Kazan Federal University
Zavoisky Physical-Technical Institute

ACTUAL PROBLEMS OF MAGNETIC RESONANCE AND ITS APPLICATION

XXV International Youth Scientific School

ACTUAL PROBLEMS OF MAGNETIC RESONANCE AND ITS APPLICATION
KAZAN

Program and Proceedings

Kazan
September 28 – October 02, 2026

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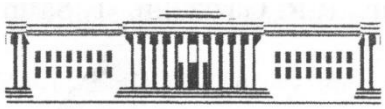

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P R O G R A M

13:00 – 13:10 Opening Ceremony

13:10 – 13:20 ***Dmitry Afanasyev***, "Ultrathin Nanocomposite Layers of Porous Silicon with Nickel Inclusions and Perpendicular Magnetization"

13:20 – 13:30 ***Alexander Alexandrov***, "Synthetic approaches for controllable size, morphology, and phase composition of $NaLnF_4$ submicroparticles as MR contrast agents"

13:30 – 13:40 ***Viktor Blinov***, "Two types of local environment of Cs^+ ions in modified averievite $CsBrCu_3Zn_2O_2(VO_4)_2$ according to NMR data"

13:40 – 13:50 ***Gleb Dolgorukov***, "EPR study of aqueous TEMPO solution confined in closed pores of LaF_3 nanoparticles"

13:50 – 14:00 ***Adeliya Garaeva***, "Magnetocaloric properties of DyF_3 powder as a promising material for cooling at liquid hydrogen and helium temperatures"

14:00 – 14:10 ***Diana Glushchenko***, "Investigation of the functional properties of novel organic MRI contrast agents based on nitroxide radicals"

14:10 – 14:20 ***Yaroslav Isaev***, "Predicting NMR Chemical Shifts of Transition Metals (^{55}Mn, ^{57}Fe, ^{93}Nb, ^{95}Mo) in Coordination Compounds Using Machine Learning"

14:20 – 14:30 ***Aidar Khusanzyanov***, "Study of the thermoelectric properties of ludwigite $(Cu, Mn)_3{}^{11}BO_5$"

14:30 – 14:40 ***Aleksey Kovalev***, "Spatial structure of indomethacin in DMSO-d_6 by NOESY and quantum chemical calculations"

14:40 – 14:50 ***Anna Lavrova***, "^{11}B NMR spectroscopy of $Ni_3B_2O_6$ single crystal"

14:50 – 15:00 ***Maksim Menshikov***, "Using capacitive dilatometer for measuring magnetostriction at cryogenic temperature and in strong magnetic field."

15:00 – 15:10 ***Anna Mololina***, "Analysis of the Spatial Structure of Etoricoxib Using NOESY Spectroscopy"

15:10 – 15:20 ***Yulia Motygina***, "Excluded volume and instantaneous diffusion at the observer frequency: two effects breaking the standard DEER analysis"

15:20 – 15:30 ***Bulat Mukhamadullin***, "Time-depended ^{1}H NMR relaxation during DyF_3 nanoparticle agglomeration"

15:30 – 15:40 ***Mikhail Murygin***, "Development of a Program for Controlling NMR Experiments Based on a Multichannel Interval Programmer, Including the Organization of Global Sequences"

15:40 – 15:50 ***Anastasia Roy***, "Design and testing of the cycling adiabatic demagnetization cell with frustrated magnet $LiGdF_4$ as a cooling agent"

15:50 – 16:30 **Coffee break**

16:30 – 16:40 ***Leonid Rybalkin***, "Application of Nuclear Magnetic Resonance Methods for the Study of Core Material Fluid Saturation Under Gas Pressure"

16:40 – 16:50 ***Leonid Rybalkin***, "Study of the Effect of Liquid Nitrogen Treatment on Gas Filtration in Low-Permeability Anisotropic Coal"

16:50 – 17:00 ***Innokenty Serdyuk***, "Investigation of the relationship between NMR spectra and structural features of fractured coals"

17:00 – 17:10 ***Yulia Slesareva***, "^{1}H NMR Analysis of Confined Acetonitrile Mobility in Graphite Oxide"

17:10 – 17:20 ***Mark Smirnov***, "Application of NMR DOSY to the Study of the "Aromatic Amino Acid–Metal Nanoparticle" System"

17:20 – 17:30 ***Valentina Sobornova***, "Structural and Sorption Properties of Nanocrystalline Cellulose Aerogel Composites Impregnated with Fenamates: Insights from Nuclear Magnetic Resonance Spectroscopy"

17:30 – 17:40 ***Ekaterina Suvorkova***, "^{13}C NMR Determination of Carbon Localization in Ni@C and CoNi@C Nanoparticles"

17:40 – 17:50 ***Artem Talantsev***, "Remote sensing of anisotropic magnetoresistance by non-resonant microwave absorption, detectable in EPR spectrometer "

17:50 – 18:00 ***Almaz Zinnatullin***, "Investigation of nuclear gamma-resonance on ^{57}Fe nuclei in Fe-implanted ZnO thin films"

Ultrathin Nanocomposite Layers of Porous Silicon with Nickel Inclusions and Perpendicular Magnetization

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Layered structures with perpendicular magnetization are of interest for implementing special localized spin configurations that are promising in new magnetoresistive and magneto-optical spintronics structures [1,2]. These include layers with cylindrical magnetic domains in epitaxial films of mixed ferrite-garnets $RFeO_3$, where R is a rare-earth element, or in amorphous films of d- and f-metal alloys Gd-Co and Gd-Fe [4]. Another example is $(Co/Pt)_n$ structures with n=5 [4,5] exhibiting perpendicular magnetization. Such magnetization was observed in layers of germanium doped with manganese and aluminum deposited from laser plasma, which is associated with needle-like inclusions of a high-temperature ferromagnetic phase with Curie temperature T_c>293 K [6]. Finally, in work [7], porous silicon (PS) layers with a channel system of diameter nm and length 30 μm by electrochemical anodization were obtained. The pores were filled with nickel along their entire length by electrochemical deposition. Based on angular dependences of ferromagnetic resonance (FMR), the presence of magnetization oriented normal to the PS layer plane was established. In [8], changes in photoluminescence and electron paramagnetic resonance were experimentally investigated with increasing time of electrochemical formation of nanoscale porous silicon, starting from ultrathin layers on Si p- and n-type monocrystalline wafers. Signs of cascade growth of porous silicon layers were found, where within the cascade, pores develop with similar growth rate and diameter. This allows for the formation of narrower channels in silicon with higher density. It is of interest to repeat the experiment [7] with ultrathin nanocomposite PS layers containing ferromagnetic metal inclusions of Ni, Co, or Fe and perpendicular magnetization. The results of FMR measurements of such layers are presented. Based on the numerical solution of the Landau-Lifshitz-Gilbert equations, the results of analyzing patterns in FMR spectra of ferromagnetic filaments are presented, taking into account exchange interaction. A comparison of FMR data and numerical modeling is provided.

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Synthetic approaches for controllable size, morphology, and phase composition of $NaLnF_4$ submicroparticles as MR contrast agents

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Submicro- and nanoparticles of lanthanide fluorides $NaGdF_4$ and $NaYF_4$ are attracting the attention of researchers due to their unique combination of magnetic and optical properties. It is known that $NaGdF_4$ nanoparticles can be used as T_1 and T_2 contrast for magnetic resonance imaging [1]. Gd^{3+} ions provide high T1 relaxation, which makes the material promising for MRI contrast enhancement, and doping of the matrices with REE activator ions, for example, the Yb^{3+}/Er^{3+} pair, produces intense upconversion luminescence for optical imaging of particles.

The key parameters determining the properties of such highly dispersed materials are size, morphology, and phase composition. For $NaLnF_4$ matrices, two modifications are known: cubic (α-phase) and hexagonal (β-phase), which actually represent non-stoichiometric phases: cubic $Na_{0.5-x}Ln_{0.5+x}F_{2+2x}$ and $Na_{3x}Ln_{2-x}F_6$, respectively. Ultrasmall nanoparticles (<10 nm) are preferred for MRI, while submicron nanoparticles (100–1000 nm) are promising as multimodal platforms. The aim of the work is to generalize approaches to the controlled synthesis of $NaLnF_4$ particles with specified characteristics.

A large number of methods for synthesizing highly dispersed fluorides have been developed [2]. Such methods include hydrothermal and solvothermal synthesis, precipitation and molten salt synthesis allowing the particle size to be tuned from a few to hundreds of nanometers depending on the chosen medium and temperature. Aqueous and solvothermal processes yield nanoparticles but suffer from agglomeration, hydration, or require high temperatures (up to 350 °C) with organic ligands, whereas molten salt methods afford crystalline products with low specific surface area and high up-conversion luminescence intensity. In this context, control over phase composition, morphology, and the degree of agglomeration is achieved by varying the temperature, time, concentration, reagent feed rate, and component ratios, while organic residues are removed by an additional heat treatment step.

