mechanism includes the generation of protonated species **A**, which reacts with an arene via electrophilic aromatic substitution. Resulting cation **B** cyclizes intramolecularly to species **C** which subsequently dehydrates to yield indene **2**. The intermediate **B** that does not undergo cyclization hydrolyzes to ketone **3**.

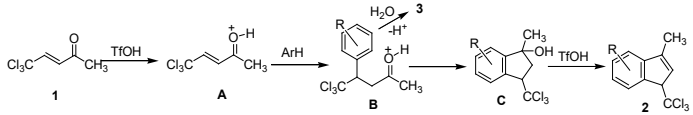

Fig. 2. Proposed reaction mechanism.

Acknowledgments: This work was supported by Russian Scientific Foundation (grant no. 21-13-00006).

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Plasmon Nanoparticles Dimers Obtained by Molecular Crosslinking with Diaminotolane

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Development of plasmonic nanomaterials with high localization of electromagnetic field is an actual task in optical spectroscopy and nanophotonics. Substrates with dimers and larger aggregates of nanoparticles (NPs) are advantageous due to their higher optical activity compared to substrates with single NPs [1]. Particularly, controllable preparation of nanoparticle dimers is important for further development of optical sensors with a detection limit up to single-molecule level. Using a systematic approach to the study of surface modifiers with properties of molecular linkers, we studied four classes of compounds, one of those is tolanes. Tolanes are well-known structure-forming units in the field of metal-organic frameworks [2]. In this work, we considered the possibility of their use for controlled self-organization of silver NPs.

To modify the surface of silver NPs, 4,4'-diaminotolane (DAT) was used. Obtained NPs were studied by SERS (surface-enhanced Raman scattering), UV-Vis, fluorescence spectroscopy and transmission electron microscopy (TEM).

TEM study of the morphology, size and dispersion of silver NPs modified by DAT showed a presence of oblong di- and trimers of NPs formed, probably, due to bridging by organic molecules. Percentage of NPs aggregates in relation to individual NPs displayed direct dependence on the concentration of DAT in initial solution, but only in the range of 10^{-7}–2.5×10^{-6} mol/l. At higher concentrations of the modifier, significant decrease in the number of NPs dimers was observed in the TEM images. The absorption spectra recorded for silver colloid at different DAT concentrations, agreed with the TEM results. They demonstrated a long-wavelength shift of the plasmon resonance band during the formation of NPs aggregates. The SERS spectra of NPs modified by DAT showed a non-monotonic character of the concentration dependence with a maximum at 2.5×10^{-6} mol/l.

Comprehensive analysis of the obtained data suggests that the efficiency of crosslinking of silver NPs with DAT is determined by the degree of surface coating and occurs at sub- or monolayer coverage only.

Acknowledgments: The authors are grateful to Saint Petersburg State University Research Park: OLMSM, MACM, PMSR, XRDRM and Nanotechnology.

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Luminescent Nanomarker Based on Gd_2O_3: Nd^{3+}, Er^{3+}, Tm^{3+} Particles: Synthesis and Characterization

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Materials doped with rare earth ions (REI) can be used in solid-state lasers, energy conversation and image generation devises. Systems with REI are promising in creating smart materials that able to deliver information on their elapsed life cycle, specific environmental influences conditions when it requires no constant power supply [1]. Oxide particles doped with a several REI have a complex optical system in which a unique identification (ID) signal can be created.

The weakly-agglomerated Gd_2O_3: Nd^{3+}, Er^{3+}, Tm^{3+} particles of single-phase were obtained in the work. The synthesis was carried out in three different ways based on Pechini method. The results of the X-ray diffraction analysis (XRD), morphology (SEM), static light scattering was obtained. ID code markers have been proposed based on the investigated luminescent properties (Fig. 1).

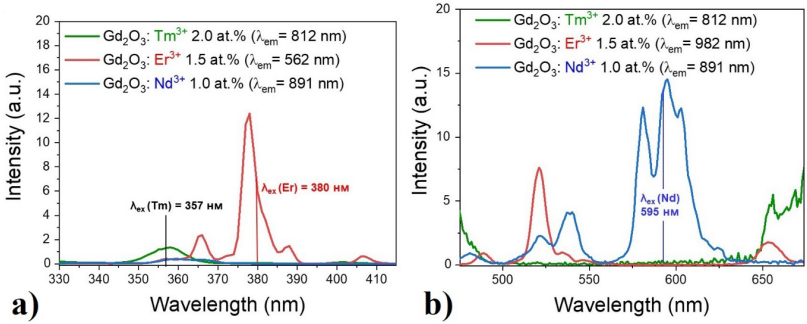

Fig. 1. Excitation spectra of single doped Gd_2O_3: Nd^{3+}/Er^{3+}/Tm^{3+} samples.

Acknowledgments: The authors are also grateful to Saint-Petersburg State University Research Park. The research has been partially funded by the Russian Science Foundation № 20-79-00101.

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Correlation Between Structural Parameters and Photocatalytic Activity of V or Ti-Doped SnO_2 Spherical Nanoparticles

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At the moment there is an actual problem of water pollution by cyclic organic compounds (COC) such as antibiotics and dyes, which poses a threat to the environment. Cheapness, environmental friendliness and the absence of need to use a complex plant are important for water purification. In this regard, the process of COC photodegradation using wide band gap semiconductor nanoparticles (NPs) is becoming a growing trend, but for these materials only the UV part of the solar spectrum can drive photocatalytic reactions, which is unsafe and increases operating costs in the case of artificial light sources. Doping allow diminish the band gap value and to shift the photocatalytic activity towards visible part of the spectrum. Among a large number of semiconductor materials, tin dioxide stands out with a rutile-type structure, which is tolerant to tin atoms substitution in the crystal lattice. But there is a lack of information about the impact of dopants with the same oxidation state as for tin (V^{4+}, Ti^{4+}) on the NPs structural parameters and photocatalytic properties.

Spherical doped NPs were synthetized by co-precipitation method. The synthesis temperature and reaction media composition were varied to change the rate of NPs formation. All samples were characterized by XRD, FTIR, TEM, XPS, Raman spectroscopy and SSA estimation. The band gap values were calculated from absorption spectra. The organic dye Methylene Blue (MB) solution was taken as a model system for kinetic of photodegradation under visible light irradiation study. For both dopants the crystallite sizes become smaller with the decrease of temperature and increase of pH value. The increase of dislocation density leads to the exponential growth of oxygen vacancies (Vo): defects (D) amounts ratio. The most effective for photocatalysis are NPs with V 11 mol %, which were synthesized by fast reaction and at a temperature of 25°C (82% of MB decomposed in 60 minutes). For the first time the impact of Vo: D ratio on samples photocatalytic activity was taken under consideration. It was shown that the enhanced behavior was demonstrated by the samples with higher amount of vacancies and a lower amount of defects simultaneously.

Acknowledgments: The author expresses his gratitude to the Resource Center of the Science Park of St. Petersburg State University: "Centre for X-ray Diffraction Studies", "Chemical Analysis and Materials Research Centre", "Centre for Optical and Laser Materials Research", "Centre for Physical Methods of Surface Investigation". The authors are thankful for the financial support provided by the RFBR (no. 20-03-00762 A).

The Methods of Phase Equilibrium Research

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Phase transformations cover a wide range of phenomena that are widespread in nature and are often used in industrial practice. Many methods of separation of substances and technological processes are based on phase transformations.

The purpose of this work is to obtain data on phase equilibrium by various methods. Data on the liquid-vapor equilibrium in the system - acetic acid - ethyl alcohol - ethyl acetate - water were calculated on the basis of the UNIFAC group model (Fig. 1).

Another research method is a continuation of a series of studies aimed at studying the liquid-liquid phase equilibrium and the extraction properties of Deep eutectic solvents (DESs) based on choline chloride in alcohol ether systems [1]. The purpose of this study is to analyze phase diagrams and evaluate the effect of alcohol and ester on the insolubility region, as well as to determine the efficiency of alcohol extraction using the investigated DESs.

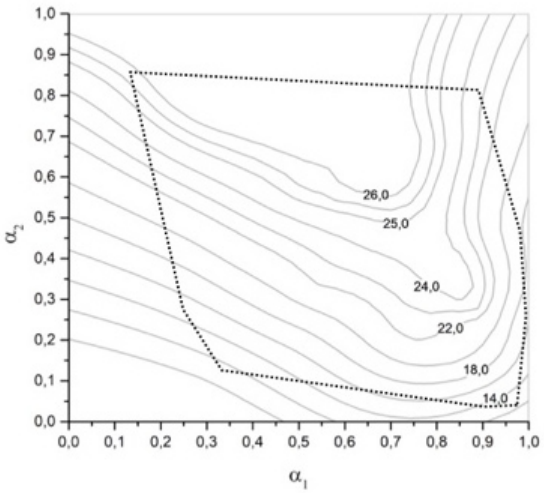

Fig. 1. Isotherm–isobar (kPa) lines on the chemical equilibrium surface for the system acetic acid – ethanol – ethyl acetate – water at 313.15 K (b): ····· - curve limiting the area of the calculated data. Beyond this curve, isotherms-isobars are approximated to the boundaries of the square of variables.

Acknowledgments: The authors are very grateful to the Russian Scientific Foundation (grant 20-73-10007) for their support in the study of liquid-liquid equilibrium and the extraction properties of DESs, and the authors are also grateful to the Russian Foundation for Basic Research for support in the study of liquid-vapor equilibrium: the data were obtained for the RFBR project 19-03-00375. The authors are grateful to Saint-Petersburg State University Research Park.

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Peculiarities of Phase Behavior of Chemically Equilibrium Mixtures in the Critical Region under Isothermal Conditions

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The development and introduction into industrial production of processes with supercritical fluids is currently an urgent and interesting task. Its study helps to discover new information about homogeneous and heterogeneous systems, to establish new physicochemical laws, which is of considerable interest for the development of physical chemistry. Processes with critical transitions are used in various industries, from pharmaceuticals to perfumery, biodiesel production and supercritical fluid chromatography.

The purpose of this work is to study chemical equilibria and critical phenomena in acetic acid – *n*-butyl alcohol – *n*-butyl acetate – water system at 318.15 K and 101.3 kPa. Fig. 1 (square of transformed compositions variables α) reflects obtained data on homogeneous, heterogeneous and critical chemically equilibrium compositions. The concentration and thermodynamic constants were calculated for the homogeneous chemically equilibrium mixtures.

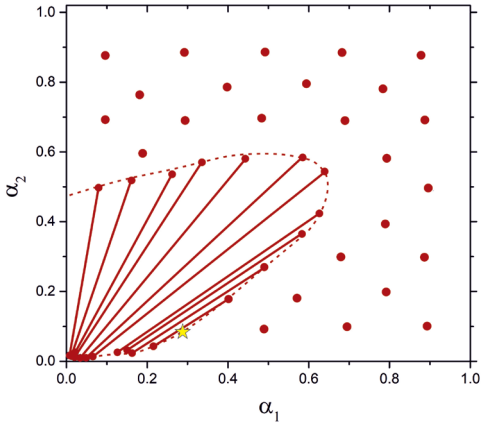

Fig. 1. The compositions of chemically equilibrium mixtures for the acetic acid – n-butyl alcohol – n-butyl acetate – water system (homogeneous (●), heterogeneous (●—●) and critical point (yellow star)) at 318.15 K and 101.3 kPa.

Acknowledgments: The authors are grateful to Russian Science Foundation (grant 20-73-10007) for the support in the liquid-liquid equilibrium study and to the financial support of Russian Science Foundation (grant 21-13-00038) in study of critical phenomena.

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Increased Plasticity of Chalcogenide Glasses While Maintaining a High Glass Transition Temperature

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Chalcogenide glasses are a promising material for creating elements of IR optics. However, at the same time, they have low plasticity due to the high degree of covalence of the bonds forming them. This fact, in particular, significantly limits the use of optical fiber based on chalcogenide glasses due to the difficulties associated with its bending. An increase in the plasticity of glass at room temperature can be achieved by changing the composition, significantly lowering the glass transition temperature. However, often in practice this means a narrowing of the permissible temperature range of glass operation, a decrease in chemical resistance, or an increase in toxicity.

As it turned out, there is another way to increase plasticity: the introduction of silver chalcogenides into the glass. In these compounds, along with a grid of directed covalent Ag-Se bonds, there is a grid of non-directional Ag-Ag metallophilic bonds [1], which explains their abnormal plasticity [2]. Thus, the introduction of Ag_2Se into the glass of the composition ($0.27Sb_2Se_3$*$0.73GeSe_2$) leads to a significant increase in the plasticity (more than in three times) of the glass while maintaining a high (for chalcogenide glasses) its glass transition temperature. At the same time, the glass retains transparency in the near IR range, which is its main functional property.

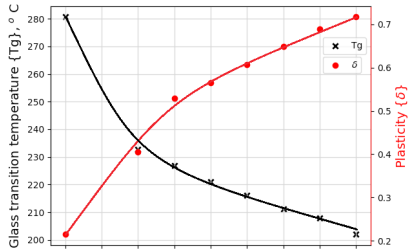

Fig. 1. Concentration dependence of the glass transition temperature (left) and plasticity (right).

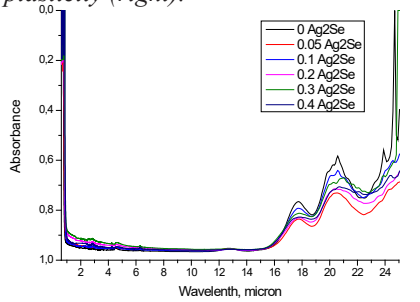

Fig. 2 Optic absorption spectra of lasses with different Ag_2Se content.

Acknowledgments: This work was supported by RFBR (№ 20-03-00185). The authors are grateful to SPbSU Research Park: COLMR, CXRDS, TGCRC.

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Electrochemical Sensor Platform to Detect of Viruses and Bacterial Pathogens in Biological Fluids

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The location and timing of detection of viruses and bacteria that cause pandemic situations are significant. The development of electrochemical test devices, due to the possibility of miniaturization of equipment, opens possibilities for the determination of the micro-content of biological substances [1].

There are various strategies for antibody function for specific antigen detection. In this work to solve these problems, the use of biomolecules in polyelectrolyte structures. This method provides a unique and novel way to use biosensors for viruses and bacteria detection. Immobilized antibodies have higher binding constants due to an increase in the number of active sterically mobile centers. Isolation of the sensitive layer of antibodies from the analyzed one by the adsorbed layers of polyelectrolytes prevents nonspecific actions by back-ward repulsion. In this case, the interaction between the antigen of the target analyte and the antibody preserved. Nanoarchitecture $(PEI/antibody/PSS)_2$ on screen-printed carbon electrode provides a wide sensor linear range from 10^3 to 10^9 parts/mL of Tick-borne encephalitis virus has been shown. The limit of de-tection was 5 parts/mL. Modification of antibodies to the Tick-borne encephalitis virus into polyelectrolyte layers made it possible to achieve high selectivity by preventing nonspecific and non-selective interactions.

The proposed approach allows avoiding preliminary preparation of a sample for analysis. The choice of an electrochemical method for obtaining a signal is due precisely to the creation of precision instruments for an electrochemical signal - mini-potentiostats [2].

The developed potentiostat showed the possibility of detecting viruses by cyclic voltammetry with the presence of Prussian blue nanoparticles on the electrode. Bacterial pathogens are identified using impedance spectroscopy. Potential ranges from -10 V to 10 V, input signal up to 1000 μA. Testing of sensor platform was shown of great reproducibility and precision.

Acknowledgments: This work was supported by RFBR- 20-04-60495.

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Silver and Gold Nanoparticles Modified with Cyclene and Tetraxetane Chelators: Preparation and Optical Properties

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Systems in which noble metal nanoparticles (NPs) forming organized structures of controlled size are promising for a wide range of applications. For this reason, their synthesis and further stabilization from uncontrollable aggregation are of interest. For such systems, it is also advisable to study their optical response. As shown earlier [1], stilbene derivatives proved to be effective molecular linkers for silver NPs, making it possible to achieve reproducible formation of plasmonic nanostructures capable of effectively localizing the electromagnetic field. In this work, modification of silver and gold NPs was carried out with two compounds belonging to azamacrocycle class which can potentially act as a molecular linker: cyclene (1,4,7,10-Tetrazacyclododecane) and DOTA (2,2′,2″,2‴-(1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrayl)tetraacetic acid).

Transmission electron microscopy (TEM) images of freshly prepared modified NPs proved the formation of their agglomerates. It is evident that cross-linking of NPs under addition of DOTA occurs, but it is accompanied by further aggregation. NPs agglomerates obtained with cyclene appeared to be stable. In the absorption spectra, the emergence of new band in the long-wave range was observed. Visual observations showed a discoloration of silver and gold NPs solutions in the presence of DOTA after one day. The most intense surface-enhanced Raman scattering (SERS) spectra were obtained for DOTA, for which a non-monotonic concentration dependence is revealed. At the second stage of works the stabilization of agglomerates of NPs with DOTA by cetyltrimethylammonium bromide (CTAB) was attempted. Several stabilization schemes led to the same result: in the presence of CTAB the SERS response from DOTA was not detected.

Acknowledgments: This work was supported by the Russian Foundation for Basic Research (project No 20-33-70034). The authors thank the Resources Centers of Saint-Petersburg State University: the Interdisciplinary Center for Nanotechnology, the Center for Optical and Laser Materials Research, the Computing Centre, the Thermogravimetric and Calorimetric Research Center.

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Electroanalytical Detection of Zinc in Running Water Using Machine Learning

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Zinc is naturally present in water, but anthropogenic impact can increase the legal limit of the metal. Fast and accurate way of detection helps to identify any changes in the amount of zinc in water.

Anodic stripping voltammetry (SV) analysis is a powerful and straightforward tool for continuous monitoring of trace target metal species [1]. One of SV types is anodic stripping voltammetry (ASV). Using this method, you can detect metals in running water.

Mercury-graphite film electrode were chosen as a working electrode for Zn detection. Anodic stripping voltammetry allows to see the concentration of zinc in the analyzed water (Fig. 1). A background electrolyte and a GaIn solution are added to the analyzed water to make the determination of zinc more accurate. The solution of GaIn helps to prevent the formation of amalgams in the zinc-copper system on the electrode surface [2]. Using algorithms of machine learning improved the accuracy of Zn determination.

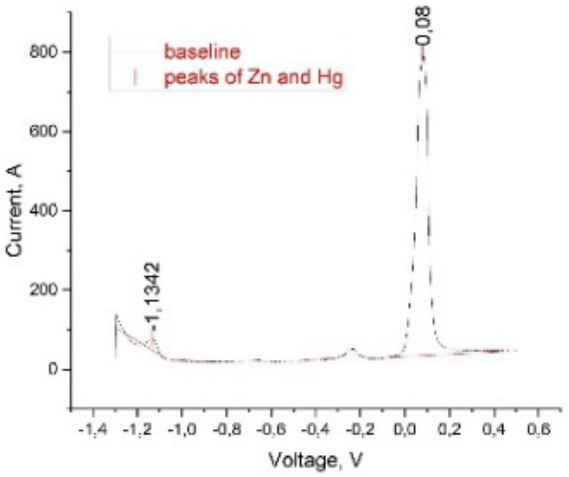

Fig. 1. Voltammetric response (A) from square-wave anodic stripping voltammetry of water sample

We consider a method for the quantitative determination of zinc in running water on a mercury-graphite film electrode by anodic voltammetry (ASV). Such an electrode let detect even small concentration of zinc and anodic voltammetry make the process of monitoring faster and enough sensitive.

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SERS Detection of Proteins on Substrates Basing on Hydroxyapatite Doped With Silver Nanoparticles

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Development of new methods for selective analysis of micro-quantities of bio-analytes is under demand. The idea of present study consists in using of hydroxy-apatite (HA) doped with silver nanoparticles (NPs) for simultaneous sorptional isolation and optical determination (qualitative and quantitative) of proteins by surface-enhanced Raman spectroscopy (SERS).

HA modified by silver NPs (HA@AgNPs) was obtained via the method [1]. The resulting powder was pressed into tablets which were placed in quartz cuvette with test solution. Laser was focused on the tablet surface for SERS measurements. Lysozyme, myoglobin and transferrin were selected as test proteins.

The SERS spectra showed that myoglobin adsorbs better on HA@AgNPs tablets among the selected proteins. Normalization of the spectral signal of myoglobin on internal standard significantly improved the accuracy and reproducibility of the quantitative determination of myoglobin by the SERS method (Fig.1). But, further improvement of the analysis procedure and / or sample preparation to increase sensitivity is required for possibility of using SERS spectroscopy for the analysis of myoglobin in physiological fluids.

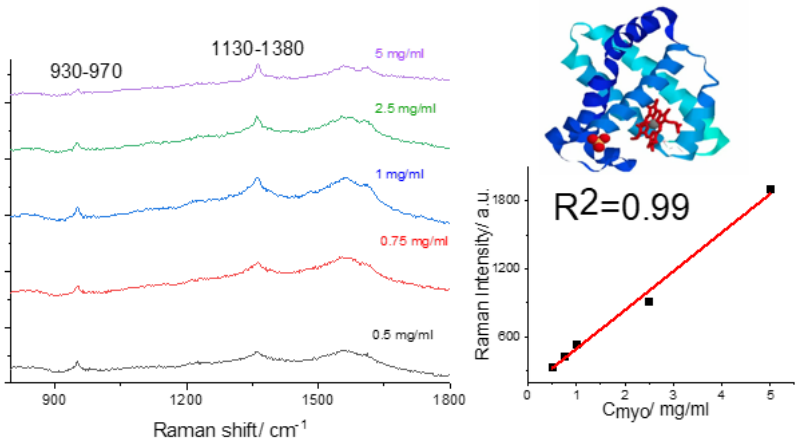

Fig. 1. The SERS spectra, calibration curve and structure of myoglobin.

Acknowledgments: The authors are grateful to Saint Petersburg State University Research Park: OLMSM, MACM, PMSR, XRDRM and nanotechnology.

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Supramolecular Assemblies for Biomolecules Encapsulation

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During previous studies, it was shown that the developed supramolecular material melamine barbiturate [1], like its close analogue melamine cyanurate, is capable of trapping and long-term storage of active components, such as organic dyes [2, 3].

We assumed that short DNA strands could also be encapsulated into melamine cyanurate; however, for slower nucleation of melamine cyanurate and more efficient encapsulation, we used a diffusion control method, namely, an agar gel-based system.

Encapsulation of short DNA strands is primarily aimed at long-term storage of the inserted component. In addition, the formation of these capsules is reversible, DNA can be released with a slight change in pH.

To analyze the efficiency of DNA encapsulation, we proposed to use the modification of the introduced component with a fluorophore.

Thus, we were able to analyze the amount of the encapsulated component according to the data obtained by the method of fluorescence microscopy.

A comparison of melamine cyanurate capsules with / without an encapsulated component was carried out using electron microscopy methods, and regularities were revealed in the difference in capsule sizes depending on the concentration of the incorporated component.

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Reactions of Diazo Compounds with 2*H*-azirine-2-carboxylic Acids Under Metal Catalysis and Photolysis Conditions

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Diazo compounds are convenient precursors of carbenes used in organic synthesis both for the synthesis of heterocycles and for their functionalization. In the presence of several reaction centers in the substrate interacting with carbene, the problem of the reaction chemoselectivity arises. One of these substrates are 2*H*-azirine-2-carboxylic acids, which contain two reactive fragments: an azirine ring and a carboxylic group.

The aim of this work is to study the reactions of 2*H*-azirine-2-carboxylic acids **1** with diazo compounds **2** under photolysis and metal catalysis conditions. It is noteworthy that under the blue light photolysis, the reaction proceeds selectively with the formation of O-H insertion products **3** in a diastereomeric ratio of 1:1, while catalysis with rhodium acetate leads to the formation of 1,3-oxazin-6-ones **4**.

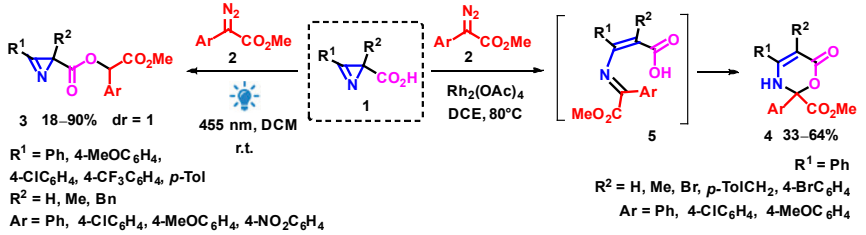

Fig. 1. Reactions of 2H-azirine-2-carboxylic acids with diazo compounds.

The formation of oxazinone **4** probably proceeds through the cyclization of the intermediate 2-azadiene **5**. In the case of $R^2 \neq H$, the yield of the final product **4** is significantly increased, which indicates the predominance of isomer **5** required for the cyclization.

Acknowledgments: We gratefully acknowledge the financial support of the Russian Science Foundation (grant no. 19-73-10090). This research used resources of "Magnetic Resonance Research Centre" and "Chemical Analysis and Materials Research Centre" of St. Petersburg State University.

Co-Doped $LuVO_4:Nd^{3+},Yb^{3+}$ Nanoparticles as Ratiometric Luminescent Thermometers

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New way of non-contact thermal sensing is a method of temperature measurement based on luminescence intensity ratio (LIR) between of two thermally coupled lines [1]. Using nanoparticles (NPs) doped with rare earth ions as luminescent thermometer allows the real time temperature measurements with high temperature resolution and sensitivity. Main idea of this work is study of $LuVO_4:Nd^{3+},Yb^{3+}$ NPs under different excitation mechanism by LIR technology.

Synthesis of $LuVO_4:Nd^{3+},Yb^{3+}$ was provided by modified Pechini method. Detailed process of obtaining NPs was described in [2]. Study of $LuVO_4:Nd^{3+},Yb^{3+}$ NPs were carried out by X-ray analysis, scanning electron microscopy, and luminescence spectroscopy. Sample characterized phase purity and low agglomeration of NPs with average size of 60 nm. Excitation spectra of both doped Yb^{3+} (983 nm) and Nd^{3+} (1064 nm) ions were measured and analyzed. All excitation spectra include a strong UV band and several weak peaks centered at 533 nm, 595 nm, 751 nm, and 809 nm. Emission spectra upon 300 nm and 808 nm excitations were recorded at different temperatures from 123 K to 573 K with step 50 K. Emission spectra consist of bands at 879 nm ($^4F_{3/2}$–$^4I_{9/2}$), 983 nm ($^2F_{5/2}$–$^2F_{7/2}$), 1064 nm ($^4F_{3/2}$–$^4I_{11/2}$), and 1342 nm ($^4F_{3/2}$–$^4I_{13/2}$). Different temperature behavior of Nd^{3+} and Yb^{3+} emission intensities makes it possible to use synthesized NPs as ratiometric thermal sensors. The best relative thermal sensitivity was determined to be 0.18 % K^{-1}@299 K direct Nd^{3+} excitation (808 nm), while the best temperature resolution of 2.4 K was obtained upon upon host excitation (300 nm).

Acknowledgments: This work was supported by the Russian Science Foundation (№ 21-79-10018). Experimental measurements were performed in "Center for Optical and Laser materials research", "Research Centre for X-ray Diffraction Studies", "Interdisciplinary Resource Center for Nanotechnology" (St. Petersburg State University).

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Hybrid TEMPO-Containing Redox-Conductive Polymers for Organic Batteries

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Nowadays lithium-ion batteries are the most widely used class of energy storage devices for both portable electronics and electric vehicles. Currently used inorganic electrode materials, suitable mainly for lithium-containing electrolytes, lead to gradual increase in the mining volume to satisfy the growing demand. The production of such batteries, as well as their disposal, requires much more energy than they can store, and generates a large amount of thermal and CO_2 emissions [1]. This problem of ecological safety stimulates the creation of new environment friendly energy technologies that would be devoid of the disadvantages of the commonly used batteries [2].

Redox-conductive nitroxyl-containing polymers (RCP) are promising candidates for replacement of inorganic-based energy storage materials, due to their high energy density and fast redox kinetics [3]. Unfortunately, charge transfer processes in such materials are poorly studied. Herein the main features of two novel RCPs are reported. The in-depth analysis of these features provided insight into the link between RCPs structure and properties.

