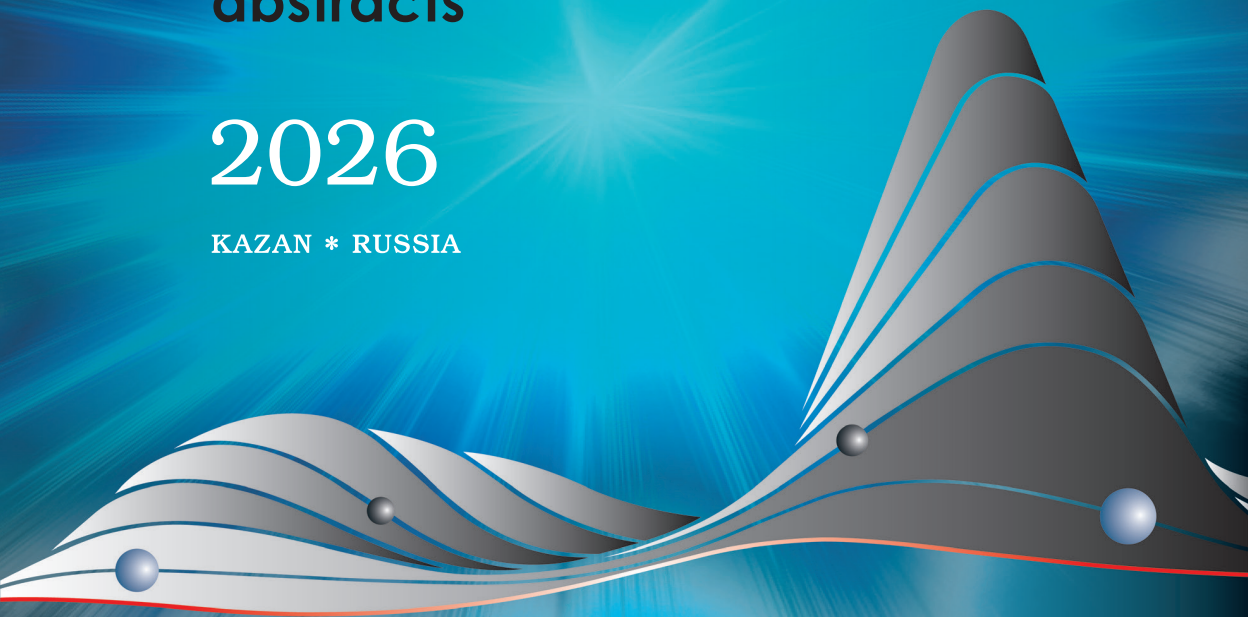


MODERN DEVELOPMENT OF MAGNETIC RESONANCE

abstracts

2026

KAZAN * RUSSIA



MODERN DEVELOPMENT OF MAGNETIC RESONANCE

ABSTRACTS OF THE
INTERNATIONAL CONFERENCE

THE CONFERENCE IS ORGANIZED AS PART
OF THE ANNUAL "KAZAN SCIENCE WEEK"

KAZAN, SEPTEMBER 28 – OCTOBER 02, 2026

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Криоприбор



ЭЛЕМЕНТ

ООО "Криогенные приборы" – ведущий российский производитель криостатов и криогенного оборудования.

За 17 лет работы нами поставлено более 200 криостатов и множество сопутствующего оборудования (гелиевых переливных линий, систем выдачи азота, систем сбора гелия, генераторов жидкого азота и т.п.).

Проточные гелиевые криостаты



Проточные гелиевые криостаты предназначены для проведения исследований образцов в диапазоне температур от <1.6 до 325 К.

Образец в таком криостате может быть расположен в вакууме либо в парах гелия (в динамическом потоке). В первом случае криостат может работать в любой ориентации, во втором – вертикально (с отклонением не более $\pm 30^\circ$ от вертикали), так как сам образец крепится на специальной загружаемой сверху вставке, которую можно извлечь для быстрой смены образца без необходимости отогрева всего криостата.

Существует специальная версия для микроскопии. Она имеет плоскую оптическую головку малой высоты (около 3-4 см) для размещения на предметном столике микроскопа, малое рабочее расстояние от поверхности окна до образца и специальную систему устранения термического дрейфа образца вдоль осей X и Y. Важным преимуществом



проточных криостатов является низкий уровень вибраций. Помимо этого, они имеют наиболее низкую цену среди всех систем, работающих при гелиевых температурах, и компактные размеры, что дает возможность легко перемещать криостат между лабораториями.

Азотные криостаты



Преимуществом азотных криостатов является простота конструкции (по сравнению с гелиевыми), низкая цена, широчайшие возможности по кастомизации, возможность применения недорогих, в т.ч. отечественных, температурных контроллеров. Такие криостаты просты в работе и не требуют сервисного обслуживания.

Обычно азотные криостаты изготавливаются в заливном исполнении, что обеспечивает низкий расход жидкого азота, а также устраняет необходимость в переливном устройстве. Однако возможна работа только в вертикальном положении (с отклонением не более $\pm 30^\circ$ от вертикали).

Базовая температура составляет 78К, однако в ряде случаев (при откачке паров азота) возможно ее снижение до ~ 65 К. Существуют модификации заливных криостатов для специальных применений, которые могут работать в любом положении (на рисунке слева).

В большинстве случаев образец в таких криостатах размещается в вакууме, реже

– в парах азота или в жидком азоте. Возможны как оптические, так и неоптические исполнения, в том числе под большие размеры образцов или с узким наконечником для использования совместно с магнитами.



Криостат открытого потока



Криостат открытого потока предназначен для охлаждения образцов, находящихся в атмосферном воздухе. Криостатирование образца производится в диапазоне температур 4,5 — 120 К при работе с жидким гелием, и от 80 до 150К при работе с жидким азотом. Возможно исполнение с охладителем замкнутого типа, которое позволяет использовать для работы газ из баллона, охлаждать его криорефрижератором и далее подавать на образец.

Конструкция криостата позволяет встроить его в рентгеновский дифрактометр, обеспечить равномерное захлаживание образцов и предоставить круговой доступ к образцу (во всех положениях гониометра) на близкой дистанции.

Между образцом, источником и детектором дифрактометра нет никаких преград, что существенно упрощает процесс исследований.

Заливные гелиевые криостаты

Заливные гелиевые криостаты предназначены для проведения исследований образцов в диапазоне температур от <2 до 325 К и выше. Преимущества: возможность работы при очень низких температурах (до 1.3 К), малый расход жидкого гелия, наименьшие вибрации среди всех стандартных криостатов.

Недостатки: возможность работы только в вертикальном положении и относительно высокая цена.

Образец в заливном гелиевом криостате может быть расположен в вакууме, в парах либо в жидком гелии. Во втором и третьем случае обычно доступна возможность быстрой смены образца без необходимости отогрева криостата. Криостат может быть выполнен как с азотной рубашкой, так и без нее, но первый вариант обеспечивает меньший расход гелия.



Криостаты замкнутого цикла (стандартное исполнение)

Это наиболее простые и бюджетные «сухие» криостаты. Они обеспечивают пользователю возможность термостатирования образца в диапазоне температур от 3...20 К до 325 К (опционально — до 500 К). Образец находится в вакууме. Замкнутый цикл позволяет полностью отказаться от жидких хладагентов (азота и гелия), из-за чего криостаты и называют «сухими». Криостаты на криорефрижераторах с циклом Гиффорда-МакМагона, могут работать в любом положении.



Такие криостаты не имеют подавления вибраций, они передаются на образец напрямую от криорефрижератора. В случае ГМ криорефрижераторов, вибрации на образце составляют ~20...800 мкм, а при использовании пульсационной трубы – 1...5 мкм.

Существуют как оптические, так и неоптические исполнения. Оптический доступ в стандартном исполнении к образцу возможен по двум взаимно-перпендикулярным осям. Доступна возможность установки дополнительного окна в торец криостата, либо

разработка оконного блока под задачи пользователя.



«Сухой» криостат с образцом в газе, или криостаты с верхней загрузкой образца («top-loading cryostat»)

Такие криостаты применяются в двух случаях: при частой смене образцов и при температурных исследованиях образцов с низкой теплопроводностью (например, порошков, теплоизоляторов или ячеек с жидкими образцами).

В конструкции такого криостата криогенный рефрижератор термически связан с нижней частью шахты. В шахту устанавливается шток (вставка) с держателем образца и напускается гелиевый газ, который выполняет функцию теплового проводника. Это позволяет эффективно термостатировать образцы с плохой теплопроводностью и/или образцы сложной формы, например, порошки различных материалов. Быстрая смена образцов возможна за счет того, что для не требуется отогревать весь криостат. Имеется возможность исполнения с низким (< 100 нм) уровнем вибраций, когда шток устанавливается на отдельный суппорт, расположенный, например, на оптическом столе. Отдельно стоит отметить криостат для Мессбауэровской спектроскопии, где криорефрижератор расположен снизу, и над ним расположена шахта под образец.