Determining the particle size, phase composition, and other physicochemical characteristics of the resulting powders is possible due to the use of such analytical methods as: X-ray powder diffraction, scanning and transmission electron microscopy, luminescence spectroscopy, and magnetization. Using a specific synthesis method, it is possible to obtain multifunctional materials.

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Two types of local environment of Cs^+ ions in modified averievite $CsBrCu_3Zn_2O_2(VO_4)_2$ according to NMR data

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Frustrated magnetic systems with dominant antiferromagnetic exchange interactions may host a quantum spin-liquid ground state [1]. The kagome lattice is a classic example where strong antiferromagnetic exchange interactions, combined with the corner-sharing triangular geometry, suppress long-range magnetic ordering down to the lowest temperatures.

We have studied a polycrystalline sample of modified averievite $CsBrCu_3Zn_2O_2(VO_4)_2$. Unlike in the parent averievite compounds, where copper ions occupy both kagome planes and interplane positions, in this compound the apical Cu^{2+} ions are fully substituted by nonmagnetic Zn^{2+}, effectively isolating the kagome layers formed by Cu^{2+} (spin 1/2) ions. Bulk magnetic susceptibility and heat capacity measurements reveal no magnetic transitions down to 2 K, and the large lower bound of the frustration parameter indicates strongly suppressed magnetic order, making this compound a promising candidate for a spin liquid state.

Nuclear magnetic resonance (NMR) is a powerful tool for probing local magnetic properties in such systems [2]. ^{133}Cs (spin 7/2) spectra were recorded in a 9 T magnetic field in the temperature range from 2.95 K to 300 K. At high temperatures, the spectral line shape indicates absence of resolved quadrup splitting, so the spectra predominantly directly reflect the distribution of local magnetic fields at Cs sites.

The spectra were fitted by a sum of two Gaussian components with fixed intensity ratio, illustrating two distinct contributions from crystallographically equivalent Cs nuclei with different local magnetic environments. The shift of the main component decreases sharply down to zero within experimental error at low temperatures, indicating singlet formation in defect-free kagome regions, characteristic of a gapped spin liquid [3]. The second component follows the temperature dependence of bulk susceptibility, showing an increase upon cooling. This is attributed to regions near defects where residual Cu^{2+} is not replaced by Zn^{2+}, inducing unpaired magnetic moments that break singlets, similarly to other kagome systems [4]. The absence of significant line broadening upon cooling provides evidence against the long-range magnetic order [5].

Thus, modified averievite $CsBrCu_3Zn_2O_2(VO_4)_2$ serves as a convenient model system for investigating spin liquid physics on the kagome lattice, and the proposed NMR analysis enables the separation of defect and intrinsic magnetic contributions.

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EPR study of aqueous TEMPO solution confined in closed pores of LaF_3 nanoparticles

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Nanoscale confinement can strongly modify phase transitions and molecular mobility of liquids. Here, closed-pore LaF_3 nanoparticles containing an aqueous solution of the nitroxide radical TEMPO were synthesized using a fluoride precipitation route with microwave treatment in water with added TEMPO compound [1] and studied by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectroscopy. The isolated water-filled nanoclusters inside the fluoride matrix protect the spin probe from the external environment and make it a local reporter of confined-liquid dynamics.

Transmission electron microscopy showed LaF_3 particles of about 30-40 nm with aqueous clusters not exceeding 5 nm. X-band EPR spectra recorded during cooling and heating differ markedly from bulk aqueous TEMPO. Spectral simulations [2] yielded the rotational correlation time τ_{corr} and revealed a transition near 210 K on cooling and near 230 K on heating (Fig. 1). The observed hysteresis indicates supercooling and a distribution of local environments in closed pores. The Gibbs-Thomson estimate gives pore sizes of 2-7 nm, consistent with microscopy.

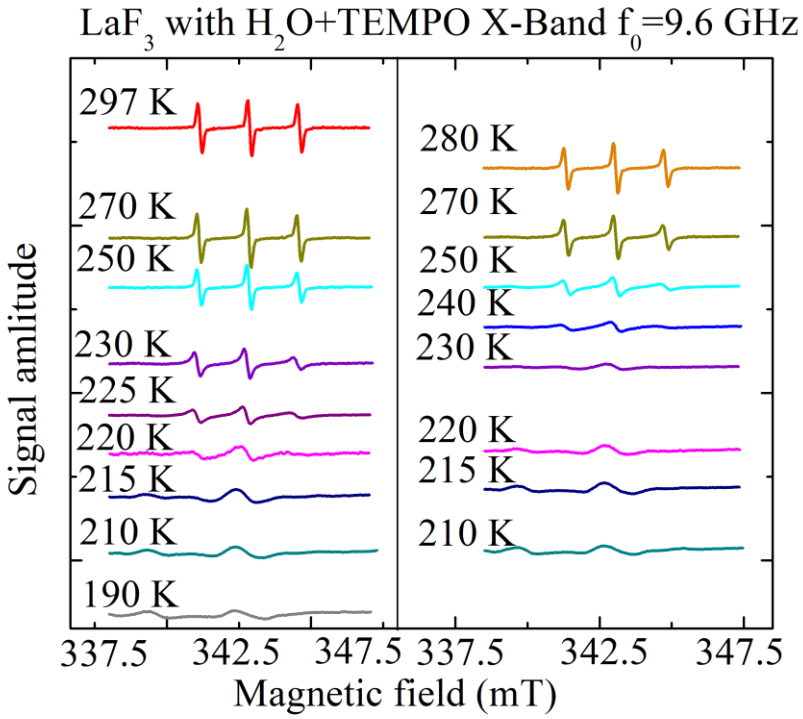

Fig. 1. Temperature dependence of X-band EPR spectra of TEMPO water solution inside the LaF_3 nanoclusters during cooling and heating.

Pulsed ENDOR spectroscopy confirmed that the radical signal originates from TEMPO inside the aqueous clusters rather than from molecules adsorbed on the particle surface. The ^1H ENDOR spectrum corresponds to direct solvation by confined water, whereas the ^{19}F response

reflects interaction with the LaF_3 lattice through an intervening water layer. The estimated distances, 0.38 nm for ^{1}H-TEMPO and about 0.72 nm for ^{19}F-TEMPO, support encapsulation of TEMPO inside the clusters.
Thus, spin-labeled LaF_3 nanoparticles provide a model system for probing phase behavior and molecular dynamics in sealed nanoscale cavities. Owing to the protected and persistent TEMPO signal, such particles may also be useful as EPR contrast agents for low-field imaging and nanoparticle tracking.

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Magnetocaloric properties of DyF_3 powder as a promising material for cooling at liquid hydrogen and helium temperatures

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The development of eco-friendly cryogenic cooling near liquid hydrogen (20.15 K) and helium (4.2 K) temperatures is crucial for hydrogen energy and quantum computing [1,2]. Magnetocaloric refrigeration offers a highly efficient alternative to gas-compression systems, but its adoption depends on finding suitable materials. Due to their large magnetic moments, compounds based on tightly packed Dy^{3+} ions are exceptionally promising. DyF_3 (orthorhombic Pnma, T_C = 2.55 K [3]), which also serves as an MRI contrast agent [4] and a coercivity enhancer for Nd-Fe-B magnets [5], can be a perspective candidate.

DyF_3 powders with characteristic sizes of 30 nm x 16 nm, 50 nm x 30 nm, 70 nm x 40 nm, 220 nm x 150 nm were obtained by hydrothermal synthesis via chloride reaction [6], powder size of 7 μm x 5 μm – by crushing a single crystal. Chemical composition control and crystallinity confirmation were carried out using X-ray diffraction analysis on Bruker D8 Advance Cu Ka, λ=1.5418 Å. The shape and characteristic size of the particles in the powders were determined from photographs obtained using transmission electron microscopy on a HitachiHT Exalens microscope.

In this work, the low-temperature magnetic and magnetocaloric properties of DyF_3 micro- and nanopowders were investigated. Field-dependent magnetization curves (0–7 T) and heat capacity under fields up to 9 T were measured using a magnetic property measurement system and MPMS-9 (Quantum Design) at St. Petersburg State University and PPMS-9 at Kazan Federal University, respectively. Theoretical modeling of the crystal-field energy spectrum, magnetization, and lattice dynamics was performed using the exchange charge model (in the full basis of the Dy^{3+} $4f^9$ configuration) and density functional theory (DFT). The theoretical modeling reveals that the magnetization behavior of the powder is well described by taking into account both surface and clustering effects. It was shown, dysprosium fluoride demonstrates outstanding promise as an efficient material for magnetocaloric cooling at liquid hydrogen and liquid helium temperatures. Furthermore, the systematic evaluation of the particle size influence on the magnetocaloric properties allowed for determining the optimal particle dimensions for maximizing cooling performance.