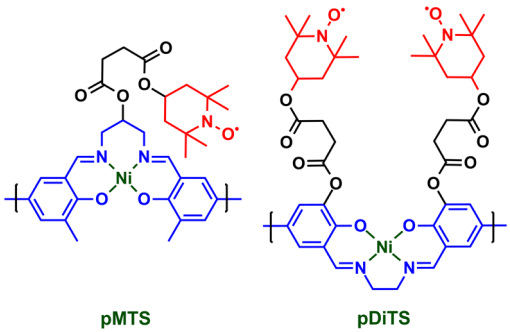

Fig. 1. Structure of studied RCPs.

Acknowledgments: Scientific research was partially performed at the centers of GEOMODEL, Chemistry Educational, Nano-technology, Magnetic Resonance, Chemical Analysis and Materials Research of SPSU Research Park. Project was funded by RFBR (#20-33-90122) and supported by scholarship of the President of the Russian Federation No. SP-691.2021.1.

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Theoretical and Experimental Investigation of the Peculiarities of the Interaction of Pyridines with Organolithium Reagents

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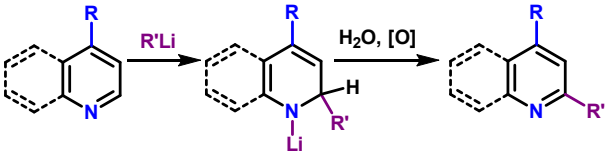
The reaction of pyridines with organolithium reagents generally leads to nucleophilic addition to position 2(6) (Scheme 1). However, to date for no examples of nucleophilic addition of organometallic to other positions are known.



Scheme 1.

In this work, we considered the effect of a bulky trimethylsilyl group at the pyridine nitrogen atom and a dimethylamino group at the position 4 on the reactivity of pyridines in nucleophilic addition reactions. Performed calculations of electrostatic potentials on carbon atoms demonstrate that introduction of trimethylsilyl group expectedly results in increasing of positive charge at all carbon atoms, but most significantly at the positions 2(6) (Fig. 1). Surprisingly the presence of electron donating NMe_2 group to the position 4 results in dramatic charge redistribution with the carbon atom at the position 4 being the most positively charged. This feature together with the steric hindrance of positions 2(6) by $SiMe_3$ group should lead to the nucleophilic addition of organolithiums predominantly to the position 4. Indeed, this prediction was confirmed experimentally upon the treatment of *N*-trimethylsilylated 4-dimethylaminopyridine with *n*-BuLi and PhLi.

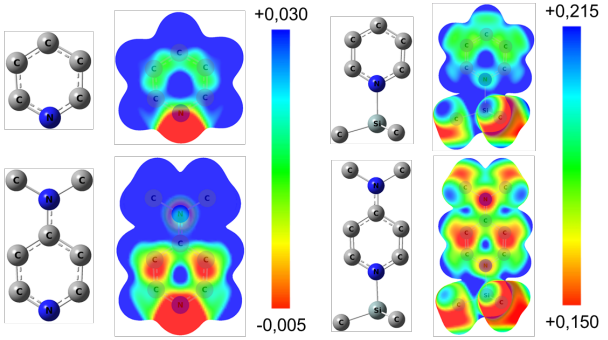


Fig. 1. Isosurfaces of electron density mapped by electrostatic potential.

Acknowledgments: This work was supported by the Russian Science Foundation (project 21-73-10040).

Synthesis and Electrochemical Properties of Conducting Polymer-Coated Molybdenum Disulfide

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Electrode materials based on molybdenum disulfide (MoS_2) have been extensively researched in various energy storage devices, including metal-ion batteries, lithium-sulfur batteries, and supercapacitors [1].

The advantage of MoS-based anodes in lithium-ion batteries is high theoretical specific capacity (up to 670 mA h g^{-1}), which is provided by a series (1-3) of conversion reactions:

$$MoS_2 + x \cdot Li^+ + x \cdot e^- \rightarrow Li_xMoS_2 \quad (1)$$

$$Li_xMoS_2 + (4 - x) \cdot Li^+ + (4 - x) \cdot e^- \rightarrow Mo + 2Li_2S \quad (2)$$

$$S + 2Li^+ + 2e^- \rightarrow Li_2S \quad (3)$$

The latter reaction also makes this material suitable for use in lithium-sulfur batteries. Yet, the challenge is in stabilizing high specific capacity values over hundreds of recharging cycles and at high current densities. The factors that cause the loss of capacity in MoS_2-based electrodes include conversion of initially present components to Li_2S/S redox pair, agglomeration of particles, loss of electric contact, dissolution of the materials via polysulfide shuttling, and volumetric expansion of the material.

Approaches to enhancement of MoS_2-based electrodes include nanostructuring, addition of graphene and other carbon particles, introduction of N-doped components and creating the composites with conducting polymers [1, 2].

In this work, we present an electrode material based on MoS_2 nanoparticles coated by PEDOT poly(3,4-ethylenedioxythiophene) (PEDOT) and its mixture with polystyrene sulfonate (PEDOT:PSS). The nanoparticles are synthesized via hydrothermal method with addition of the polymer. The polymer layer is intended to encapsulate the particles, both providing conductivity and trapping the particles to prevent dissolution.

The prepared particles samples have been characterized by SEM, XRD and XPS, and the electrochemical properties of the electrode materials have been studied using cyclic voltammetry and galvanostatic charge-discharge methods.

Acknowledgments: This work was supported by Russian Foundation for Basic Research, project number 20-33-90143. The authors are grateful to Centre for X-ray Diffraction Studies, Centre for Physical Methods of Surface Investigation, and Interdisciplinary Resource Centre for Nanotechnology of Research Park of St. Petersburg State University

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Investigation of Perovskite-like Niobate $HCa_2Nb_3O_{10}$ Exfoliated into Nanolayers as a Photocatalyst for Hydrogen Production from Aqueous Methanol

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The depletion of fossil fuels stimulates the search for alternative energy sources such as hydrogen. In this regard, at present, the photocatalytic hydrogen production from water and plant biomass is becoming an especially urgent scientific and technical problem. Layered perovskite-like oxides, an important property of which is the ability to exfoliate into nanolayers, are among the most actively studied photocatalysts. It is well known that the efficiency of heterogeneous photocatalysis directly depends on the specific surface area of the photocatalyst. Exfoliation into nanolayers leads to a sharp increase in its value, significantly magnifying the number of active centers involved in the process of hydrogen production. At the same time, the small size of perovskite nanolayers makes it possible to reduce the bulk charge recombination, which also explains the multiple increase in photocatalytic activity [1].

The present study is devoted to the photocatalytic properties of the perovskite-like niobate $HCa_2Nb_3O_{10}$, previously exfoliated into nanolayers via sonication in diluted TBAOH, in the reaction of hydrogen evolution from 1 mol. % aqueous methanol. The exfoliated sample was decorated with Pt nanoparticles as a co-catalyst to improve the efficiency of charge separation. It has been shown that the photocatalytic performance of the platinized niobate nanolayers exceeds that of the bulk precursor up to 3 times and strongly depends on the reassembly technique used. Particularly, the simple filtering of the nanolayers followed by their redispersing in aqueous methanol and in situ platinization allowes obtaining a composite photocatalyst, providing the apparent quantum efficiency of hydrogen generation of 20.4%. However, the nanolayers, restacked via the suspension acidification, demonstrate ceteris paribus only 6% efficiency, which is apparently associated with their pronounced aggregation and, consequently, lower specific surface area.

Acknowledgements: The study was conducted using the equipment of the Saint Petersburg State University Research Park: Centre for X-ray Diffraction Studies, Centre for Optical and Laser Research, Centre for Magnetic Resonance, Centre for Chemical Analysis and Materials Research, Centre for Thermal Analysis and Calorimetry, Interdisciplinary Centre for Nanotechnology, Centre for Innovative Technologies of Composite Nanomaterials.

The study was supported by grants of Russian Scientific Foundation (20-73-00027) and President of Russian Federation (MK-480.2020.3).

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Multipurpose Detector Based on High Frequency Inductor

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An urgent task of modern analytical chemistry is the development of simple and inexpensive sensor devices for the analysis of real objects under in-field conditions. In this study we propose a sensor device based on an inductance coil connected to a high-frequency electric field generator (4-114 MHz). When a sample is introduced inside the coil, it becomes the core of the inductor, changing the properties of the electrical signal flowing through the coil. A receiver connected to the coil registers these changes that depend on the properties of the sample (in particular on the dielectric permittivity and conductivity of the sample) and can serve as a source of information for qualitative and quantitative analysis.

In this work we have studied the possibility of using the developed sensor to distinguish between the substances with different physical and chemical properties. The applicability of the device to distinguish between different inorganic salts solutions (KCl, NH_4Cl, KNO_3, $Cu(NO_3)_2$, $Pb(NO_3)_2$, Na_2SO_4, KBr) was demonstrated. Moreover, it was shown that the detector is able to distinguish between various concentrations of the electrolytes in the concentration range $10^{-4} – 10^{-1}$ M. It was also shown that the sensor is able to detect the differences in the dielectric properties of organic solvents and it was shown that linear calibration model relating the registered signal and solvent's dipole moment can be constructed.

The applicability of the detector to real samples was demonstrated in the experiment with milk and cream samples with various fat contents. The device was shown to yield the signal linearly related to these values.

Donor-Acceptor Complexes of Lewis Acid $Ga\{N(C_6F_5)_2\}_3$ with Acetonitrile and Pyridine

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Lewis acids play a key role in many areas of modern chemistry. The widespread use of Lewis acids in synthetic chemistry aroused interest in the creation of very strong Lewis acids, the so-called super acids. The value of the energy of affinity for the fluoride ion in the gas phase (FIA, kJ/mol) was proposed by Haarz and McDaniel in 1973 as a parameter that quantitatively characterizes the strength of the Lewis acid [1]. A convenient method for the design of Lewis superacids is to use strong electron-acceptor substituents such as perfluorinated alkyl or aryl groups. One of the promising Lewis acids with a high FIA value is the compound $Ga\{N(C_6F_5)_2\}_3$, first described in 2018 [2].

In this communication, synthesis and reactions of the Lewis acid $Ga\{N(C_6F_5)_2\}_3$ with Lewis bases acetonitrile and pyridine in non-aqueous solution (Fig. 1) are reported. The products of the interaction were characterized by ^{19}F NMR spectroscopy. It was shown that the $Ga\{N(C_6F_5)_2\}_3 \cdot AN$ complex partially dissociates in solution, which is consistent with the results of quantum chemical computations [3].

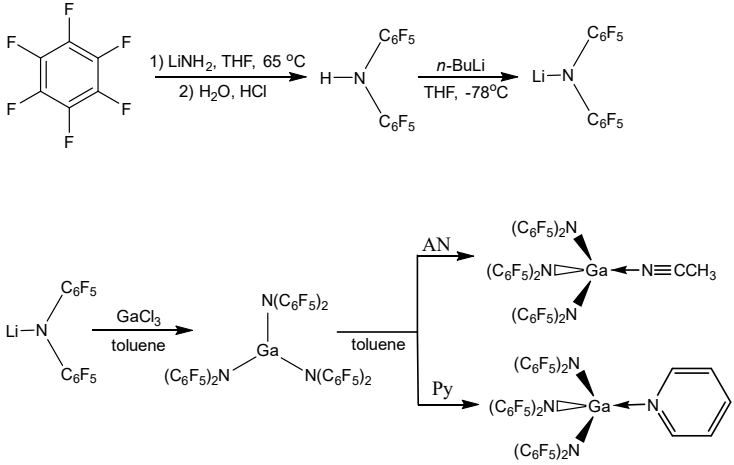

Fig. 1. The synthetic routes to $Ga\{N(C_6F_5)_2\}_3$ and its complexes.

Acknowledgment: This work was supported by the RSF grant 18-13-00196.

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Photophysical Properties of C^N*N^C-cyclometalated Platinum(II) Complexes

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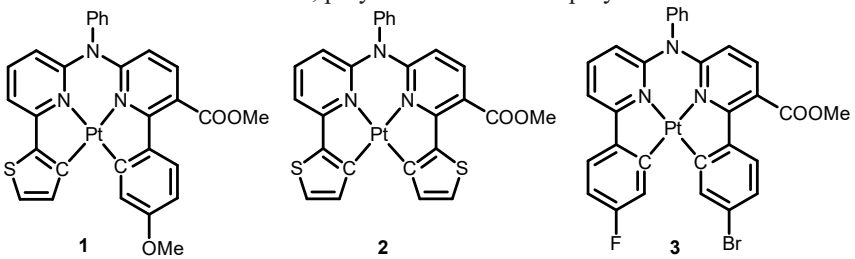
Cyclometallated platinum(II) complexes are organometallic compounds that include chelating ligands forming at least one carbon-metal covalent bond. The development of novel materials based on cycloplatinates, which are able to efficiently emit from an excited state with formally triplet character, is an intriguing field of scientific research. Owing to their rich photophysical properties, such materials have been successfully used in the design of nanoscale sensors, optoelectronic devices, smart materials and bioimaging agents [1]. The tendency of cycloplatinates to form molecular assembles due to the flat geometry, allowing efficient "axial" and "non-axial" intermolecular non-covalent interactions, is attractive [2]. These interractions lead to a change in the nature of the radiative excited state with a red shift of the photoemission.

Herein we report the synthesis and photophysical properties of a series of C^N*N^C-cyclometalated square-planar Pt-complexes 1-3 (Scheme 1). Their emission and excitation spectral profiles, quantum yields, and lifetime of excited state were studied in solution, polymer matrix and in polymeric micelles.



*Scheme 1. Structure of complexes **1-3**.*

Acknowledgments: This work was supported by RSF grant №19-73-20055 and RFBR+ MOST grant №20-53-S52001. The authors are grateful to Saint-Petersburg State University Research Park: Center for Magnetic Resonance, Center for Optical and Laser Research, Center for Chemical Analysis and Materials Research, and Centre for X-ray Diffraction Studies.

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Deep Eutectic Solvents as a Medium for Chemiluminescent Reactions Based on Luminol

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Deep eutectic solvents are increasingly used in various fields of analytical chemistry. They have proven themselves to be effective extractants for the isolation of organic and inorganic analytes from various objects of analysis. The possibility of using eutectic solvents in electrochemical analysis, for the modification and synthesis of various sorbents, and as stationary and mobile phases in chromatography was also demonstrated. However, the possibility of using deep eutectic solvents as a medium for conducting chemiluminescent analytical reactions has not yet been presented in the literature.

Chemiluminescence is one of the most sensitive methods of chemical analysis, but the disadvantage of this method is the significant influence of various chemicals on the processes of chemiluminescence reactions [1-2].

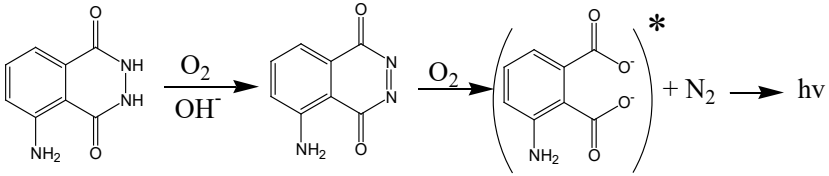

Fig. 1. Luminol oxidation reaction.

Fig. 1 shows the mechanism of the luminol oxidation reaction, which underlies chemiluminescence analysis.

In this work, the possibility of using deep eutectic solvents simultaneously as extractants and as a medium for chemiluminescent reactions is demonstrated for the first time. The main types of eutectic solvents based on alcohols, acids and urea were studied. The reaction of oxidation of luminol with hydrogen peroxide was chosen as the analytical reaction. An illustration of the analytical capabilities of this approach was demonstrated when developing a method for determining hydrogen sulfide in various objects of analysis.

Acknowledgments: This work was supported by the Russian Science Foundation (project No 20-73-00043).

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Multifunctional MRI and Luminescence Agent Based on Magnetite Nanoparticles: Correlation between Shell Parameters and Signals Intensity

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Surface modified magnetite nanoparticles are a promising material to develop medical multifunctional agents for magnetic resonance and fluorescence diagnostic methods. We chose hydroxyapatite (HAp) as a material for the shell production, guided by our previous results obtained for Fe_3O_4@HAp nanoparticles [1] and terbium doped bare HAp nanoparticles with fluorescent properties.

Morphological parameters of multifunctional fluorescent nanoparticles Fe_3O_4@ Tb-HAp were characterized using XRD, FTIR, HRTEM, BET, XPS and Mössbauer spectroscopy. We studied the effect of the synthesis temperature (100, 140 and 200 °C) and the shell material amount (10 and 20 mol.% HAp) on the nanoparticles morphology. It is shown that with an increase in the molar content of HAp, the thickness of the shell increases with the retention of crystallinity. In the case of a decrease in the shell thickness upon temperature increase (or with an increase in the HAp content), the crystallinity of the surface layer becomes more expressed.

The MRI visualization behavior of nanoparticles was tested in T1 and T2 modes and relaxation times were calculated for both. It was shown that the relaxation time T2 decreases linearly with the shell crystallinity increase. The photoluminescence spectra were recorded and it was found that doping leads to an increase in luminescence intensity. Optimal luminescence parameters (high intensity for all detected peaks) and the lowest (more optimal) relaxation times were demonstrated by samples obtained at 200 °C with 20 mol.% HAp.

The established correlations indicate that the dopant, and shell thickness and crystallinity impact on MRI and photoluminescence signals, which makes it possible to recommend as-prepared nanoparticles for multifunctional diagnostic.

Acknowledgments: This work was supported by Russian Foundation for Basic Research (project No 18-03-01066-a). Scientific research was performed using the equipment of the Research Park of St. Petersburg State University (Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Centre for Innovative Technologies of Composite Nanomaterials, Centre for Optical and Laser Materials Research, Centre for Magnetic Resonance).

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Novel Ultrafiltration Membranes Based on Polyvinylidene Fluoride Modified by Titanium Dioxide

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Polyvinylidene fluoride (PVDF) is a highly non-reactive thermoplastic fluoropolymer, used in processes requiring the highest purity, due to its good resistance to solvents, acids and hydrocarbons.

UF membranes from PVDF have found wide industrial application in biotechnology and medicine. However, during the filtration process, the membrane becomes contaminated and productivity decreases. To solve this problem, ultrafiltration membranes based on PVDF modified with titanium oxide have been developed.

Titanium dioxide (TiO2) is the most commonly used semiconductor for photocatalytic membranes, due to its chemical and thermal stability, low cost, high reusability, and excellent yield in the degradation of organic pollutants.

The improvement of the transport properties of polymer membranes could be achieved due to the inclusion of TiO2. Two types of modification of ultrafiltration membranes with nano-sized and micro-sized TiO2 have been developed: (1) the solid-phase method (2) the solution method. The structure and physicochemical properties of the developed PVDF-TiO2 membranes were studied by various methods of analysis (FTIR spectroscopy, atomic force microscopy, scanning electron microscopy, porosity and contact angle). The transport properties of the developed membranes were studied by ultrafiltration separation of the bovine serum albumin (BSA) and cutting fluid. The introduction of TiO2 into the polymer matrix led to significant changes in the properties of PVDF-based membranes.

Acknowledgments: The reported study was funded by RFBR, Sirius University of Science and Technology, JSC Russian Railways and Educational Fund “Talent and success”, project number 20-38-51022. The experimental work of this study was facilitated by the equipment from the Resource Centre of Geomodel, Chemical Analysis and Materials Research Centre, Centre for X-ray Diffraction Methods, Magnetic Resonance Research Centre, Centre for Innovative Technologies of Composite Nanomaterials, Nanophotonics Centre, Cryogenic department, Thermogravimetric and Calorimetric Research Centre and the Interdisciplinary Resource Centre for Nanotechnology at the St. Petersburg State University.

The Accuracy of the Critical States Prediction in Multicomponent Systems by NRTL Modeling

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Within the framework of this work, the possibilities of determining critical states in liquid-liquid systems using NRTL modeling [1] were studied. The objects of the study were binary, ternary and quaternary systems ester - acid - alcohol - water with large areas of immiscibility under isothermal-isobaric conditions.

Experimental determination of critical states in liquid systems is usually a complex and painstaking task [2]; therefore, the possibility of predicting critical states is of interest, including to facilitate search in experimental verification.

The main idea is to use classical results of chemical thermodynamics [3] to predict critical states based on the NRTL model. The paper investigates the dependence of the position of the critical point in a binary system on the parameters of the model. The conclusion is drawn at which values of the parameters the upper and at which the lower dissolution temperature is observed. The question of the possibility of describing systems with the simultaneous existence of these points is discussed. It is shown that for some combinations of parameters, modeling leads to non-physical results. For ternary and quaternary systems, the emphasis is shifted towards processing data on liquid-liquid equilibrium and identifying patterns that allow predicting the composition of the critical state from a limited sample of experimental data.

Acknowledgments: This work was funded by the Russian Foundation for basic research (RFBR), grant 19-03-00375. Alexander Toikka is grateful to the Russian Science Foundation (grant 21-13-00038) for the support of this study.

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Studying the Cell-Cell Communication Via Ion Channels

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Ion channels are commonly represented as integral membrane proteins that control the channel of several ions (Na^+, K^+, Ca^{2+}, and Cl^-) through lipid membranes in cells. Ion transport through an open ion channel is determined by an electrochemical gradient for specific ions through the considered membrane [1]. Various electrophysiological, biochemical, pharmacological, genetic, and other methods are used to study ion channels in excitable tissues. Electrophysiological methods consist of registration of potentials and currents flow through the membrane of an excitable cell. The cellular currents are usually subdivided into intra- and extracellular [2].

This research aims to study the cell-cell communications and interactions via ion channels using ion-selective electrodes. We will focus on the measurement of the extracellular current using ion-selective electrodes. This approach has advantages such as high efficiency, accuracy, and selectivity. Moreover, it is most suitable for studying calcium channels.

The ion-selective electrodes (ISEs) were prepared on carbon fiber and modified with polyelectrolytes by layer-by-layer (LbL) deposition. The LbL assembly was successfully implemented on cation exchange membranes, which includes an ionophore that reversibly binds to a specific ion. This approach provides high stability during sensor measurement and storage. The ISEs were immersed into solutions of the corresponding salts (KCl, NaCl, $CaCl_2$). The concentration of the solution was changed step-by-step after each addition of the standard solution. The potential values were monitored continuously using the potentiostat. The electromotive force was measured between the working ISE and the reference electrode.

The C2C12 muscle cells were selected for the study as the control cell line due to their sensitivity to Ca^{2+} ions. After calibration, the electrodes were immersed in a medium with cells to detect the current originated calcium ions. These current jumps could be associated with cell communication.

Thus, the developed system is promising for monitoring cell-cell communication. Moreover, this system will be optimized for the detection of cell communication.

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B. Geo- and Astrophysics

Identification of Carbonaceous Aerosol Sources in Central Siberia Using PSCF and CWT Methods

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The importance of atmospheric composition research and modelling for various applications has increased considerably. One of the main factors influencing climate change is carbonaceous aerosol. Carbon is part of aerosols both in its elemental form (EC) and as part of various organic compounds (OC). In Central Siberia the main sources of carbonaceous aerosols emitted into the atmosphere are forest fires, biogenic emissions over boreal forests and emissions from industrial centres.

OC and EC concentrations for the period from 01.12.2017 to 29.02.2020 are presented. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to calculate air mass backwards trajectories at 60,47°N latitude and 89,21°E longitude [1]. For further analysis and better visualization, MeteoInfoMap software was applied, allowing for PSCF and CWT calculations.

The potential source contribution function (PSCF) method is a qualitative method based on the conditional probability function of the HYSPLIT model. It is widely used to identify potential pollution source areas. PSCF calculates the probability that a source is located at a certain latitude and longitude [2]. CWT method recovers the spatial distribution of the average impurity concentration to the receptor from a potential source. This method can easier distinguish source strength than PSCF one [3].

The conclusions based on spatial distributions of EC and OC concentration reveal the main sources during different seasons: boreal wildfires, big industrialized cities, fires on agricultural land and etc. The obtained results will be used in further researches.

Acknowledgments: The authors are grateful to Saint-Petersburg State University Research Park.

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Response of the Upper Atmosphere to the Increase in Radiation After the Solar Flare on September 6, 2017

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On 6 September 2017, at 12:20 UT, the most powerful X9.3 flare of the solar activity cycle 24 flared up. The flare was generated by the large active region of the Sun AR2673, which was the beginning of series of other intense solar-terrestrial disturbances in September 2017.

Solar flares can influence the mesosphere and thermosphere depending on the flare's spectral irradiance. Photoionization of the atmosphere by solar flares can occur at altitudes from approximately mesosphere up through the layers of the ionosphere.

Using chemical-climate modeling, we investigated how enhanced photoionization during the strong flare on September 6, 2017 influenced the formation of the odd nitrogen group NO_y ($N + NO + NO_2 + NO_3 + N_2O_5 + HNO_3$). Fig. 1 shows the latitudinal distribution of NOy concentration. These NOy values persist for several days.

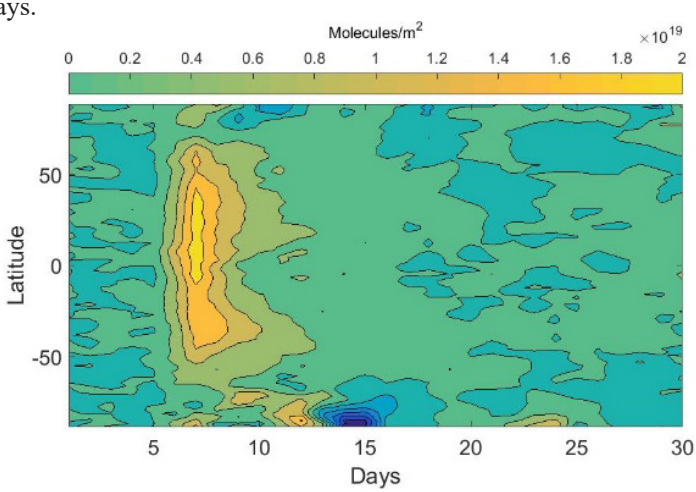

Fig 1. Distribution of NO_y concentrations above 60 km (10 Pa) after the solar flare on September 6, 2017.

Acknowledgments: This work was supported by a grant from the Russian Science Foundation (Project RSF No. 20-67-46016). The work of ER was done in the SPBU "Ozone Layer and Upper Atmosphere Research Laboratory" supported by the Ministry of Science and Higher Education of the Russian Federation under agreement 075-15-2021-583.

Changes in the Content and Transport of Atmospheric Heat and Moisture Over the Waters of the Oceans of the Northern Hemisphere

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Over the past three decades, satellites in low Earth orbit have become the main components of climate change monitoring. Passive microwave measurements are used as one of the methods for measuring the atmospheric moisture content in the vertical column of the atmosphere (integral moisture content, IMC) [3]. Its concentration is highest in the lower atmosphere. Latent heat is inextricably linked with water vapor, the distribution of which determines the energy balance of the ocean-atmosphere system. Therefore, the purpose of this work is to study water vapor as a factor in the heat-moisture turnover of the atmosphere and variations in the propagation of IMC according to satellite microwave observations.

According to the reanalysis data, the most important factor in increasing polar warming is meridional heat - moisture transfer from low to high latitudes [1]. IMC longitudinal-temporal diagrams of the distribution of moisture content were constructed to identify the nature of the change in the latitudinal range of 40° - 70° N. They are based on data from microwave satellites of the DMSP series for the period 1988-2020. As it turned out, the nature of the trends in the North Atlantic and the North Pacific Ocean is different. In the Atlantic, the rapid increase in the ISS until the early 2000s is replaced by a slight decrease. In the Pacific Ocean, the moisture content increases relatively evenly, having changed by about 1.5 mm over the past 30 years.

A decrease in the ice cover area and an increase in the near-surface temperatures of the Arctic in the North Atlantic region may indicate the prevalence of the role of a decrease in albedo over a relative decrease in polar transport. In the Arctic, global warming is increasing, probably due to an increase in the meridional heat and moisture transfer from low latitudes and an increase in the concentration of water vapor [2].

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C. Mathematics and Mechanics

Peculiarities of NiTi Nanofilms Functional Behavior

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Shape memory alloys (SMAs) are able to accumulate large inelastic strain on cooling and then recover it on heating. This is possible due to SMAs undergo thermoelastic martensitic transformation on temperature variation. This unique property of SMAs allow them to be used as working element for different drives, sensors and actuators. There is no clear advantage of SMA actuators over traditional ones on macro level, however at micro level they boast compared to conventional types much higher generated forces, larger strain recovery, ease of production, smooth and reliable actuation. To minimalize such SMA drives, different techniques were developed, and one of them is film deposition on a flexible substrate. The aim of the present work is to study the one-way and two-way shape memory effects in thin films pre-deformed by bending around the mandrel.