Криостат замкнутого цикла с образцом в вакууме с низким уровнем вибраций



Для снижения вибраций на образце в криостатах на базе криорефрижераторов на цикле Гиффорд-МакМагона разработаны специальные интерфейсы для устранения прямого контакта между самим рефрижератором и держателем образца. При этом блок образца монтируется на одной базе (например, на оптическом столе), а криорефрижератор — на другой (обычно на напольном суппорте). Типичный уровень вибраций в таких криостатах — менее 100 нм (согласно материалам зарубежных производителей и собственным тестам).

Из недостатков таких криостатов следует выделить достаточно большой размер, необходимость установки двух суппортов, а также снижение мощности охлаждения и повышение базовой температуры из-за наличия теплопередающего интерфейса.

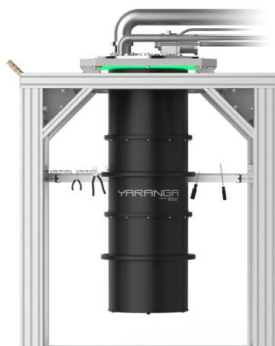
Есть специальная версия для оптической микроскопии, когда образец расположен в L-образно вынесенном блоке. Оптическая ось при этом может быть как параллельна, так и перпендикулярна оптическому столу (и может быть изменена в процессе эксплуатации).

Криостаты для работы с температурами ниже 1К

В этом диапазоне температур можно выделить 3 основных типа криостатов:

- криостаты на откачке паров ^4He (до ~0.9К) либо ^3He (до ~0.3К). Такие системы основаны на принципе конденсации жидкого ^3He либо ^4He с последующей его откачкой турбомолекулярным насосом. Имеют три ступени охлаждения (50К, 4К, 1/0.3 К);
- криостаты растворения ^3He - ^4He . Не работают до температур <20 мК. Имеют четыре ступени охлаждения (50К, 4К, 1К, <50 мК);
- криостаты с модулем ядерного размагничивания, которые позволяют работать с температурами ниже 1 мК. Имеют пять ступеней охлаждения (50К, 4К, 1К, 20 мК, NDR).

Основные применения: физика сверхнизких температур, исследования кубитов, построение квантовых компьютеров. Образец находится в вакууме, при этом медная пластина для размещения образцов обычно имеет диаметр от 200 до >500 мм. В предлагаемых нами системах к этой пластине можно подвести до 200 коаксиальных проводов.



Помимо этого, наша компания готова изготовить нестандартные криостаты практически под любые задачи пользователя. Мы открыты к сотрудничеству с научными группами по созданию новых приборов.

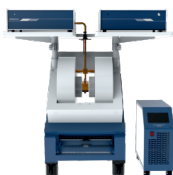
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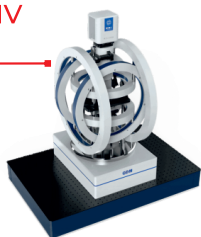
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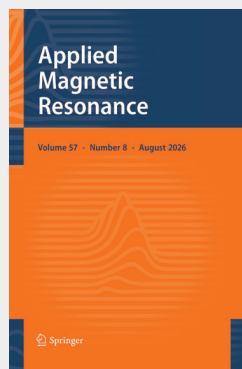
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Columns



Applied Magnetic Resonance



Applied Magnetic Resonance provides an international forum for the application of magnetic resonance methodology in physics, chemistry, biology, medicine, geochemistry, ecology, engineering, and related fields.

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This special issue welcomes papers demonstrating applications of magnetic resonance spectroscopy. Topics covered include, but are not limited to:

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- Chemical and biological systems
- Defects and spin qubits
- Magnetic resonance imaging and applications in medical physics

The submission deadline is 30 November 2026.

Please make sure to choose the special issue article tab “MDMR2026”.

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SECTIONS

- ADVANCES IN MAGNETIC RESONANCE THEORY AND INSTRUMENTATION
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- LOW-DIMENSIONAL SYSTEMS, NANO-SYSTEMS AND MOLECULAR MAGNETS
- SPIN-BASED INFORMATION PROCESSING AND OPTICAL QUANTUM TECHNOLOGIES
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- CHEMICAL AND BIOLOGICAL SYSTEMS
- DEFECTS AND SPIN QUBITS
- MAGNETIC RESONANCE IMAGING AND APPLICATIONS IN MEDICAL PHYSICS
- MÖSSBAUER SPECTROSCOPY AND ITS APPLICATIONS
- RELATED PHENOMENA

SECTION COLOR SCHEME

ADVANCES
IN MAGNETIC
RESONANCE
THEORY AND
INSTRUMENTATION

MODERN
METHODS OF
MAGNETIC
RESONANCE

LOW-DIMENSIONAL
SYSTEMS,
NANO-SYSTEMS
AND MOLECULAR
MAGNETS

SPIN-BASED
INFORMATION
PROCESSING AND
OPTICAL
QUANTUM
TECHNOLOGIES

STRONGLY
CORRELATED
ELECTRON
SYSTEMS

CHEMICAL AND
BIOLOGICAL
SYSTEMS

DEFECTS
AND
SPIN QUBITS

MAGNETIC
RESONANCE
IMAGING AND
APPLICATIONS IN
MEDICAL PHYSICS
SYSTEMS

MÖSSBAUER
SPECTROSCOPY
AND ITS
APPLICATIONS

RELATED
PHENOMENA

CONTENTS

ZAVOISKY AWARD LECTURE

ESR spectroscopy of quantum-disordered states in spin chains <i>A.I. Smirnov</i>	2
---	---

PLENARY LECTURES

Optically detected cross-relaxation in dielectric and semiconductor crystals <i>R.A. Babunts, N.G. Romanov, P.G. Baranov</i>	5
Application of new spin labels to the study of biomolecular structure <i>E.G. Bagryanskaya</i>	6
The Landau-Lifshitz equation, the Gilbert equation, and the description of EPR using semiclassical magnetization dynamics: breaking stereotypes and new effects <i>S.V. Demishev</i>	7
Nano-scale clustering of mono-spin-labeled molecules from double electron-electron resonance data <i>S.A. Dzuba</i>	9
Inversion recovery EPR characterizes the impact of Heisenberg exchange on nitroxide T_1 in low viscosity solutions <i>S.S. Eaton, G.R. Eaton</i>	10
Multi-extreme THz ESR: Developments and future directions <i>H. Ohta, S. Okubo, T. Sakurai, E. Ohmichi, M. Fujiwara</i>	11
On the narrowing effect of EPR spectra due to particle motion and its potential implications for other scientific disciplines <i>K.M. Salikhov</i>	12
Study of the photophysics of the compact electron donor-acceptor compounds using time-resolved electron spin resonance spectroscopy <i>Jianzhang Zhao, A.A. Sukhanov, V.K. Voronkova</i>	14

SECTION 1

ADVANCES IN MAGNETIC RESONANCE

INVITED

Emerging ODMR techniques for spin dynamics in solids <i>V.V. Belykh</i>	16
Short-lived cation radicals visualized by CIDNP <i>O.B. Morozova, N.N. Fishman, I.V. Zhukov, M.P. Geniman, A.V. Yurkovskaya</i>	17
Nuclear hyperpolarization in electron transfer in chiral systems <i>N.E. Polyakov, I.M. Magin, T.V. Leshina, K.M. Salikhov</i>	18
A quantitative EPR method based on electron relaxation time distribution tested on the dual NMR/EPR spectrometer <i>Wenyu Li, Yang Chen, Yong Li, Haijun Yang</i>	19
Using nuclear hyperpolarization in photoinduced electron transfer to study chiral induced electron spin selectivity <i>K.M. Salikhov</i>	20
Spin 3/2 paramagnet, spin 1/2 quantum chains and a weakly ordered antiferromagnet in Cs_2CoCl_4 <i>A.I. Smirnov, T.A. Soldatov</i>	21
Features of ESEEM in the study of photosystem I in trehalose matrix <i>A.A. Sukhanov, M.D. Mamedov, G.E. Milanovsky, A.Y. Semenov, K.M. Salikhov</i>	23
π -Topology, spin alignment, DEP generation and ESPT of photogenerated organic multi-spin π -systems <i>Y. Teki</i>	24
Dimerization of NO molecules as the initial stage of iron dinitrosyl complexes formation in animals and humans <i>A.F. Vanin</i>	25
Multi-pulse protocols in EPR: From spectral diffusion suppression to quantum zeno analogy <i>R.B. Zaripov, K.M. Salikhov</i>	26
ORAL	
Broadband ESR spectrometer based on VNA and its application for FM materials <i>I.I. Gimazov, I.N. Khamidullin, M.N. Markelova, I.E. Graboi, A.R. Kaul</i>	27
Photoinduced spin dynamics in rigid chromophore–radical compounds <i>Yu.E. Kandrashkin</i>	28
Low-field NMR of ^{129}Xe at low temperatures: frequency and temperature dependences of spin-lattice relaxation in liquid and solid phases near triple point <i>K.O. Sannikov, A.V. Klochkov</i>	29