The work was carried out by the Russian Science Foundation (Project No. 23-72-10039-П).

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Investigation of the functional properties of novel organic MRI contrast agents based on nitroxide radicals

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Despite the widespread use of Gd-based contrast agents, their clinical application is limited by the risk of nephrogenic systemic fibrosis, which drives the search for safe alternatives. In this context, organic agents based on stable nitroxide radicals attract attention due to their biocompatibility and metal-free composition [1].

Previously, we studied a series of novel hydrophobic polynitroxyl dendritic radicals containing from 1 to 45 radical centers [2]. It was shown that the maximum relaxation efficiency is achieved at 42-45 centers; however, poor solubility in aqueous media restricts their biomedical potential.

In the present work, a new series of water-soluble polynitroxyl dendrimers with 4 to 580 radical centers has been investigated. The introduction of hydrophilic groups provided complete solubility in water without organic cosolvents, which is critically important for further in vivo studies.

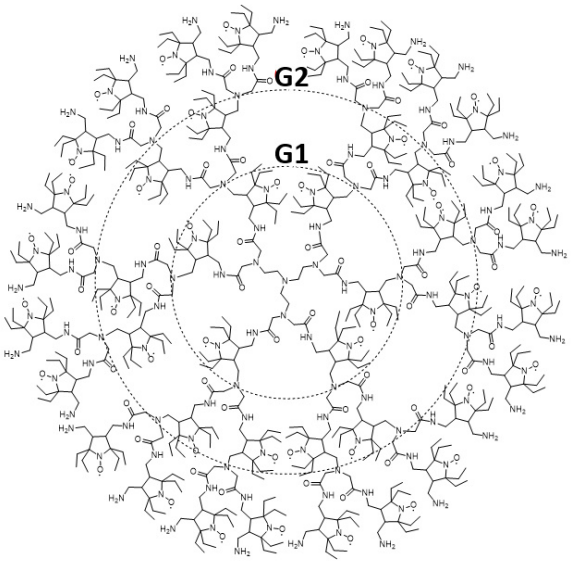

Fig.1. Structure of a polynitroxyl dendrimer bearing 42 nitroxide moieties

A key feature of the compounds is that the nitroxide fragments act not as peripheral substituents but as building blocks of the dendritic structure itself (Fig. 1), providing a high local density of paramagnetic centers within a single macromolecule and simultaneously enhancing the resistance of radicals to reduction under physiological conditions [3-5].

For all compounds, spin-lattice (T_1) and spin-spin (T_2) relaxation times of water protons were measured at 37 °C by NMR relaxometry. Dependences of $1/T_1$ and $1/T_2$ on dendrimer concentration were constructed, and longitudinal (r_1) and transverse (r_2) relaxivities were calculated. The radical concentration in each sample was determined by EPR spectroscopy using a monoradical standard of known concentration.

The resulting polynitroxide structures demonstrated high r_1 and r_2 relaxivities, exceeding those of conventional gadolinium-base CA.

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Predicting NMR Chemical Shifts of Transition Metals (^{55}Mn, ^{57}Fe, ^{93}Nb, ^{95}Mo) in Coordination Compounds Using Machine Learning

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Accurate structural characterisation of coordination compounds containing transition metals such as Mn, Fe, Nb, and Mo remains a significant challenge in modern physical chemistry. Nuclear magnetic resonance (NMR) spectroscopy is widely employed because chemical shifts are highly sensitive to the local coordination environment and can reliably indicate structural changes. However, direct experimental NMR measurements for these nuclei present substantial obstacles: ^{55}Mn signals often broaden in larger molecules, ^{57}Fe exhibits inherently low sensitivity, and both ^{93}Nb and ^{95}Mo require specialised measurement conditions that restrict their routine application. Machine learning provides a promising alternative, enabling rapid chemical shift predictions that rival the accuracy of conventional density functional theory (DFT) calculations.

In this study, we developed machine learning models to predict ^{55}Mn, ^{57}Fe, ^{93}Nb, and ^{95}Mo NMR chemical shifts in coordination compounds, utilising a liquid-phase experimental database. The final dataset included 1956 measurements across 1728 unique structures: ^{55}Mn (429), ^{57}Fe (235), ^{93}Nb (173), and ^{95}Mo (1119).

We investigated several modelling approaches, including descriptor-based models (CatBoost), neural network architectures (Chemprop, Transformer-CNF, MolEncoder), and a hybrid method (TabPFN). The descriptors comprised RDKit-derived features, smooth overlap of atomic positions (SOAP) representations from DScribe, and geometric parameters. Model performance was assessed using five-fold cross-validation and root mean square error (RMSE) as the evaluation metric.

Among all evaluated methods, TabPFN combined with RDKit descriptors achieved the best performance, yielding RMSE values of 300 ± 60, 650 ± 180, 260 ± 50, and 320 ± 60 ppm for ^{55}Mn, ^{57}Fe, ^{93}Nb, and ^{95}Mo, respectively. We further assessed the impact of incorporating global versus local structural information on the ^{93}Nb subset (158 entries, excluding 15 systems with unreliable optimised geometries). The comprehensive descriptor set (RDKit, SOAP, and geometric features) outperformed RDKit descriptors alone, reducing the RMSE from 280 ± 50 to 250 ± 60 ppm.

The developed methodology provides a robust and interpretable computational framework to support experimental NMR spectral interpretation, facilitating more reliable structural characterisation of coordination compounds containing Mn, Fe, Nb, and Mo. We anticipate that this approach can be readily extended to additional nuclei and integrated into routine coordination chemistry research.

Study of the thermoelectric properties of ludwigite (Cu, Mn)$_3$^{11}BO$_5$

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Oxides are promising materials for the development of thermogenerators operating at high temperatures [1]. From our perspective, it is of interest to consider ludwigite-type compounds as a possible working substance for thermoelectric power generation [2]. Oxyborates with the formula *MM'*BO$_5$, where *M* and *M'* are di- and tri- valent metal ions, respectively, are called ludwigites. These metal ions occupy four non-equivalent crystallographic positions per unit cell, which leads to the random distribution of magnetic ions, mixed valence of ions, strong electron correlations, and unusual charge ordering. As a result, they have extremely unusual magnetic properties [3].

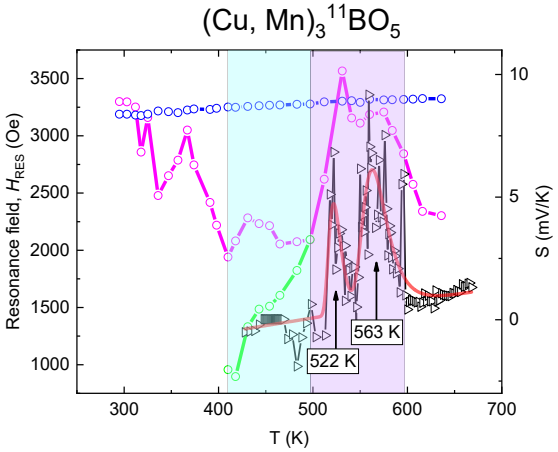

Fig. 1. Temperature dependence of the resonance fields for the EPR spectrum lines — circles (blue, margenta, green) — and of the Seebeck coefficient — triangles — in a (Cu, Mn)$_3$^{11}BO$_5$ sample.

The temperature dependence of the EPR spectrum and the Seebeck coefficient were obtained. Figure 1 shows the temperature dependence of the resonance fields of three lines in the EPR spectrum and of the Seebeck coefficient. It can be seen that at a temperature of about 400 K, an additional EPR signal appears (the green line in Figure 1) and becomes indistinguishable at a temperature of 500 K. We assume that this signal originates from a polaron, and at 500 K the polaron is destroyed, which subsequently leads to the release of charge carriers, clearly observed as a sharp increase in the Seebeck coefficient. In the temperature dependence of the Seebeck coefficient, two peaks are observed at temperatures of 522 K and 563 K, which we attribute to phonon drag of charge.

This work was supported by the Russian Science Foundation, project no. 23-72-00047.

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Spatial structure of indomethacin in DMSO-d_6 by NOESY and quantum chemical calculations

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Some small molecules have high conformational lability, leading to the formation of various solid forms with different physicochemical properties. In this regard, establishing the characteristics of spatial structure and calculating the proportions of conformer groups in various environments are urgent problems in pharmaceutical chemistry, the solution of which can serve as the basis for developing approaches for the controlled production of conformationally determined solid forms. An integrated approach combining nuclear magnetic resonance (NMR) spectroscopy techniques, particularly nuclear Overhauser effect spectroscopy (NOESY), with quantum chemical calculations provides a powerful tool for solving these problems.