The thin NiTi films with a thickness of 500 nm were flash evaporated on Kapton. After deposition X-ray analysis showed that NiTi layer was amorphous. To obtain the flat crystalline samples, two ribbons were pressed to each other by the NiTi layers and vacuumized in quartz glass vials (10^{-4} bar). After that vials with samples were heated up to a temperature of 350 °C and held for two hours.

To characterize the functional properties, heat treated ribbons were preliminary deformed by bending around the mandrel with a diameter of 2, 1.2, 0.5 or 0.2 mm. After preliminary deformation, samples were installed in a holder and subjected to heating – cooling - heating in thermal chamber with a rate of 7 °C/min in the temperature range of 120÷0 °C. During temperature variation, the shape of the samples was photographed with constant time interval to estimate the strain variation and the sample temperature was measured with thermocouple attached to the sample. To calculate the strain after unloading, the photograph of the bent samples were digitized with OriginPro™ software and the bending radius was measured. The strain was calculated as $\varepsilon = (h/2r)\cdot 100\%$, where h is film thickness and r is a bending radius.

The one-way and two-way shape memory effects were studied in the NiTi films deposited to Kapton substrate and subjected to heat treatment at 350 °C for 2 hours. It is shown that the heat treated NiTi films demonstrate the one-way shape memory effect in the temperature range of 40÷85 °C and the maximum recoverable strain of 2% was observed after the pre-deformation by bending to 2.8 %. The two-way shape memory effect was not found in NiTi films deposited to Kapton.

Acknowledgments: This work was supported by joint DST-RSF project (RSF # 19-49-02014, DST#DST/INT/RUS/RSF/P-36).

On Index of Elliptic Boundary Value Problems Associated with Isometric Group Actions

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Let M be a smooth compact manifold with boundary X. We suppose that M is endowed with a Riemannian metric. In a neighborhood of the boundary we use local coordinates $x = (x', x_n)$ on M, where $\dim M = n$, $x' = (x_1, \ldots, x_{n-1})$ are local coordinates on X, and the boundary is locally defined by $x_n = 0$, while M is defined by inequality $x_n \neq 0$. We fix a Riemannian metric on M.

Let us consider Boutet de Monvel operators of zero order and type. We write such operators as follows

$$\begin{pmatrix} A+G & C \\ B & A_X \end{pmatrix} : \begin{matrix} L^2(M) & L^2(M) \\ \oplus & \to & \oplus \\ L^2(X) & & L^2(X) \end{matrix}, \tag{1}$$

where

- A is a classical pseudodifferential operator of order zero on M; its complete symbol satisfies the transmission property;
- A_x is a pseudodifferential operator of order zero on X;
- B,C and G are boundary, coboundary and Green operators, respectively (or trace, potential, singular Green operators in the terminology of Boutet de Monvel [1]).

Let us denote the algebra of matrices (1) by $\Psi_B(M) \subset \mathcal{B}(L^2(M) \oplus L^2(X))$.

Let Γ be a discrete finitely generated group of isometries $\gamma : M \to M$, which preserve the boundary $\gamma(X) = X$. We suppose that the local coordinates near the boundary are chosen such that x_n is a Γ – invariant function. Given $\gamma \in \Gamma$, we define the shift operator

$$T_\gamma : L^2(M) \oplus L^2(X) \to L^2(M) \oplus L^2(X).$$

Elements $\{D_\gamma\}_{\gamma \in \Gamma}$ in the smooth crossed product (see [2]) $\Psi_B(M) \rtimes \Gamma$ define operators

$$\{\boldsymbol{D}_\gamma\}_{\gamma \in \Gamma} \mapsto \sum_{\gamma \in \Gamma} \boldsymbol{D}_\gamma T_\gamma : L^2(M) \oplus L^2(X) \to L^2(M) \oplus L^2(X). \tag{2}$$

Operators in (2) are called Γ-Boutet de Monvel operators.

We define the conditions under which Γ-Boutet de Monvel operators are elliptic and give the index formula for elliptic Γ-Boutet de Monvel operators.

Acknowledgments: This work was supported by RFBR (grant no. 21-51-12006).

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The Discrete Problems of Selfish Parking

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The problem known as the "Parking problem" has a long history. First steps in tackling this problem have been made by Renyi A. in 1958. In our work we investigated two models of discrete analogues of this problem.

The first part of the work is dedicated to considering the following model. Let n, k be non-negative integers. If $n>k$, then on the segment $[0,n]$ we place an interval $(i,i+1)$, where i is a random variable with equal probability taking the values $0,1,\ldots, n-1$, so that there is a free space of the length not less than k to the left or right from the placed interval. Otherwise, we say that the interval does not fit. Having placed the first interval, we continue to fill segments $[0,i]$ and $[i+1,n]$ with unit intervals according to the same rule, independently of each other. Let $X(n)$ denote the number of placed intervals. We obtained an expression for expected value of random variable $X(n)$, when $n>2k$.

In the second part of the work we proceed to investigate another discrete model. Let n be a non-negative integer. If $n<4$, we say that the interval does not fit. On the segment $[0,n]$ we place an interval $(i,i+2)$, where i is a random variable with equal probability taking the values $1,\ldots,n-3$ (leaving a free space of at least unit length from interval to the ends of the overall segment). Having placed the first interval, we continue to fill segments $[0,i]$ and $[i+2,n]$ with intervals according to the same rule, independently of each other. Let $Y(n)$ denote the number of placed intervals. We obtained the results concerning the asymptotic behaviour of the expected value of random variable $Y(n)$.

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Martensite Stabilization Effect in $Ti_{50}Ni_{50}$ Alloy after Incomplete Direct Transformation

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The martensite stabilization effect is that the first heating of preliminary deformed alloy leads to increase the temperatures of strain recovery which are significantly higher than the temperatures of the reverse transition in undeformed sample or on the second heating. It has been suggested that martensite stabilization effect may be caused by damage of intermartensitic boundaries. So the following idea appeared that if in the process of preliminary deformation, the boundaries of martensitic crystals did not contact with each other, then the martensite stabilization effect would not be observed. On cooling under a stress, the oriented martensite crystals appear. At the beginning stage of cooling, the isolated crystals form which interfaces are not damaged. On a decrease in sample temperature, the crystals grow and touch to each other that leads to the damage of the intermartesnitic boundaries. Thus, one may assume that the martensite stabilization effect should depend on the fraction of the martensite appeared on cooling. The aim of this work is to check this hypothesis.

Flat samples of $Ti_{50}Ni_{50}$ alloy with a thickness of 0.8 mm, width and length of working part of 4 mm and 40 mm were quenched at 850 ^{o}C for 10 minutes to water and annealed at 500 ^{o}C for 2 hours. After heat treatment, alloy underwent the B2 ↔ B19' martensitic transformation at the temperatures of M_s = 70 ^{o}C, M_f = 56 ^{o}C, A_s = 79 ^{o}C, A_f =99 ^{o}C. The samples were cooled under a stress of 100 MPa or 200 MPa through an incomplete temperature range of the forward transition, unloaded and subjected to a cycle "heating-cooling-heating" to investigate the displacement of the reverse transition temperatures during the first heating.

Upon cooling under stress 100 MPa, the martensite stabilization effect is not observed for the A_s temperature. The shift in the A_f temperature is observed if more than 80% of the forward transition is realized upon cooling. An increase in stress acting on cooling leads to the martensite stabilization effect is observed for the A_s temperature if more than 70% of the forward transition has been realized. The Af temperature increases during the first heating regardless of the fraction of the forward transition on cooling. Thus, obtained results confirm the hypothesis about the influence of damage intermartensitic boundaries on the value of martensite stabilization effect.

Acknowledgments: This work was supported by RSF №18-19-00226-P.

On Using Singular Spectrum Analysis in Machine Learning for Time Series Prediction

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We consider the problem of time series forecasting by using the machine learning methods, in particular, Artificial Neural Network (ANN) methods. In several papers, singular spectrum analysis (SSA) [1] is involved in the ANN algorithms as a preprocessing of time series to improve the accuracy of the forecast. However, [2] contains a critic of a number of papers with the hybrid SSA-ANN approach related to so-called data leak in the algorithm testing.

We show for both model data (a noisy sinusoidal time series) and real-life data from [2] that the correct application of the SSA-ANN approach with no data leak do improve the forecasting accuracy.

We consider the task of predicting the next 13th value using the previous 12 values on data from [2]. The data are divided into training, validation, and test samples. We consider the application of SSA to the training and validation data as a preprocessing step to select the signal from the time series. During the task, the ANN model is trained on the training sample. Using validation sampling, the optimal number of epochs to train the model is established. The RMSE error is counted on the test sample. There is no data leaking problem in our experiment. The computational experiment showed that using SSA as preprocessing reduces the RMSE error.

Acknowledgments: The reported study was funded by RFBR, project number 20-01-00067.

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Stability of Strain Variation During Repeating Isothermal Holding of the $Ni_{51}Ti_{49}$ Shape Memory Alloy under a Stress

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It was lately shown that the $Ni_{51}Ti_{49}$ quenched alloy demonstrated the variation in recoverable strain on holding under a stress due to the isothermal martensitic transformation. This effect can be successfully used in actuators, however the application of such mechanisms often requires numerous working cycles. Thus, the aim of this work is to study the stability of strain variation during repeating holding of the quenched $Ni_{51}Ti_{49}$ alloy under a constant stress.

The $Ni_{51}Ti_{49}$ alloy wire samples with a diameter of 1.5 mm and a length of 100 mm were water quenched from 850 °C for 15 min and subjected to 100 thermal cycles to stabilize the martensitic transformation temperatures. After thermal cycling, the samples underwent the B2 ↔ B19' martensitic transformations at temperatures of M_s = -43 °C, M_f = -63 °C, A_s = -24 °C, A_f = -9 °C. To study the stability of strain variation during isothermal holdings, the following procedure was repeated: samples were cooled from 100 °C to the holding temperature T*, kept at T* for a duration of 40 min to stabilize temperature in the sample, loaded by a stress of σ, held for a duration of 60 min under stress and unloaded. A stress was chosen at a value of 300 MPa. The holding temperatures were chosen both within the range of forward martensitic transformation and outside of this range.

The results of study show that strain increases during the first isothermal holding under a stress and recovers on unloading. In the second cycle strain increases during loading but hardly changes during holding. An increase in the number of cycle suppresses the strain variation during holding and this stops since the 4th loading. Thus, it can be concluded that the strain variation during isothermal holding under a stress is unstable in quenched $Ni_{51}Ti_{49}$ alloy and this should be considered while NiTi sample applications.

Acknowledgments: The work has been supported by Russian Science Foundation (# 18-19-00226).

Modeling the Temperature-time Dependence of the Cavitation Strength of Water

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The strength of a fluid is closely related to cavitation, which is interpreted as a disruption in fluid homogeneity due to a decrease in pressure. In the case under consideration, the tensile strength of water is interpreted as the minimum amplitude of the acoustic wave pressure at which cavitation occurs. To analyse the dependences of the cavitation threshold of water, the cavitation criterion is used, based on the concept of incubation time. The work uses a modified incubation time criterion, which takes into account the effect of liquid temperature and background pressure. This criterion allows one to obtain analytical curves the dependence of the threshold value of cavitation pressure on temperature [1]. Also, the results of plotting the curves were compared taking into account the compressibility of the liquid.

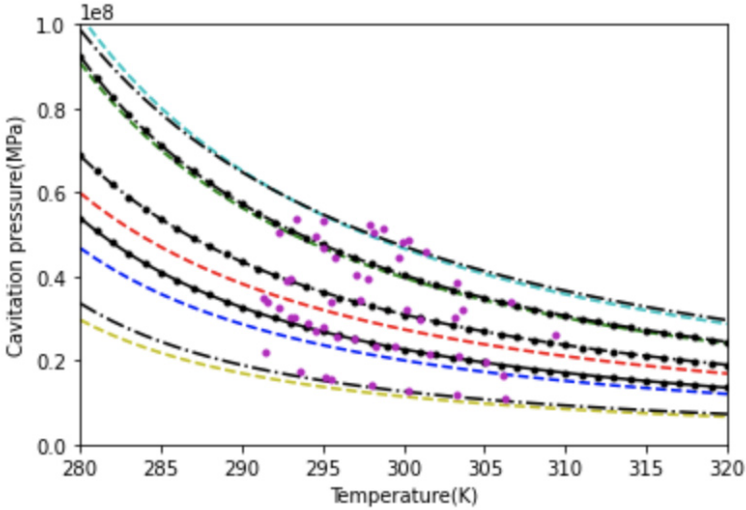

Fig. 1. Temperature dependence of the acoustic cavitation threshold for water: (points) experimental data [2], (colored lines) the results of calculations of the dependence of the binding energy on the background pressure, (black lines) the results of calculations taking into account the compressibility of the liquid.

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Modeling of State-to-State Oxygen Kinetics behind Reflected Shock Waves

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Chemical and vibrational nonequilibrium in high-temperature shock-heated oxygen (O_2) strongly influences the thermodynamic state of air in the flowfield around hypersonic vehicles and reentering space crafts. Therefore, development of reliable theoretical models for nonequilibrium flow simulations is of vital importance for aerospace applications.

The aim of this study is to find the best model of strongly coupled dissociation and vibrational energy exchange, which would give the best agreement with the recent experimental data [2].

State-to-state vibrational-chemical kinetics of a binary mixture of oxygen molecules and atoms behind the reflected shock wave is modeled. The processes of vibrational energy exchange are described on the basis of the first-order perturbation SSH theory and the forced harmonic oscillator model (FHO). Dissociation of oxygen molecules is simulated using the generalized Treanor–Marrone model with various values of the parameter U available in the literature. The 1D code developed earlier in [1] is used for numerical simulations.

All numerical results are compared with experimental data [2]. The key advantage of new experiment is that the processes of oxygen relaxation are investigated behind the reflected shock wave. In our previous numerical studies [1], the relaxation processes were modeled behind an incident shock wave. In the present study, we simulate both incident and reflected shocks and compare the gas temperature, vibrational temperature and mixture composition with those measured experimentally. Based on this comparison, the most accurate models suitable for hypersonic flow simulations are recommended.

Acknowledgments: This study is supported by Saint Petersburg State University, project ID 84912260.

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Poroelastic Model of the Scleral Layer for Studying the Growth of Intraocular Pressure after Intravitreal Injection

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One of the main ways to treat various eye diseases is intravitreal injection. However, the administration of the drug can cause a significant increase in intraocular pressure (IOP).

Many living tissues are solids saturated with physiological fluid. For a correct description of the processes occurring inside the scleral layer after an intravitreal injection, it is proposed to use the poroelastic transversely isotropic model based on the theory of poroelasticity described in [1]. This mathematical model extends the study [2] by applying a two-phase model and specific boundary conditions.

It is necessary to formulate boundary conditions on the inner and outer surfaces of the shell to solve the problem. It is assumed that the outer surface is free from external forces and impermeable. The latter condition is equivalent to the radial derivative of the pore pressure being equal to zero. Two types of boundary conditions are set on the inner surface:

1. Impenetrable wall. The displacements are set based on the incompressibility of the fluid. The radial derivative of the pore pressure is equal to zero.

2. Permeable wall. The displacements are set based on the incompressibility of the fluid and an unknown quantity associated with seeping into the scleral layer. The radial component of the effective stress tensor is equal to the IOP value up to sign.

Static and dynamic problems for a spherical layer are considered in this research. The dependence of IOP on various volumes of drugs injected into the eye was obtained. For a dynamic task, the IOP rise is 18.6% greater than for a static one. For the poroelastic model, qualitative changes are observed in the radial displacements of the scleral layer. For boundary conditions with a permeable wall only 29.4% of the injected liquid is filtered into the scleral layer when the specified physical constants are selected. Also the theory of poroelasticity is in good agreement with clinical data. In addition, the degree of influence of anisotropy on IOP was assessed.

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Monte Carlo SSA for Signal Detection: Comparing Test Versions by ROC Curves

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The problem of signal detection in noisy time series is considered. The null hypothesis is that the observed time series is red noise and do not contain a signal. For testing this hypothesis against the presence of a sine-wave signal, Monte Carlo singular spectrum analysis (MC-SSA) [1] can be applied.

In [2], several modifications of MC-SSA were discussed in terms of statistical tests. Both the type I and the type II errors were investigated for a fixed significance level equal to 0.2.

In this work, these test versions are compared by power and ROC curves. For example, comparing a set of single tests from [1] with Bonferroni correction and Multiple MC-SSA test proposed in [2] gives a result depicted in Fig. 1. Fig. 1 (right) contains the plot of the dependence of test power against the presence of a sine wave signal on the significance level. One can see that the multiple version is much more powerful. Fig. 1 (left) demonstrates that the ROC curve (dependence of power on significance level) shows the power, which can be achieved if an adjustment of the significance level to the conservativeness of the Bonferroni correction. After this adjustment, the multiple version is still more powerful; however, the difference is smaller.

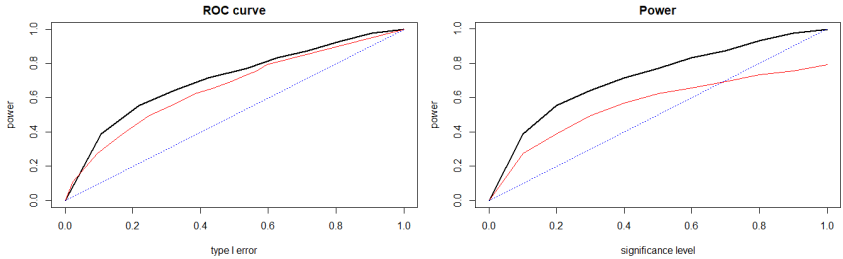

Fig. 1. ROC curves (left) and power (right) curves for Single MC-SSA with Bonferroni correction (red line) and Multiple MC-SSA (bold blackline).

Acknowledgments: The reported study was funded by RFBR, project number 20-01-00067.

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Strain Variation during Isothermal Martensite Transformation under Stress in the $Ti_{40.7}Hf_{9.5}Ni_{41.8}Cu_8$ Alloy

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Shape memory alloys can recover unelastic strain during heating (shape memory effect) or unloading (pseudoelasticity effect). This behavior is due to thermoelastic martensitic transformations – the first-order phase transitions that occur during temperature or stress variation. If the transformations take place on cooling under a stress, the oriented martensite appears that is accompanied by a strain increase. On subsequent heating this strain completely recovers during the reverse transition.

It has been found that in some NiTi-based shape memory alloys, isothermal formation of the martensite phase can be observed. Moreover, it has been shown that during isothermal holding under a constant stress, the isothermal martensitic transformation is accompanied by variation in reversible strain. Before holding, the samples have been cooled under the stress, however, the sample can be cooled to the holding temperature without stress and then to be subjected to loading and holding under a stress. The aim of the present work was to study the influence of regimes before holding to the reversible strain variation during isothermal martensitic transformation in the $Ti_{40.7}Hf_{9.5}Ni_{41.8}Cu_8$ alloy.

To study the isothermal strain variation in the $Ti_{40.7}Hf_{9.5}Ni_{41.8}Cu_8$ alloy, two series of experiments were carried out. In the first one sample was loaded up to 240 MPa at holding temperature equals 75 °C or 100 °C, held for an hour, unloaded and heated. In the second series, a sample was cooled under 240 MPa to the holding temperature, kept at a constant temperature for an hour, and then heated. The holding temperatures were chosen from 29 °C to 44 °C, which was within the range of the forward transformation under stress.

The results obtained showed that during isothermal holding of the $Ti_{40.7}Hf_{9.5}Ni_{41.8}Cu_8$ alloy under stress an increase in strain occurred in both regimes. The strain was completely reversible upon subsequent heating. In the first regime, the maximum isothermal strain of 3.8% was observed at a temperature of 75 °C. In the second regime, the maximum isothermal strain was 3.2% and it was found at a temperature of 40 °C. Thus, the results of the study showed that the regimes of the sample cooling before holding (cooling under a stress or cooling without stress and loading) hardly affect the isothermal strain but they significantly influence the holding temperature at which the maximum recoverable strain is observed.

Acknowlegments: This work was supported by Russian Science Foundation (grant number 18-19-00226)

Deformation Tensor and Crystallographic Resource for Martensitic Transformation in TiZr Shape Memory Alloy

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Stricter requirements for medical devices have led to the need to replace potentially carcinogenic nickel in titanium based SMA with other elements such as zirconium, molybdenum etc. The TiZr alloy can be used as a high-strength and biocompatible alternative to titanium. This alloy has a high creep resistance at high temperatures and excellent corrosion resistance which can be improved with proper processing.

For effective use of SMA in various applications models are needed which allow to calculate the deformation behavior of these materials correctly. One of the most important material constants of the microstructure model [1] used in this work is the strain tensor of the crystallographic lattice transformation of the initial high-temperature austenitic phase into a low-temperature martensitic one.

In this paper, the strain tensor matrix for (ordered BCC and ordered HCP, correspondently) martensitic transformation in the TiZr alloy was calculated. The deformation gradient and the matrix of Green-Lagrangian were calculated based on known data for crystal lattices in α and β phases. The deformation tensor matrix was used to model the functional and mechanical properties of this material. The crystallographic resource for this transformation was estimated as the maximum value of the principal strains. The orientation of a single crystal providing the value of strain that is close to the calculated value of the crystallographic resource during realization of the pseudoelasticity effect was found.

Acknowledgments: The study was supported by the Russian Foundation for basic research (RFBR) 19-01-00685. The author expresses his thanks to his scientific adviser Dr. Margarita E. Evard, Prof. Aleksandr E. Volkov and Dr. Fedor S. Belyaev for useful discussion of the obtained results.

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Robust Versions of the Complex SSA Method

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The analysis of complex-valued time series is important due to its prevalence in engineering tasks. The SSA [1] method is used for real- and complex-valued time series analysis; however, Basic SSA is not robust to strong outliers.

In [2], two robust versions of SSA were considered for the signal extraction from real-valued data. Since Basic SSA can be considered as a combination of two projections in the L_2 norm, the robust approaches are based on the change of this norm to a weighted L_2 norm or the L_1 norm.

Here the same approaches are extended to the complex-valued time series. The implementation of the methods has been done and a method from [3] was used to implement the projection by norm L_1. Fig. 1 demonstrates estimating the signal using Basic SSA and SSA with the L_1 norm for a noisy complex exponential with complex normal noise and outliers. The RMSE errors of the signal estimates are 39.9 for Basic SSA and 7.5 for SSA with L_1 norm.

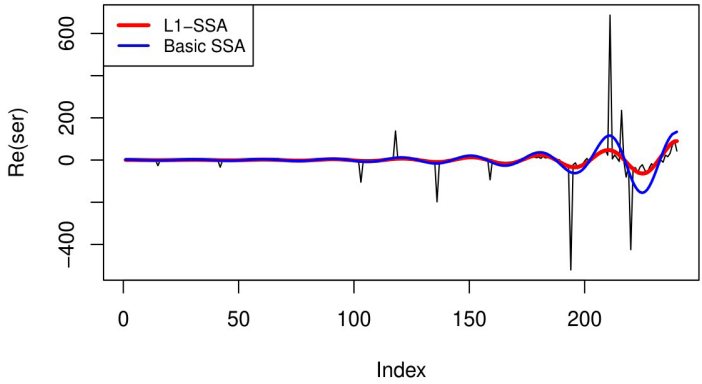

Fig. 1. Real parts of the original series and signal estimation.

Acknowledgments: The reported study was funded by RFBR, project number 20-01-00067.

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Boundary Conditions for Non-Equilibrium Gas Flows in Slip Regime

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As it is known, for proper description of the gas mixture, initial and boundary conditions should be determined. Current work focuses on the development of the last ones for strongly non-equilibrium gas flows in slip regime near the solid surface. The gas mixture is described in the state-to-state approach and the solid wall presumed to be partially catalytic. Boundary conditions for macroscopic parameters are obtained using two different approaches. First approach is based on the developed kinetic boundary condition for described gas mixture, the another one – on the method, initially proposed by Grad. On the basis of specular-diffusive reflection model, the equivalency of approaches is sustained. The derived equations for velocity slip, temperature and concentration jumps equations tend to correspond to known equations in one-temperature model. It is shown that approach for deriving slip/jump equations from kinetic boundary condition gives more rigorous mathematical description of the problem.

Acknowledgments: This study is supported by Saint Petersburg State University, project ID 84912260.

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Hidden Attractors and Transient Chaotic Sets in Complex Lorenz Systems

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In this work, we study possible existence of hidden attractors and transient chaotic sets in the complex Lorenz system, which describes physics of a detuned laser and can be written as follows [1]:

$$\dot{X} = \sigma (Y - X),\ \dot{Y} = r X - a Y - X Z,\ \dot{Z} = - b Z + 1/2 (X^* Y + XY^*), \quad (1)$$

where $X = x_1 + ix_2$, $Y = x_3 + ix_4$ are complex variables, $Z = x_5$ is real, and " * " denotes complex conjugation operator. Parameters σ, $b > 0$ are real, $r = r_1 + ir_2$ and $a = 1 - ie$ are complex with r_1, e are real. Following [2], we first apply the special transformation for system (1). If the conditions: $2\sigma > b$, $\sigma (r_1 - 1)\ e^2/4 \equiv \eta > 0$ are satisfied, system (1) in the form:

$$\dot{X}' = Y',\ \dot{Y}' = (1+ik) X' - \mu Y' - X' Z' - \rho X' |X'|^2,\ \dot{Z}' = - \beta Z' + |X'|^2, \quad (2)$$

where $k = (2 \sigma r_2 + e (\sigma-1)) / 2\eta$, $\mu = (1 + \sigma) / \eta^{1/2}$, $\rho = \eta^{1/2} / (2\sigma - b)$, $\beta = b / \eta^{1/2}$. Next, introduce the following real variables ξ', υ', w', Z':

$$\xi' = (|X'|^2 - |Y'|^2) /2,\ \upsilon' + iw' = X'^* Y'. \quad (3)$$

Expression (3) defines the projection map: $\Pi: \mathbb{H} \to \mathbb{P}$. The derivative of expressions (3) with respect to the dynamics of system (2) defines the projective system [2]. Using projective system, it is convenient to study and visualize the dynamics of the initial system (1). By the numerical continuation method (NCM), it is possible to visualize a hidden transient chaotic set in projective system (see Fig. 1) [3].

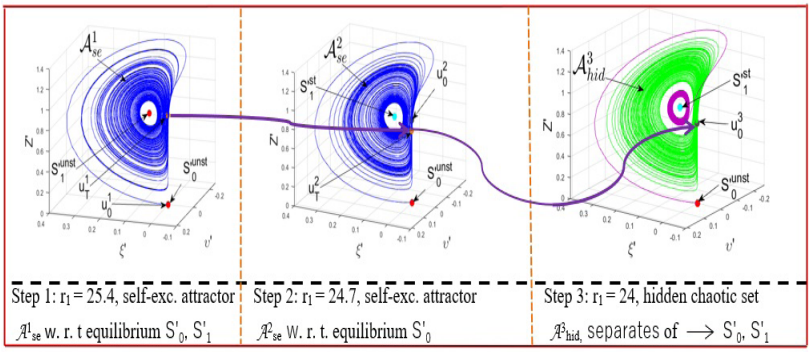

Fig. 1. Localization, by NCM, of hidden chaotic set in projective system with (*r1, r2, e, b*) = (*10, 24, 0.001, -0,001 8/3*).

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Lattice Deformation Tensor and Crystallographic Resource for D03-18R Martensitic Transformation in Cu-Al-Be Shape Memory Alloys

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Shape memory alloys of system Cu-Al-Be are distinguished among other Cu-based shape memory alloys (SMAs) by their relatively low temperatures of martensitic transitions, high mechanical strength, corrosion stability and advanced fatigue failure resistance [1]. They can be used not only in single-crystal but also in the oligo- and polycrystalline form for seismic dampers, pipe coupling, actuators and other devices.

A previously developed microstructural model [2] is used to simulate the functional and mechanical behavior of this SMA. One of the most important material constants of this model is the lattice deformation tensor for D03-18R martensitic transformation of the initial high-temperature austenite phase into a low-temperature martensitic phase. Matrices of the deformation gradient and Green-Lagrange tensors for the Cu-Al-Be SMA were calculated based on X-ray data for the lattice parameters of austenite and martensite [3]. The obtained matrix of the deformation tensor was used to simulate stress-strain diagrams for tension and compression and the two-way shape memory effect after training. The obtained data are in a good agreement with the available experimental results.