Infrared spectroscopy with the advantages of synchrotron radiation sources: global experience and prospects for the “IR-diagnostics” beamline at the skif facility <i>S.L. Veber, A.R. Melnikov, N.A. Tashkeev, A.V. Borodulina, I.A. Milekhin, A.G. Milekhin, E.S. Zhimuleva, A.V. Soldatenko, N.A. Vinokurov, K.V. Zolotarev, Ya.V. Zubavichus</i>	30
Transferred hyperfine interactions in $\text{CaF}_2\text{:Pu}^{3+}$ according to ENDOR <i>R.R. Ziatdinov, M.V. Eremin</i>	31
Quantum dynamics in Krylov space and operator growth: a study using multiple-quantum NMR <i>V.E. Zobov, A. A. Lundin</i>	32
POSTER	
Pulsed and steady-state thermal annealing of sapphire single crystal implanted with chromium ions: Optical and EPR studies <i>R.I. Batalov, V.F. Valeev, H.A. Novikov, N.V. Kurbatova, K.I. Gerasimov, R.B. Zaripov</i>	34
Simulation of a specialized dual-frequency sensor for MRI 0.4 T <i>A.A. Bayazitov, A.R. Fakhrutdinov, Ya.V. Fattakhov, V.L. Odivanov, V.A. Shagalov</i>	35
Features of the search for an analytical solution of Bloch equations with nonlinear coefficients for describing the modulation technique for recording a nuclear magnetic resonance signal <i>R.V. Davydov, D.S. Provodin, V.V. Davydov</i>	36
EPR spectroscopy of rare earth ions in a CsCaF_3 crystal <i>M.L. Falin, V.A. Latypov, S.L. Korableva</i>	40
Orientational motions of nitroxide molecules in glassy ethanol and dibutyl phthalate studied by CW and pulsed EPR <i>S.V. Komlina, A.N. Atnyukova, S.A. Dzuba</i>	41
Magnetic properties of ludwigite $\text{Mn}_{0.53}\text{Mg}_{2.47}\text{BO}_5$ in the temperature range 300–570 K <i>A.A. Rakhmonov, R.M. Eremina, I.I. Fazlizhanov, E.M. Moshkina</i>	42
Exchange and dipolar interactions in some photoexcited systems <i>A.A. Sukhanov, V.K. Voronkova, Zhanjun Li, J. Zhao</i>	44
Effect of quantum interference under simultaneous excitation of magnetic dipole and electric quadrupole resonance transitions <i>V.F. Tarasov, R.B. Zaripov, B.A. Ulanov</i>	46

SECTION 2

MODERN METHODS OF MAGNETIC RESONANCE

ORAL

- Semiconductors: parameters and possible nature of CIDNP
I.A. Frolov, P.A. Purtov 48

- Weighted least-squares approach to the weak-signal problem
 in orientational studies of graphene oxide membranes
G.E. Slivin, N.A. Chumakova 49

- Dispersion shape of the EPR spectra lines of the impurity Gd^{3+} ions
 in the narrow-gap $Pb_{1-x}Ag_xS$ semiconductors: parameters and possible
 nature of the effect
V.A. Ulanov, R.R. Zainullin, I.V. Yatzyk, I.I. Fazlihanov 51

POSTER

- Simulation of chirp pulse inversion performance in an inhomogeneous
 RF field
I.T. Khairutdinov 53

- High-field EPR spectroscopy for measuring magnetic resonance parameters
 of heterospin complexes of Cu(II)
A.A. Samsonenko, S.E. Tolstikov, S. Wu, Z.Wang, S.L. Veber 55

SECTION 3

LOW-DIMENSIONAL SYSTEMS, NANO-SYSTEMS AND MOLECULAR MAGNETS

INVITED

- Low-lying electronic energy levels correlate with faster electron spin
 lattice relaxation rates for lanthanide complexes in diverse coordination
 environments
G.R. Eaton, S.S. Eaton 57

- ODMR based mapping of diamond and silicon carbide with nanometer
 resolution
*V.V. Yakovleva, M.V. Uchaev, A.M. Skomorokhov, K.V. Likhachev,
 A.V. Nikitina, I.P. Veyshkort, A.S. Gurin, P.G. Baranov, R.A. Babunts* 58

ORAL

- Magnetic properties of PrF_3 nanoparticles
E.M. Alakshin, A.M. Garaeva, B.M. Mukhamadullin, E.I. Boltenkova 60

- ^3He NMR based measurement of the paramagnetic layer depth
 in $LaF_3:Gd^{3+}$ delta doped nanoparticles
*G.A. Dolgorukov, A.S. Makarchenko, A.M. Garaeva, E.I. Boltenkova,
 V.V. Kuzmin* 61

Polarized neutron reflectometry in oscillating magnetic fields: resonant phenomena in low-dimensional magnetic systems <i>E.D. Kolupaev, V.D. Zhaketov, A.N. Chernikov, Yu.V. Nikitenko</i>	63
Modeling of the magnetic response of low-scaled spin structures <i>E.I. Kovychева, K.B. Tsiberkin, V.K. Henner</i>	65
The influence of graphene oxide membranes architecture on their functional properties <i>M.V. Matveev, N.A. Chumakova</i>	67
¹ H NMR monitoring of DyF ₃ nanoparticle agglomeration <i>B.M. Mukhamadullin, A.M. Garaeva, E.I. Boltenkova, M.Yu. Volkov, E.M. Alakshin</i>	68
Modeling of structural and magnetic properties of Gd _{1-x} R _x MO ₃ compounds <i>I.V. Romanova, V. A. Achintseva, O.V. Nedopekin</i>	69
Dependence of the ferromagnetic–paramagnetic transition temperature on microwire size in Co ₈₃ Fe ₇ C ₁ Si ₇ B ₂ and Fe ₄₅ Co ₃₀ Si ₁₀ B ₁₅ <i>A.V. Shestakov, I.I. Fazlizhanov, R.M. Eremina, S.V. Demishev, V.V. Rodionova, V.G. Kolesnikova</i>	70
Transition between transverse relaxation and regular spin dynamics in dipole chain <i>K.B. Tsiberkin</i>	72
POSTER	
Control of temperature dependence of coercive force in multilayer epitaxial films Pd _{96-x} Fe ₄ Co _x <i>D.K. Davlyatshina, I.V. Yanilkin, A.I. Gumarov</i>	73
Melting of the surface layer of the implanted GaAs and Si by the halogen incandescent lamps <i>B.F. Farrakhov, Ya.V. Fattakhov</i>	74
Influence of anions on the magnetic properties of mixed-valence heptanuclear iron complexes <i>E.N. Frolova, O.A. Turanova, A.R. Sharipova, E.E. Batueva, L.V. Bazan, R.F. Likerv, R.G. Batulin, M.A. Cherosov, A.A. Sukhanov, A.N. Turanov</i>	75
Observation of an unusual double quantum transition in the EPR spectrum <i>R.T. Galeev, R.B. Zaripov</i>	76
Study of the magnetic properties of micro and nanosized DyF ₃ powder <i>A.M. Garaeva, I.V. Romanova, E.I. Boltenkova, E.M. Alakshin</i>	77
Resonance response of finite two-dimensional ising-like ferromagnets <i>S.A. Klimova, A.A. Goldberg, R.V. Davydov, V.V. Davydov</i>	78
Engineering electronic and magnetic behavior in functionalized MXene nanoclusters via first-principles calculations <i>H. Mohammadi, I.V. Romanova, I.G.S. Acosta, O.V. Nedopekin</i>	80
Conditions of 180° switching of the quasiuniform magnetization in planar Ni particles by thermally induced magnetoelastic effect <i>N.I. Nurgazizov, D.A. Bizyaev, A.A. Bukharaev, A.P. Chuklanov</i>	81

Compositional structure influence on FMR properties of epitaxial $\text{Pd}_{1-x}\text{Fe}_x/\text{Pt}$ thin film bilayers <i>Zh.Kh. Pulotov, B.F. Gabbasov, I.V. Yanilkin, A.I. Gumarov, A.G. Kiiamov, L.R. Tagirov, R.V. Yusupov</i>	82
Synthesis and magnetic properties of dysprosium-doped lutetium titanates and lanthanum zirconates with pyrochlore structure <i>M.A. Severina, T.Z. Sharifullin, P.E. Kazin, A.V. Vasiliev</i>	85
The shape change of Neel's skyrmion as a result of an electric field <i>T.S. Shaposhnikova, R.F. Mamin</i>	86
^1H NMR study of acetonitrile fractions and relaxation in graphite oxide <i>Yu.V. Slesareva, M.Yu. Volkov, D.A. Astvatsaturov, N.A. Chumakova, E.L. Vavilova</i>	87
Spin 1/2–3/2 crossover in a chain antiferromagnet Cs_2CoCl_4 <i>T.A. Soldatov, A.I. Smirnov</i>	88
Low temperature magnetism and g-factor anisotropy in the compound $\text{CaCuSi}_4\text{O}_{10}$ <i>R. Tagirov, A. Azarevich, A. Samarin, S. Kozyukhin, S. Bezzubov, A. Semeno, V. Glushkov</i>	90
Anisotropic magnetoresistance in magnetic tunnel junctions <i>N.Kh. Useinov</i>	93

SECTION 4

SPIN-BASED INFORMATION PROCESSING AND OPTICAL QUANTUM TECHNOLOGIES

POSTER

A selective pulse sequence for implementing associative memory on two qutrits via quantum annealing <i>I.S. Pichkovskiy, V.E. Zobov</i>	95
Control of the states of quadrupole nuclei through hyperfine interaction with electrons <i>V. E. Zobov, V. P. Shauro</i>	97