Indomethacin (IND) is a non-steroidal anti-inflammatory drug used to treat rheumatic diseases; its molecules are potentially suitable for studying conformational lability. However, it is characterised by several gastrointestinal side effects, including gastritis and ulcers. IND is known to exhibit conformationally determined polymorphism, in which the nucleation processes of solid forms directly depend on the prevalence of syn- or anti-conformations (depending on the position of the parachlorobenzoyl fragment relative to the indole backbone) of the target molecules in solution (see Figure 1). Because of its high conformational lability, the subject of study can exist in nine polymorphic forms that differ in physicochemical properties and water solubility. This makes it important to study the compound's structure in solution, which could be the first step toward understanding the processes that form polymorphic forms with improved biopharmaceutical characteristics.

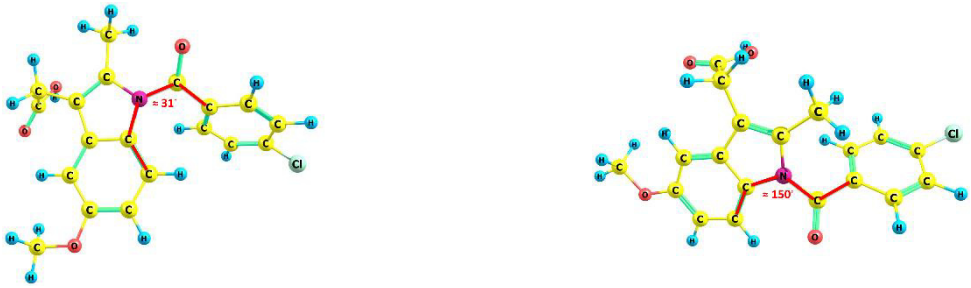

Figure 1. Molecular structure of IND with the highlighted dihedral angle τ_1 defining the syn- (left) and anti- (right) conformations

In this study, the structure of IND molecules was analysed using 1D (^{1}H and ^{13}C) and 2D (^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{1}H NOESY) NMR spectra in DMSO-d_6. We present and analyse the NMR spectral characteristics and compare them with calculated conformer structures obtained from quantum chemical calculations using density functional theory (DFT). We obtained information on the characteristic internuclear distances that determine conformational changes of IND in DMSO-d_6, and determined the ratio of syn- (72.2%) and anti- (27.8%) conformer groups. These results can be used to select a solvent for producing solid forms of IND with improved characteristics to enhance the therapeutic effect.

^{11}B NMR spectroscopy of $Ni_3B_2O_6$ single crystal

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One of the most prominent representatives of the entire class of oxyborates is the compounds with the general formula $Me_3B_2O_6$ (Me = Ni, Co, Mn) featuring the kotoite structure [1]. Compared to other oxyborates, the kotoite structure is one of the simplest, which allows them to be considered as model systems. In kotoites, significant differences in the magnetic properties of isostructural compounds are observed [2], which opens up the possibility of targeted modification through the mutual substitution of transition metal ions at various concentrations [3].

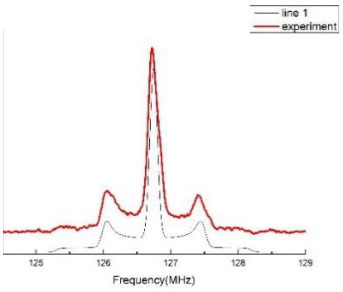

Fig.1. ^{11}B NMR spectrum of $Ni_3B_2O_6$ powder.

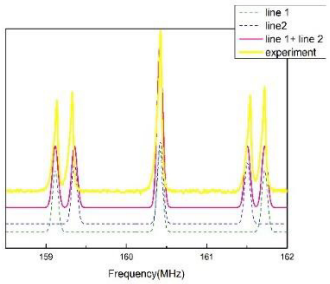

Fig.2 ^{11}B NMR spectrum of $Ni_3B_2O_6$ single crystal.

The aim of the work was to study the local charge environment of the boron atom nuclei in the $Ni_3B_2O_6$ system using ^{11}B NMR spectroscopy. The spectra were recorded on powder and single crystals with the external magnetic field $H_0 = 11.7$ T applied along three crystallographic directions.

Fig. 1 shows the ^{11}B NMR spectrum of the powder and its fitting with a theoretical curve. The structure of the spectrum is due to the interaction between the nuclear quadrupole moment ($eQ = 0.04 \times 10^{-24}$ cm²) and the electric field gradient (EFG) created by its charge environment. The spectrum is satisfactorily fitted with the quadrupole frequency value $^{11}\nu_Q = 3e^{11}QV_{zz}/6h = 1.47\ MHz$ and the asymmetry parameter $\eta = |V_{xx} - V_{yy}|/V_{zz} = 0$, which determines the components of the EFG tensor at the location of the boron nuclei.

Fig. 2 shows the spectrum obtained when the external magnetic field is directed along the **a**-axis of the crystal. The spectrum is satisfactorily described by the sum of two lines of equal intensity and the position of the central transition (1/2 ↔ -1/2), but with different positions of the satellites (3/2 ↔ 1/2 and -1/2 ↔ -3/2). The presence of two lines in the spectrum may be related to the orientational disorder of the structural planar triangles formed by oxygen atoms (anion complex $(BO_3)^{3-}$).

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Using capacitive dilatometer for measuring magnetostriction at cryogenic temperature and in strong magnetic field.

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In this report we present the construction of capacitive dilatometer and the results of measuring the magnetostriction of the Van Vleck dielectric single crystal of lithium-thulium double fluorides $LiTmF_4$ along the [100] crystallographic axis.

The capacitive dilatometer was designed and assembled according to the design proposed by G. M. Schmiedeshof et al [1] and was used with a PPMS system and a capacitive bridge [2]. The design of the capacitive dilatometer cell offers an open architecture that allows for convenient placement of samples for testing. The samples can be in the form of cylinders and rectangles with a maximum size of 6 mm along the dimension of the sample being tested, and they can also be less than perfectly shaped with selected parallel planes.

The $LiTmF_4$ single crystal was grown using the Bridgeman-Stockbarger method. After evaluating the single crystallinity and axis orientation, two parallel planes perpendicular to the crystallographic axis [100] were selected and polished using a brass mandrel and water-based abrasives.

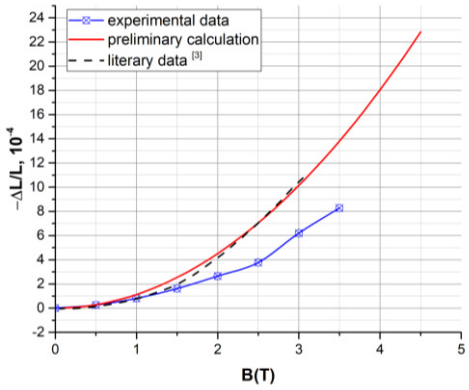

Fig.1. Comparison of the obtained (symbols) and calculated (solid line) data with the literature data [1] (dashed line) for the field dependence of the magnetostriction of the single crystal LiTmF4 at T=5 K and B || [100].

Using a capacitive dilatometer, the magnetostriction of the $LiTmF_4$ single crystal was obtained at a temperature of T=5 K. Our data are consistent with previous studies up to 3 T [3], and also qualitatively consistent with preliminary calculation in a single crystal up to 3.5 T.

This work was supported by RSF grant #22-12-00259-П

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Analysis of the Spatial Structure of Etoricoxib Using NOESY Spectroscopy

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The development of solid forms of active pharmaceutical ingredients (APIs) represents a key strategy for modifying drug compounds to impart new physicochemical and biopharmaceutical properties and to stabilize existing ones. The structure and molecular packing within the crystal unit cell are critical factors in the formation of these solid forms. Therefore, the development of monitoring methods that provide spatial structural information at the early stages of nucleation enables more effective adjustment of processes for obtaining and modifying API forms. A comprehensive approach that integrates computational data from conformational screening with experimental nuclear magnetic resonance (NMR) spectroscopy is particularly effective in addressing these challenges.

This study presents the results of a spatial structure analysis of the nonsteroidal anti-inflammatory drug etoricoxib (ETR), a highly selective cyclooxygenase-2 (COX-2) inhibitor with pronounced analgesic and anti-inflammatory activity. For the first time, a detailed assignment of resonance signals in the one- and two-dimensional NMR spectra of this compound has been performed [1]. Utilizing a comprehensive approach based on NOESY data and quantum chemical calculations, information was obtained on the internuclear distances that characterize changes in the position of the γ-ring of the ETR molecule relative to the plane of the β-ring (see Figure 1). Given etoricoxib's significant potential for forming various solid forms, including solvates and polymorphs, these results may inform future developments aimed at modifying drug compounds.