Acknowledgments: This work was supported by the grant of Russian Foundation for Basic Research 19-01-00685. The author is grateful to her scientific supervisor Dr. Margarita E. Evard, Prof. Aleksandr E. Volkov and Dr. Fedor S. Belyaev for useful discussion of the obtained results.

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Qualitative Analysis of a Shallow Lake Model

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In this talk, we consider a shallow lake model that describes the essential dynamics of the eutrophication process. This model is used to carry out a qualitative analysis of the eutrophication in relatively shallow lakes.

The amount of nutrients in algae is governed by the non-linear differential equation (normalized form) [1]:

$$\dot{x} = a(t) - bx(t) + \frac{x^2(t)}{x^2(t)+1}, x(0) = x_0.$$

A qualitative analysis of this model is carried out. Specifically, we consider the effect of variation in the parameters *a* and *b* to the steady state behavior of the system. It is shown that for the certain values of parameters, the system may undergo a double saddle-node bifurcation, which results in a hysteresis-like behavior. We analyzed the values of parameters and described the regions of the parameter space in which different scenarios occur (Fig. 1).

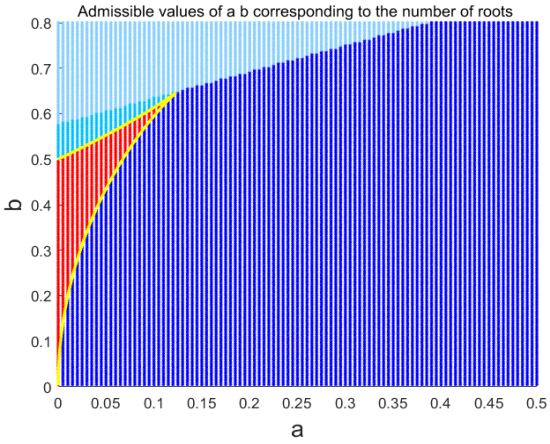

Fig. 1. Parameter space.

The preformed analysis helps to better understand the processes of eutrophication of lakes and develop measures to counteract this harmful process.

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Cavitation Threshold Dependence on Temperature and Static Pressure

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This work investigates the problem of modeling acoustic cavitation inception. Two models of the onset of cavitation were considered. The first model is based on the Rayleigh equation [1]. This approach considers the collapse of a bubble in a liquid. The second model is based on the structural-temporal approach [2], which uses macro parameters of the liquid.

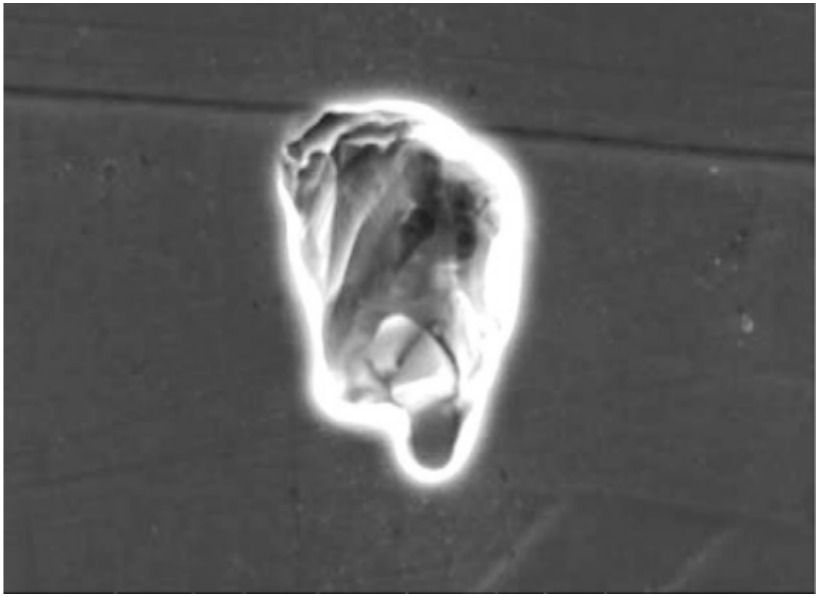

Fig. 1. Cavitation erosion pit.

The predictions of the presented models were compared with experimental data. Possible relationships of parameters between these approaches are found.

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An Index Theorem for Operators on the Real Line Periodic at Infinity

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This work is devto the index problem for elliptic pseudodifferential operators (ΨDOs) on the real line with coefficients periodic at infinity. Such operators have the form

$$D = \chi_- D_- \chi_- + \chi_0 D_0 \chi_0 + \chi_+ D_+ \chi_+, \qquad (1)$$

where

$$1 = \chi_-^2 + \chi_0^2 + \chi_+^2$$

is a partition of unity subordinate to the cover

$$\mathbb{R} = (-\infty, -T + \varepsilon) \cup (-T - \varepsilon, T + \varepsilon) \cup (T - \varepsilon, +\infty)$$

with $T > 0$, D_- and D_+ are $N \times M$ matrix ΨDOs with periodic coefficients and D_0 is a $N \times M$ matrix ΨDO on the real line. Here the symbols of the operators D_-, D_0 and D_+ satisfy certain compatibility conditions.

Using Melrose's approach [1], we introduce the η-invariants (cf. [1, 2]) of periodic operators D_- and D_+ as regularized winding numbers for families of parameter-dependent ΨDOs of Shubin type [3] and establish their main properties. In particular, it is proved that the η-invariant satisfies logarithmic property and a formula for the derivative of the η-invariant of an operator family with respect to the parameter is obtained.

Further, we establish an index formula of operator (1) in terms of the symbol of D_0 and the constructed η-invariants, which give the contribution of plus and minus infinity to the index formula. Finally, we compute η-invariants of differential operators in terms of the spectrum of their monodromy matrices.

Acknowledgments: This work was supported by RFBR and DFG, project number 21-51-12006.

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D. Solid State Physics

Influence of Annealing Conditions and HfO_2 Impurity Material on Nitrogen and Oxygen Diffusion at the HfO_2 / TiN Interface

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Due to the possibility of creating ferroelectric properties, thin films of hafnium dioxide (HfO_2) are the main candidates for use in non-volatile storage devices. The phenomenon of ferroelectricity in HfO_2 is a direct consequence of the formation of a non-centrosymmetric orthorhombic phase in the crystal structure, unstable under normal conditions [1], which is achieved by deposition of electrodes (TiN or TaN) followed by temperature annealing and doping with impurities.

It was revealed that processes at the HfO_2/TiN interface (redistribution of nitrogen and oxygen) play an important role in the formation of orthorhombic modification in the HfO_2 film [2]. In this regard, the dependence of the redistribution of nitrogen and oxygen at the film / electrode interface on the conditions of annealing and alloying with impurities was studied in this work.

During the measurements, it was revealed that TiN_xO_y titanium oxynitride is formed at the HfO_2/TiN interface. With an increase in the annealing temperature, its amount decreases, since part of the oxygen is returned to the hafnium dioxide film. In addition, temperature annealing promotes the transition of nitrogen from the titanium nitride film to the underlying layers. The analysis of the obtained X-ray diffraction measurement data allows us to assert that the introduction of an aluminum impurity leads to the formation of an orthorhombic phase in the crystal structure of HfO_2, while samples with an admixture of silicon demonstrate the dominance of a non-magnetoelectric tetragonal crystal modification.

Acknowledgements: The experimental part of this work was carried out at the Petra III synchrotron Radiation Center, on the P22 synchrotron radiation output channel in Hamburg, Germany. The authors express their gratitude to their German colleagues.

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Optical Tuning of the Charge Sign of the GaAs / AlGaAs Quantum Well

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Long-lived optical memory could be created by a photon echo on charged exciton complexes (trions). In connection with this it is necessary to tune the sign of the charges in the quantum well (QW), using above-barrier optical illumination [1]. In this work, we have studied the photoluminescence spectra (PL) of a GaAs / AlGaAs QW with presence over-barrier optical illumination (E=2.33 eV). Resident holes were present in the QW without illumination; therefore, features associated with positive trions were observed in the PL spectra. As the illumination intensity increases, the signal from positive trions (T^+) decreases, a signal from excitons (X) appears and then gives way to a signal from negative trions T^- (Fig. 1 (a)). Thus, using above-barrier optical illumination, one can control the sign and concentration of trions in the QW (Fig. 1 (b)).

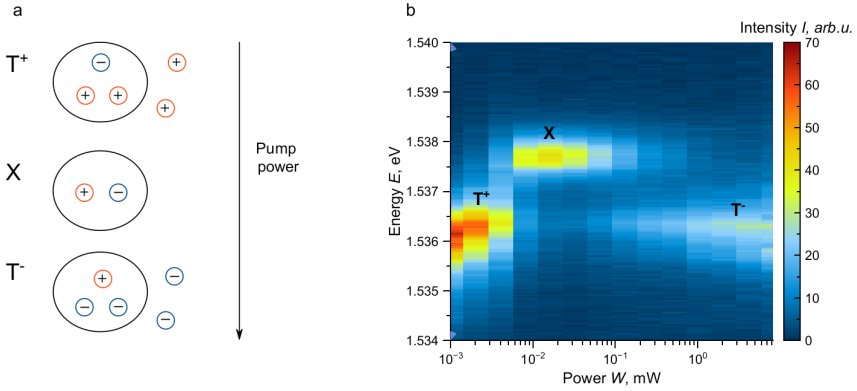

Fig. 1. Pumping process (a), dependence of the PL spectra on the pump power (b).

Acknowledgments: This work was supported by RFBR №19-52-12046 nnio_a. This work was carried in the SPBU resource center "Nanophotonics".

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Contribution of the Electronic Mechanism to the Formation of Thermoelastic Stresses in Metals under Pulsed Laser Action

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The paper presents an analysis of the contribution of the heat transfer process in metals to the formation of thermoelastic stresses and thermoelectric processes under pulsed laser exposure.

The dynamic problem of thermoelasticity is considered as a two-stage process, the first stage of which is determined by the duration of the radiation pulse, the second by the dynamics of the heat transfer process after the end of the laser pulse.

At the first stage, the thermoelastic response is described by the traditional solution of the dynamic thermoelasticity problem, in which the influence of thermal conductivity gives only an insignificant change in thermoelastic stresses from time [1, 2].

It is shown that the increase in tensile stresses in metals at the second stage of the process is due to the electronic mechanism of heat transfer [3]. The difference in the mechanisms of heat transfer determines the fundamental difference in the parameters of thermal stresses in metals and dielectrics (Fig. 1).

It is demonstrated that in the models of the formation of elastic stresses and electric current pulses in metals, it is necessary to take into account the total derivative of the temperature change at the heat transfer stage.

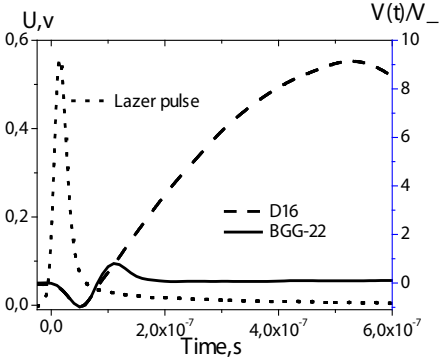

Fig. 1. Laser pulse and typical forms of thermal stress pulses in a dielectric (colored glass BGG-22) and metal (aluminum alloy D16).

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Optical Properties of InGaAs/GaAs Quantum Wells with a Low Indium Content

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A3B5 semiconductor heterostructures with quantum wells (QW) are important building blocks for optical communications and computing. In this work we study optical properties of InGaAs/GaAs quantum wells with low indium content (3%). We use inhomogeneous broadening of exciton resonances as a quality factor. At a temperature close to 0 K, this broadening is determined by the homogeneity and defectiveness of the QW [1]. The studied sample was a heterostructure with two $In_{0.03}Ga_{0.97}As$/GaAs Qws 190 nm (QW1) and 4.5 nm (QW2) thick. The photoluminescence excitation (PLE) spectrum was studied at 10 K (Fig. 1). PLE spectrum made it possible to determine the spectral position of heavy-hole (HH) and light-hole (LH) exciton resonances in QWs, as well as to estimate their spectral widths. Resonances associated with spatial quantization of excitons in QW1 are well-resolved in the spectrum, which confirms the high quality of QWs of this composition.

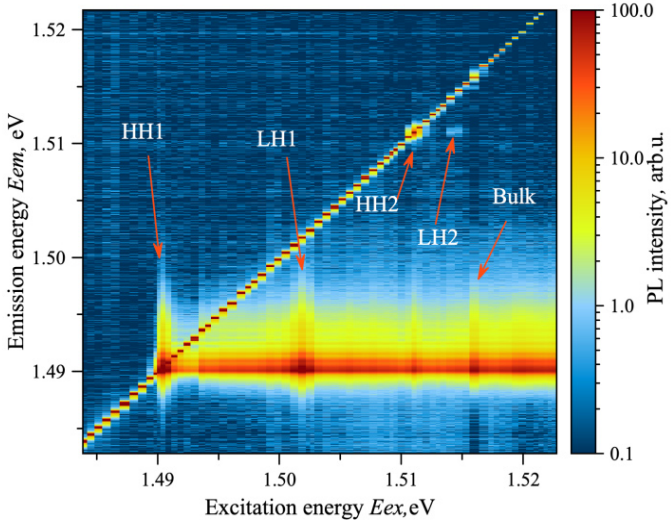

Fig. 1. PLE spectrum of InGaAs/GaAs QW at T = 10 K.

Acknowledgments: This work was carried out on the equipment of SPbU Resource center “Nanophotonics” and was supported by the RFBR project (20-32-70163).

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Effect of Barrier Layers on the Chemical Composition and Reflectivity of Multilayer Cr/Be Mirrors

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Currently, multilayer periodic mirrors are the crucial elements in X-ray optics. The search for novel materials for the manufacture of multilayer structures that would provide higher reflection coefficients has become an important research field in recent years. Cr-based mirrors can be used to obtain reflection in the short-wave range (3 – 6 nm). Such mirrors are promising for the elemental analysis of materials and can be used to create microscopes in the spectral regions of the "transparency windows" of water and carbon (2 – 5 nm), which opens up opportunities for studying carbon-containing substances and biological structures.

Interlayers formed at the interfaces as a result of diffusion, mechanical penetration of incident atoms during the manufacturing of mirrors, chemical reactions and other factors significantly reduce the theoretically expected reflectivity of the multilayer structure. To reduce the interaction between the main layers of the mirror such a method as the introduction of a barrier layer is used.

The work is focused on the investigation of multilayer X-ray mirrors based on Cr/Be with ultrathin layers. The structural features of extended interzones were explored using X-ray photoelectron spectroscopy, as well as the possibilities of influencing them by introducing barrier layers C and B_4C. In addition, the effect of the barrier layers on the reflectivity of the mirrors was analyzed. It was established:

- In the multilayer nanostructures, the chromium and beryllium layers are completely mixed to form $CrBe_2$ and $CrBe_{12}$ beryllides;
- The introduction of a barrier layer (C, B_4C) reduces the amount of the $CrBe_2$ beryllide with a simultaneous increase in the amount of $CrBe_{12}$ beryllide. In addition, chromium and beryllium carbides and chromium boride (in the case of the B_4C interlayer) are formed;
- The mirror $[C/Cr/Be]_{x180}$ demonstrates the best reflectivity.

Acknowledgments: This work was supported by RSF grant 19-72-20125.

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Theoretical Interpretation of the Interface Formation in Multilayer X-ray Mirrors Synthesized by Magnetron Sputtering

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The study of multilayer X-ray mirrors synthesized by magnetron sputtering indicates the formation of asymmetric transition layers in them at the interfaces. Asymmetry can be expressed in the extent of layers or different stoichiometry and / or extent depending on the order of deposition of layers [1, 2]. To explain the resulting asymmetry of the interfaces a theoretical analysis of the exchange process between film atoms and substrate atoms during film growth was carried out and a model for the synthesis process of a multilayer structure by magnetron sputtering was offered. The formation of transition layers as a result of mixing of adjacent layers can be considered as a result of two mechanisms arising during the deposition of layers: mechanical penetration of incident atoms into the layer and exchange of positions of surface and subsurface atoms caused by minimization of the surface free energy.

The energies of sputtered atoms were calculated using the Stopping and Range of Ions in Matter (SRIM) software package [3] for Mo / Si and Mo / Be multilayer systems without / with barrier layers (B_4C and Si). Despite the limitations inherent in the program it allows one to establish the main factors affecting the resulting asymmetry of interface zones in layered systems.

It was found that the formation depth of the interface is comparable to the penetration depth of atoms during the synthesis process. The influence of the introduction of barrier layers on the formation of the interface is analyzed.

Acknowledgments: This work was supported by the Russian Science Foundation grant 19-72-20125.

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Dynamic Magnetization of the Eutectic Bismuth-Tin Alloy under Nanoconfinement

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Over the years, it has been a tendency for reducing the size of electronic components. It has led to increasing demands on physical properties of solder alloys. A suitable solder material should have low melting point, good wettability, high strength of joints, etc. Tin-based alloys are being thoroughly investigated due to their promising application as a superconducting solder [1]. One of the methods to create a nanostructured superconductor is to insert a superconductive material into the voids of a dielectric mesoporous matrix such as opal, porous alumina, silicate glass, etc. [2].

We present the study of the eutectic Bi-Sn alloy, which was embedded into the silicate glass with the average pore size of 10 nm. The temperature dependence of the dynamic (ac) magnetization was measured by Physical Properties Measurement System PPMS-9 (Quantum Design Inc.) in the temperature range from 1.9 to 10 K in bias magnetic fields up to 20 kOe. The magnetization dependence on the amplitude and the frequency of the ac driving field was obtained.

The upper critical field line on the plotted H-T phase diagram showed a positive curvature at low magnetic fields, which was explained within the framework of the proximity effect. The evaluated activation energy at different bias fields showed the existence of the thermally activated creep of superconducting vortices in the dirty type-II superconductor. The temperature dependence of the imaginary part of ac magnetization demonstrated the anomalous second peak at bias magnetic fields from 3 to 15 kOe.

Acknowledgments: This work was supported by RFBR (grant No. 19-07-00028). The measurements were carried out in the Resource Centre «Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics» Saint-Petersburg State University Research Park.

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Diffuse Reflectance Spectroscopy of Halide Perovskites: New Methods and Solutions

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In this work, we propose a new method for obtaining true absorption spectra of powder samples based on the diffuse reflectance spectra of pure and diluted samples with a non-absorbing material (absorption of $BaSO_4$ is taken as 0). Crushed single crystals of halide perovskites, such as $MAPbI_3$, $MAPbBr_3$ and $MAPbBr_3$ doped with bismuth, as well as one-dimensional perovskite $PyPbI_3$, were chosen as the studied samples.

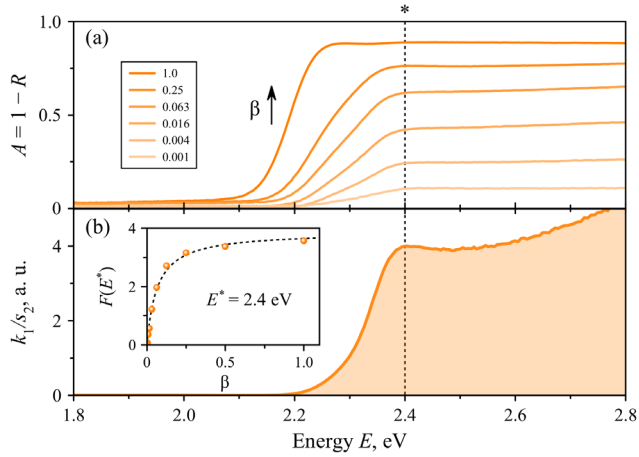

*Fig. 1. (a) Absorption (A) obtained from diffuse reflectance spectra (R) of $MAPBr_3$ when diluted with $BaSO_4$ (β – concentration of $MAPBr_3$); inset (b) fit of the dependence of the Kubelka-Munk function $F(E^*)$ on the β for the energy E^* marked with *; (b) true absorption spectrum obtained during data processing.*

With dilution, the true structure of the diffuse reflectance spectra becomes visible (Fig. 1(a)), otherwise hidden behind the strong absorption of the material. Further processing (inset Fig. 1(b)), based on the Kubelka-Munk transformation, allows one to obtain true absorption spectra (Fig. 1(b)) that are consistent with the literature [1].

Acknowledgments: The work was carried out using the equipment of St. Petersburg State University resource center «Nanophotonics» with the support of the Russian Foundation grant 19-72-10034.

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Coherent Dynamics of Excitons and Their Complexes in a GaAs / AlGaAs Quantum Well

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One of the possible ways to implement quantum logic gates is to process information using light signals. Photon echo is a phenomenon that can be used in the basis of a quantum logic gate.

In this work, we study the character of coherent dynamics by the method of four-wave mixing and photon echo from excitons in an AlGaAs / GaAs quantum well under optical pumping by constant wave laser radiation. A theoretical model is constructed and computer simulations are carried out to determine the spectral position of the exciton resonance.

The obtained experimental data allow us to speak about the presence of a photon echo in the sample. Various spectral positions of the photon echo signal were assigned to ensembles of excitons and their complexes. In the course of the experiment, it was possible to increase the time of irreversible phase relaxation of the exciton ensemble by pumping with constant wave laser radiation.

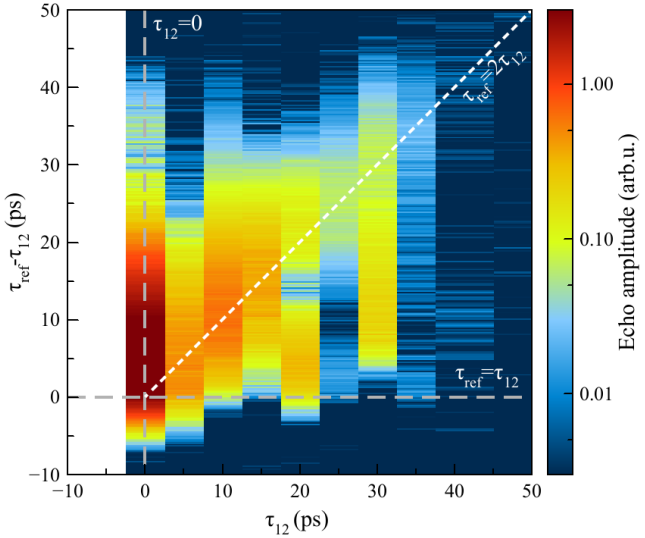

Fig. 1. Dependence of the temporal envelope of the photon echo amplitude on the delay between 1 and 2 impulses. The dotted line $\tau_{ref} = 2\tau_{12}$ corresponds to the echo position, $\tau_{ref} = \tau_{12}$ corresponds the second exciting pulse.

Acknowledgments: This work was carried out on the equipment of SPbU Resource center “Nanophotonics” and was supported by the RFBR project 19-52-12046 nnio_a.

Optical Properties of Core-Shell Structure in AlGaAs Nanowires

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In this work, the studied sample was grown by molecular beam epitaxy on semiconductor substrates using a metal growth catalyst. As a result, a sample of one-dimensional AlGaAs nanowires (NWs) with a single filament height of 5–7 μm and a thickness of 2 μm was obtained. In turn, the wires were overgrown with a wider-gap material, resulting in the formation of a two-component structure (see Fig. 1a) [1].

We create an experimental setup for the excitation and subsequent registration of photoluminescence (PL) from the NWs, either as-grown vertically-standing or randomly-bestrewn on the substrate. It is possible to measure the PL of the ensemble of NWs. The results were analyzed and presented in Figs. 1b and 1c. Fig. 1b shows the PL spectra at different pumping power of the laser. One can see that the PL spectra have two distinct maxima. This two-peak structure, presumably, can be associated with the radiation of the core-shell structure of each single NW (Fig. 1a) [1]. The shift of one peak relative to the other is associated with the spreading of Al content in the NW (the composition $Al_{0.1}Ga_{0.9}As$ of a core and $Al_{0.3}Ga_{0.7}As$ of a shell). At the same time, the peak broadening most probably originates from spreading of NW sizes in the ensemble. This may also be attributed to the emission of direct and spatially indirect excitons created thank to a spontaneous crystal-phase transition in single NWs.

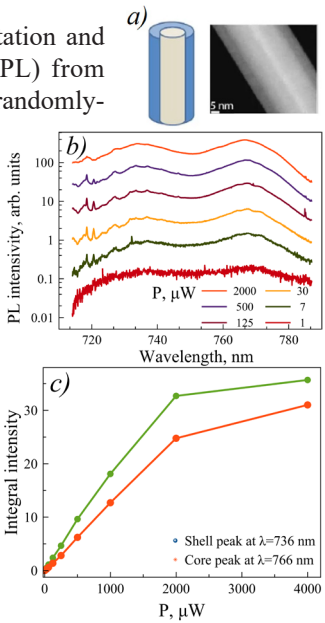

Fig. 1. (a) Schematic (left) and the transmission-electron-microscopy image (right) of the core-shell structure in a single NW. (b) Power dependences of the PL intensity. (c) Integral intensities of the core and shell peaks measured at different radiation power.

Acknowledgments: The authors acknowledge the RSF grant No. 19-72-30004.

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First Hybrid Organic-Inorganic Halide Post-Perovskite

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In this work we present a first hybrid organic-inorganic halide post-perovskite $[C_6H_5N_2]PbBr_3$ (Fig. 1a,b) [1]. The crystal structure makes the material anisotropic, what observed in Raman scattering spectra.

The photoluminescence excitation (PLE) and photoluminescence (PL) spectra (Fig. 1c) demonstrate the band gap of the material as 3.25 eV and the broadband emission of self-trapped excitons are the typical features of low-dimensional lead bromide hybrids.

The tilt of inorganic octahedrons along the *y*-axis creates a tight packing of organic cations in the system. It leads to the appearance of a weak bonding interaction between them and the formation of two uncuppied organic-related bands in the theoretical electronic band structure (Fig. 1d, e). These bands are not flat, but they also do not participate in optical transitions. The band gap is formed by inorganic-related bands, and the calculations show the possibility of both direct and indirect transitions between them.

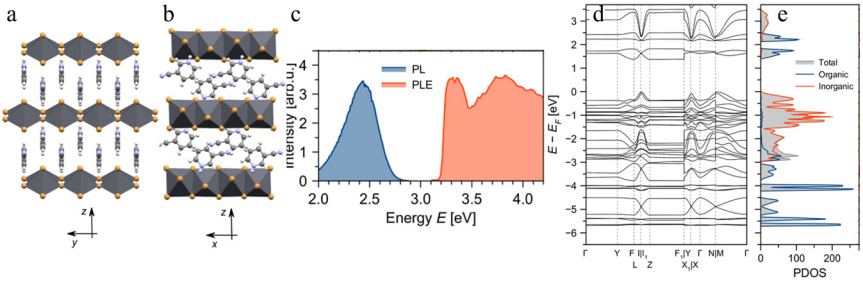

Fig. 1. Crystal structure of $[C_6H_5N_2]PbBr_3$ *seen in (yz) (a) and (xz) (b) planes. (c) PL and PLE spectra at T = 77 K. Calculated electronic band structure (d) and total density of states (e).*

Acknowledgments: This work was supported by RFBR №19-03-00836 A and RSF №19-72-10034 on the equipment of the resource center "Nanophotonics".

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Dynamic Susceptibility of the Nanocomposite Porous Glass/Ga-In-Sn in the Superconducting Region

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Recently, there has been an increase in interest in studies of gallium alloys in connection with their possible applications for self-healing superconducting contacts and wires. Particular attention is paid to the superconducting properties of nanostructured alloys. In the present paper, the study of the dynamic (ac) susceptibility of the porous glass/Ga-In-Sn nanocomposite in a temperature range of 1.9 - 8 K and bias fields up to 5 T is reported. The phase diagram is constructed (Fig. 1). Two superconducting transitions with temperatures of 5.6 and 3.1 K are found. The sections of positive curvature of critical lines interpreted within the framework of a model that takes into account the proximity effect [1] are demonstrated. Activation barriers for the vortex mobility are found from the shift of the maxima of the imaginary part of the susceptibility with the frequency of the ac field. A bend on the field dependence of activation barriers is shown.

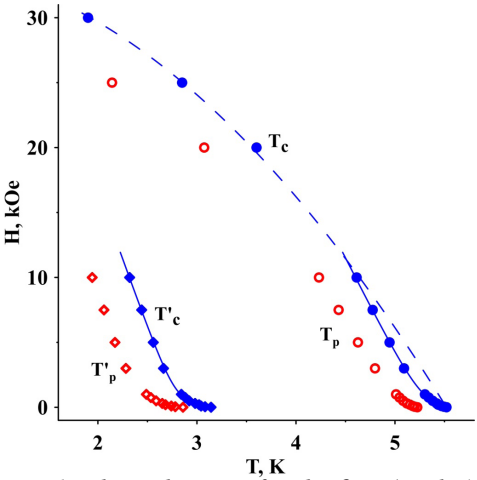

Fig. 1. Phase diagram for the first (circles) and second (diamonds) superconducting transitions. Filled symbols are transition temperatures, empty symbols are temperatures of the maxima of the imaginary part of susceptibility. The dashed line is a theoretical dependence for the two fluid model. Solid lines are theoretical curves for the model developed in [1].