SECTION 5

STRONGLY CORRELATED ELECTRON SYSTEMS

INVITED

Magnetic order in nabokoite family compounds <i>I.N. Glazkov, M.A. Dubovitskii, Ya.V. Rebrov, M.M. Markina, A.F. Murtazoev, P.S. Berdonosov, A.N. Vasiliev</i>	99
---	----

High field ESR measurements of the interacting spin dimer systems <i>S. Kimura, M. Matsumoto, M. Akaki, Y. Narumi, M. Hagiwara, K. Kindo, H. Tanaka</i>	100
Topological foundations of the scaling behavior of superconductors <i>V.R. Shaginyan</i>	101
ORAL	
A new permanent macroscopic coherent quantum state at room temperature <i>Yu. Bunkov</i>	102
Properties of ludwigite Cu_2MnBO_5 <i>R.M. Eremina, I.I. Fazlizhanov, I.V. Yatsyk, A.V. Khusanzyanov, E.M. Moshkina</i>	103
Electron paramagnetic resonance and magnetic oscillation modes described by semiclassical spin dynamics with combined relaxation term <i>A.V. Popov, S.V. Demishev,</i>	104
Impact of manganese ions on magnetic and structural properties of cobalt containing ludwigites <i>D.V. Popov, R.G. Batulin, M.A. Cherosov, I.V. Yatsyk, V.A. Shustov, E.M. Moshkina, R.M. Eremina</i>	106
Electron spin resonance probing of antiferromagnetic state in CeB_6 <i>A. Semeno</i>	107
Electron-polaron transition and high-temperature phonon drag in $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{Ti}_{0.3}\text{Mn}_{0.3}\text{O}_{3-\delta}$ perovskite <i>I.V. Yatsyk, A.V. Khusanzyanov, R.F. Likero, A.V. Shestakov, R.M. Eremina</i>	109
POSTER	
The effect of a superconducting spin valve in a Py/Pb/Py heterostructure with oxidized interfaces <i>D. Arbuzov, A. Kamashev, N. Garifyanov, I. Garifullin</i>	111
ESR investigation of magnetic inhomogeneities in the pentaborate $\text{GdMnB}_5\text{O}_{10}$ <i>T.P. Gavrilova, A.R. Gafarova, R.B. Zaripov, I.V. Yatsyk, A.I. Zaitsev, A.V. Cherepakhin, E.M. Moshkina</i>	112
Spin nematicity in the Eu ternary pnictides: the ESR viewpoint <i>Yu. Goryunov, A. Nateprov</i>	114
Critical temperature of thin superconducting films within the proximity-effect theory in the dirty limit <i>B.R. Mukhamaturov, T.D. Kremlev, V.A. Tumanov, Yu.N. Proshin</i>	116
Magnetisation and magnetic resonance in relaxor ferroelectrics with double perovskite structure $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbCo}_{1/3}\text{Nb}_{2/3}\text{O}_3$ <i>M.I. Nasyrova, I.A. Sotnikov, M.A. Cherosov, A.A. Rodionov, R.V. Yusupov, S.G. Lushnikov</i>	118

Processing and analysis of the electron paramagnetic resonance line shape in the noncentrosymmetric magnet $\text{Mn}_{1-x}\text{Rh}_x\text{Si}$ <i>A.E. Os'kin, S.V. Demishev</i>	119
Fabrication of photomasks using combined photo- and scanning probe lithography techniques <i>A.A. Validov, D.A. Bizyaev, D.A. Arbuzov, N.N. Garyf'yanov, A.A. Kamashev, I.A. Garifullin</i>	122

SECTION 6 CHEMICAL AND BIOLOGICAL SYSTEMS

INVITED

Water molecules and biologically active substances in RBC on NMR data <i>I.A. Avilova, D.L. Melnikova, V.D. Skirda, V.I. Volkov</i>	124
Comprehensive use of NMR methods in studying microstructure and molecular mobility in ionic liquid systems <i>V.I. Chizhik</i>	126
Applications of EPR spectroscopy to heterojunction photocatalysts <i>M.V. Fedin</i>	128
Structural reorganization of VO^{2+} complexes on the surface of TiO_2 <i>A.I. Kokorin, S.O. Travin, A.I. Kulak</i>	129
Photoelectronic properties of optical sensor platforms based on anodic aluminum oxide <i>E.A. Konstantinova, E.V. Kytina, O.A. Shalygina, V.B. Zaitsev, Yu.V. Nazarkina, P.P. Shcherbakov</i>	131
Structural characterization of conformationally heterogeneous biomolecular complexes with photoactive ligands by pulsed dipolar EPR spectroscopy <i>O.A. Krumkacheva, N.E. Sannikova, M.I. Kolokolov, S.A. Dementev, R.A. Podarov, M.V. Fedin</i>	133

ORAL

EPR study of graphite oxides with different oxidation levels <i>D.A. Astvatsaturov, E.L. Vavilova, M.Yu. Volkov, Yu.V. Slesareva, N.A. Chumakova</i>	134
MRI investigation of the development of bird embryos <i>Ya.V. Fattakhov, A.R. Fakhrutdinov, V.L. Odivanov, A.A. Bayazitov, V.A. Shagalov, V.O. Ezhkov, A.M. Ezhkova</i>	135
EPR study of nitric monoxide content in the brain of rats after combined brain and spinal cord injury <i>Kh.L. Gainutdinov, V.V. Andrianov, A.I. Arslanov, L.V. Bazan, T.K. Bogodvid, I.B. Deryabina, L.N. Muranova, D.I. Silantyeva, G.G. Yafarova, S.G. Pashkevich, Yu.P. Tokalchik, T.A. Filipovich</i>	136

Comparative analysis of paramagnetic centers in nanosized anodic aluminum oxide synthesized in organic and inorganic acids and subjected to additional etching and annealing <i>E.V. Kytina, Yu.V. Nazarkina, P.P. Shcherbakov, E.A. Konstantinova</i>	138
Disentanglement of intra- and inter-molecular pathways of photoinduced electron transfer in biomimetic Trp-Pro _n -F dyads by time-resolved and field-cycling CIDNP <i>O.B. Morozova, A.S. Kiryutin, I.V. Zhukov, A.V. Yurkovskaya</i>	140
NMR study of supramolecular drug delivery systems and drugs interaction with lipid membranes <i>N.E. Polyakov, O.Yu. Selyutina, Q. Zhang, A.V. Dushkin, Can Jin</i>	142
Analysis and simulation of EPR spectra of iron-doped bioactive glasses using the Czjzek distribution <i>D.A. Saritsky, D.N. Grishchenko, M.A. Medkov, A.M. Ziatdinov</i>	143
Automated prediction of natural carbohydrate structure from 2D NMR data <i>Ph.V. Toukach</i>	145
POSTER	
2D noesy NMR spectroscopy study of mechanoactivated Ca and Mg gluconates <i>M.M. Akhmetov, M.Yu. Volkov, G.G. Gumarov, D.S. Rybin</i>	146
Multinuclear ¹ H and ³¹ P NMR characterization of hydrogen-bonded complexes of phosphine oxide <i>O. Alkhuder, M.A. Kostin, P.M. Tolstoy</i>	147
Differences in the hydrodynamic radius of block and gradient copolymers in dilute solution <i>A.A. Elizarova, O.V. Malyshkina, O.V. Shavykin</i>	149
Features of the EPR spectra of serum ceruloplasmin in patients with undifferentiated connective tissue dysplasia <i>M.I. Ibragimova, A.I. Chushnikov, I.V. Yatsyk, D.Kh. Khaibullina, G.G. Gumarov</i>	150
NMR spectroscopy of the interaction between 4,6-dinitro-7-chlorobenzofuroxan and an oligonucleotide <i>L.A. Kontorina, E.M. Gibadullina, E.A. Chugunova, B.I. Khairutdinov</i>	152
Analysis of the anticancer potential of novel (hetero)aromatic derivatives using NMR spectroscopy and molecular modeling methods <i>I.R. Nigmatullin, E.A. Ermakova, E.M. Gibadullina, E.A. Chugunova, B.I. Khairutdinov</i>	153
Is local mobility in lysine-based dendrigrafts similar to that in dendrimers or chains? <i>O.V. Shavykin, E.I. Fatullaev, I.M. Neelov, D.M. Markelov</i>	154
Features of T ₂ behavior of water in aqueous sugar solutions <i>D.A. Tsukhlova, D.L. Melnikova, E.A. Shchitova, V.D. Skirda</i>	155

2D NMR study of phthalazole <i>M.Yu. Volkov</i>	156
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Observation of noise-like magnetic resonance fine structure in spectra of biological tissues <i>S.V. Yurtaeva, I.V. Yatsyk, A.A. Rodionov</i>	157
--	-----

SECTION 7

DEFECTS AND SPIN QUBITS

POSTER

Electron-nuclear interactions of V_B^- centers and ^{11}B shells in hexagonal boron nitride <i>E.V. Dmitrieva, G.V. Mamin, F.F. Murzakhanov, I.N. Gracheva, M.R. Gafurov, V.A. Soltamov</i>	160
---	-----