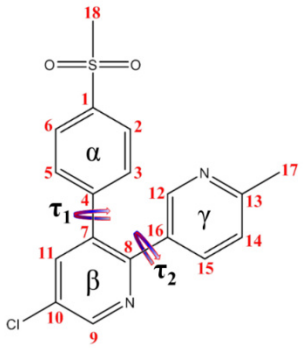

Figure 1. Structure of the ETR molecule with labeling of the cyclic fragments α, β, and γ.

This research was funded by the grant of the Russian Science Foundation (project no. 22-13-00257-II)

[1] A.A. Mololina, I.A. Khodov Role of non-covalent interactions in the conformational stability of bicalutamide in different solvent environments: Insights from quantum-chemical calculations and NMR spectroscopy // Journal of Molecular Liquids, 2025, 423, 126921

Excluded volume and instantaneous diffusion at the observer frequency: two effects breaking the standard DEER analysis

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Modern structural biology needs methods capable of measuring distances in mobile, conformationally heterogeneous systems. One such method is double electron-electron resonance (DEER), which recovers the distance distribution between spin labels in the range of 1.5–8 nm. The DEER signal of a doubly labeled molecule is a product of two contributions. **The intramolecular contribution** describes interactions between labels within one molecule (concentration-independent). **The intermolecular contribution** arises from interactions with labels of neighboring molecules (concentration-dependent). The DEER guidelines for biomolecules [1] recommend low concentrations so that the intermolecular contribution can be treated as exponential – i.e., originating from point particles uniformly distributed in space. However, real molecules have finite volume. Moreover, in biradicals, the label distribution is spatially correlated – unlike in monoradicals – which breaks the exponentiality of the intermolecular contribution. This leads to a systematic error in extracting the intramolecular one. Incorrect signal processing can compromise the reliability of the resulting structural data.

Here we used an **alternative approach** – the Milov dilution method with correction for the non-reproducibility of P_B, based on dividing signals at two sample concentrations to isolate the pure intermolecular contribution. The dilution method was confirmed to provide correct separation of contributions for all studied systems: rigid and flexible model biradicals and the therapeutic antibody trastuzumab. For the antibody (240 μM), the approach recommended by the guidelines leads to negative probabilities in the distance distribution at 6–10 nm, whereas the dilution method yields a physically meaningful distribution over the entire range. The pair distance distribution P(r) was reconstructed from the intramolecular contribution. For the biradical, the mean distance is 1.8 nm, and the shape of P(r) agrees with molecular dynamics. The intermolecular contributions were found to be non-exponential for both objects.

The origin of the non-exponentiality was identified for *biradicals*: **instantaneous diffusion at the observer frequency**. Observer pulses, like pump pulses, flip surrounding spins, and the correlated distribution of these spins leads to non-exponential decay. The effect was confirmed experimentally and by numerical simulation. Additionally, numerical simulations were performed to study the manifestation of the effect at different distances and concentrations.

For the *antibody*, the non-exponentiality was explained by **the excluded volume effect**. The molecule was modeled as a sphere with a label on its surface; the best agreement with experiment was achieved for a diameter of 6 nm, corresponding to the size of the Fc-fragment from X-ray data. The native protein structure was confirmed by two independent results: an excluded volume of ~6 nm and a fixed mean label distance of ~5 nm.

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Time-depended ^{1}H NMR relaxation during DyF_3 nanoparticle agglomeration

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The transverse relaxation of water protons is highly sensitive to the local environment in dispersions of paramagnetic nanoparticles. In DyF_3-containing aqueous systems, the proton relaxation rate is influenced by interactions with nanoparticle surfaces, molecular diffusion, and spatial variations of the local magnetic field. Therefore, changes in nanoparticle agglomeration may be reflected in the evolution of the transverse relaxation behaviour even when no visible changes occur in the sample.

The aim of this work is to investigate how the state of an aqueous DyF_3 nanoparticle dispersion affects the ^{1}H transverse relaxation response during storage after ultrasonic redispersion. Particular attention is given to the evolution of the relaxation-time distribution as an indicator of changes in the nanoparticle–water interfacial environment.

The experiments are performed at room temperature using the Carr-Purcell-Meiboom-Gill pulse sequence. After ultrasonic treatment, the transverse magnetization of the samples is recorded repeatedly over time. The resulting decays are analyzed by regularized inverse Laplace transformation, allowing the contribution of different relaxation modes to be resolved.

The obtained relaxation distributions are non-single-component and change systematically with storage time. The evolution of both relaxation times and signal amplitudes demonstrates that the NMR response is sensitive to gradual changes in the nanoparticle agglomerates. A longer relaxation-time component becomes more pronounced with time, while the relative contribution of the shorter relaxation component decreases. This behavior is consistent with progressive redistribution of water environments accompanying the formation of nanoparticle clusters.

The results demonstrate that ^{1}H transverse relaxometry can be used as a sensitive probe of the physical state of DyF_3 nanoparticle dispersions. Analysis of relaxation-time distributions provides a convenient way to follow dispersion stability and distinguish different stages of particle organization without disturbing the sample. The approach may be useful for studying the colloidal behaviour of paramagnetic nanoparticles and for comparing their stability under different preparation and storage conditions [1, 2].

This work was financially supported by the Russian Science Foundation (Project No. 26-22-20043).

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Development of a Program for Controlling NMR Experiments Based on a Multichannel Interval Programmer, Including the Organization of Global Sequences

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Abstract. This paper discusses the development of a highly scalable C++ software system designed for the automation and visual control of nuclear magnetic resonance (NMR) experiments. The relevance of this study stems from the need for flexible tools to construct complex pulse sequences, manage multi-channel systems, and process experimental data. The aim of this work is to create a software suite that enables the visual design and execution of complex pulse sequences-including nested loops, macros, and supersequences for multidimensional NMR, organized through a dedicated SupSeq module interface (Fig. 1). Crucially, the system supports both synchronous and asynchronous control of up to 200 distinct peripheral devices within a single pulse sequence, including dozens of gradient and radiofrequency channels, positioning stages, and temperature regulators. This architecture provides extensive scalability, making the system highly effective for discovering and testing novel MRI techniques. The developed software is currently being evaluated on a newly engineered hardware-software system optimized for studying relaxation, self-diffusion, and magnetic resonance imaging (MRI) of complex natural objects, such as full-size core samples. Built upon object-oriented programming methods and graphical user interface principles, the system allows users to visually monitor the experiment structure and save custom configurations. The obtained results can be applied to the development of advanced control systems for complex multi-channel research NMR and MRI equipment.

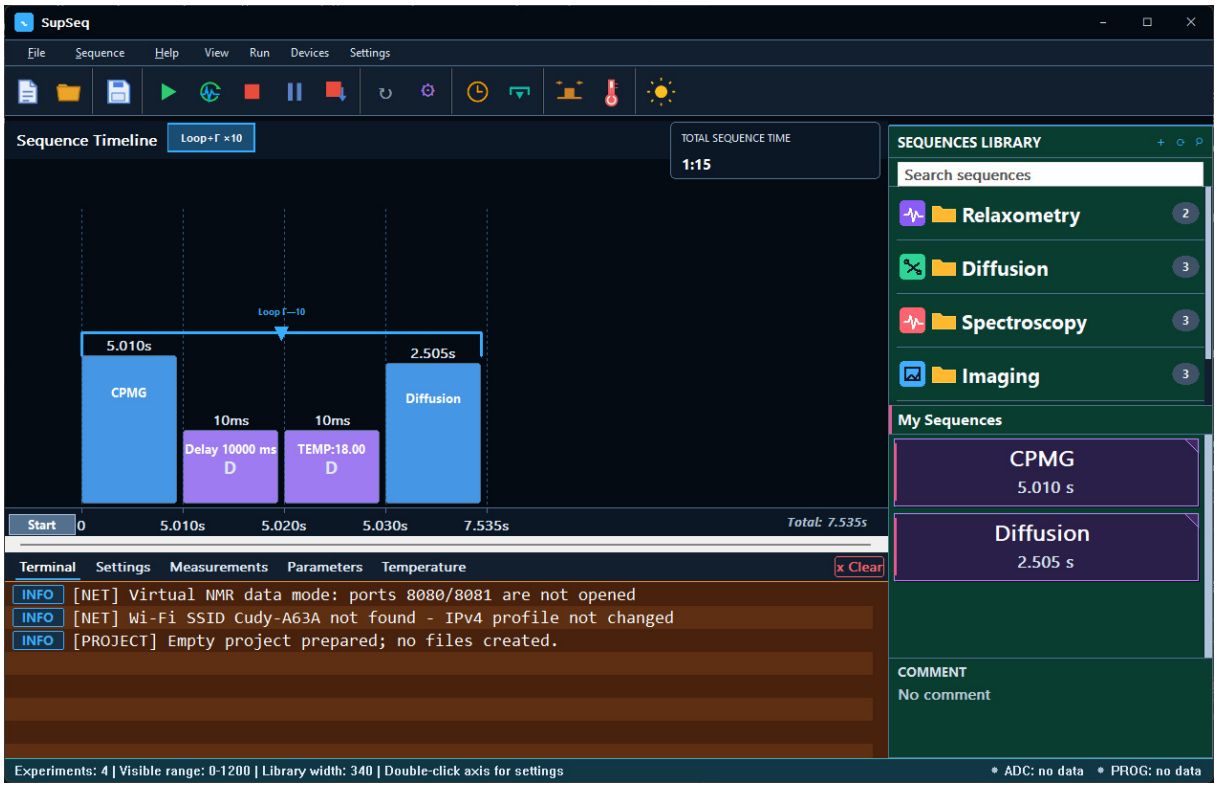

Fig. 1. The SupSeq module interface: a global sequence timeline (left) is built from experiments organized in the Sequences Library (right), grouped by category (Relaxometry, Diffusion, Spectroscopy, Imaging).