Acknowledgments: The present study was supported by RSF, grant 21-72-20038. The measurements were performed on the equipment of the Research Park of St. Petersburg State University.

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Effect of Annealing Conditions on the Composition of Interlayer Regions in Mo/Be Multilayer Structure

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Due to its high reflectivity, Mo/Be based multilayer X-ray mirrors are promising optical elements for maskless EUV lithography technologies. In addition to lithography, these mirrors are actively used both in space exploration and in synchrotron radiation sources where they are exposed to high temperatures and impressive energy flows. Heating at high temperatures leads to an increase in thermal diffusion, which further affects the formation of interlayer regions and ultimately leads to a violation of the periodic structure of multilayer mirrors, which makes them unusable. In this connection the purpose of this work was to study the influence of the high temperatures on the thermal stability of Mo/Be multilayer systems with/without a barrier layer using X-ray photoelectron spectroscopy.

According to [1], two types of beryllide are formed at the interfaces of the Si/$[Mo/Be]_{110}$ structure at room temperature depending on the order of layer deposition ($MoBe_{12}$ are formed at the Be-on-Mo interface and $MoBe_2$ are formed at the Mo-on-Be interface). Heating the structure to only 100 °C leads to a decrease in pure beryllium content, accompanied by an increase in $MoBe_{12}$, in the system. At annealing temperatures above 300 °C, the $MoBe_2$ content increases sharply and is 90% at 500 °C.

Analysis of the effect of the interlayer (B_4C or Si) inserted between molybdenum and berillium reveals that regardless of the material the introduction of barrier layer: i) limits the formation of beryllides with an increase in the annealing temperature at the Be-on-Mo interface; ii) prevents the formation of $MoBe_2$, while forming a $MoBe_{12}$ beryllide at the interface Mo-on-Be; iii) does not limit beryllium oxidation process at the Mo-on-Be interface; iv) both system are thermally stable up to 300 °C.

Acknowledgments: This work was supported by the Russian Science Foundation grant 19-72-20125.

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Incremental Relaxation Plasticity Model for Analytical Study of Nonmonotonic Behavior of Dynamic Yielding Diagram

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Many temporal phenomena of high-rate plastic deformation of metals, such as the yield drop phenomenon and subsequent non-monotonic behaviors or the oscillating behavior of the stress-strain diagram, were found in many experiments under rapid tension. These phenomena cannot be explained by the existing classical models and theories of plasticity. Thus, the modeling of the irreversible deformation diagram under dynamic loading is an actual and important problem. The relaxation plasticity model [1] based on the incubation time concept was aimed to explain some phenomena of dynamic yielding diagram such as strain-rate sensitivity of the yield limit and the yield drop effect, but this version sometimes works well only in the strain range close to the yield point. The modified incremental approach does not have such restriction and it is capable to simulate a wider class of problem of dynamic plasticity. It was also demonstrated that this approach can predict the nonstable oscillating behavior of the diagram at the stage of the developed yielding process. The obtained results of the incremental approach applied to the linear one-dimensional problems are compared with experimental data and simulation results of the original relaxation approach [2] and Johnson-Cook model. The better coincidence to the experimental data is reported for the incremental approach.

Acknowledgments: This work was supported by RFBR. The authors are grateful to Saint-Petersburg State University Research Park.

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E. Electromagnetic and Acoustical Processes

Applicability of the Dynamic Current-Voltage Characteristics for Diagnostics of Transformer Oils

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High-voltage oil-filled equipment is actively used in power distribution systems. One of the actual and significant problems is an absence of a technique that allows one to diagnose the necessity to replace oil as accurately as possible and with an extremely low risk of missing a breakdown. For each approach, criteria are needed to determine whether the measurement results must be interpreted as the need for an oil replacement [1]. Researchers of St. Petersburg State University have developed a method of dynamic current-voltage characteristics of liquid-filled systems to diagnose their high-voltage conductivity. The possibility of using the technique to assess the condition of oils is an open and very actual question [2].

An investigation was carried out to measure the dynamic current-voltage characteristics (DCVC) of the blade-plane system filled with transformer oil taken from a high-voltage power transformer (clean liquid and that after some time of being in use). The issue discussed in detail here is devoted to the possibility of applying the DCVC method for diagnosing changes in the properties of transformer oil during its operation. In the present work, the dynamic current-voltage characteristics and ampere-second characteristics of oils were measured, and the technique and methodology for measuring DCVC were described. The comparison of DCVCs of oils at different stages of operation was carried out. In the course of the work, several problems were identified that make it difficult to interpret the study results. In particular, the effect of the contact between oil and electrode on the electric current levels in the system was found. A clear advantage of the DCVC technique over the classical current-voltage characteristic was shown. The effect of microparticles on the shape of DCVC was also evaluated. The conclusion is that a correlation between the type of DCVC and the state of the oil exists.

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Applicability of the Effective Magnetization Curves Method for Calculating the AC Resistance

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Recent developments in the numerical calculation of harmonic electromagnetic problems with nonlinear magnetic materials have heightened the need for computational costs reduction, as the most accurate approach of solving such problems consists in conducting nonlinear transient analysis requiring significant resources [1]. One of the methods of lowering resource consumption is the method of effective magnetization curves in combination with finite element modeling. Although it has been known over twenty years, the limits of its applicability are not completely clear [2].

To determine these limits, parametrization and solution of the problem of harmonic current passing through a nonlinear magnetic wire as well as the calculation of its resistance were carried out. Analysis was conducted with nonlinear transient and effective magnetization curves methods. Calculations have shown that when the wire material is nonlinear and the current is distributed inhomogeneously, the latter does not give an exact value of the resistance, the maximum deviation from it was 28%. Thus, effective magnetization curves can be used where it is necessary to consider the nonlinearity of magnetic materials, spending a minimum of resources.

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Comparison of Positive Corona Discharge Computer Models Based on Drift-Diffusion and Unipolar Approximations

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Corona discharge is an electrical discharge appearing in inhomogeneous electric fields nearby electrodes of great curvature. Unwanted corona discharges on transmission lines may cause significant waste of energy. However, the discharge can also be used, for instance, in cleaning gases from dust, cracks diagnostics, as well as copiers and laser printers.

Simulation of the discharge is necessary, since analytical solutions exist only for simple geometries. Simulations, considering all phenomena included in actual corona discharges, are quite resource-intensive, so various approximations are being designed.

The work considers two approximations: drift-diffusion and unipolar. They are applied to a system of coaxial cylinders, using finite-element method in COMSOL Multiphysics software. The results are compared to theoretical ones, as well as experimental data in analogous geometries, and a conclusion on pros and cons of the models are made.

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F. Optics and Spectroscopy

DFT Modeling of the Zwitterionic Structure of Amino Acids and Their Raman Spectrum

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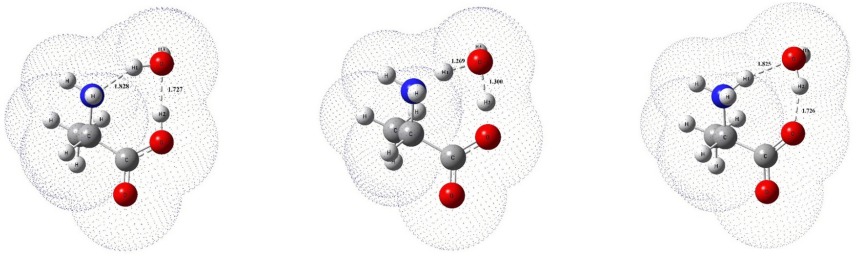
Many of the important biochemical reactions involving α-amino acids are associated with proton transfer. Each free α-amino acid also plays a fundamen-tal role in the vital cycle of the organism. To model vital biological processes with their participation, it is necessary to understand how the zwitterionic struc-ture itself is formed at the molecular level. Modern methods of quantum chem-istry allow to do this elegantly, and optical spectroscopy of biomolecules sug-gests extensive experimental material for a comprehensive study of their elec-tronic structure.

In this work, it is shown that the formation of the zwitterionic state (ZW) of alanine from the most stable conformer of the ground state (GS) occurs with the participation of a single water molecule. This molecule is responsible for the transfer of a proton from the –COOH group to the $–NH_2$ group through the transition state (TS) with the hydroxonium ion $(H_3O)^+$ (Fig. 1). To test this discrete-continuum model of the zwitterionic state, the Raman spectra of alanine is calculated and compared with the experimental ones. All calculations were performed using the GAUSSIAN 16 package [1], installed on the Huawei cluster of the Computational Center at the St. Petersburg State University [2].



Ala + H_2O (GS) **Ala + H_3O^+ (TS)** **Ala + H_2O (ZW)**

Fig. 1. The optimized at level method B3LYP/6-311++G (3df, 2p) geometry of the molecular system Ala + H_2O in the ground (GS), transition (TS), and zwitterionic (ZW) states.

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Spectroscopic and Quantum Chemical Study of Adsorbed Ozone

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Coordinate bond to surface cations of TiO_2 shifts the band of ν_3 vibration to lower wavenumbers, while the two terminal oxygen atoms become not equivalent. We succeeded to obtain frequencies for ν_1, ν_3 and ν_{1+3} combination modes for all eight isotopomers of chemisorbed ozone [1, 2]. All the isotopic species have different bands of ν_{1+3} combination, while the ν_1 and ν_3 bands are split into three or four maxima containing several unresolved close lines. Several variants of ozone adsorption on anatase clusters by DFT method have been calculated. Two models: TiO_2 molecule and a $Ti_{20}O_{40}$ cluster have been compiled, two stable conformations: bidentate and monodentate were found for each surface Ti site.

The calculated frequencies of the combination ν_{1+3} mode for the bidentate and monodentate conformations on the five and four coordinated titanium atoms multiplied by the scaling factor are shown in fig. 1. All the 5 investigated ozone complexes well reproduce the experimentally observed splitting of ν_{1+3} band and the decrease in anharmonicity.

The most energetically favorable conformation turns out to be a monodentate adsorbed ozone molecule on a 4-coordinated titanium atom. However, the separation between the bands of ν_1 and ν_3 vibrations is better reproduced for the bidentate molecule on the same site. The explanation of this seeming contradiction we see in simultaneous interaction of the molecule with two adjacent sites. Further work is in progress.

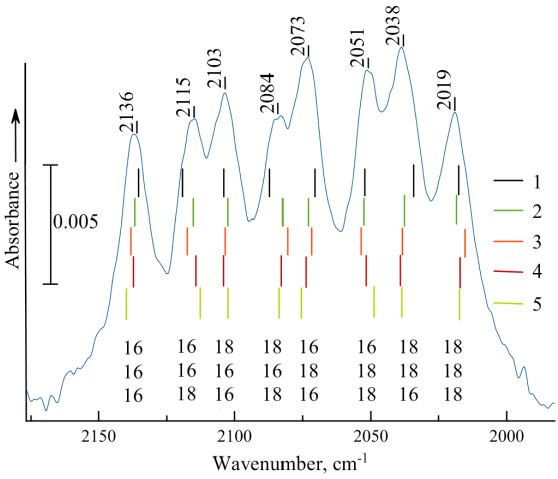

Fig. 1. Experimental spectrum and calculated frequencies.

Acknowledgments: The work was supported by RFBR and CITMA, grant No. 18-53-34004. The author thanks A.A.Tsyganenko and I.V.Krauklis for assistance and the Computing Center of SPSU for the computing facilities.

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Luminescent Properties of Lanthanide Metal-Organic Frameworks (MOF-76)

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Metal-organic frameworks (MOFs) represent a relatively new class of hybrid crystalline solids, which are formed by the binding of organic ligands (linkers) and metal ion clusters [1]. The combination of the various organic linkers and metal ions allows to create a large number of various MOF compositions with different morphology and topology and therefore opens a wide range of possibilities for their application in different areas such as gas storage, separation, catalysis, magnetism, as well as chemical sensors, bioprobes, sorbents, markers in forensics science, primarily owing to luminescent properties of such compounds. Most of lanthanide (III) ions demonstrate f–f luminescent emission from ultraviolet (UV) to visible and near-infrared (NIR) ranges, because of the $[Xe]4f^n$ configuration [2].

In this work, the series of lanthanide metal-organic frameworks $Ln(BTC)(DMF)_2(H2O)$ (Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) were synthesized under solvothermal conditions. The lanthanide nitrates and 1,3,5-benzenetricarboxylic acid (BTC) were used as a metal ion center and ligand, respectively.

Synthesized compounds were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) method and atomic absorption and emission spectroscopy.

Furthermore, we explored the luminescent behavior of these MOFs. Emission and excitation spectra were recorded. The quantum yield of the luminescence and photoluminescence lifetime were also measured with the most impressive results obtained for europium- and terbium-based samples.

Acknowledgments: The present study was supported by Saint-Petersburg State University (Pure ID 73032813). The authors are grateful to Saint-Petersburg State University Research Park.

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Diagnostic of ICF Target Inhomogeneous Compression by He-α Line Emission Radiography

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This report proposes He-a line radiation source for diagnosing Inertial Confinement Fusion (ICF) primary target compression. The secondary target (iron plate), as a source of X-ray radiation, is irradiated with a sequence of laser pulses at an intensity of ~10^{17} W/cm^2 and pulse duration of ~15 ps. As a result, this target emits He-α line radiation with an intensity of ~10^{16} W/cm^2 during ~25 ps. Such X-ray source, operating in a pulsed mode, can be used to determine the spatial distribution of the primary target plasma density with a high temporal resolution. In this report by developing the approach of [1], we have analyzed the scheme with another line emission for radiography of the compressed state of a thermonuclear target. The optimal parameters of the secondary laser target, for which the conversion factor of (sub)picosecond laser radiation into X-ray He-α radiation reaches a maximum, have been determined. With these parameters, the spatial resolution in the radiogram obtained by such a source reaches few microns, at picosecond temporal resolution. This diagnostic allows one to identify large-scale instabilities of the ICF target. In this research, the geometrical parameters of an ellipsoid-shaped target are determined such in its dynamics as the lengths of its semiaxes and the angle of inclination relative to the secondary target. The results obtained in [2] showed that the approximation of perturbation of ICF target by an ellipse makes it possible to predict with sufficient accuracy hot-spot temperature, hot-spot velocity and fusion yield depending on the ratio of the lengths of the semiaxes of the ellipsoid.

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Short-Arc Zenon Discharge at Super High (Ultra-High) Pressure

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A short-arc xenon discharge of super high (ultra-high) pressure, which is widely used as a light source, has been studied taking into account the evaporation of cathode material (thorium) into the discharge volume [1, 2]. The high electric current, typical for such discharge lamps, leads to the high cathode temperature that, in turn, could lead to thorium atom evaporation into a discharge gap and, due to the low ionization and excitation energies of thorium atoms, to strong influence on plasma properties, first of all, on the ionization balance. The earlier study [3] has shown that the presence of thorium near the cathode reduces the plasma temperature and ensures prevailing of the thorium ion density over that of xenon, the latter being close to zero in this region of the discharge.

A model of a short-arc xenon discharge has been developed for a real geometry taking into account evaporation of thorium atoms from a thoriated tungsten cathode into the discharge volume, the ellipsoidal coordinates as the most appropriate being used. The strong influence of thorium atoms on plasma properties is shown. Addition of thorium to the plasma decreases the plasma temperature, increases the strength of the electric field, and changes the composition of ions in the discharge gap. The data obtained are in reasonable agreement with the known ones [1, 2] and the results for the one-dimensional model [3]. The results can be valuable for the study of high pressure arc discharges with electrodes doped with some lightly ionized additives.

Acknowledgments: The work is supported by the Russian Foundation for Basic Research (RFBR), the grant No 20-32-90055 Aspiranty, 03 September 2020.

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Numerical Simulations of Nanosecond Pulsed Gas Discharges for Design and Optimization of Soft X-ray Sources and EUV Lasers

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Soft X-ray microscopy of biological objects is based on the use of X-ray radiation in the "water window" – the wavelength range from 2.3 to 4.4 nm. In this range, water is transparent to X-rays, while carbon (and organic compounds) absorbs it, which makes it possible to visualize the internal structure of cells in vivo [1]. The current level of development of the methods of X-ray microscopy and nanotomography has been mostly achieved with extremely expensive and bulky sources of synchrotron radiation. Achieving a comparable level of image quality and detalization but with simpler and more accessible soft X-ray sources could lead to a great progress in a number of fields in biology and medicine [2]. As potential water-window radiation sources nanosecond pulsed gas discharges of specific configurations have been considered [2, 3]. Great expectations have been placed on developments of gas-discharge sources of EUV radiation for lithography applications. However, shorter wavelengths require drastically different discharge conditions. Although X-rays in the “water window” and first magnified images have been obtained using capillary discharges in nitrogen [3], the current state of development of such sources is far from meeting the requirements set by nanotomography methods.

Numerical simulations could prove a valuable tool in design and optimization of discharge-based Soft X-ray sources and provide reliable estimations and scaling laws for plasma parameters. In this work we consider problems of discharge simulations when applied to relevant experimental setups of discharge-based soft X-ray sources, cover recent developments in corresponding numerical and physical models and present preliminary estimations of plasma dynamics for a specific source configuration.

Acknowledgments: This work was supported by RFBR-DFG. The authors are grateful to Saint-Petersburg State University Research Park.

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Diagnostic of OH···N Hydrogen Bond by IR Spectroscopy

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Modern supramolecular chemistry develops soft materials with adaptive properties based on non-covalent binding of monomeric blocks. Thus, the investigation of strength and geometry of non-covalent interactions such as hydrogen bonds is essential for materials chemistry. For solid state geometry of a hydrogen bond can be evaluated experimentally by X-ray diffraction, but for soft matter it is difficult. The alternative way is using spectral parameters (IR, NMR etc.) for evaluation of hydrogen bond geometry and strength. Pioneer researches of correlations between IR spectral parameters and hydrogen bond properties was performed by Badger, Bauer and A. V. Iogansen [1, 2]. However, equations proposed in their works are limited by a narrow range of geometries of investigated complexes.

In this work we continue our investigation of the applicability of IR spectral parameters for estimations of a hydrogen bond strength and geometry [3]. On the example of a set of complexes with OH···N hydrogen bond, formed by substituted methanol and acetic acid as a hydrogen bond donor, pyridines and amines as a hydrogen bond acceptor (Fig. 1).

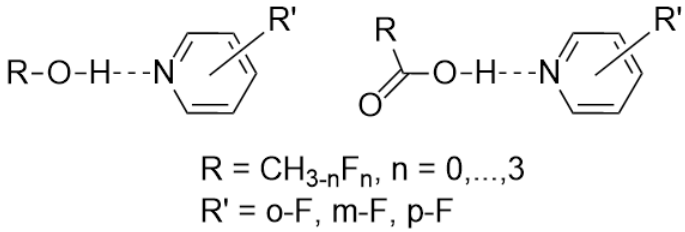

Fig. 1. Scheme of studied complexes.

Acknowledgments: This work was supported by grant of the President of the Russian Federation number MK-946.2020.3.

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Second Harmonic Generation Spectroscopy in Silver Nanorods-Based Hyperbolic Metamaterials

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Hyperbolic metamaterials (HMMs) are artificially created nanocomposite materials, where components of the permittivity tensor are of opposite signs [1]. An array of metal nanorods deposited in a dielectric template is a traditional design for HMMs. Special dispersion of HMMs possesses two spectral features of the real part of the effective permittivity: (i) a pole of the perpendicular to the nanorods axes component of dielectric function (Epsilon-Near-Pole, ENP) and (ii) a sign change of the parallel to the nanorods axes permittivity tensor component, when it crosses a zero value (Epsilon-Near-Zero, ENZ) [2]. Unusual optical and nonlinear optical effects can be observed in the spectral vicinity of these points, such as enhanced second and third harmonic generation [1] or giant optical birefringence [2].

In the experiment the sample contains ordered arrays of silver nanorods, prepared by templated electrodeposition of Ag in porous anodic aluminum oxide film. The pore diameter and interpore distance were 30 nm and 102 nm, respectively, corresponding to the porosity of 8%. ENZ and ENP features are at $\lambda = 800$ nm and $\lambda = 400$ nm. Studies of the second harmonic generation (SHG) were performed with the p-polarized fundamental radiation of a Ti:Sa laser with tunable wavelength 730 - 900 nm, with the FWHM of the spectral line of about 10 nm, the pulse duration of 50 fs, the repetition rate of 80 MHz, and the average power of 70 mW.

The wavelength-angular spectrum of the p-polarized SHG measured for the p-polarized fundamental beam demonstrates two maxima: (i) at $\lambda = 760$ nm for the angle of incidence $\theta = 30° - 40°$; (ii) at $\lambda = 850$ nm. Peaks in SHG are associated with the fulfillment of the eee phase-matching condition for the wavevector: $n_e(\lambda, \theta) = n_e(\lambda/2, \theta)$. We have shown the crucial role of the two specific spectral points, ENZ and ENP, which govern the dispersion of the composite metamaterial and, thus, the SHG formation.

Acknowledgments: The work was supported by Russian Science Foundation (grant number 18-73-10151), I.V.M. acknowledges the financial support of the Foundation for the advancement of theoretical physics and mathematics BASIS.

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Determination of the Carbon Monoxide Extinction Coefficient, Adsorbed on Titanium Dioxide

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The process of carbon monoxide adsorption on the titanium dioxide surface at room temperature was studied by *in situ* IR spectroscopy and volumetry methods. It was found that the data obtained on CO adsorption on exponentially heterogeneous surface can be satisfactorily described by the Freundlich isotherm [1]. This finding is in the agreement with the presence of two CO bands adsorbed on TiO_2 surface, at 2210 cm^{-1} and at 2193 cm^{-1} .

The extinction coefficient of adsorbed CO in the CO/TiO_2 system was also calculated with the use of Bouguer – Lambert – Beer law giving value of 110.6 $km \cdot mol^{-1}$ at minimum coverage. Experimental data showed that the extinction coefficient value of adsorbed carbon monoxide decreases with coverage increase, approaching the value of gaseous CO (65.5 $km\text{-}mol^{-1}$). The data were obtained under the condition that the optical path is equal to the thickness of the sample. The applicability of the Bouguer-Lambert-Beer law for determining the CO extinction coefficient in heterogeneous systems is obviously limited by the mismatch between the sample thickness to the real optical pathway.

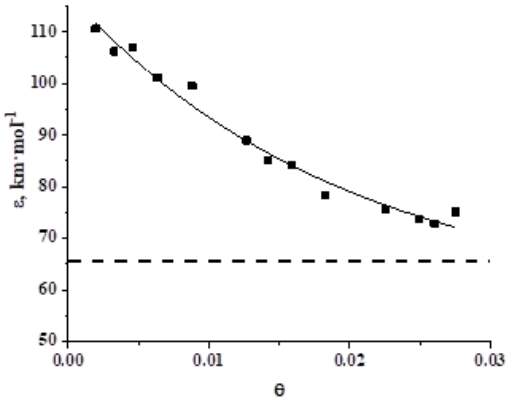

Fig. 1. Coverage dependence of the extinction coefficient of adsorbed CO. The dotted line indicates the CO extinction coefficient value in the gas phase at 293 K, equal to 65.5 km-mol-1.

The effect of the Lorentz field was also evaluated for this "adsorbate-adsorbent" system. It was found that the value of the extinction coefficient corrected in this way (81.5 $km\text{-}mol^{-1}$) is in agreement with the value obtained experimentally.

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DFT Study of the Adsorption Properties of Ca Cation

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Adsorption properties of the cations in zeolites dramatically differ from those of the oxides of the same elements. To explain this effect FTIR spectra of CO adsorbed on CaO exposed to different gaseous acids has been carried out [1]. It was shown that transformation of the surrounding O^{2-} ions into carbonate, sulfite or sulfate ions results in the blue shift of C-O stretching band of molecules bound to Ca^{2+} cation, approaching the value characteristic of Ca zeolites. In the zeolites adsorption of two or even three CO molecules at the same cation is possible. In the spectra of CO adsorbed on Ni-USY zeolites such mono-, di-, and tricarbonyls exhibit one, two or three well resolved bands which shift in a certain way on ^{13}C substitution [2]. However, for CO adsorbed on CaY zeolite [3] adsorption of two molecules on the same cation, manifested in a shift of CO band with coverage, does not lead to its splitting in two maxima as expected for the dicarbonyl. Band assignment in the spectra of adsorbed ^{12}CO-^{13}CO mixtures faced some difficulties, in particular, at elevated temperatures when the spectra reveal linkage isomerism – a part of molecules become bound via O atom.

For better understanding the experimental results we have carried out a DFT calculation of CO molecules interacting with Ca cation in clusters modelling either a fragment of zeolite framework or the oxide, pure and modified by CO_3^- ions, as well as with the free Ca^{2+}. The calculated values of harmonic frequencies were multiplied by scaling coefficients different for C- or O- bonded molecules. Besides the frequencies, the intensity of C-O band was calculated

In accordance with [4], the increase of CO stretching frequency is accompanied by intensity decrease of the corresponding absorption band.

For the Ca dicarbonyl complex in zeolite, as compared with Ni dicarbonyl, due to weaker interaction between the molecules, splitting of CO band is small and the second band of CO vibration coincides with that of monocarboonyl.

Unlike CaO, where strong field of O^{2-} anions prevents the formation of O-bonded complexes, for larger anions linkage isomerism becomes possible, and the higher are the frequencies of C-bonded complexes, the greater is the low-frequency shift of the O- bonded CO.

Acknowledgments: The work was supported by RFBR and CITMA, grant No. 18-53-34004. The author thanks A.A. Tsyganenko and I.V. Krauklis for assistance and the Computing Center of SPbSU for the computing facilities.

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Dynamics of the ArICl Van-der-Waals Complex Decay

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The most of the existing research is devoted to complexes of Rg with dihalogens, RgXY/RgX_2 – mainly $RgHaI_2$. According to the literature, complexes such as RgICl and RgIBr, Rg = He, Ne (for example, [1]) have been studied in the ground and electronically excited states, while the ArICl complex has been studied in the ground state only.

In this work, we investigated the dynamics of the ArICl complex decay in exited states as a result of electron photoexcitation. It is known that the RgXY complex, where XY is halogen atoms, as a result of excitation dissociates into a free molecule and an Rg atom or three Rg, X and Y atoms. The reason for the decay is the internal redistribution of excitation energy.

The IP (ion-pair) states of the ArICl complex and the free ICl molecule were excited by the double optical resonance method with different delay times of the second pulse relative to the first. A model of the kinetics of all photoprocesses with the ArICl complex has been build (Fig. 1). An analysis of the rotational structure of the decay products of the complex was also carried out [2].

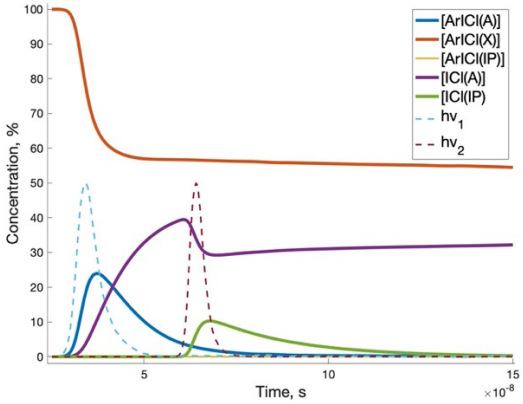

Fig. 1. Changes in the concentration of the ArICl complex in the ground and excited states and of the ICl molecule with a second pulse delay of 30 ns.

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Numerical Simulations and Parametric Analysis of Longitudinal Structure of DC Glow Discharges

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DC glow discharges are one of the more studied types of low-temperature plasma sources. Their distinctive feature is the peculiar glow structure and specific distributions of plasma parameters, which allow distinguishing different regions: negative glow, Faraday dark space, positive column, cathode and anode sheaths [1]. The strive to understand the processes of current transfer and plasma self-organization has contributed to the development of discharge models and plasma simulation methods in general.