Spin properties and electron-nuclear interactions of axial NV centers in 6H-SiC: spectroscopic and theoretical study <i>Yu.E. Ermakova, E.V. Dmitrieva, D.V. Shurtakova, F.F. Murzakhanov, I.N. Gracheva, M.A. Sadovnikova, G.V. Mamin, M.R. Gafurov</i>	161
---	-----

Comprehensive studies of magnetic and optical spectroscopic properties of PbGa_2S_4 crystals doped by Ho^{3+} and Na^+ ions <i>V.I. Kolesnikova, G.S. Shakurov, V.V. Semashko, D.V. Badikov</i>	163
--	-----

Research of oxygen vacancies in two types of $\alpha\text{-SiO}_2$ (G2 fused silica and G3 natural silica) using EPR under γ -radiation <i>L.V. Nikiforov, D.V. Dmitrieva, D.S. Dmitrieva, V.V. Davydov</i>	164
---	-----

Spin dynamics and local structure in $\text{Pb}_{1-x}\text{Cu}_x\text{S:Mn/Gd}$ probed by pulsed EPR <i>R.B. Zaripov, V.A. Ulanov, R.R. Zainullin</i>	166
--	-----

SECTION 8

MAGNETIC RESONANCE IMAGING AND APPLICATIONS IN MEDICAL PHYSICS SYSTEMS

POSTER

Mixed-valence heptanuclear iron complex as a potential MRI contrast agent <i>E.E. Batueva, L.I. Savostina, O.A. Turanova, A.N. Turanov</i>	168
---	-----

Improving the structural correspondence of MRI studies using a modified TransMorph neural network <i>N.A. Nefediev, N.E. Staroverov, R.V. Davydov</i>	169
--	-----

Gradient pulse shaper for NMR or MRI installation <i>V.L. Odivanov, A.R. Fakhrutdinov, Ya.V. Fattakhov, V.A. Shagalov, A.A. Bayazitov</i>	171
--	-----

CTCF as a backbone-agnostic cascade plug-in for deformable 3D brain MRI registration <i>D.V. Pasenko, R.V. Davydov</i>	172
Computer simulation of hydroxyapatite doping with vanadium: search for thermodynamically stable configurations <i>A.A. Petrova, L.I. Savostina, M.R. Gafurov</i>	174

SECTION 9

MÖSSBAUER SPECTROSCOPY AND ITS APPLICATIONS

ORAL

Increasing the efficiency of a special wireless communication system based on the stochastic gamma-ray flow <i>F.G. Vagizov, A.L. Zinnatullin, R.N. Shakhmurov</i>	176
Nanoscale magnetic inhomogeneities in Fe–Al alloys with Ga and B additions: structure, stability, and temperature evolution <i>E.V. Voronina, A.F. Abdullin, A.V. Korolev, A.K. Arzhnikov</i>	177
Combined Mössbauer effect and DFT studies of the hyperfine interactions and lattice dynamics in phosphaferrrocenes <i>A.L. Zinnatullin, A.A. Zagidullin, I.A. Bezkishko, V.A. Milyukov, F.G. Vagizov</i>	179

SECTION 10

RELATED PHENOMENA

ORAL

Magnetic hysteresis of paramagnetic LiDyF_4 : a magnetocaloric model <i>G.Iu. Andreev, E.I. Baibekov, I.V. Romanova</i>	181
Entropy: a perspective based on NMR relaxation times <i>L. Grunin, M. Ivanova</i>	182
Conducting and superconducting films with local electric field on interphases <i>R.F. Mamin, V.V. Kabanov, A.S. Sigov</i>	184

POSTER

Electron spin resonance and magnetic properties of ZnO and Cu-doped ZnO: Effect $\text{As}^{3+}/\text{As}^{5+}$ treatment <i>T.P. Gavrilova, A.R. Gafarova, D.V. Mamedov, I.V. Yatsyk, O.I. Gyrdasova</i>	185
High-entropy perovskite-like oxide $(\text{BaCaSrLaNa})_{0.2}\text{FeO}_3$: Synthesis, EPR and magnetometry measurements <i>R.F. Likеров, I.V. Yatsyk, R.M. Eremina, R.G. Batulin, M.A. Cherosov</i>	187
Prospects for the use of LiHoF_4 microparticles in LIR^2 thermometry <i>A.D. Shishkin, V.V. Semashko, V.I. Kolesnikova, G.S. Shakurov</i>	189

ZAVOISKY
AWARD
LECTURE

ESR spectroscopy of quantum-disordered states in spin chains

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$S = 1/2$ spin chains with antiferromagnetic exchange have a peculiar quantum-disordered ground state, featured by the absence of a classic magnetic order. By classic order we mean the spin structure with an ordered spin component, as, e.g., in a ferro- or antiferromagnet. The quantum-disordered (or quantum spin-liquid) ground state is strongly correlated and may be described as an ensemble of delocalized quasiparticles with spin $S = 1/2$. The spins at the lattice sites are strongly fluctuating which destroys the anticipated classic order. The quasiparticles are not like magnons in systems with a long-range spin order. They have spin $S = 1/2$, they are fermions and are called spinons see, e.g., [1–3]. In experiments on inelastic neutron scattering or electron spin resonance the quasiparticle-hole pairs are created by a spinon transfer from a position inside the Fermi-surface to a position outside. Thus the spectrum of the transmitted energy at a fixed transmitted pulse is a continuum, radically different from the sharp magnon peaks in a conventional antiferromagnet.

To search for the details of spinon physics we study, in particular, the low-temperature absorption spectra of microwaves in crystals $\text{K}_2\text{CuSO}_4\text{Br}_2$ [4], Cs_2CuCl_4 [5] and others, hosting chains of Cu^{2+} -ions ($S = 1/2$). We obtain experimental evidence for the concept of spinons and their chirality. Besides, we detect the Fermi-liquid interaction between the spinons. The temperature of experiments should be much lower than the intra-chain exchange energy J/k_B to get the intra-chain correlations as in a hypothetical single chain studied in theory. On the other side, the temperature should be higher than the temperature of 3D ordering which appears under the action of a weak interchain exchange J'/k_B . Practically, for the above crystals the temperature range of experiments should cover the interval between 0.1 and 10 K. The interaction of spinons with the chiral crystal surrounding results in the fine structure of the spinon continuum. The fine structure has a form of a doublet of ESR absorption which is due to a difference of energies of spinons moving to the right and to the left in the same chain [5]. We observe a doublet split for about 10 GHz which is about 1% of the typical spinon energy. The interaction of spinons of the “backscattering” type, provides an additional shift of the boundaries of the spinon continuum in presence of a magnetic field. This shift reveals the Fermi-liquid interaction of spinons. From the experimental position of the continuum boundaries and their dependence on the magnetic field, we deduce the probability of scattering of spinons and the change of the spinon spectrum due to interaction of the Fermi-liquid type [6]. The Fermi-liquid interaction was detected to give a shift of the spectrum of about 10% of the Larmor energy.

The results indicate the specific kind of a Fermi-liquid (not a Fermi-gas) of spinons. In contrast to the known fermionic systems like Fermi-liquid of electrons in metals or liquid ^3He , where fermions are microparticles of matter, the fermions in $S = 1/2$ spin chains are collective dynamic structures of localized spins.

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PLENARY LECTURES

Optically detected cross-relaxation in dielectric and semiconductor crystals

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Cross-relaxation occurs due to energy-conserving spin flips between two distant paramagnetic defects tuned to resonance by the magnetic field. Since the early work of Bloembergen et al. [1], in which the theory of cross-relaxation was formulated, cross-relaxation has been extensively studied. Optically detected magnetic resonance (ODMR) has proven to be very effective in studying such processes. Of particular interest at present are cross-relaxation resonances in diamond (first described in [2]) and silicon carbide. The report summarizes the results of observations of cross-relaxation resonances discovered during our studies of ODMR in dielectric and semiconductor crystals at the Ioffe Institute. The following phenomena are considered:

1. Cross-relaxation between optically pumped F-centers and impurity defects in irradiated crystals of alkali halides doped with thallium and indium, detected by monitoring magnetic circular dichroism in the absorption of F-centers;
2. Manifestation cross-relaxation Ce^{3+} - Gd^{3+} in the luminescence of Ce^{3+} in garnet crystals co-doped with cerium and gadolinium;
3. Cross-relaxation resonances in the photoluminescence of localized heavy-hole excitons in GaAs/AlAs superlattices;
4. Cross-relaxation between NV centers and loosely coupled pairs of substitutional nitrogen atoms in diamond;
5. Cross-relaxation between optically active $S = 3/2$ vacancy centers and other defects in silicon carbide.