Design and testing of the cycling adiabatic demagnetization cell with frustrated magnet $LiGdF_4$ as a cooling agent

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Adiabatic demagnetization is one of the first techniques to reach low temperatures. Entropy of the spin system can be suppressed by the applied magnetic field. Switching off magnetic field adiabatically leads to sample cooling. Cooling performance of this method is limited by spin-spin interactions. To reduce this effect paramagnetic salts are usually used as a cooling agent for low temperature magnetic refrigeration [1].

Magnetic frustration results in compensation of the spin-spin interactions, which in turn yields high residual magnetic entropy in a concentrated spin system. This makes frustrated magnets promising magnetic cooling agents. $LiGdF_4$ is unique for this purpose: due to almost exact compensation of exchange and dipolar couplings and single-ion anisotropy effects this magnet behaves as an ideal paramagnet down to ~ 1 K at H||c providing potentially record cooling power per unit volume [2, 3].

To demonstrate advantages of $LiGdF_4$ for low temperature magnetic refrigeration we have designed experimental magnetic cooling cell with $LiGdF_4$ single crystal as a cooling agent. $LiGdF_4$ crystal is mechanically switched between the helium bath and the cooled body providing possibility to repeat cooling cyclically. Magnetic field up to 3 T was provided by a superconducting cryomagnet.

Test experiments demonstrate operational functionality of this design. Cooling of the large (~2 cm^3) $LiGdF_4$ single crystal and cycling «cold transfer» from the cooling agent to the cooled body were successful. Magnetic cooling from the starting temperature of 7 K down to almost 1 K was demonstrated. Cooling performance of the test setup was limited by the unaccounted radiative heat link. We plan to remove this issue in ongoing experiments.

The work was supported by the RSF Grant 22-12-00259-П.

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Application of Nuclear Magnetic Resonance Methods for the Study of Core Material Fluid Saturation Under Gas Pressure

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The application of Nuclear Magnetic Resonance (NMR) methods is one of the most informative non-destructive approaches for investigating porous media and fluid saturation in the mining industry [1, 2]. The authors have developed a specialized sealed chamber for NMR measurements of samples subjected to external gas pressure, thereby expanding the range of information that can be obtained from conventional NMR studies.

The NMR analyzer Micro12-040V (Niumag, China) was selected as the basis for the technical design of the chamber. The main component of the chamber is a cylindrical body made of fluoroplastic (Fig. 1). One end of the body is sealed with a cover. A threaded opening is provided at the center of the cover for mounting the crack initiator.

The crack initiator consists of a rod fabricated by stereolithography (SLA/DLP) using an engineering photopolymer. A conical tip is formed at its free end, while the opposite end is externally threaded and provided with a slot for a hex key. The compressed-gas saturation system consists of a gas cylinder equipped with a pressure regulator and a gas supply line made of flexible polyamide tubing, which is connected to a dedicated adapter mounted on the chamber cover.

The prepared sample is placed inside the chamber. Then, the chamber cover is screwed into place, and the threaded connection is sealed with PTFE tape. The crack initiator is screwed into the center of the cover and adjusted so that it is just in contact with the core sample. The compressed-gas supply system is connected, and the pressure inside the chamber is increased to the required value, up to 10 atm. The chamber is carefully positioned inside the bore of the NMR analyzer, and a series of standard measurements of the core is performed.

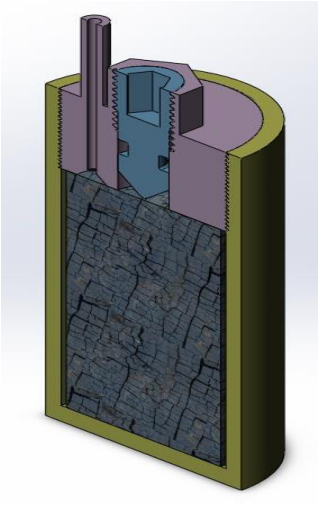

Fig.1. General view of the developed cell.

If modification of the pore and fracture network is required, the chamber is removed and a longitudinal fracture is induced using the crack initiator. The fracture opening is controlled by linear displacement of the initiator. The core material with the altered structure is then subjected to repeated measurements.

This work was carried out within the framework of the Youth Laboratory for Research into Electromagnetic Properties of Coal and Rocks at the Institute of Mining Process Physics.

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Study of the Effect of Liquid Nitrogen Treatment on Gas Filtration in Low-Permeability Anisotropic Coal

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The effect of liquid nitrogen (LN_2) treatment on coal has been actively studied over the past 10-15 years. The studies are required due to the insufficient effectiveness of existing coal seam degassing methods [1]. The authors of this paper investigated the effect of liquid nitrogen treatment on gas filtration in low-permeability anisotropic coal. Laboratory experiments were conducted on layered, fine-pored D-grade (DG) gas coal.The treatment consisted of 1–5 freeze–thaw cycles. During each cycle, the coal samples were immersed in liquid nitrogen for 30 minutes, until boiling ceased, and were subsequently thawed at room temperature for 1–2 hours. Changes in porosity and fracture development before and after LN_2 treatment were characterized using nuclear magnetic resonance (NMR) techniques.

The effect of LN_2 treatment on the open porosity of cores drilled parallel to the bedding is negligible. The open porosity of samples containing macrofractures (Nos. 1, 4, 5, 7, and 8) is consistently higher, both before and after LN_2 treatment, by an average of 5.4% compared with that of intact samples (Nos. 2, 3, 6, and 9). The intact samples have an average open porosity of 9.9% and a total porosity of 17.3%. In our view, the oberseved increase in open porosity of the cores is not attributable to changes in the pore-space structure, but rather to differences in the degree of water saturation.

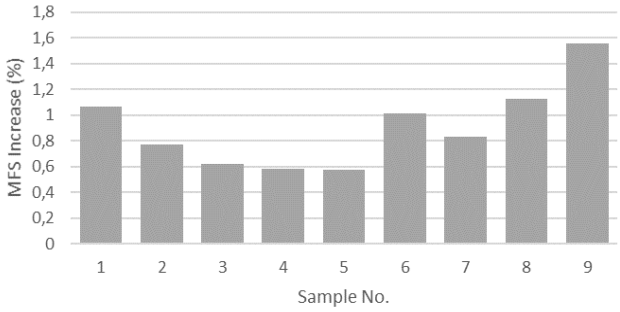

Fig.1. Change in the proportion of mobile water within the saturated volume (MFS parameter) of samples drilled parallel to the bedding as a result of liquid nitrogen treatment.

The low sensitivity of the NMR method to changes induced by LN_2 treatment can be attributed to the fact that, against the background of the relatively high total porosity of the tested coal (17–18%), the increase in void volume resulting from the development of microfractures is relatively small and therefore difficult to detect. This effect is manifested as a slight increase in the proportion of mobile water within the water-saturated pore volume (Fig. 1).

The obtained results differ from those reported in most previous studies of liquid nitrogen treatment of unstressed coal. This discrepancy may be attributed to the specific characteristics of the coal tested, as well as to the use of confining sleeves during the experiments, which prevented the core samples from fracturing during freezing.

The study was funded by the Russian Science Foundation under grant project No. 25-27-00060, https://rscf.ru/project/25-27-00060/.