The key requirement for the numerical model of a DC glow discharge is to account for non-local ionization produced by the electrons accelerated in the strong electric field of the cathode sheath. This ionization mechanism is dominant in the cathode regions of a DC discharge and cannot be described in terms of local parameters of plasma. Previously a full longitudinal structure of a glow discharge has been obtained using a hybrid Monte-Carlo/fluid model [2]. The issue with the proprosed approach to this day remains its technical complexity in terms of numerical realization that significantly limits its potential for parametric analysis of discharge.

We have previously developed a unique approach that is capable of reproducing the longitudinal structure of a DC glow discharge and which can be easily implemented in most low-temperature plasma simulation software packages [3]. Here we present the results of a parametric study of a DC glow discharge using the approach and discuss how the ability to compare with an experimentally obtained glow structure can extend our understanding of the physics behind formation of different discharge regions.

Acknowledgments: This work was supported by the Council on grants of the President of the Russian Federation (Grant № 075-15-2021-374).

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Kinetic Theory of Stability of the Electron Beam-Plasma System at Knudsen Numbers of Order One

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The paper is devoted to the development of the kinetic theory of stability of the fast electron beam – gas-discharge plasma system developed in [1, 2], considering the beam and plasma noise. It is shown that in this case the problem is of a mixed type. In particular, taking into account the shot noise of the beam and the plasma's own noise, stability problems arise with boundary conditions and initial conditions, respectively.

It is found that, in the linear approximation, the increment of the increase of beam perturbations in the plasma frequency region is significantly higher than that for plasma noise. At the same time, at lower frequencies of disturbances, the increments are equal (see Fig. 1). At the same time, the loss of stability of the system occurs simultaneously for both problems.

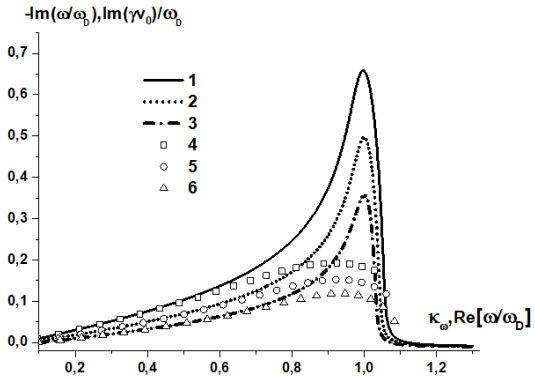

Fig. 1. Dependence on the frequency of increments in a problem with boundary (1 - 3) and initial (4 - 6) conditions for different parameters κ_b = 0.04 (1,4); 0.02 (2,5); 0.01 (3,6); $\kappa_b = \kappa_E$=0.02; ν_{ed}/ω_D = 0.01.

Therefore, perturbations of the beam, which increase along the direction of its propagation, play an important role in the dynamics of perturbations at the linear stage after the loss of stability.

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G. Theoretical, Mathematical and Computational Physics

Nonresonant Effects in Spectroscopic Experiments on Measurement of Transition Frequencies in Hydrogen and Helium Atoms

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Being a key instrument in understanding fundamental physical processes, spectroscopic experiments play an important role in verifying the results of calculation and theoretical hypothesis in various fields of physics. Development of experimental technique has led to a level of accuracy of spectroscopic measurements of order 10^{-15} of relative uncertainty, which requires taking into account effects so subtle that they can only be described in frames of the most accurate theory of atomic physics − Quantum Electrodynamics (QED).

Thus, relativistic QED corrections have long been included in the CODATA base of fundamental physical constants. However, it was found that as precise as experiments are, there is a discrepancies between results of various experiments, that could not be for unaccounted QED corrections. This leads to the necessity of rigorous theoretical analysis of processes used in these experiments, example of which are investigations of photon scattering processes on atomic systems and, as a result, calculations of so-called Nonresonant (NR) effects, which is a distortion of the spectral line profile due the presence of different transitions, and their interference, to close-lying levels, affecting significantly on definition of transition frequency.

For the first time, NR effects were considered in [1], and with [2] the whole new branch of investigations aimed at these effects were opened. From [2] and later works [3-6] it follows that NR effects can either reach or even become higher than level of experimental accuracy, and, moreover, have specific properties, characteristic for a given particular experiment. This work is devoted to analysis of NR effects in one- and two-photon scattering processes and their role in modern precision spectroscopy.

Acknowledgments: This work was supported by Russian Science Foundation (Grant No. 20-72-00003).

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RKKY-Interaction in Weyl Semimetal with Non-Symmorphic Symmetry

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Weyl semimetals attract the interest of scientists for their unique properties. These materials have a gapless spectrum. The valence and conduction bands touch each other at symmetry points called Weyl nodes. The spectrum is linear in the vicinity of these points. In the presence of additional symmetry, pairs of Weyl nodes can form one Dirac point, where the spectrum is doubly degenerate. The most famous two-dimensional material with a Dirac-type of spectrum is graphene.

We consider the model of 2D Weyl semimetal proposed in [1]. The system contains three Dirac cones at the boundary of the Brillouin zone. An important characteristic of this system is the existence of Dirac points in the presence of significant spin-orbit coupling. Dirac points are stable in the proposed model due to the non-symmorphic symmetry. In contrast, the spin-orbit interaction in graphene leads to the appearance of a gap in the spectrum.

We are interested in calculating the RKKY-interaction in the above model. It is considered as the second order of perturbation theory with respect to the exchange interaction of the localized moment and the local spin density of conduction electrons. Usually RKKY-interaction is characterized by $2k_F^*$-oscillations, where k_F^* is an effective Fermi momentum, and decrease with the distance between localized moments as R^{-d} (d is a dimensionality) [2]. In systems with zero k_F^*, such as pure graphene, the period of the oscillations is related to the distances between the Dirac points in reciprocal space [3]. Here the RKKY decreases as R^{-3}, what distinguishes graphene from other two-dimensional systems. We have obtained closed expressions for the RKKY-interaction in the model under consideration. The final formulas contain terms with both types of oscillations and corresponding degrees of decay. The existence of different types of terms is due to the presence of a nonzero effective Fermi momentum in a system with a Dirac spectrum. It should also be noted that the RKKY in the proposed model is not an isotropic Heisenberg exchange. The presence of spin-orbit coupling leads to magnetic anisotropy of the crystal.

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Analytical and Numerical Analysis of the Isotope Shift in Spectra of Superheavy Ions

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Isotope shift is the difference of atomic energy levels between isotopes of the same element. Nowadays, the isotope shift is widely used in study of the nuclear structure, astrophysical objects and laboratory plasma isotope composition [1]. Precision isotope shift spectroscopy can help in searching new physics beyond the standard model such as a new force carrier particle [2] and variations in time of the fundamental constants [3]. Another application of the isotope shift spectroscopy is the search of metastable superheavy element (SHE) transitions in astrophysical data [4]. To predict these atomic transition energies for stable neutron-rich isotopes of SHEs, the calculated isotope shifts must be added to the atomic transition energies measured in laboratories for the neutron-poor unstable isotopes.

The isotope shift is given by a sum of the mass shift and the field shift. The first one arises due to the finite nuclear mass, the second one takes into account the finite nuclear size effect. Within the framework of the one-electron approximation, the previously derived analytical formulae for evaluation of the isotopic shift lead to rather large deviations from the exact results when the nuclear charge number becomes larger than Z=100.

In the present work, an analytical analysis of the field shift in hydrogen-like ions with Z>100 is performed. The nuclear model of the uniformly charged sphere is employed. Simple approximate formulae based on the analytical results are obtained for 1s and $2p_{1/2}$ states of hydrogen-like ions using numerical methods.

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Calculation of the Electronic Structure of Atoms and Molecules Using a Quantum Computer

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The complexity of simulating the quantum system grows exponentially with number of particles. As a consequence, it is impossible to simulate efficiently large systems on classical computer. However, quantum computers have exponential supremacy over classical. On classical hardware a number of bits for storing the quantum state scales exponentially. On a quantum computer, in contrast, the number of qubits required to compute the system increases polynomially with the size of the system [1]. There exist several algorithms for electronic-structure calculations.

One of the main goals of electronic-structure problem is to obtain the ground-state energy of many-body fermionic Hamiltonians. In the present work, we consider (Iterative) Quantum Phase Estimation (QPE) [2] and Variational Quantum Eigensolver (VQE) [3]. It's expected the run-time and physical resources required by these algorithms to scale polynomially with both the size of the considered system and the accuracy required.

First algorithm we consider is QPE, which is based on phase evaluation of wave function with usage of quantum Fourier transform. However, to obtain the chemical accuracy with QPE we need a considerable amount of qubits, which can be reduced in Iterative Quantum Phase Estimation (IQPE) via multiple circuit iterations.

The VQE approach uses a parameterized quantum circuit to prepare a wave function. The parameters are obtained by optimizing the energy with the hybrid quantum-classical algorithm. But, Variational Quantum Eigensolver scales worse than IQPE and QPE. This method has low requirements for a quantum computer due to the usage of a classical computer along with a quantum one.

Using the described algorithms the electronic structure simplest molecules and atoms is calculated. The results obtained by different algorithms are compared with each other.

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5-loop Calculation of Critical Exponent z of Model A

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The second order phase transitions and critical phenomena are accompanied by anomalous increase of correlation radius and relaxation time. On the approach of a system to its critical point, these values are described by power law and characterized by critical exponents. These universal constants depend on the dimension of the space and the number of components of the order parameter, but remain the same for all matter. The renormalization group method allows to obtain an asymptotic ε-expansion for the critical exponent, where ε=4-d is formally small parameter, which shows the deviation of the dimension of the space from its critical value d_c=4. Alternative expansion with parameter ε'=d-1 could be done as well [1]. Expansion coefficients have a factorial growth therefore the resummation procedure is required in order to obtain more reliable theoretical predictions, which effectiveness strictly depends on the amount of known expansion terms.

This work is focused on estimation of the critical exponent z that is responsible for relaxation time behavior $t_c \sim r_c^z$ (r_c is correlation radius) using resummation techniques for recently calculated 5-loop ε-expansion [2] and 2-loop ε'-expansion. For this purpose, Pade approximation and new modification of Borel resummation method proposed in [2] were applied. Accounting the parameter which is in control of the asymptotics of the strong coupling along with the exact value of critical exponent for certain dimension [3] significantly increases result precision. However, both of these quantities are unknown for exponent z. The idea of the modification is to use the convergence criterion for determining optimal values of these parameters from the condition of the fastest convergence of the summation procedure.

Overall, obtained results demonstrate that account of new 5-loop term of ε-expansion and 2-loop ε'-expansion for critical exponent z provides a rapprochement of RG estimations with other results of Monte-Carlo simulations. The fact that two fundamentally different methods are in agreement denotes high degree of reliability of obtained estimates, effectiveness of the modification of Borel summation technique and argues in favor of advancing to higher orders of ε'=d-1 expansion.

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Quantum Effects in the Glauber Model of Nuclear Interactions at High Energies

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Currently, Glauber's model is widely used to describe the hadronic interactions at high energies. At such energies, the dominant is the contribution of the partial waves corresponding to the large values of the orbital quantum number l which is proportional to the impact parameter b. Therefore, the unitarity condition for a given partial wave l of nucleon-nucleon scattering leads to the unitarity condition for the Glauber amplitude at a fixed value of the impact parameter b.

In [1] it was shown that when applying the so-called optical approximation to describe the nucleus-nucleus interaction, correct answers are obtained for the average number of nucleons-participants and the number of binary NN collisions, however, for the variance of these quantities, the results are incorrect. Nevertheless it was shown that in the classical probabilistic approach outside the optical approximation the correct results for these variance can be obtained. In this regard, the question arose of how to obtain these results in the quantum version of the Glauber model.

As a first step the simple approximations for the NN amplitude was studied. It was shown that the simplest Gauss approximation, for a purely imaginary scattering amplitude, allows one to quantitatively describe the appearance of the effect Halo - "darkening" in the cross section of inelastic NN interaction at zero impact parameter. At the same time, this approximation also well describes the growth of a diffraction cone with energies from ISR to LHC. It was also shown that the effect Halo itself is a general quantum phenomenon that is not related specifically to the Gauss approximation for the amplitude and takes place for a sufficiently large amplitude of any shape.

For pA and AA collisions within the framework of the quantum Glauber approach, it was found that the non-diffraction scattering cross section is really expressed only in terms of the probability of inelastic nucleon-nucleon interaction at a given value of the impact parameter. At that, in the case of AA interaction, complex loop contributions occur already in the leading approximation. They contain convolutions of the profile functions of the inelastic NN interaction with each other.

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Two-Particle Correlation Function in the Geometrical Model of String Fragmentation

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Experimental and theoretical studies of pp and AA collisions at high energies has become an essential part of modern fundamental physics, and, especially, particle physics. One of the models used for theoretical analysis of such collisions is the geometrical model of string fragmentation, which successfully describes experimental data for low particle production densities, using apparatus of classical physics.

Based on the simplest model of string fragmentation [1] and the definition of two-particle correlation function:

$$\Lambda(\eta_1, \eta_2) = \lambda_2(\eta_1, \eta_2)/[\lambda_1(\eta_1)\lambda_1(\eta_2)] - 1, \quad (1)$$

where λ_1 and λ_2 are inclusive and double-inclusive distribution functions, we calculated two-particle correlation function between two separated windows in a mid-rapidity region. Those results gave us a base line for further investigations, when we moving away from simplest model and taking into consideration the details of Schwinger mechanism [3].

After introducing the Schwinger mechanism, we discuss the restrictions it removes from a simplest version of the model [2] and recalculate the distribution function for different separation between particles in rapidity. This enables us to use the same approach that we used earlier to calculate the two-particle correlation function in the case of the considered Schwinger mechanism.

As the result we present the final formula for two-particle correlation function between two separated windows in mid-rapidity region. This formula agrees with the simplest model [2] in the limit when all string segments have the same mass.

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A Four-Loop Order Approach to Flat Polymerized Membranes

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In recent years, the study of the critical properties of polymerized membranes has become an important area of research. The unique properties of such structures are of fundamental and practical interest in such areas as biophysics, solid state physics, and string theory. In recent years, calculations of renormalization group functions up to the second and third orders of perturbation theory with dimensional regularization in the minimum subtraction scheme were performed [1, 2].

The work is aimed at developing the already available results up to the fourth order of perturbation theory. To achieve this goal, all two-tailed diagrams up to four loops were generated using the QGRAF [3] package and their epsilon decomposition was calculated using the FORM [4] and FORCER [5] packages. The connection between the renormalization constants provided by the Ward identity allows us to restrict ourselves to this set of diagrams and not calculate three- and four-tailed diagrams.

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Asymmetries of Two-Photon 2s→1s Transitions in H-like Ions

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In this study, the differential transition probability for two-photon 2s→1s decay with respect to the polarization of the emitted photons was investigated. The angular distribution of the emitted photons is determined by the dominant E1E1 transitions, which gives $1+\cos^2\theta$ distribution, where θ is the angle between the momenta of the emitted photons. The deviation from this distribution was investigated in the nonrelativistic limit in [1]. The asymmetry for unpolarized emitted photons was investigated in [2].

We found that the differential transition probability can be approximated by two parameters: the total two-photon transition probability and the asymmetry factor. The difference between our relativistic calculation of the asymmetry and the calculation [1] reaches three times for the superheavy elements. In the case of light ions, the asymmetry is small, but important for evaluating the nonresonant corrections [3].

We also investigated the asymmetry of the emission of the left- and right-hand photons in the two-photon 2s→1s decay, which appears due to special geometry of the process [4]. For this geometry the left- and right-hand photons are emitted differently by ions with different polarizations that can be used in the measurement of the ion-beam polarizations. In the case of 2s → 1s transition, the asymmetry is a relativistic effect.

Acknowledgments: The work of Knyazeva V.A. and Andreev O.Yu. was supported solely by the Russian Science Foundation under Grant No. 17-12-01035.

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Natural Transition Spinors in Heavy-Element Compounds: Visualization and Analysis

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Natural transition spinors (NTS) are relativistic counterparts of natural transition orbitals, which could play an analogous role in the interpretation of ab initio calculation results in studies of heavy-element compounds. In the present work approximate (model) NTS [1] for low-energy transitions in several simple molecules of Ra or Pa compounds were constructed using Fock space coupled cluster electronic structure calculations as implemented in [2] in the frames of the small-core shape-consistent relativistic pseudopotential model.

A new approach to visualize complex two-component NTS and their cross-sections has been implemented. Correlations between the peculiarities of resulting plots and transition properties are investigated, focusing on the characteristics essential for the direct laser coolability of the studied systems. Advantages of using the presented graphical technique over that employing the RGB color wheel to represent the phase of complex orbitals [3] are discussed.

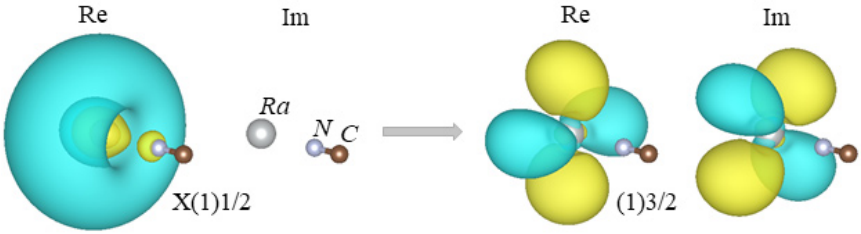

Fig. 1. Spin-up components of the NTS for the X(1)1/2 – (1)3/2 transition in the RaNC molecule. The corresponding spin-down components are much smaller and not shown. Strict localization of both spinors corresponds to the parallelism of potential energy surfaces.

Acknowledgments: The studies of Ra compounds are supported by the Russian Science Foundation (Grant No. 21-42-04411 RSF-DFG).

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Analytical Evaluations of Gas Cooling of the Latest Large-Area Pixel Detectors for Future Installations at Colliders

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Newest high-energy physics experiments will be equipped with detector complexes based on recently developed CMOS imaging sensor technologies. A compact, next-generation multipurpose detector ALICE 3 at the LHC [1, 2] will use arrays of silicon pixel very thin sensors, with an area of up to 14 cm×14 cm. This will allow to reach the ultra soft region of phase space, to measure the production of very-low transverse momentum lepton pairs, photons and hadrons at the LHC and to investigate properties of the Quark-Gluon Plasma (QGP) in details. More generally, it would open a new window for studies of soft phenomena in hadronic collisions, allowing to address fundamental physics questions [2]. Several cylindrical and disk-type layers (see Fig. 1) of ultra-thin (~40 micron) pixel silicon sensors, will be installed in a compact, next-generation multipurpose detector ALICE 3 at the LHC [1]. These layers of large area sensors are a source of heat release, which is about 20 mW/cm^2 on the surface of silicon sensors and 140 mW/cm^2 is a heat dissipated by electronics.

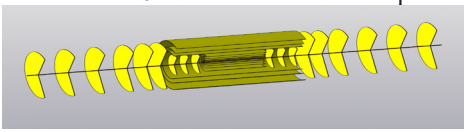

Fig. 1. Conceptual design of thin, large area, silicon pixel layers for the novel charged particle tracking system [1. 2].

Therefore, it is very important to consider the issue of heat removal from the surface of the detector. The following requirements are imposed to a cooling system: it must provide an operating temperature of no more than 30 degrees Celsius, the system should be very lightweight, and also vibration of the sensors must be excluded. To implement all of the above requirements, it is proposed to use a gas cooling system with low-speed laminar air flows. In the present study analytical evaluations have been performed to test the effectiveness of such approach and the estimates of cooling system performance were obtained.

Acknowledgments: This work is supported by the SPbSU grant ID:75252518.

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Combined Impact of the Weak Annihilation and Long-Distance Contributions on $B^+ \to \pi^+ \ell^+ \ell^-$ Decay

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The physics of bottom hadrons plays a fundamental role both in the precision tests of the Standard Model (SM) and in searches of New Physics (NP). Rare B-meson decays, which are induced by the Flavor-Changing Neutral Currents (FCNCs) $b \to s$ (d) transitions, provide a stringent test of the SM in flavor physics. The interest in B-physics is greatly stimulated by the LHCb, CMS, and ATLAS experiments at the LHC, and Belle-II at the B-factory SuperKEKB, which provide a huge amount of experimental data for different characteristics of the bottom hadron decays.

In this talk we consider $B^+ \to \pi^+ \ell^+ \ell^-$ decay, where $\ell = e, \mu, \tau$ is a charged lepton, and present its dilepton invariant-mass spectrum and decay rate calculated in the effective electroweak Hamiltonian approach for b$\to$ d $\ell^+\ell^-$ transitions in the SM, with account of both weak annihilation and long-distance contributions for different types of the $B \to \pi$ formfactor parameterizations. Our main result for the $B^+ \to \pi^+ \mu^+ \mu^-$ decay (green boxes) in comparison with experimental data by the LHCb collaboration [1] (black crossed lines) and known theoretical predictions [2] (red boxes) is shown in Fig. 1. Theoretical predictions for the $B^+ \to \pi^+ \tau^+ \tau^-$ decay are also presented.

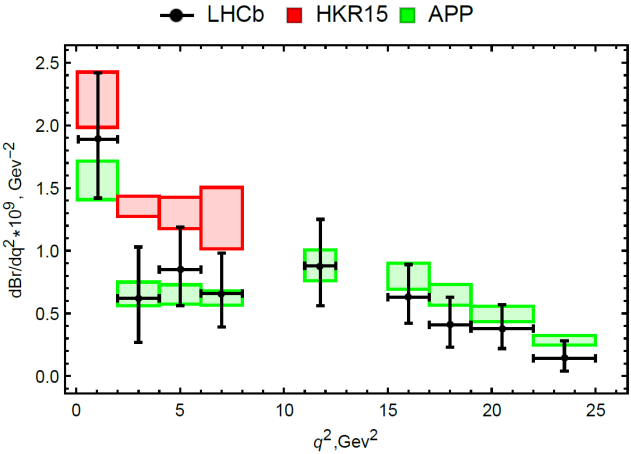

Fig. 1. Differential branching fraction of the $B^+ \to \pi^+ \mu^+ \mu^-$ decay in bins of dilepton invariant mass squared for the BGL parameterization.

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Calculation of TaO^+ Electronic Structure as a Means of Studying the Neutron Quadruple Moment of Nuclei

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In order to probe the standard model, as well as to set constraints on the parameters of its extensions, one can use different approaches of studying the effects of spatial parity non-conservation effects (P) in atoms and molecules. Such experiments, devoted to study P-odd effects, were most successfully conducted for the Cs atom [1]. Later it was suggested that it is possible to obtain the quadrupole term of neutron density from expanding the expression for the P-odd electron-nuclear weak interaction in series of multipole moments of the nuclear density [2, 3]. Taking into account that the weak charge of the neutron is by more than an order of magnitude larger than the one of the proton, the main contribution to the P-odd interaction is caused by the neutron subsystem of the nucleus. It means that if we study the interaction of this type, then it will allow us to extract the quadrupole distribution of neutrons in a nucleus.

Using a two-step approach for calculating the properties of atoms in compounds of heavy elements [4], we study the P-odd tensor interaction of the electrons with the neutron quadrupole moment of the nucleus in the TaO^+ cation. Finally, the energy levels of the TaO^+ molecule are predicted.

Acknowledgments: This work was supported by a grant from the Russian Science Foundation (project No. 19-72-10019).

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Renormalization Group Analysis of the Kardar – Parisi – Zhang Equation with Quenched Noise

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We study the Kardar-Parisi-Zhang (KPZ) model that describes kinetic roughening of randomly growing interfaces; examples of the roughening include a wide range of phenomena: propagation of solidification and flame fronts, spread of epidemics, tumor growth, etc., [1, 2]. KPZ model is defined by a non-linear differential equation for the height of an interface profile h(x)=h(**x**,t):

$$\partial_t h = \varkappa_0 \partial^2 h + (\partial h)^2/2 + f,$$

where **x** is d-dimensional spatial coordinate, t is time, $\partial_i = \partial/\partial x_i$ (here i = 1,..,d), $\partial_t = \partial/\partial t$, $\partial^2 = \partial_i \partial_i$ (summation over repeated indices is implied), and parameter $\varkappa_0 > 0$ corresponds to surface tension. The last term f = f (**x**, t) is a random noise that we assume to be "quenched", i.e., it is time-independent with zero mean and correlation function of the form $\langle f(x)\, f(x')\rangle = D_0\, \delta^{(d)}(\mathbf{x} - \mathbf{x}')$, $D_0 > 0$. According to experimental data [3], such type of noise is better suited for describing growth processes.

We also take the turbulent motion of the environment into account as it can dramatically affect the system's behavior. We use the Kazantsev – Kraichnan statistical ensemble for an incompressible fluid [4] with a pair correlation function $\propto \delta (t - t')/k^{d+\xi}$, where k is the wavenumber and ξ is a positive arbitrary exponent with the most realistic value ξ = 4/3 (Kolmogorov turbulence).

Stochastic problem under consideration is equivalent to a field theory, which is logarithmic at spatial dimension d = 4. Renormalization group analysis reveals that the theory must be modified in order to become renormalizable (a new term quadratic with respect to the velocity of the environment must be added). We calculate critical exponents (that determine asymptotic behavior of correlation functions) for all regimes of critical behavior predicted by the modified theory. Calculations are performed to the first order of the double expansion in ξ and ε = 4 − d (one-loop approximation).

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The Radial Index of Laguerre-Gaussian Modes in a Quantum Memory Scheme

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Quantum memory is a way to store and change quantum states, located in a memory cell in a controlled manner [1]. This makes it possible to control the quantum states of light, which, of course, is one of the main tasks of the quantum information theory. The usage of Laguerre-Gaussian modes makes it possible to use the space of state vectors of high dimension. Two Laguerre-Gaussian mode indices are used as a discrete value for information representing: radial *p* and azimuthal *l*. In our work, it was shown that for a certain beam configuration, the usage of a radial index is more preferable than an azimuthal (Equation 1).

$$z_{max} << z_R << R_z \quad (1),$$

where z_{max} – the maximum modulo distance from beam waist, z_R – Rayleigh range, R_z – radius of curvature.

Also, was shown the possibility of usage Laguerre – Gaussian modes, differing in the radial number p, as the basis states of the quantum signal field in the Raman model of quantum memory. This model was considered on the example of the Λ – scheme of energy levels (Fig. 1).

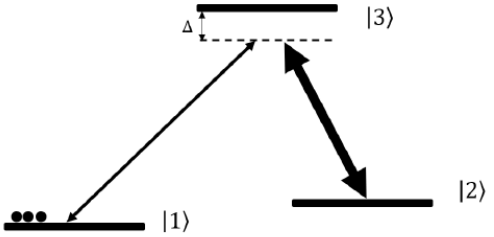

Fig. 1. Λ – scheme of energy levels in the Raman model of quantum memory.

A system of Heisenberg equations for field and atomic variables was obtained with using the dipole approximation, the approximations of a slowly varying amplitude and a rotating wave, and the evolution of each individual Laguerre-Gaussian mode in interaction with an atomic system was considered.

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Ground State g-factor of Highly Charged ^{229}Th Ions: Determination of the Mixing Coefficient and M1 Transition Probability Between the Isomeric and Ground Nuclear States of ^{229}Th

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A method is proposed to determine the M1 nuclear transition amplitude and hence the lifetime of the "nuclear clock transition" between the low-lying (~ 8 eV) first isomeric state and the ground state of ^{229}Th from a measurement of the ground-state g factor of a few-electron ^{229}Th ions.

In highly charged ^{229}Th ions, the ground and isomeric states can mix with each other due to a strong hyperfine interaction and small energy difference [1–3]. The nuclear hyperfine mixing (NHM) shifts the energies of the hyperfine sublevels (Fig. 1) and can strongly increase the transition probability between the "up" and "low" states of the ion [2]. The NHM coefficient b, which contains information about the M1 transition probability between the nuclear states, affects also the ground state g factor of the ion. In the present paper, we show that the mixing coefficient and therefore the M1 transition probability can be found to a good accuracy from high precision measurements of the ground state g factor of H- or Li-like thorium ions [4].

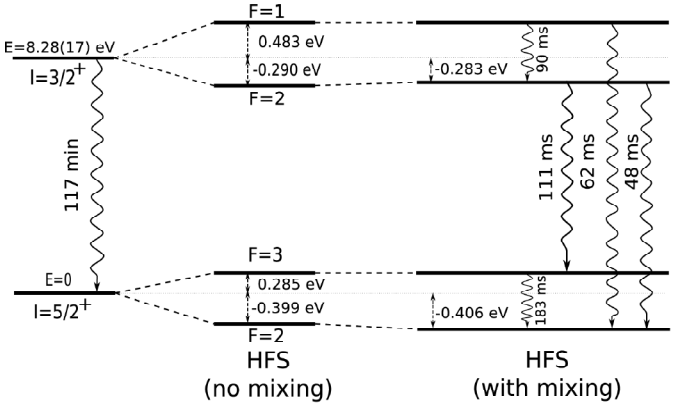

Fig. 1. Energy levels of $^{229}Th^{89+}$, g.s. and i.s. without NHM (*in the middle*) *and with NHM* (*on the right side*).