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Application of new spin labels to the study of biomolecular structure

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The method of pulsed dipole EPR spectroscopy is widely used to study the structure and functions of biological molecules – proteins and nucleic acids [1]. The method is based on the use of special pulse sequences PELDOR, DEER, SIFTER, which allow measuring nanometer distances between spin labels selectively introduced into biomolecules. Nitroxyl and triarylmethyl radicals, as well as gadolinium and copper complexes, are used as spin labels. The report provides an overview of work with the participation of the Institute of Organic Chemistry SB RAS in the field of using spin labels based on triarylmethyl [2, 3] and stereosubstituted nitroxyl radicals [4] for studying the complex of enzyme, DNA and inhibitor [5–8]. The first application of a triply orthogonal PELDOR/DEER approach to investigate the TDP1-DNA-inhibitor system [8]. By measuring the dipolar couplings between the three distinct labels, we not only confirm the formation of the ternary complex in solution but also reveal its conformational dynamics. To robustly interpret the experimental distance distributions, we complemented our EPR data with extensive molecular dynamics (MD) simulations. As a result of molecular modeling, a stable model of the complex of the labeled Tdp1 enzyme with the labeled oligonucleotide was successfully constructed, reproducing the experimentally measured distance between the spin labels. This integrated approach provides unprecedented structural insights into the inhibition mechanism of TDP1 by usnic acid derivatives and establishes a powerful methodological framework for studying similar multi-component enzymatic systems.

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The Landau-Lifshitz equation, the Gilbert equation, and the description of EPR using semiclassical magnetization dynamics: breaking stereotypes and new effects

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This paper examines the semiclassical description of magnetization dynamics by the Landau-Lifshitz (LL) and Gilbert (G) equations. Our studies [1–5] have revealed a number of aspects of the application of this approach to the calculation of electron paramagnetic resonance (EPR) that go beyond the stereotypes established in the literature [6]. The paper will show that:

- The difference in the form of the relaxation term makes the LL and G equations fundamentally different, and therefore the standard formal reduction to a unified Landau-Lifshitz-Gilbert equation has no physical meaning [1]. Simultaneously, a new form of semiclassical master equation for the description of dynamical magnetic properties may be suggested [1].
- The LL and G equations predict different types of magnetization dynamics when taking into account classical and quantum magnetic fluctuations [1,2].
- In the case of semiclassical magnetization dynamics described by the Landau-Lifshitz equation, more interesting and rich physical behavior arises than in the case of the Gilbert equation. For example, anisotropic spin fluctuations in the LL equation lead to an anisotropic relaxation time, resulting in a strong dependence of the EPR amplitude on the direction of the microwave field vector causing the magnetic oscillations (polarization effect [1,3]).
- The LL equation in the regime of strong magnetic fluctuations predicts a universal relationship between the line width and the g-factor [1,2].
- The LL equation with an anisotropic relaxation time and g-factor predicts "negative EPR absorption," in which energy is transferred from the magnetic oscillator to the electromagnetic field [3].
- If Landau-Lifshitz relaxation and Gilbert relaxation act simultaneously, a number of new effects arise in the EPR spectra, emulating magnetic transitions and the fictitious appearance of several magnetic oscillators [4].
- In the case of EPR, the structure of the mode of magnetic oscillation is complex [3] and, in general, differs significantly from the circular or elliptical precession of the magnetization vector, which may be found in textbooks typically.

These results are primarily of interest to the physics of strongly correlated electron systems (in which a rigorous quantum-mechanical description of dynamic susceptibility is difficult) and can be used to study spin-nematic effects, polarization effects, relationships between spectroscopic parameters, and a new group of magnetic phenomena, the spin-fluctuation transitions [5]. Given the widespread use of semiclassical spin dynamics

to model various spintronic devices, it is important to keep in mind that the choice of one equation or another can lead to radically different calculation results.

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Nano-scale clustering of mono-spin-labeled molecules from double electron-electron resonance data

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Guest molecules in soft media of different kind may assemble in nanometer-size clusters. The important example is clustering of antimicrobial peptides in bacterial membranes, which is crucial for the antibacterial action of these peptides. Double electron–electron resonance (DEER, also known as PELDOR) is a pulsed electron paramagnetic resonance (EPR) technique with the unique ability to study the distances between spin labels in the nanometer range.

DEER has been successfully applied to the study of the conformations of doubly spin-labeled biomolecules. However, when applied to clusters with a number of spin labels $N > 2$, DEER encounters certain difficulties both in the proper implementation of measurements and in the interpretation of the data. The most important issue here is the emerging dependence on the time interval between echo-forming pulses, an effect that is usually not considered when analyzing experimental DEER data. The report analyzes this and other existing problems and gives recommendations on the proper use of the DEER method and interpretation of its data when studying clusters of spin-label molecules [1, 2].

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Inversion recovery EPR characterizes the impact of Heisenberg exchange on nitroxide T_1 in low viscosity solutions

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The impact of Heisenberg exchange on nitroxide relaxation times is key to optimizing conditions for dynamic nuclear polarization (DNP). Although the impact on T_{2e} has been studied extensively, less data are available for T_{1e} . For low viscosity solutions Freed pointed out that nitroxide-nitroxide collisions have two potential outcomes. Collision with a nitroxide with a different nuclear spin (m_i) relieves saturation by moving the spin off resonance (Heisenberg exchange). Collision with a nitroxide with the same nuclear spin state has no impact on T_{1e} [1]. The effective spin lattice time constant observed in a CW power saturation experiment was shown to be the weighted average of the possible outcomes [1]. Three-pulse inversion recovery experiments have now been performed to distinguish the contributions from these two outcomes [2]. For deoxygenated toluene solutions of tempol with concentrations between 0.015 and 5.9 mM, inversion recovery curves were fitted with a stretched exponential, the sum of two exponentials, and with a distribution of exponentials. These analysis methods show that there are two distinct contributions to the recovery curves. The concentration-dependent contribution is attributed to Heisenberg exchange, and the concentration-independent contribution is the ‘true’ T_{1e} . The ratios of the contributions to the recovery curves are 2:1 for ^{14}N nitroxide and 1:1 for ^{15}N nitroxide, consistent with the statistical probabilities of collisions between radicals with the same or different nitrogen T_1 .

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Multi-extreme THz ESR: Developments and future directions

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THz ESR systems under multi-extreme conditions, such as high magnetic fields, high pressures, and low temperatures, have been developed in Kobe. It covers a frequency range of 0.03 to 7 THz [1] and a temperature range of 1.8 to 300 K [1], and it generates magnetic fields up to 55 T [1]. Furthermore, the pressure range can be extended from 1.5 GPa [2] to 2.5 GPa using a hybrid-type piston-cylinder pressure cell [3]. It also includes mechanically detected ESR measurements using a commercially available membrane-type surface stress sensor [4], which is an extension of our micro-cantilever-based ESR [5]. In addition, the development of high-pressure THz ESR up to 25 T [6] has facilitated its application to the triangular antiferromagnets Cs_2CuCl_4 [7] and CsCuCl_3 [8]. Finally, we report the successful observation of ODMR from the NV-centers of nanodiamonds in the pressure medium of a diamond anvil cell (DAC). This is a crucial first step toward observing THz ESR under extreme high pressures using a DAC.

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On the narrowing effect of EPR spectra due to particle motion and its potential implications for other scientific disciplines

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In dilute solutions, the shape of the EPR spectra of paramagnetic particles can exhibit significant changes with increasing rate of random bimolecular collisions of these particles. During these collisions, the Heisenberg exchange interaction is switched on, changing the spin state of unpaired electrons during the collision. This process is called spin exchange.

What is phenomenologically this exchange spectrum narrowing effect? Imagine an EPR spectrum, which, under slow spin exchange, consists of a set of hyperfine components associated with the interaction of unpaired electrons with the magnetic nuclei of colliding paramagnetic particles. As the spin exchange rate increases, the spectrum's resonance lines broaden, and the resonance frequencies shift. However, as the spin exchange rate increases further, a phase transition occurs: the entire original spectrum visually transforms into a single resonance line, the resonance frequency equals the statistical average frequency of all spins in the system, and the contribution of spin exchange to the resonance broadening decreases (tends to zero!) with increasing spin exchange rate. This is called the exchange narrowing effect of the spectrum.

At first glance, one might think that under conditions of exchange narrowing, the spectrum becomes uninteresting and uninformative. Therefore, for many years, the exchange narrowing effect remained unanalyzed in detail. This effect was explained using the Krylov-Bogolyubov mean value theorem.

But it turns out that the exchange narrowing effect reveals interesting physics in the nature of the spin motion of paramagnetic particles undergoing random bimolecular collisions. In recent years, K.M. Salikhov formulated a new paradigm for spin exchange and its manifestations in EPR spectroscopy, which presented a completely different interpretation of the exchange narrowing effect [1–4].

According to the new paradigm, due to the transfer of quantum coherence from the partner during random bimolecular collisions of paramagnetic particles, the motion of an ensemble of spins with different resonant frequencies exhibits well-defined organized modes, collective degrees of freedom. These collective modes are the normal coordinates of the system of linear kinetic equations for the magnetizations of electron spin subensembles, which replace the quantum mechanics equations of spin dynamics, given that in dilute solutions, the exchange interaction is switched on at random moments in time.

The exchange narrowing effect of the spectrum does not mean that only one resonant frequency remains in the system. The number of possible resonances does not change with the spin exchange rate.