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Investigation of the relationship between NMR spectra and structural features of fractured coals

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Nuclear magnetic resonance (NMR) relaxometry is an effective non-destructive tool for analyzing the porosity and filtration properties of coal. This study investigates the influence of coal properties and cyclic cryogenic treatment (geo-loosening) on NMR T2 spectra [1-3]. Cylindrical samples (30×60 mm) of coal were drilled parallel and perpendicular to the natural layering. NMR measurements were performed using a Micro1 2-040V analyzer (0.28 T, 12 MHz). Transverse magnetization decay curves were converted into T2 spectra, where T2 < 2 ms corresponds to micropores, 2–200 ms to mesopores, and > 200 ms to macropores. The relation between relaxation time and pore size is governed by the surface-to-volume ratio and surface relaxivity.

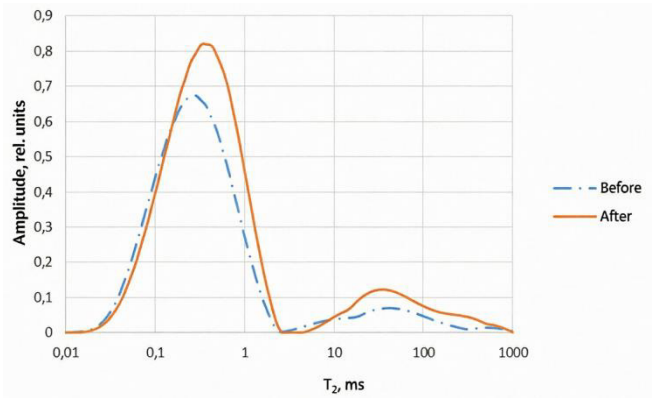

Fig. 1. Normalized T2 spectra of the water-saturated sample drilled perpendicular to the layering, before and after treatment.

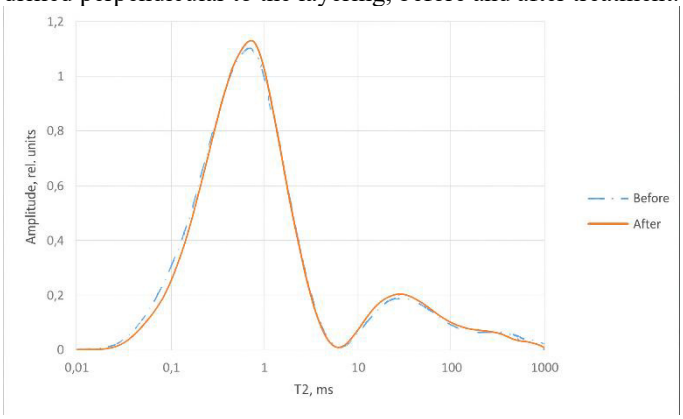

Fig. 2. Normalized T2 spectra of the water-saturated sample drilled along the layering, before and after treatment.

The T2 spectra of water-saturated cores before and after treatment are presented in Fig. 1 and Fig. 2. For the sample drilled perpendicular to the layering, the treatment led to an apparent increase in amplitudes in the 0.5–1 ms and 500–2000 ms intervals (Fig. 1). However, normalizing the micropore amplitudes reveals that the spectra in the meso- and macropore regions nearly converge. The spectrum of the sample drilled along the layering remained almost unchanged after liquid nitrogen treatment (Fig. 2).

In conclusion, the treatment weakly affects the primary pore size distribution. The observed increase in permeability and apparent open porosity is primarily associated with the formation of new micro-fractures rather than the transformation of the existing pore space.

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^{1}H NMR Analysis of Confined Acetonitrile Mobility in Graphite Oxide

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Graphite oxide (GO) is a promising material for the separation and purification of polar liquids. However, its practical application requires an understanding of molecular mobility within its heterogeneous interlayer space. In this work, acetonitrile intercalated into GO was studied by ^{1}H NMR spectroscopy as a function of temperature and saturation level. Field-dependent measurements showed that the side features in the spectra originate from incompletely averaged dipole–dipole interactions. Spectral modeling revealed two acetonitrile fractions with different mobilities. Increasing the acetonitrile content increased the relative proportion of the mobile fraction and reduced the effective dipolar splitting. Molecular motion in both fractions persisted below the freezing point of bulk acetonitrile, which is characteristic of nanoconfined liquids. These findings are consistent with independent EPR results [1].

Nuclear relaxation measurements provided additional information about the dynamics of the confined acetonitrile. The combined analysis of the NMR spectra and relaxation behavior confirmed the coexistence of acetonitrile fractions with different motional regimes and indicated strong interactions between the low-mobility molecules and the GO structure.

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Application of NMR DOSY to the Study of the "Aromatic Amino Acid–Metal Nanoparticle" System

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Aromatic amino acids (AA) are of considerable interest as model compounds for studying the interaction of biological molecules with nanostructured surfaces. In this work, a comparative study of the dynamic parameters of L-tyrosine (L-Tyr) and L-tryptophan (L-Trp) in aqueous solutions in the presence of noble metal nanoparticles was performed out using diffusion-ordered NMR spectroscopy (2D NMR DOSY).

The study examined aqueous solutions of two aromatic amino acids: L-tyrosine (L-Tyr) and L-tryptophan (L-Trp). L-Tyr and L-Trp were studied in combination with platinum and gold nanoparticles, with gold NPs occurring in three different morphologies: spherical (Au NP), star-shaped (Au SNP), and rod-shaped (Au RNP).

The measured values of the D-coefficient for the studied L-Trp samples are presented in Table 1, and for the L-Tyr samples in Table 2. The molecular hydrodynamic radius was calculated using the Stokes–Einstein equation [*A. Einstein, Ann. Phys. (1905)*].

	L-Trp	**+ Au SNP**	**+ Au RNP**
D-coeff., * 10^{-10} м²/с	6,5	5,9	5,5
R_h, Å	3,71	4,16	4,54

	L-Tyr	**+ Au NP**	**+ Pt NP**
D-coeff., * 10^{-10} м²/с	5,05	5,11	4,84
R_h, Å	3,96	3,77	4,27

Analysis of the 2D NMR DOSY data presented in Tables 1 and 2 demonstrated that the interaction of the two studied AAs with metal NP is accompanied by a change in their translational mobility.

For L-Trp, the addition of Au SNP leads to a decrease in the D-coefficient by approximately 9%, while the addition of Au RNP results in a decrease of about 15%. At the same time, the hydrodynamic radius increases by approximately 12% and 22%, respectively. The most pronounced effect is observed for rod-shaped Au NPs, which is due to their anisotropic morphology and the heterogeneity of surface binding sites. The obtained results are consistent with the assumption that the indole fragment of L-Trp interacts with the surface of gold NP through π-π stacking [*G. Kupriyanova et al., Appl. Magn. Reson. 57, 37 (2026)*].

For L-Tyr, the influence of NP of different nature is complex and depends on the type of NP. In the presence of Au NP, the D-coefficient increases by approximately 1%, and the hydrodynamic radius decreases by approximately 5%, which may indicate molecular compaction. Conversely, Pt nanoparticles cause a decrease in the D-coefficient by approximately 4% and an increase in the hydrodynamic radius by approximately 8%, which indicates molecular stretching and a reduction in its translational mobility [*M. Smirnov et al., JMOL 420, 126822 (2025)*].

When interpreting the results for Au SNP and Au RNP, it is necessary to take into account the additional influence of the CTAB stabilizer.

The results obtained confirm the important role of the type and morphology of NPs in determining the dynamic properties of aromatic amino acids in aqueous solution.

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Structural and Sorption Properties of Nanocrystalline Cellulose Aerogel Composites Impregnated with Fenamates: Insights from Nuclear Magnetic Resonance Spectroscopy

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Microporous aerogel-based matrices produced via supercritical fluid (SCF) technologies have attracted significant attention as carrier systems. Immobilising poorly soluble active pharmaceutical ingredients (APIs) within carrier pores in an amorphous state represents a promising modification strategy. The mechanisms by which the local microenvironment affects the properties of incorporated compounds remain insufficiently understood, necessitating further investigation. In this study, composite materials comprising nanocrystalline cellulose (NCC) aerogel impregnated with mefenamic acid (MA) and flufenamic acid (FA) were examined using nuclear magnetic resonance (NMR) spectroscopy in supercritical carbon dioxide ($scCO_2$).

Analysis of the ^{13}C NMR spectra recorded in $scCO_2$ for both pristine aerogel and composite samples revealed an upfield shift of the CO_2 carbon signal from 121.17 to 120.73 ppm in the FA-containing composite. This shift suggests increased shielding of the carbon nuclei, which is associated with CO_2 sorption and dopant incorporation into the NCC pores. The characteristic sorption time was 0.15 hours for the pristine aerogel, compared with 0.38 and 0.25 hours for the MA- and FA-containing composites, respectively. These results indicate altered matrix sorption properties following impregnation.

Solid-state ^{13}C NMR spectroscopy with magic-angle spinning (MAS) confirmed that the structure of the NCC matrix remained unchanged after dopant incorporation. The spectrum of the FA-containing composite exhibited weak signals in the 110 – 170 ppm range, corresponding to carbon atoms of FA. Broadening of these signals, relative to pure FA, is attributed to the distribution of hydrogen bonds between the acid molecules and the hydroxyl groups of the cellulose matrix.