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Multiple Ionization Binding-Energy Difference of Ho-163 and Dy-163 Atoms

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One of the most intriguing open question within Standard Model is the absolute scale of the neutrino masses [1]. Within the Standard Model framework neutrinos are considered as massless particles, however modern experiments on the neutrino oscillations demonstrate that neutrinos do have a mass. A direct laboratory estimation of the electron neutrino effective mass can be obtained from experiments based on studies of the spectra of the beta decay or the electron capture processes. Currently, the laboratory limit on the electronic neutrino mass is about 1 eV for the tritium beta decay [2–4] experiments and 225 eV for the electron capture experiments [5].

One of the most promising ways to substantially lower the laboratory limit on the electron neutrino effective mass is the experiments proposed by several collaborations (ECHO, HOLMES, NuMECS) to study the electron capture (EC) process in the Ho-163 isotope. These collaborations are planned to establish the upper limit of 1 eV on the mass of the electronic neutrino, and then improve it to 0.1 eV level. For this kind of experiment, it is necessary to know in advance the mass excess of Ho-163 in EC process. However, the mass difference between Ho-163 and Dy-163 can be measured with the required accuracy only for highly charged ions [6]. In this regard, the mass difference of ions must be recalculated into the mass difference of the neutral atoms.

In this work, the corresponding calculations of the multiple ionization binding-energy difference are performed within the Breit approximation for the Ho-163 and Dy-163 ions with 30+, 48+ and 56+ degrees of ionization by means of the configuration interaction method in the basis of Dirac-Fock-Sturm orbitals [7].

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Two-loop Calculations in Statistical Model of Passively Advected Vector Field: RG Analysis and Techniques

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The renormalization group (RG) approach to the stochastic Navier-Stokes equation has received growing attention over the years. This approach allows us to get a good description of fully developed fluid turbulence in $d > 2$ dimension and reveals some interesting properties of turbulent fluid critical behaviour. The asymptotics of the two-point correlation functions obtained within the RG approach are in good correspondence with the experimental data [1].

In this work the behaviour of the model of passively advected vector field is investigated within the RG framework in two-loop approximation. The external velocity field is considered transverse and satisfying the Navier-Stokes equation. From one-loop calculations it follows that it is not needed to renormalize three-particle one-irreducible Green function [2]. This fact follows from cancellation of the divergent parts of three independent Feynman graphs and can be accidental (just an artefact of one-loop approximation) or can happen due to some underlying symmetry of the model. To establish which assumption is correct one should calculate three-particle Green function in two-loop approximation.

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On the One-Dimensional Stefan Problem: Numerical Solution and Potential Applicability to Modelling of Basal Melting of Glaciers

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Basal melting of glaciers may be one of the reasons for the appearance of subglacial lakes. Their formation is of interest both in itself and in an applied aspect. Some subglacial lakes pose a potential threat of an outburst flood, causing significant material damage to the adjacent territory [1].

From a mathematical point of view, the process of basal melting of glaciers can be considered as a problem of heat propagation with the participation of phase transitions. One of the ways to model these processes is to solve the Stefan problem.

In this paper we consider the numerical solution of the one-phase and two-phase variations of one-dimensional Stefan problem. The boundary immobilization method is used to fix the moving boundary. An implicit difference scheme of the second order of accuracy in time and space is used.

Numerical results were obtained, taking into account experimental data from Antarctic glaciers: temperature fluctuations and accumulation of precipitation on the glacier surface.

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Electronic Structure of Super Heavy Elements Nihonium (Z=113) and Flerovium (Z=114) Compared with Their Lighter Homologues

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Elements with atomic number Z > 103, which are usually referred to as superheavy elements (SHEs) [1], are especially interesting and promising systems to study. The increasing influence on the electronic structure of the relativistic and electron-electron interaction effects may lead to exotic physical and chemical properties of SHEs compared to their lighter homologues [2], where these effects are less prominent. However, the experimental study of SHEs is difficult due to short half-lives and low production rates. The most available way to study SHEs is the theoretical calculations within the framework of the relativistic quantum mechanics.

At the moment, elements with the atomic number up to 118 have been synthesized. In 2019, Superheavy Element Factory was opened at the Joint Institute for Nuclear Research in Dubna [3]. The experiment aims to increase the product rates of SHEs to make, in particular, the experimental studies of their physical and chemical properties available.

The present work is dedicated to calculation of the electron affinity (EA) and ionization potentials (IPs) of the superheavy elements Nihonium (113) and Flerovium (114). The relativistic Fock-space coupled cluster method equations with single and double excitations are solved with the method implemented in the DIRAC package [4]. Fully iterative triple excitations are computed by means of the EXP-T program [5]. The influence of the relativistic effects on the EA and IPs is studied through comparison of the relativistic results with the results obtained within the non-relativistic framework. The properties of these SHEs are compared with the properties of their lighter homologues.

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The Shirokov Effect in the Kottler and Reissner–Nordström Metrics

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The geodesic deviation equation for circular orbits was considered in the spherically symmetric Reissner – Nordström and Kottler metrics. Solutions of these equations were found, they describe the evolution of geodesic deviation vector with respect to proper time. The geodesic deviation vector describes the relative divergence of two close geodesics. It turns out that the oscillation periods of the radial and polar deviation vector components in the Reissner – Nordström and Kotler metrics coincide as in Schwarzschild spacetime. Therefore, we find the difference in the oscillation periods of the angular geodesic deviation vector components and compare the results obtained for Reissner – Nordström (1) and Kottler (2) cases with results for Schwarzschild spacetime [1].

$$\Delta T = T_\theta - T_\varphi = T_0\left(-\frac{3M}{r}+\frac{q^2}{2Mr}\right)+O\left(r^{-2}\right) \tag{1}$$

$$\Delta T = T_\theta - T_\varphi = T_0\left(-\frac{3M}{r}-\frac{\Lambda r^3}{2M}\right)+O\left(\Lambda^2\right) \tag{2}$$

This allows us to make quantitative estimations of the influence of the charge of a gravitating object and the cosmological constant on the Shirokov effect (articles [2] and [3] generalize the description of the effect for the metric of a rotating Kerr black hole and an arbitrary static axially symmetric asymptotically flat spacetime). We managed to find out that the influence of a non-critical charge does not exceed one-sixth of the difference in periods caused by the gravitating mass. Whereas the influence of the cosmological constant is determined not only by its magnitude but also by the distance to the massive object. However, for all known massive bodies and the closed orbits surrounding them, the correction due to the cosmological constant turns out to be negligible.

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New Approach to the Canonical Formalism for Description of Gravity in Terms of the Embedding Theory

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The embedding theory is an approach to gravity description which operates the so-called embedding function, the four-dimensional surface $y^a(x^\mu)$ in a flat space time of higher dimension [1]. The embedding function is treated as an independent variable. The action of the theory is the Einstein-Hilbert action with metric considered to be induced. The canonical formalism for this theory was constructed in [2]. Despite of the fact that it was impossible to present the exact expressions for the constraints within this framework, the algebra of the constraints was calculated.

The alternative way of the embedding theory canonical formalism construction was presented. The introduced approach appeals to the fact that the action of the embedding theory can be splitted into two summands: the standard GR action and the action of some extra matter. The difficulties related to this approach were discussed, as well as the relations between the canonical formalism constructed using the proposed method and the one constructed in [2].

Acknowledgments: The work was supported by RFBR grant 20-02-00081.

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Obtaining Reliable Estimates of the Dynamic Critical Exponent ν of the φ^4 Model with n=0

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The statistical characteristics of chain polymers can be specified by the Flory radius R_F. The difficulty of estimation the dependence of the R_F on the number of links - N of the chain essentially depends on the dimension of the space d. In the case $d < 4$, the prohibition of self-intersections leads to a law of the form $R_F \sim N^{0.5}$, where $\nu(d) > 0.5$. The objective of the theory is to substantiate this law and calculate $\nu(d)$.

The behavior of ferromagnets near the Curie point also becomes complicated for $d < 4$, it is necessary to take into account the fluctuations growing around T_c and characterized by the correlation radius $\xi \sim \tau^{\nu(d)}$. The renormalization group method allows within the φ^4 model, to calculate this exponent in the form of a series in the degrees of deviation $\varepsilon = 4-d$ of the space dimension from the critical value $d_c = 4$. The ferromagnet model transforms into a random walk model without self-intersections if we take $n = 0$, where n – the number of order parameter components [1–2].

The series of ε expansion are asymptotic and should be resummed. The purpose of this work was to perform such a resummation of the ε-expansion series. Testing the hypothetical assumption $\nu = 0.75$ for $d = 2$, expressed in article [3] was also the goal of this work. The value in $d = 1$ can be used in two ways – it can serve as a test for checking the efficiency of the used summation methods in determining the value of ν for $d = 3$ and $d = 2$ and can be used as information supplementing the ε-expansion. The resummation was implemented by various methods based on the Borel resummation and Padé approximation.

Based on the results, we can conclude that taking into account boundary value $\nu = 1$ for the case $d = 1$ significantly improves the convergence to the supposedly correct value. The results at $d = 1$ and $d = 3$, obtained by various resumming methods, are in good agreement with the results of other works [4]. At the same time, at $d = 2$ for all resumming methods the results contradict the value of 0.75. This circumstance is possibly connected with the presence of additional symmetries appear in the system at $d = 2$, which are not taken into account in the ε - expansion.

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Lambda Hyperons Polarization, Vorticity and Helicity Structure and Hubble Low in Heavy-Ion Collisions

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The calculation of the Λ–hyperons polarization is performed in the chiral vortical effect approach. It is a macroscopic manifestation of an axial anomaly that leads to an induced axial current of strange quarks which can be transformed into the polarization of Λ-hyperons. The effect is proportional to the vorticity and hydrodynamic helicity of strongly interacting media:

$$<\Pi_0^{\Lambda}> = <m_{\Lambda}/(N_{\Lambda}p_y)> N_c/2/\pi^2 \int d^3x \mu_s^2(x)\gamma^2\varepsilon^{ijk}\upsilon_i\partial_j\upsilon_k, \quad (1)$$

where $\partial_j\upsilon_k$ is the vorticity, $\varepsilon^{ijk}\upsilon_i\partial_j\upsilon_k$ is the helicity, μ_s is the strange chemical potential, and p_y is the transverse momentum of hyperons.

The simulation of Au-Au collisions is done in the Parton Hadron String Dynamics transport model [1]. After passing from kinetic equations to the hydrodynamic description, dipole and quadrupole structures of the medium vorticity are discovered in the longitudinal and transverse reaction planes. The helicity separation effect by octant is found in both the momentum and position spaces. The longitudinal helicity component contributes significantly to the polarization ~ $\upsilon_z\omega_z$. In CVE approach [2], the polarization of Λ-hyperons is ~ 8% at the energy of 7.7 GeV, which exceeds the result obtained in the experiment and is associated with the approach sensitivity to a determination of the strange chemical potential.

The method based on local thermodynamic equilibrium [3] and hydrodynamic calculation of vorticity gives the polarization ~ 4%, which can be associated with its inverse dependence on temperature and, accordingly, its lower sensitivity to thermodynamic calculations.

We observe a linear dependence of the particle velocity on the radius in the middle region of the fireball at times exceeding 15 fm/*c* at energies of 7.7 GeV, which corresponds to the chemical freezout time. The velocity divergence in this region is kept at a constant level which indicates that the explosion is isotropic and makes it possible to determine the Hubble constant $H \sim 0.05$ fm^{-1}.

Acknowledgments: The reported study is funded by RFBR according to the research project number 20-32-90205.

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Investigation of the Interaction of the Coordination Compound of Cobalt with DNA in Vitro

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The finding the effective anticancer drugs is currently one of the main problem of modern medicine. Among the huge number of dosage forms, drugs based on coordination metal compounds occupy a major place. One of the main directions for the search for anticancer drugs is the identification of substances whose action is aimed at suppressing DNA replication by forming complexes with a macromolecule in a cell. The first step in testing the effectiveness of such drugs is to study their action in a water-salt DNA solution.

The aim of this research was to study the complexation of DNA with coordination compound of Co(II) using various methods, such as spectrophotometry, DNA melting, low-gradient viscometry. High molecular DNA from Sigma Aldrich company was used. DNA molecular mass was determined from the value of DNA intrinsic viscosity in 0,15 M NaCl.

In the course of this work, it was shown that cobalt compound forms complexes with DNA in 0.005 M NaCl. The influence of salt concentration om DNA-cobalt interaction was analyzed.

The melting of DNA in complexes with cobalt compound in 0,005 M NaCl demonstrates the shift of melting temperature to higher value versus melting of free DNA. This effect depends on the ratio of DNA and cobalt concentration in solution. An increase of cobalt concentration in DNA solution leads to the raising the melting point. It was shown that the saturation of cobalt binding to DNA is observed at r>0,3 (r is the ratio of molar concentrations of cobalt and DNA base pairs in 0,005 M NaCl). Fig. 1 demonstrates this result. Spectrophotometric titration gives the possibility to determine the binding constant. In our work the value of binding constant was defined as $K_b = (2,7 \pm 1,6) \cdot 10^5\ M^{-1}$

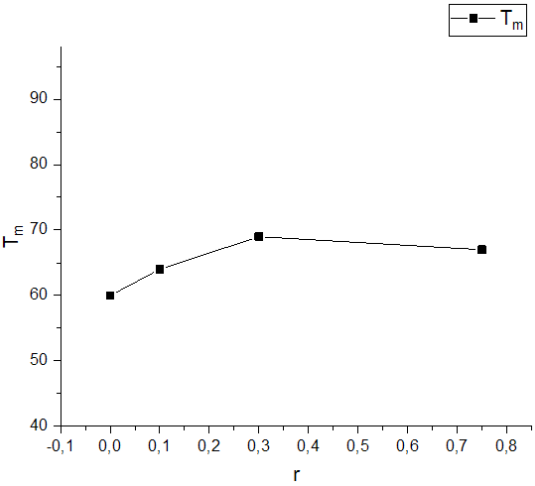

Fig. 1. Dependence of the DNA melting temperature on r.

Application of The Principal Component Analysis for The Diagnosis of Cancer Diseases

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Multiple myeloma (MM) and chronic lymphocytic leukemia (CLL) are considered incurable malignant diseases. The diagnostic methods available today do not allow detecting these diseases at an early stage or they require a time-consuming blood test. Machine learning model will help to diagnose the disease faster, having only the spectrum of the patient's blood serum on hand.

In this paper, we studied how a machine learning algorithm principal component analysis (PCA) can help classifying IR spectra into groups of diseases. IR spectra of serum solutions obtained from healthy donors (HD), MM and CLL patients were analyzed using PCA. The most informative classification of the samples was observed in the plot of the third vs fourth main components (15% of the information) (Fig. 1), which clearly demonstrated separation of the CLL patients from other studied samples.

We believe that the method described here has a great potential in the diagnosis of tumor diseases, however it is still necessary to further improve this approach and test it on other larger number of samples.

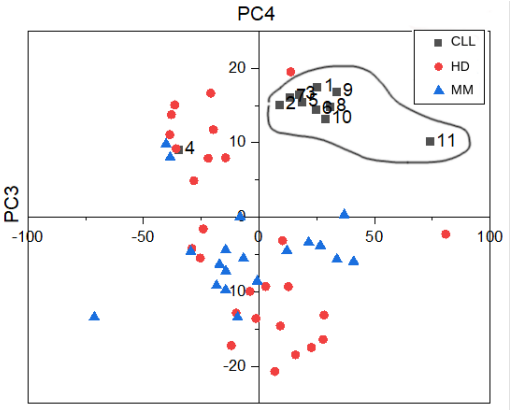

Fig. 1. The graph of the third and fourth main components.

Acknowledgments: The authors are grateful for the Russian Research Institute of Hematology and Transfusiology (St. Petersburg) for providing the serum samples. Part of the work was performed using the equipment of the Research Park of Saint Petersburg State University ("Centre for Optical and Laser Materials Research", "Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics", "Cryogenic Department").

L-DOPA Detection by Silver Nanoparticles

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L-3,4'-Dioxyphenylalanine (L-DOPA, levodopa) is an important compound in the human body. Therefore, it is desirable to develop a method for L-DOPA detection. In recent years, many methods have been created for the small biomolecules determination in biological fluids such as electrochemistry and colorimetry [1].

Silver nanoparticles (Ag NPs) exhibit a strong UV–vis extinction band that is not present in the spectrum of the bulk metal, it is known as the surface plasmon resonance (SPR) [2]. To check the selectivity of the method, Tyrosine (Tyr), L-DOPA, phenylalanine (Phe), and tryptophan (Trp) were used as similar compounds.

Typical synthesis: $AgNO_3$ was added to the AA dissolved in MiliQ water, then pH was adjusted to 8.5 by NaOH. Then the absorption spectra were measured an hour later.

At pH 8.5 L-DOPA reduces silver ions to nanoparticles with noticeable absorption band at 400-410 nm. For other amino acids, this band was not observed (Fig. 1, left). Ag NPs plasmonic band can be observed even in the mix of all chosen amino acids (Fig. 1, middle).

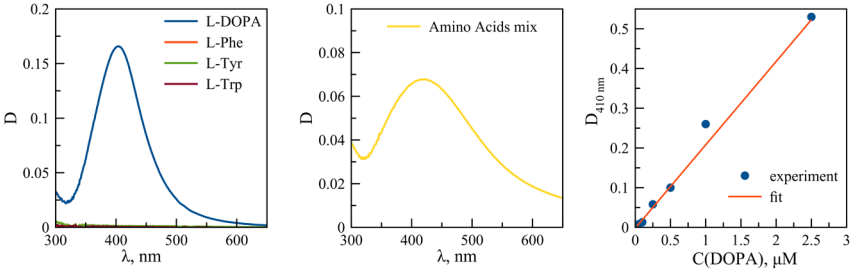

Fig. 1. Absorption spectra of amino acids complexes with silver at pH 8.5 (left), absorption spectra of AA mix at pH 8.5 (middle) and $D_{410\,nm}$ vs C(DOPA).

The optical density of silver NPs complexes with DOPA recorded at 410 nm showed a linear dependence in the range 0.1-2.5 uM of L-DOPA concentration (Fig. 1, right).

In conclusion, a simple and cheap method for L-DOPA detection *in vitro* was developed. Further optimization of this method is currently in progress.

Acknowledgments. This work was supported by the Russian Science Foundation (project 20-73-10029).

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Light-Induced Generation of Static and Dynamic Supramolecular Patterns in Photosensitive Chiral Liquid Crystals

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At present, chiral localized structures in a birefringent anisotropic liquid crystal medium are of particular research interest, since they can provide an additional level of information embedding into an optical memory cell or a complex interaction of a transmitted light beam with an optical material [1, 2]. However, activation of such structures by optically induced reorientation of liquid crystal molecules requires a typical optical power budget in the range of tens and hundreds of milliwatts [3, 4], which is rather awkwardly for future technological developments, especially those related to the simultaneous manipulation by a set of miniaturized birefringent optical elements.

Recently [5, 6], an opto-molecular approach to the creation of light-induced localized structures in frustrated chiral nematics was proposed, based on the photoisomerizarion of chiral dopant molecules. The first dynamic revolving pattern and several static localized structures have been obtained at a recording light beam power of only 10-100 nW.

We conduct the first detailed study of the relationship between the structure and behavior of light-induced localized supramolecular patterns in frustrated chiral nematics with the spatio-temporal characteristics of a recording light beam. In order to demonstrate the possibilities of structural rearrangement of localized chiral patterns, we explore the light-controlled reconfiguration of the generated structures. The high relevance of our research is ensured by intensive scientific and technological developments in the field of adaptive, tunable, reconfigurable optical elements for photonic devices, optical memory cells and light structuring by optically anisotropic complex materials.

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The Interaction of DNA with L-Lysine and Poly-L-Lysine in Water Solutions of Different Ionic Strength

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DNA is an extremely rigid and highly charged polymer. The high-molecular weight DNA in water solution has the conformation of a highly swollen statistical coil. There are a number of agents that cause DNA shrinkage and compaction in solution to form discrete, sometimes highly ordered structures. DNA packaging is necessary, for example, for gene vectors and other nanostructures construction.

It is known that, under certain conditions, polycations can cause DNA condensation (DNA packaging with the formation of spherical particles). In our research, the polylysine was used as a polycation. Amino acid Lysine was also used to compare the effect of electrostatic interaction between amino acid on peptide chain and phosphate groups on DNA nucleotides. The purpose of this work was to study the interaction of DNA with L-Lysine and poly-L-Lysine.

Calf thymus DNA with a molecular mass $M = 4\times10^6$ Da determined from the intrinsic viscosity of DNA in 0.15M NaCl, L-Lysine hydrochloride and poly-L-Lysine hydrobromide (all chemicals from Sigma Aldrich company) were used.

To analyze DNA interaction with positively charged compounds some experimental methods were used: UV absorption spectroscopy, DNA melting study and low gradient viscometry.

Absorption spectra of systems at room temperatures in 0.005M NaCl solution show that DNA condensation is accompanied by an increase in absorption.

Melting curves of systems in 0.005M NaCl solution were registered. Melting temperatures of DNA in solutions with poly-L-lysine increases along with the growth of polycation concentration. Hyperchromic effect (as a result of DNA melting) was about 34% for DNA-poly-L-lysine complexes.

Reduced viscosity of DNA solution as a function of relative molar concentration of the monomers of peptide and DNA in solutions of different ionic strengths indicates DNA shrinkage. The binding of poly-L-Lys and L-Lys with DNA does not affect its secondary structure. The addition of poly-L-Lys to a DNA solution of low ionic strength causes the DNA packaging. But DNA compaction was not observed when poly-L-Lys was added to a DNA solution in 0.15 M NaCl. The addition of L-Lys to a DNA solution in 0.005 M NaCl does not cause the DNA packaging.

Some Acute Phase Proteins Affect Neutrophils Functional Activity

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Neutrophils are the key players of the innate immune system, its first defending line. Various infectious particles are destroyed by neutrophils through phagocytosis and the following cascade of reactions called respiratory burst reaction (RBR). Neutrophils generate reactive oxygen species (ROS) during RBR and use them to kill and destroy captured agents. It is crucial to regulate such a process strictly due to the damaging effect of ROS overproduction on surrounding tissues.

The study conducted at the NRC «Kurchatov Institute» - PNPI [1] showed that the necessary for the normal course of pregnancy decrease in the functional properties of neutrophils was accompanied by an increase of the acute phase protein ceruloplasmin several times compared to healthy non-pregnant donors. Based on the data from this study, it was suggested that other APPs may also be involved in the priming stage of neutrophils.

In this work, the influence of some acute-phase proteins (namely, C-reactive protein (CRP), serum amyloid A (SAA), and alpha 1-acid glycoprotein (a1AGP) on peripheral blood neutrophils' capacity to RBR was investigated for the first time. It was shown they are involved in both activation mechanisms and mechanisms for reducing the intensity of RBR of neutrophils in terms of their ability to produce ROS. Respiratory burst reaction (RBR) was measured using the original flow cytometric technique as in [2].

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Photosensitive Azobenzene Containing Cationic Surfactants in DNA Solutions of Different Ionic Strengths

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Trans-cis reversible isomerization of azobenzene group induced by UV and VIS radiation can be used for creating various photosensitive nanoobjects such as gene vectors or other DNA-nanostructures [1]. The choice of cationic surfactants for experiments (C4-Azo-OC6TMAB and C4-Azo-OC6TEAB) was associated with the great difference in critical micelle concentration (CMC) for the trans- and cis-isomers. We have focused on the peculiarities of the interaction of cis-surfactants with DNA. It has been shown [2] that surfactants interact with phosphates and form pseudomicelles on DNA at surfactant concentration lower than CMC.

The difference between cis- and trans- surfactant micelles in solutions was regarded. DNA interaction with trans- and cis- isomers have been studied. Spectrophotometry, luminescent spectroscopy, low-gradient viscometry, flow birefringence and dynamic light scattering (DLS) methods were applied. The difference in the sizes of cis- and trans- associates of surfactants was determined. The comparison of cis- and trans- isomer complexes with DNA was done [3]. The influence of salt concentration on the formation of surfactant complexes with DNA was carried out. It was shown that cis- isomers interact with phosphate groups of DNA, and that their molecules were also located along the minor groove of DNA. Three fundamentally different types of behavior of DNA-surfactant complexes were observed. DNA shrinkage ($Z < 1$), DNA condensation ($Z > 2$) and region of thermodynamic instability of DNA solution ($1 < Z < 2$) (Z means charge ratio). The ionic strength of solution influences on DNA-surfactant interaction and thermodynamic stability of DNA-surfactant solution. For a low ionic strength of 0.005 M in the $Z < 1$ region, it was shown that the DNA rigidity and optical anisotropy of the DNA segment does not depend on Z.

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Investigation of the Stability of Metal Clusters in Solution

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Luminescent silver clusters (Ag NCs) on oligonucleotide templates are promising objects in bioimaging [1] and in vivo probing [2]. However, when DNA-Ag complexes interact with living systems, the luminescence may disappear. Therefore, it is necessary to check the influence on NCs stability of the following factors: burnout due irradiation, temperature and pH. The studied objects were Ag complexes with DNA1- (CCCACCCCTCCCGTTTT) and DNA2 (TTCCCACCCACCCCGGCCC) (Fig. 1).

To assess the burnout effect, two complexes of clusters were irradiated in a spectrofluorimeter Shimadzu RF-6000 at typical experimental conditions. With each measurement, the luminescence intensity decreases by no more than 1% in the case of DNA1-Ag and by no more than 2% in the case of DNA2-Ag. The drop in intensity is most likely associated with the destruction of fluorophores. Accordingly, the complexes showed high photostability. To reveal the temperature dependence, Ag NCs synthesized on DNA1 were investigated. The study showed that the DNA1-Ag complex remains stable when exposed at temperature up to 60 ° C. At higher, temperatures the clusters begin to disintegrate. To determine the effect of the pH of the medium, a solution of sodium hydroxide (NaOH) or nitrous acid (HNO_3) was added to the DNA-Ag complexes. The complexes were found to be sensitive to changes in the pH value: with the deviation from neutral pH, the intensity of the luminescence peak decreased.

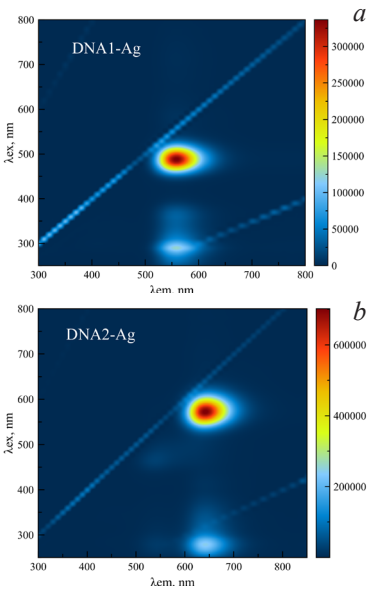

Fig. 1. 3D luminescence spectra DNA1-Ag (a) and DNA2-Ag (b).

Acknowledgments: This work was supported by by the Russian Foundation for Basic Research (Project No. 19-53-51005 NIF_a RFFI-Korea).

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MicroRNA Sensing Using DNA-templated Silver Nanoclusters

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Metal nanoclusters are small particles with unique electro-optical properties consisting of 2-10^2 atoms. The most common matrices for the synthesis of silver nanoclusters are DNA oligonucleotides. Fluorescent properties of silver clusters depend on the DNA stabilizing matrix. Fluorescent nanoclusters are widely used in various fields of science due to the simplicity of synthesis. At the moment, the most promising field of application of precious metal clusters is bioimaging and biosensing [1]. Nanostructures are also used for the detection of biopolymers, in particular, nucleic acids.

In this work, we developed a sensor for detecting microRNAs. MicroRNA is a small RNA molecule about 20 nucleotides long. Changes of the expression of these molecules in body fluids occur earlier than changes found in other currently known biomarkers, which makes it easier to diagnose such diseases as cancer or Alzheimer disease as quickly as possible [2]. Extracellular (circulating) microRNA can be detected in various biological fluids, for example, in blood plasma or in follicular fluid. In this regard, the development of a sensor for the detection of this molecule can simplify the procedure for the diagnosis and treatment of various diseases.