However, the “oscillator strength” for excitation of a given collective degree of freedom depends on the spin exchange rate. At high spin exchange rates, only one collective degree of freedom contributes essentially to the observed spectrum, namely,

the collective degree of freedom which asymptotically tends to the sum of the spin magnetizations of all subensembles. This asymptotic behavior corresponds to the Krylov-Bogolyubov mean value theorem. However, if the spin exchange rate does not tend to infinity, the new spin exchange paradigm predicts that other resonances with different frequencies should exist. Moreover, some lines can contribute negatively to the absorption spectrum. These predictions have been experimentally confirmed in recent years [4–7].

However, I would like to emphasize that different collective modes have completely different homogeneous broadening at high spin exchange rates. It has already been said that in the region of fast spin exchange there is a line whose width decreases with increasing spin exchange rate, while the excitation lines of other collective modes broaden, and in different ways.

The excited state of the collective mode that produces the exchange-narrowed line in the spectrum has the longest lifetime. In magnetometry, this is even called a special effect (SERF, spin exchange relaxation free). How can it be that there are random collisions, due to which relaxation and broadening of resonance is expected, but this does not happen!?

This raises the question of whether the theory of the exchange-narrowing effect, when the relaxation mechanism, contrary to expectations, ceases to contribute to irreversible relaxation, has any common ground with the theory of superfluidity and superconductivity.

In superfluidity, we lower the temperature and expect an increase in viscosity, but suddenly it turns out that superfluidity effect can arise. If relaxation-free relaxation is possible, why shouldn't viscosity-free, friction-free relaxation also occur?

In the new spin exchange paradigm, the elementary excitations of collective modes of motion are all bosons. Therefore, quasiparticles of excitation of collective modes of motion of spin sub-ensembles under conditions of exchange narrowing in principle open the way to the realization of a Bose condensate at room temperatures.

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Study of the photophysics of the compact electron donor-acceptor compounds using time-resolved electron spin resonance spectroscopy

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Electron donor-acceptor compounds contain two weakly coupled units in the molecular structure (the donor and acceptor are separated using long and rigid linker). The electron transfer in these molecules has been studied for decades, to mimic the natural photosynthesis center, and for study of fundamental electron transfer. Long-lived charge separated (CS) states were obtained in these compounds. The electron spin dynamics of these compounds, such as the chemically induced dynamic electron spin polarization (CIDEP) or the chemically induced nuclear spin polarization (CIDNP) were studied [1]. In recent year, the compact electron donor-acceptor compounds were developed, short linkers were used in the molecular structure to separate the donor and acceptor. These compounds show complicated photophysics, including the strong electron exchange interaction and strong spin-spin dipolar interaction. Moreover, some of these compounds show the property of thermally-activated delayed fluorescence (TADF) property, in which both the singlet excited state and the triplet excited state can be harvested for light emitting (through the emissive singlet state of S_1). Thus these compounds are promising for application in efficient organic light emitting diodes (OLED). However, one challenge in study of these compounds is the difficulty to detect the transient species formed in the molecules upon photoexcitation, some species are difficult to be discriminated using the normal optical spectroscopy.

During the long-term collaboration with the EPR spectroscopy group at Kazan, we studied a series of TADF compact electro donor-acceptor dyads, and we detected the triplet charge separated states, and from the electron spin polarization pattern of the T_1 state time-resolved EPR spectra, we propose there are two intersystem crossing (ISC) mechanisms [2, 3].

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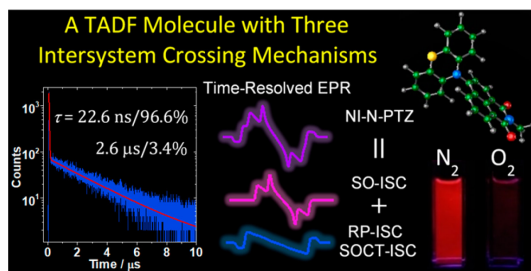


Fig. 1. The molecular structure of a representative TADF electron donor-acceptor dyad (carbon: green; hydrogen: white; sulfur: yellow; oxygen: red; nitrogen: blue), the luminescence property and the time-resolved EPR spectra.

SECTION 1

ADVANCES
IN MAGNETIC
RESONANCE

Emerging ODMR techniques for spin dynamics in solids

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Optically detected magnetic resonance (ODMR) combines the spin selectivity of electron paramagnetic resonance (EPR) with the exceptional sensitivity of optical techniques, reaching the ultimate limit of single-spin detection. A broad family of ODMR techniques has been developed, employing photoluminescence, optical absorption, and Faraday/Kerr rotation as spin-sensitive observables. Their sensitivity can be further enhanced through optical spin orientation. Some experiments use specially designed structures to facilitate spin initialization and detection using a gate voltage. Combined with arbitrary control of microwave excitation, optical detection, and external parameters such as gate voltage, ODMR provides access to virtually the complete set of spin characteristics, including the g factor, spin relaxation time T_1 , spin coherence time T_1 , and inhomogeneous dephasing time T_2 (see [1] and references therein).

There is no universal technique that can reveal the spin properties of every system, and different variations of ODMR techniques can be applied to different solid-state systems depending on their electronic level structure, optical selection rules, interlevel transition probabilities, and other factors.

In this talk, I will review recent developments in ODMR methodologies aimed specifically at measuring spin dynamics characteristics, with an emphasis on longitudinal spin relaxation and spin coherence. Particular attention will be devoted to the recently developed resonant spin inertia [2] and stimulated spin amplification [3] techniques. These methods take an advantage of experimental simplicity and are applicable to a broad range of materials possessing direct optical transitions and long-lived resident carriers, whether free, localized, or exciton-bound. Their application to rare-earth ions, conventional III–V semiconductor nanostructures, and emerging metal-halide perovskite systems [4] will be discussed.

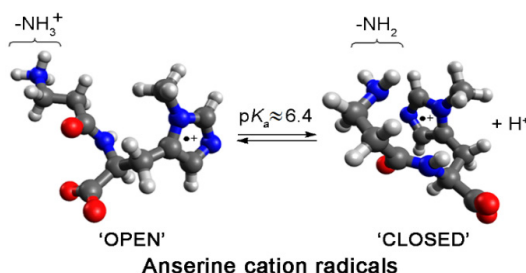
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Short-lived cation radicals visualized by CIDNP

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A histidine-containing dipeptide anserine (β -alanyl-1-methyl-histidine) is widely distributed in vertebrate animal tissues, especially skeletal muscles, underscoring its physiological relevance. The talk presents significant findings on the application of selectively hyperpolarized NMR spectroscopy for the indirect detection of optically silent anserine radicals, using chemically induced dynamic nuclear polarization in its time-resolved version (TR CIDNP) and in the version with the variable magnetic field (FD CIDNP). Our investigations revealed fundamentally different properties of anserine cation radicals depending on the protonation state of its amino group. In particular, an anserine radical with neutral amino group is not involved in the reaction of degenerate electron exchange with parent molecules, and is not reduced by aromatic amino acids on the submillisecond time scale, while an anserine radical with positively charged amino group participates in both reactions [1, 2]. We found that the pK_a of the amino group of electron-deficient anserine is 6.4, which is much lower than 9.5 of the parent molecules, and thus a significant change in the reactivity of anserine radicals occurs at physiological pH [1]. We suggest that the anserine radical with a neutral amino group is stabilized by non-covalent interaction of its functional groups, which breaks the degeneracy of electron exchange and makes the radical stable against the reduction reaction. Aiming to correlate the properties of radicals with structural features, we determined the hyperfine coupling constants (HFCCs) of anserine radicals based on the proportionality between HFCC and the amplitude of CIDNP of the corresponding nucleus in the geminate CIDNP spectrum [3]. The g -factors of the radicals were found from modeling the CIDNP field dependences. Experimental results were supported by quantum chemical calculations, which confirmed the proposed ‘closed’ geometry of the anserine radical with a neutral amino group, in which the nitrogen atom is located close to the C2 imidazolyl atom. Our findings highlight the utility of TR CIDNP in studying the structures of short-lived radicals, contributing to a deeper understanding of the role of anserine in redox processes in biochemical systems, including its potential antioxidant properties and impact on managing oxidative stress.



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Nuclear hyperpolarization in electron transfer in chiral systems

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In the 21st century, a new aspect has been added to the already known manifestations of the role of chirality in various fields of chemistry, physics and biology: spin effects in chiral systems. The first topic is chiral-induced electron spin selectivity (CISS): it was found that when electrons pass through chiral media, the electron current becomes spin-polarized [1-3]. In particular, it has been shown that the polarization of the electron spin is formed when an electron passes through a chain of chiral amino acid residues (chiral bridge). This phenomenon is currently widely discussed in the world literature keeping in mind perspective of using electron spin in the chiral systems as a qubit in quantum technologies [4].

The second topic is chiral-induced nuclear spin selectivity (NSS), which is the difference in the magnitude of hyperpolarization (CIDNP) of optical isomers during photoinduced electron transfer in chiral donor-acceptor systems in solutions [5–7].

To date, neither CISS nor NSS have proven mechanisms, but a hypothesis was formulated that nuclear spin selectivity can depend on the electron spin selectivity in systems where electron passes through a chiral bridge [7]. According to this hypothesis, in a photoexcited chiral system, a partial change in the multiplicity of the reacting excited state occurs during charge separation between the donor and acceptor (before formation of radical pair). Thus, the polarization of electrons arising in the framework of the CISS mechanism will affects the polarization of nuclear spins formed in the radical pair.