^{19}F MAS NMR spectroscopy of the NCC_FA composite containing a trifluoromethyl group produced a significant result. Two signals were observed at –62.15 and −65.09 ppm, corresponding to the amorphous state of FA within the pore volume and a liquid-like state at the pore surface, respectively. The intensity ratio was 2:1. The identification of two stable states of the same API within the porous structure represents a notable finding.

In summary, the combination of NMR techniques enabled detailed characterisation of the structural and sorption properties of NCC aerogel-based composites. The results demonstrate the potential of NCC aerogels as platforms for stabilising amorphous forms of poorly soluble APIs and suggest new opportunities for developing materials with controlled properties for targeted drug delivery.

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^{13}C NMR Determination of Carbon Localization in Ni@C and CoNi@C Nanoparticles

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Metal nanoparticles encapsulated in carbon shells are of great interest for catalysis, biomedicine, and hybrid materials design. The carbon shell ensures chemical stability and biocompatibility, while the metallic core provides magnetic functionality. For such core-shell nanoparticles, previous magnetization studies have revealed a pronounced decrease in magnetization relative to bulk metal [1]. A possible reason is the incorporation of carbon into the metal core during synthesis, occupying interstitial sites in the metal lattice. To verify this assumption, we performed a ^{13}C NMR study of carbon localization in Ni@C and CoNi@C.

For Ni@C, two signals are observed in the ^{13}C NMR spectra. The first one lies near zero shift ($\nu \approx 125.76$ MHz) and shows no temperature dependence, consistent with literature data for similar nanoparticles [2]. Its assignment to shell carbon is confirmed by an independent experiment on hollow carbon shells obtained by removing the metal cores. The second signal is shifted to higher frequencies, and this shift decreases markedly with increasing temperature. The shift originates from the additional magnetic field produced by ferromagnetic nickel cores, which also weakens with temperature. This unambiguously indicates that part of the carbon resides inside the metal core, forming an interstitial carbon impurity in the metal lattice. The absence of splitting of the shifted signal implies that carbon occupies crystallographically equivalent positions, most likely octahedral interstices of the fcc Ni lattice. From the ratio of integrated intensities, the fraction of carbon in the core is estimated at ~30%, in agreement with thermogravimetric data. After annealing at 1000 °C, the shifted signal disappears, indicating carbon release from nanoparticle cores.

In CoNi@C, the spectral pattern is qualitatively similar, but instead of a single shifted signal, several signals with different positions are observed. Their number and frequencies depend on the particle composition. This can be naturally explained by the non-equivalence of the local environment of carbon in the core: the nearest coordination sphere may contain different numbers of nickel and cobalt atoms. Each distinct configuration of the nearest environment gives rise to its own shifted line, so the observed set of signals reflects local deviations from the overall stoichiometry in the bimetallic core. Annealing at 1000 °C, as in Ni@C, leads to the almost complete disappearance of the shifted signals, confirming release of interstitial carbon from the metal lattice.

Thus, ^{13}C NMR demonstrates that in both Ni@C and CoNi@C, carbon is located not only in the shell but also inside the metal core. In Ni@C, the single shifted line indicates that carbon occupies crystallographically equivalent positions in the Ni lattice. In CoNi@C, the set of shifted signals reflects the variety of local configurations around carbon, related to the distribution of Ni and Co in the lattice. Carbon dissolution in metal cores may be a common feature of core-shell nanoparticles, which should be taken into account when interpreting their magnetic properties, and ^{13}C NMR provides a means to detect and monitor this process.

The work was carried out within the framework of the state assignment of the Ministry of Science and Higher Education of the Russian Federation for the IMP UB RAS and the youth project "m 09-25" (Suvorkova E.).

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Remote sensing of anisotropic magnetoresistance by non-resonant microwave absorption, detectable in EPR spectrometer

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Sharp change of non-resonant microwave absorption was found in exchange-biased NiFe/IrMn and NiFe/Cu/IrMn structures possessing anisotropic magnetoresistance (AMR) and planar Hall effect (PHE). Angular dependence of the microwave detected AMR and contribution of the domain expansion to AMR microwave signal were analyzed. Decrease in the microwave absorption signal caused by Cu spacer between ferromagnetic NiFe and antiferromagnetic IrMn layers was observed, when NiFe and IrMn layers become exchange decoupled. Additional characterization of the electric transport was proved by asymmetry of resonant line.

Effectiveness of non-resonant microwave absorption probe as a tool for contactless measurements of the AMR and PHE in exchange biased structures is demonstrated [1]. Microwave detection of magnetoresistance provides possibility of contactless remote reading of sensors state due to excitation of eddy currents in planar heterostructures. Several distinct features have been revealed.

True field dependences of PHE voltage V_{PHE} and derivative of AMR signal ~ dV_{AMR}/dH on magnetic field were recalculated from the field dependence of microwave absorption recorded in suitable orientation. Magnetoresistive response is frequency independent in 2 – 20 GHz range, while a FMR signal of NiFe layer manifests a frequency dependence. In magnetic field directed along easy magnetization axis, dependences $dV_{AMR}/dH(H)$, $V_{PHE}(H)$, and $dP/dH(H)$ show magnetic hysteresis accompanying domain dynamics.

Asymmetry of a simultaneously observed resonant FMR signal was used as an additional parameter characterizing skin depth and vortex currents. It appears when eddy electric current lies in a sample plane or/and Cu layer thickness becomes large enough > 0.5 nm. A FMR signal with a Dyson shape becomes a convenient tool to probe the skin layer depth and inhomogeneity of eddy currents in multilayered structure. The Dyson line parameters can be used to determine eddy currents in the NiFe layer, where the microwave detection of the AMR and PHE was carried out.

Sensitivity of the microwave AMR method is enough high to detect magnetic fields of microTesla level, that provides remote detection with a sensitivity corresponding to standard galvanic sensors. Developed technique is promising for wireless AMR sensor technology providing coordinate and angular field measurements through remote microwave absorption.

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Investigation of nuclear gamma-resonance on ^{57}Fe nuclei in Fe-implanted ZnO thin films

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Wide-bandgap semiconductors and dielectric materials doped with transition metal ions continue to be of scientific interest today. This is due to the unique properties that they acquire through doping, which make them promising for use in various devices. For instance, experimental studies have shown that doping zinc oxide with transition metal ions may result in the material exhibiting ferromagnetic properties, even at room temperature [1]. Some of these studies suggest that the observed magnetic properties stem from ferro- or ferrimagnetic secondary transition metal nanoclusters. However, other mechanisms originating bulk magnetic properties, including hole-mediated exchange between magnetic ions (the Zener model), defect-related magnetism, etc., are also discussed [2].

In this work, iron-implanted ZnO thin films were studied by nuclear gamma-resonance (Mössbauer) spectroscopy. Ion implantation makes it possible to precisely introduce ions into a relatively thin near-surface layer of a sample, thereby modifying only the near-surface region of the material. Magnetron-sputtered ZnO thin films with a thickness of 135 nm on oriented Si(001) substrates were implanted with 40 keV Fe^+ ions (enriched to 40% in the ^{57}Fe isotope content) using an ILU-3 ion accelerator. The implantation was performed to fluence (dose) values in the range of 0.5–1.5 × 10^{17} ions/cm² using a constant ion beam current density of 8 μA/cm².

Nuclear gamma-resonance studies were performed using the conversion electron Mössbauer spectroscopy (CEMS) technique at room temperature. This method enables a depth-selective study of the valence and magnetic states of the introduced iron atoms as well as their local environment in the near-surface layer of the material. CEMS measurements were performed using a WissEl spectrometer equipped with a RiKon-5 detector. A ^{57}Co(Rh) source with an activity of 50 mCi was used. The spectrometer velocity scale was calibrated using the spectrum of a thin α-Fe foil. The spectra were fitted by a sum of model components using the least-squares method. The isomer shifts of the model components were determined relative to the α-Fe spectrum center of gravity at room temperature.

The CEMS results reveal the presence of Fe^0, Fe^{2+}, and Fe^{3+} ions in the studied samples. It was found that the relative content of these ions depends on the implantation fluence. The content of magnetically ordered iron ions, which appear in the spectra as a sextet with a distribution of hyperfine magnetic field values, has a nonmonotonic dependence on the fluence. The maximum content of iron ions in the magnetically ordered state was found in the sample with a fluence of $1 \cdot 10^{17}$ ions/cm^2. Depth-selective CEMS studies were performed on this sample, and the uniformity of the state of the iron ions at various depths was demonstrated.

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List of authors

Table of contents