The developed sensor emits fluorescent light only by interaction with the target. The sensor model logically divided into three parts: a hybridization sequence, that complementary to the target, a NC-scaffold sequence, which forms the cluster and a spacer: it links these two parts together. The optimization of a spacer sequence showed that the best optical parameters of a silver nanocluster were obtained with the spacer of one adenine on each matrix strands. The DNA analog (5'-CTGT-GCGTGTGACAGCGGCTGA-3') served as a model target of mir-210. The sensor was successfully tested with DNA – target. It showed bright green fluorescence with excitation/emission at 490/560 nm, which appeared only in the presence of target. The target detection limit (LOD) was determined as 3 nM. The proposed model can be used for the detection of other nucleic acids.

Acknowledgments: This work was supported by RFBR grant № 19-53-51005.

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Application of the DNA Melting to Detection of its Structural Defects

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DNA melting, or the so-called helix-coil transition, is very important and interesting physical process. It is a reversible transition from an energetically advantageous highly ordered helix state to a disordered Gaussian coil. When DNA melts, only weak intermolecular hydrogen bonds are destroyed, and the covalent bonds inside the sugar-phosphate backbone remain intact, so the sequence of bases in the chain in the coil remains as fixed as in the helix [1].

The most common method of observing the helix-coil transition is the method of measuring the absorption of a DNA solution in the near ultraviolet region (260 nm). This method is based on the hyperchromic effect. During the helix-coil transition, due to the disappearance of the interaction of neighboring pairs of nitrogenous bases, the absorption of DNA increases. The melting curve is characterized by two parameters – the melting temperature Tm, which corresponds to the inflection point of the curve, and the width of the melting interval ΔT. These parameters depend on the integrity of the primary and secondary structure of the original DNA molecule, so they are used to detect defects in the DNA structure. One of the methods for determining the melting point is to plot the first derivative $dD_{260}/dT = f(T)$ and then find the maximum corresponding to the inflection point on the melting curve $D_{260}(T)$. The temperature value at this point will be the melting point Tm. The width of the helix-coil transition is a measure of the heterogeneity of the secondary DNA structure. The melting width is the interval between the points of intersection of the tangents to the melting curve at the interval where it exists in the native state (20-30°C) and fully denatured (70-90°C) and the tangent drawn at the point that corresponds to the melting temperature.

In this work, the parameters of Tm and ΔT were determined by the method of spectrophotometric melting for a number of DNA samples containing various violations of the primary and secondary structure: DNA irradiated with ^{241}Am γ-radiation, treated with ultrasound, heated to 50 °C with subsequent cooling, as well as after long-term storage in solution at 4 °C.

Acknowledgments: The authors are grateful to prof. I.A. Mitropolsky for γ-irradiation of DNA samples.

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Creation of Localized Twisted Structures in the Films of Light-responsive Chiral Nematic Liquid Crystals

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Liquid crystal materials are well-known to demonstrate various types of structural defects, whose optical properties can be used for a number of applications in optics and photonics. These structural defects cannot be transformed into one another by continuous changes of the material texture, that also makes such structures highly important for information storage [1].

In thin films of frustrated chiral liquid crystals, various localized defect structures can be created by optically induced reorientation of liquid crystal molecules by either structured or unstructured light beams at power levels of tens and hundreds mW [2, 3].

The aim of this study is to generate a wide wealth of localized complex structures in thin films of a light-responsive chiral nematic liquid crystal by optically inducing photochemical transformations of chiral dopant molecules. Then, the light illumination of the frustrated chiral liquid crytal a Gaussian beam enables the local winding of cholesteric helix and formation of localized twisted patterns [4]. The resulting localized space-variant birefringent structures can be used to create, for example, a multifunctional material with an arbitrary array of microscopic lenses or deflectors [5, 6].

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Calculation of the Viscosities of Polar and Nonpolar Solutions by Molecular Dynamics Method

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Calculation of viscosities of colloidal systems via molecular dynamics simulations can be done, e.g., with the help of the Stokes-Einstein formula [1, 2]. In this paper we use the method proposed by Palmer in [3] and implemented in GROMACS 2020 software package for estimating the viscosities of one- and two- component molecular liquids. This method is based on computation of the autocorrelation functions of the momentum. It has been here applied for finding the viscosities of several homogeneous molecular systems (water, pentane, heptane, decane) and that of a weakly inhomogeneous system, i.e., a small premicellar aggregate of non-ionic surfactant molecules (C12E4) in heptane. In particular, the viscosity was calculated for systems containing monomer, dimer, and tetramer of C12E4 molecules. All the systems were represented by the all-atom models within the CGenFF 4.4 force field [4] and were simulated via molecular dynamics in the NPT statistical ensemble. Good agreement of our results for the one-component liquids with the previous works was observed. For the systems containing SPC and SPC/E water molecules, the results are consistent with those in [5]. The results for the viscosity of pentane coincided well with the computer simulation results in [6]. For the system consisting of decane molecules, the general agreement of our simulation data on viscosity with the experimental data [7] was observed. We plan to use this method for calculating the viscosities of the systems containing bigger aggregates (reverse micelles).

Acknowledgments: This work was supported by a grant RFBR 20-03-00641_A from the Russian Foundation for Basic Research.

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DNA Interaction with New Palladium Compound in Vitro

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The anticancer drugs based on platinum coordination compounds: cisplatin, carboplatin and oxaliplatin are commonly used to treat different cancers. Platinum drugs cause damage of DNA and block its replication. The functional disorders induced by platinum drugs lead to cell apoptosis. However, high efficacy of platinum-based drugs is often worsened because of the toxicities and non-selectivity. Therefore, the synthesis of new compounds based on coordination compounds of metals is of considerable interest. In the presented work, the palladium compound (Fig. 1) acts as a potential antitumor compound. This compound was synthesized by Dr. Kinzhalov at the Institute of Chemistry of St. Petersburg University.

The aim of the research was to study the interaction of palladium compound with high molecular thymus DNA (Sigma Aldrich Company) in a water solution with 0,005 M NaCl. Some experimental methods were used: spectrophotometry, DNA melting, low gradient viscosity. The absorption of palladium compound is observed within wavelength region 220-400 nm. This spectrum partially intersects with the absorption band of DNA. But we can check the adsorption of palladium compound in complexes with DNA at wavelength over 300 nm, out of DNA absorption. It was shown that palladium compound interacts with DNA in solution with 5 mM NaCl. The binding causes changes in absorption spectra of DNA and palladium compound. We made the assumption that nitrogenous bases of DNA are involved in binding to palladium.

The spectrophotometric titration gives the value of binding constant $K_b = (1,3 \pm 0,6) \times 10^5$. The Wolfe – Shimmer procedure was used.

The method of DNA melting has shown that complexation has a destabilizing effect on the secondary structure of DNA. We made this conclusion based on the found melting temperatures of DNA in the complexes at different palladium concentrations.

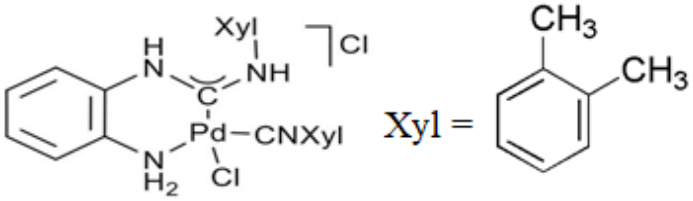

Fig. 1. Chemical structure of KM_1352.

I. Resonance Phenomena in Condenced Matter

Diffusion of Toluol and Water in Composopzite Systeme: Poly-m-Phenyleneisophthalomide and MOF by Molecular Dynamics Simulations

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Purification of material is a historically actual problem. Today, the cleaning technology consists of a several inalienable elements: energy efficiency, environmental friendliness, as we mentioned earlier high degree of purity. One of the technologies that contains each of the above elements is pervaporation. One of the ecological and energy-efficient methods of cleaning/post-cleaning is pervaporation. This method is utilized for difficult-to-separate liquids using a polymer membrane through which only one component of the mixture predominantly passes.

Using the molecular dynamics method, we have simulated two systems: a pure polymer membrane (made of poly-m-phenyleneisophthalomide) with two solvents – 36 methanol molecules and 26 toluene molecules, and a composed membrane which additionally includes MOF particles UiO-66 (NH2). First, we equilibrated the systems at 800 K, then slowly cooled it down to room temperature – 300 K, and finally simulated 140 ns at room temperature as an equilibrium trajectory.

We have established that follow important results:

1) Toluene molecules get stuck inside the MOF, and as a result its significantly diffusion reduced compared to a system without MOF;

2) Methanol passes freely through MOF even when molecules of toluene are stuck in MOF. Moreover, diffusion through MOF is several times faster than in the pure polymer.

Thus, when adding MOF nanoparticles, the characteristics of the polymer membranes are improved for separating a mixture of toluene and methanol, since it slows down the mobility of toluene through the membrane and accelerates the diffusion of methanol sever times. Our results are found on good agreement with experimental data [1].

Acknowledgments: The simulations have been performed by using the Computer Resources Center of Saint Petersburg State University.

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Kinetic Quantum Chemical Investigation of the GPx1 Catalytic Cycle Using Crystal-based Model System

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Severe health problems that are associated with selenium deficiency are widespread [1]. They can be prevented using a special designed selenium-containing drug Ebselen that acts like a mimic of a human selenoprotein glutathione peroxidase [2]. As has been demonstrated, activity of Ebselen can be modulated with an assistance of noncovalent interactions to selenium atom [3].

We looked carefully to glutathione peroxidase crystal structure and discovered the possibility of a selenium atom to be involved in numerous noncovalent interactions. Thus, we sought to *ab initio* simulate the glutathione peroxidase catalytic cycle with special attention to these interactions. Their participation may lead to dramatical changes in reaction barriers. The formation of noncovalent interactions is verified by a presence of critical points, bond paths (Fig. 1), and the values of QTAIM parameters in critical point. The selenium outer electronic shell is also analysed by electron localization function, electrostatic potential and using calculated values of selenium-77 chemical shift.

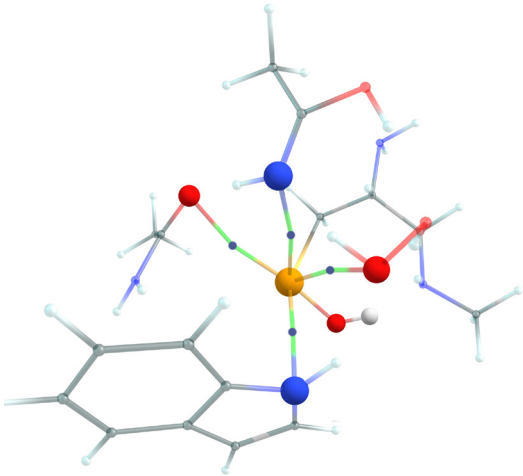

Fig. 1. Bond critical points (purple dots) and bond paths (green lines) calculated for R−SeOH fragment.

Acknowledgments: This work was financially supported by the RSF grant 20-73-00099. The calculations were performed in the Computer Center of Saint-Petersburg University Research Park (www.cc.spbu.ru).

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Investigation of the Molecular Mobility of the Ionic Liquid [Bmpyrr][NTF_2] by NMR Methods.

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Ionic liquids exhibit a unique combination of physicochemical properties that make them ideal candidates for electrolyte applications. Salt solutions containing the TFSI anion are typical and/or promising electrolytes for supercapacitors and lithium batteries. The aim of this work was to test the mobility of counterions (and the solvent if any) in order to compare the diffusion of ions and the physicochemical, in particular the electrically conductive properties of the above systems.

In this work 1-Butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) (Fig. 1) with addition of lithium ions with a concentration of 0.1 mol and 1.5 mol was studied by NMR methods on the Bruker Avance III NMR spectrometer 500 MHz.

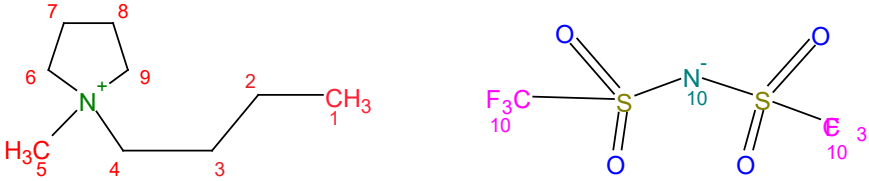

Fig. 1. BmpyrrNTF$_2$ chemical formula

During the study of the samples, measurements of the diffusion coefficients were carried out on several nuclei: 1H, Li, 19F at various temperatures in the range from 243 to 333 Kelvin. The research results will be presented at the report during the conference.

Acknowledgments: Thanks to the staff of Center for Magnetic Resonance of Research Park of St. Petersburg State University for fast and high-quality measurements.

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Diffusion Coefficients of Ionic Liquid [BMIM][SCN] Calculated by Molecular Dynamic Method

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Recently, ionic liquids (IL) have been increasingly used as components of polymer electrolytes for new current sources. One of the newest methods of studying IL is Molecular Dynamics Modelling (MDM), whcih allows to determine the physico-chemical properties of the investigated substances. Ionic liquid [BMIM][SCN] was selected, because an experimental work was provided to study its physico-chemical properties [1, 2].

One of the characteristics describing the dynamics of the system is the diffusion coefficient D .Several simulations of two systems with different charges on each atom were carried out. Modeling parameters: 100 ns, NVT ensemble. The coefficients were obtained using the Einstein's equality [3],

$$MSD = \lim_{t\to\infty}\left\langle \left\| \boldsymbol{r}_i(t) - \boldsymbol{r}_i(0) \right\|^2 \right\rangle = 6D_i t$$

The obtained coefficients are shown in Fig. 1. For comparison with experimental data, we calculated the activation energy E_a from Arrhenius dependence. As can be seen from this comparison, the difference between the simulation values and the real ones is 19-20% for 2 systems.

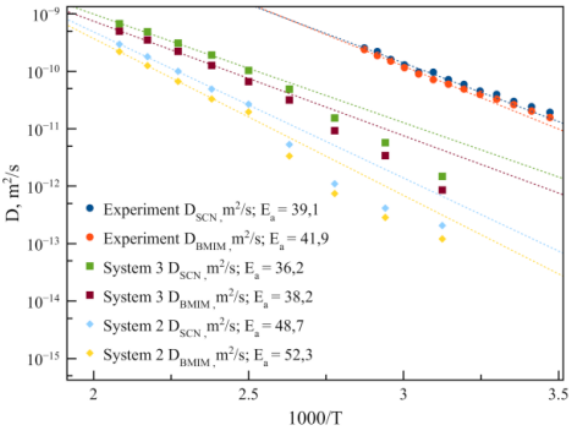

Fig. 1. Dependence of coeff. D on 1000/T.

Acknowledgments: Scientific research were performed at the «Computing Centre» of Research park of St.Petersburg State University.

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DFT Study of Electronic Structure and Water Induced Phase Transition in the $K_2La_2Ti_3O_{10}$ Photocatalyst

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The problem of global pollution is becoming important during the last years. One of the ways to solve this problem is the utilization of environment-oriented hydrogen fuel. Semiconductor photocatalysts can help to reach the aim. These substances can convert solar energy into chemical energy for water splitting reactions [1]. In particular, layered perovskites, that belong to the Ruddlesden – Popper phase with formula A_{02} $[A_{n-1}B_nO_{3n+1}]$ (A_0, A - alkali, alkaline earth or rare earth; B - transition metal), have excellent photocatalytic properties and are capable for intercalation and ionic exchange reactions. $K_2La_2Ti_3O_{10}$ is one of the most promising photocatalyst belonging to this family of materials. However, it exhibits the photocatalytic activity only under ultraviolet light irradiation due to the wide bandgap (3.5 eV) [2]. Currently, research is underway to decrease the bandgap to achieve a photocatalytic activity in visible light. To optimize the search strategy theoretical calculations of the impact of structural modifications on the energy bandgap are highly required. However, the first step is the choice of the correct calculation method.

In this contribution we report on the results of our theoretical studies of the electronic structure of the both hydrated and dehydrated forms of $K_2La_2Ti_3O_{10}$. The calculations were carried out within the framework of the full-potential linearized augmented plane wave (FLAPW) method based on the density functional theory as implemented in the WIEN2k program package [3]. The impact of the exchange-correlation potential on the calculated bandgap was studied. It was found that the PBE and LDA functionals underestimate the bandgap. For a correct description of the electronic structure of $K_2La_2Ti_3O_{10}$ the modified Becke-Johnson (mBJ) exchange potential must be used. The electron properties of the hydrated and dehydrated forms were calculated within the mBJ exchange-correlation functional. The water induced phase transformation from dehydrated to hydrated phase and its effect on the bandgap were investigated.

Acknowledgments: Calculations were carried out using resources provided by Resource Center "Computer Center of SPbU" (http://cc.spbu.ru).

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Molecular Mobility in Mixtures of Ethylammonium and Aluminum Nitrates. A Molecular Dynamics Simulation Study

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Until now, most of the studies of systems containing ionic liquids (ILs) have been devoted to mixtures of salts of monovalent metals (mainly lithium) with protic or aprotic IL. But higher valence metal ions such as Mg^{2+} or Al^{3+} might lead to more efficient energy-storage systems [1]. In the present study the mixtures of ethylammonium nitrate (EAN) with aluminum nitrate were investigated using molecular dynamics computer simulations for better understanding of the NMR data.

Two mixtures (5 % and 10 % salt molar fractions) were modeled employing the MDynaMix program package [2]. Both model systems (500 EAN and 28 or 56 salt molecules in a cubic periodic cell) were simulated in the NPT ensemble at 298 K and 1 atm. The ethylammonium cation was modeled employing the potentials described in Ref. [3]. Model nitrate anion was treated as a 4-site planar structure with the central nitrogen atom and three oxygen atoms at the distance of 1.22 Å with all O-N-O angles of 120° [4]. Its intermolecular interactions were described by the sum of Coulomb and Lennard-Jones (6-12) potentials. Three different potential parameters sets, taken from Refs. [5-7], were considered. The interaction potential of the model aluminum ion was also the sum of Coulomb and Lennard – Jones (6-12) potentials, the parameters of the latter were described in Ref. [8]. Simulation time was 1 ns.

To describe the molecular mobility, the diffusion coefficients of all ions were calculated as well as the times of rotational reorientation of various intramolecular vectors for nitrate and ethylammonium ions. The effect of the salt concentration on the dynamical properties of investigated IL was studied in detail. Special attention was paid to the question of the influence of the nitrate-anion model parameters on the simulated molecular mobility.

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Orientation and Translational Mobility in Proton Ionic Liquid Propilammonium Nitrate

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Ionic liquids (ILs) are compounds composed entirely of ions. They are liquid at the room temperature or close to it, unlike "classical" salts [1]. As it is known ILs are prospect substances in enormous number of different practical applications (such as lubricants, fuel cells, batteries, etc.) [2]. It is possible due to their remarkable properties. For example, ILs have high thermal stability and ionic conductivity, negligible vapor pressure, wide electrochemical window, etc. In the present investigation the protic IL propylammonium nitrate (PAN) was explored by NMR.

Firstly, ^{1}H NMR spectrum of the investigated sample was measured. It was found that the sample of PAN contains a certain amount of water. The sample was dried using the device consisting of a heater and fore-vacuum pump with a nitrogen trap. Dependences of the spin-lattice relaxation times (T_1) and the diffusion coefficients on the temperature were measured for the dried PAN sample. The measurements were made in the temperature range from 25 to 100 °C in increments of 5 K. The dependence of the ^{13}C diffusion coefficients on the temperature was also measured in the range from 25 to 70 °C.

Temperature dependences of the spin-lattice relaxation rate and the diffusion coefficient were plotted in order to analyze the molecular mobility of the PAN. Unfortunately, the used temperature range was not enough to reach a maximum in relaxation rates, and measurements are required at lower temperatures or at higher magnetic field. However, the correlation times were roughly estimated using the initial part of the dependence and SBPP equation [3]:

$$\frac{1}{T_{1H}} = s_H^2 A_{0H} \left(\frac{\tau_c}{1+(\omega_H \tau_c)^2} + 4\frac{\tau_c}{1+(2\omega_H \tau_c)^2} \right) \quad (1)$$

One more peculiarity of the $1/T_1$ curves is a curve break observed near temperature range from 65 to 80 °C. It is reasonable to associate this break with a change in the propyl tail conformation under the temperature increase.

Acknowledgments: The NMR measurements have been carried out in the Center for Magnetic Resonance of Research Park of Saint Petersburg State University.

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S. First Steps in Science
(for secondary school students)

Modification of the Surface of Glass Microspheres by Molecular Layering

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One of the most promising ways to create materials with new complex properties ts modifications of existing ones, i.e. creation of new ones composite material. Inorganic compounds of the silicate type, such as hollow glass microspheres, are of interest for creating composites. It is known that the performance characteristics of glass microspheres, especially strength, are determined by the state of their surface, in basically, the presence of defects [1]. Modification of the surface of glass spheres by the method of molecular layering opens up prospects for increasing the strength and the adhesive properties of such fillers in the creation of polymer glass-reinforced plastics.

The main idea of the molecular layering method is to sequentially build-up of new structural units on the surface of a solid body by implementation of chemical reactions between surface functional groups and reagents supplied to them [2]. Thus, the study of the structure and morphology of the surface of glass spheres, both original and surface modified versions are up-to-date task.

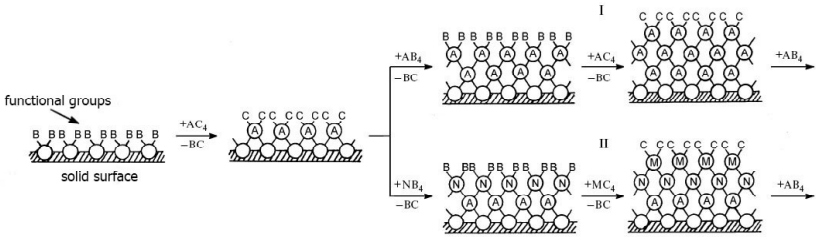

Fig. 1. Scheme of modifying the surface of a solid by the molecular layering method when creating a monolayer of new structural units, coatings of a given thickness (I), and layered nanostructures of different chemical nature (II).

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Method of Protection of the CubeSat Device Against Radiation

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One of the urgent problems of the modern development of space technology is the protection of small spacecraft (SSC), in particular CubeSat format devices, from ionizing radiation (IR), the impact of which has a significant impact on the physicochemical properties of electronic systems of spacecraft and their performance. Currently, there are physical and hardware-software methods for protecting satellites [1].

This paper presents a method for protecting the CubeSat SSC from the effects of IR. The method is based on the creation of a magnetic field by two solenoids mounted on the CubeSat body with opposite directions of current. Using of a program written in C++, the trajectories of the movement of charged particles were modeled and the effectiveness of the action of the magnetic field in deflecting ionizing radiation from the CubeSat satellite was confirmed (see Fig. 1).

The presented method will significantly reduce the likelihood of equipment failure and extend the service life of the spacecraft. In addition, the use of the proposed idea will provide an opportunity to launch CubeSat format satellites into higher orbits, where the impact of radiation is stronger [2].

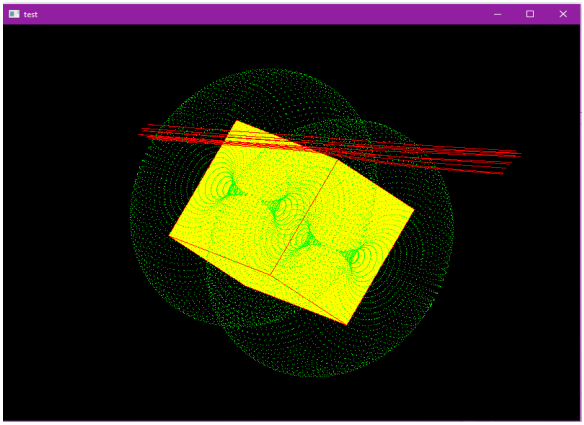

Fig. 1. Modeling particle trajectories.

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Augmented Reality in Education

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Purpose of the work**:** to improve the quality of assimilation and understanding of the material of the lessons by students, using augmented reality technology.

Scientific novelty based on the data of Russian and foreign studies, the teaching method using AR technology in education is an extremely relevant and effective way of teaching.

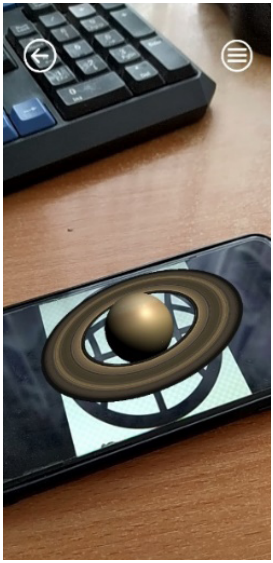

Fig.1 Augmented reality app.

Scientific significance: the research is that the developed courses of AR applications will increase the level of assimilation of the material by students.

The practical significance of the research lies in the development of augmented reality applications to solve the above problem.

Results of the study: as a result of the study, it was possible to draw the following conclusions: the AR market in education in Russia is in an empty state, since the main large market players are spread only in the western segment. That is why our project can be valuable in the Russian market.

In the course of the study, it was also possible to determine the necessary resources for the implementation of the project, namely: specialists in the field of programming and design, financial resources, premises, technical devices, software.

During the lesson, we managed to find out the interest of students in augmented reality technology; the hypothesis of the project was confirmed.

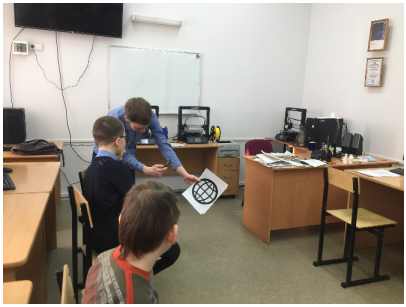

Fig.2 Carrying out lessons.

As a result of the implementation of the project, we have a product ready for mass use - an augmented reality application, which already (Fig. 1), at this stage of the project implementation, can launch Augmented Reality itself, videos and verification tests on the subject of the solar system. The project has a potential audience that is interested in using this technology in the learning process - primary school students (Fig. 2).

Complex Formation of Cobalt(II) Ions with 4,4’ -Bipyridine in Non-Aqueous Solvents

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Metal-organic frameworks (MOF) widely used nowadays in different fields of science and technology. However, the detailed mechanism and kinetics of their crystallization have not been fully understood yet. It is known from the literature that the solvent strongly effects on the composition and the topology of MOFs [1]. The most common solvents used in solvothermal synthesis are dimethyl sulfoxide, dimethylformamide, dimethylacetamide, and ethanol. In this work we studied the complex formation between cobalt(II) and 4,4'-bipyridine to understand the first step of MOFs formation – the complex formation.

Absorption spectra of cobalt(II) and 4,4’-bipyridine complexes in non-aqueous solvents were obtained by UV spectroscopy (Fig. 1). It was found that only one complex is formed in all solvents – $Co(4,4'\text{-bpy})^{2+}$. Stability constants of the complexes were determined. The values of stability constants decrease as the donor numbers [2] of solvents increase.

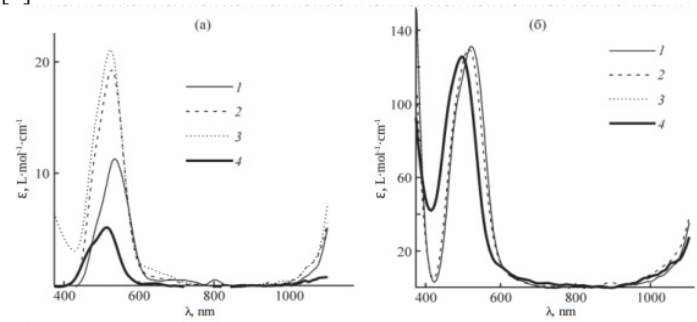

Fig. 1. Electronic absorption spectra of Co^{2+} (a) solvate complexes and cobalt(II) complexes with 4,4'-bipyridine (4,4'-bpy): $Co(4,4'\text{-bpy})^{2+}$ (b) in dimethyl sulfoxide (1), dimethylacetamide (2), dimethylformamide (3) and ethanol (4).

Acknowledgments: This work was supported by RFBR (project № 20-33-70025). The authors are grateful to Saint-Petersburg State University Research Park.

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Table of Content

Подписано в печать 09.11.2021 с оригинал-макета заказчика.
Ф-т 30х42/4, Усл. печ. л. 13. Тираж 30 экз.

Отпечатано в типографии ООО «СБОРКА»
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