In this regard, it seems useful to consider the features of stereo- and spin selectivity of photoinduced electron transfer in chiral systems to compare the contributions of direct and back electron transfer to the formation of NSS. Maybe this will allow us to build a bridge between CISS and NSS phenomena.

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A quantitative EPR method based on electron relaxation time distribution tested on the dual NMR/EPR spectrometer

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The Magnetic Resonance Laboratory of Tsinghua University, in collaboration with CIQTEK (Hefei) and NIUMAG (Suzhou), has developed the first dual NMR/EPR spectrometer in China that successfully operated at 6 K. Recently, based on this all-in-one device, we have explored a new strategy for quantitative EPR.

Conventional quantitative EPR method is mainly based on the continuous wave (cw) EPR measurements. The ratio of double integrals of different signals from cw-EPR spectrum is often related to the ratio of signal components. However, for samples with highly overlapping signals (Fig. 1a), this method is not applicable or suffers from large errors. In such cases, pulsed EPR technique could provide a new method that majorly based on the difference in relaxation times. This quantification method starts from the signal decay curves in time domain and by inverse Laplace transform (ILT), T_2 relaxation profile could be obtained and the contributions from different components with overlapping signals in cw-EPR could be quantitatively determined. In this paper, the frequently used ILT algorithm in time-domain NMR was applied in EPR and this quantitative EPR method was first validated on sample series of TEMPOL with different concentrations (Fig. 1). This new method is potentially useful for polymers, cis-trans structural metal-organic complexes, macrocyclic compounds and other samples with intrinsic relaxation time distributions.

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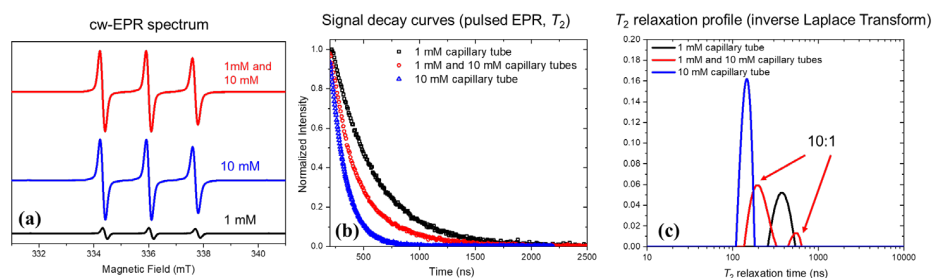


Fig. 1. (a) cw-EPR spectra of capillary tubes of TEMPOL solution, one 1 mM (black), one 10 mM (blue) and two capillary tubes with equal volumes of 1 and 10 mM TEMPOL solution (red) (b) the pulsed EPR signal decay curves (c) the corresponding T_2 relaxation profiles. The intensity ratio of two components (red) in the relaxation profile is in consistency with the ratio of their concentrations.

Using nuclear hyperpolarization in photoinduced electron transfer to study chiral induced electron spin selectivity

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A method has been proposed for extracting information about the initial spin state of a radical pair that arises during photoinduced electron transfer through a chiral bridge, from data on chemically induced nuclear polarization (CINP) observed using NMR. The dynamics of the system are divided into two stages: the formation of a pair of separated charges and the subsequent spin dynamics of the electrons and nuclei in the radical pair. As the main phenomenological assumption, it is assumed that after an electron passes through a chiral bridge, a radical pair can be generated in a coherent superposition of the singlet state and the triplet state T_0 , and not only in a pure S (T_0) state or in their incoherent mixture. For the simplest S - T_0 model, it has been shown that the nuclear polarization contains two contributions: the usual contribution, determined by the difference between the initial populations of the singlet and triplet states, and an additional contribution proportional to the imaginary part of the singlet-triplet coherence.

This makes it possible to formulate the inverse problem: to reconstruct the parameters of the initial state of a radical pair based on the polarizations of several nuclei. NMR provides the imaginary part of coherence, whereas timeresolved EPR can provide its real part. Therefore, the quantitative characterization of chirally induced spin selectivity requires a joint analysis of NMR and EPR data.

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Spin 3/2 paramagnet, spin 1/2 quantum chains and a weakly ordered antiferromagnet in Cs_2CoCl_4

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Quantum models of 1D antiferromagnetic chains exhibit remarkable ground states and excitations. The well known $S = 1/2$ Heisenberg antiferromagnetic chain has a quantum-disordered ground state with algebraically decaying spin correlations [1–3]. The feature of excitations above this ground state is the field-dependent continuum [4, 5] instead of the resonance magnon branch of a conventional 3D antiferromagnet. In this presentation we shall discuss properties of another important model of quantum magnetism, the model of $S = 1/2$ antiferromagnetic spin chain with XXZ (uniaxial) anisotropy and its experimental realization. This model is of importance since it shows phases intermediate between fluctuating and ordered ground states. In particular, we may expect here a quantum-disordered ground state in zero magnetic field and a long-range but strongly reduced order in a magnetic field, followed by a restored spin-liquid regime before saturation [6]. At the first glance the coexistence of spin $S = 1/2$ ions and a strong anisotropy seems to be not realistic because spin $S = 1/2$ has no single-ion anisotropy in a crystal field. Nevertheless, in crystals of Cs_2CoCl_4 it appears to be possible due to the following reasons.

Cs_2CoCl_4 is a quasi-1D antiferromagnet with a high degree of one-dimensionality: the ratio of intra- to interchain exchange J/J' is about of 10^2 , $J = 0.74$ K. The interaction of magnetic ions Co^{2+} ($S = 3/2$) with the crystal field (so called single-ion anisotropy) dominates over the exchange interaction and has a characteristic energy of 7 K [7,8,9]. Due to this large anisotropy the upper Kramers doublet of a magnetic ion demonstrates a freezing-out of the population at cooling below the temperature of about 10 K, which was detected in thermodynamic experiments (see, e.g., [9]). This should cause a smooth transition from spin $S = 3/2$ to an effective spin $\sigma = 1/2$ (pseudospin 1/2). This transition is accompanied by a natural renormalization of g-factor and exchange interaction with arising of an anisotropic part of effective exchange (see, e.g. [9]). This makes the $S = 1/2$ XXZ-chain model relevant for Cs_2CoCl_4 . We confirm this transformation by means of ESR technique. In a multi-frequency experiment covering the range 25–224 GHz we observe above the temperature of 15 K the clear “fingerprints” of $S = 3/2$ ions in an axial crystal field in form of a two-branch spectrum corresponding to transitions between sublevels with $S_z = \pm 1/2$ and $\pm 3/2$. The value of the anisotropy parameter $D = 7$ K supporting the easy plane type of the anisotropy is obtained from the splitting of energy levels.

At lowering the temperature down to 3 K we observe a smooth but clear transformation to a single-branch spectrum which corresponds well to uncorrelated pseudospins $\sigma = 1/2$ coupled via an effectively anisotropic exchange.

At the temperatures below 0.5 K we observe another modification of the frequency-field ESR diagram which differs from the previous one by a negative frequency shift of about 14 GHz [10]. This modification of spin oscillations points to a formation

of a spin system in a state which is close to the ground state of anisotropic $S = 1/2$ antiferromagnetic chain ($S = 1/2$ XXZ-chain model) [6]. As mentioned above, the remarkable feature of this quantum model is a quantum-disordered ground state in zero magnetic field, 1D long-range antiferromagnetic order in a moderate field transverse to the anisotropy axis and a restored spin-liquid phase before saturation [6]. The collective excitations of XXZ-chain model are spinon-like excitations forming a continuum of excitation energies for transitions with $\Delta S_z = \pm 1$.

Finally, in ultralow temperature range below $T_N = 0.2$ K, the spin system of Cs_2CoCl_4 becomes 3D-ordered due to a tiny interchain coupling. The ordered spin component is strongly reduced by zero-point fluctuations. This is fixed in [7] by the magnetic Bragg reflections appearing below T_N . There is a fundamental question on the spectrum of excitations in this strongly fluctuating system with a small ordered component. The result of our experiment [11] shows, that the spectrum of excitations evolves at T_N in two different ways. First, for frequencies about and above the exchange frequency J/h the main part of the spectral weight remains at the frequency of the XXZ-chain excitations. Only about 10 percent of the spectral weight shift to very weak satellite modes. The second way shows the transformation of resonance frequencies at low frequencies $f \ll J/h$, where the spectra of XXZ chain and of a 3D order differ essentially and are not similar to each other. This kind of the transformation of the magnetic resonance spectrum is in a qualitative agreement with the expected dynamics of a weakly ordered spin system in which quantum fluctuations of the 1D-chains persist.

Thus, in the whole perspective, we have observed two crossovers and a phase transition. Crossovers belong to a paramagnetic state – the first is between the states of separate magnetic ion and the second – between the system of uncorrelated magnetic ions and the system of intra-chain correlated but mutually decoupled spin chains. The phase transition is a 3D antiferromagnetic long range ordering evolving from 1D-correlated ground state.

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Features of ESEEM in the study of photosystem I in trehalose matrix

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For the first time we observed a shift in the frequency of dipole–dipole interaction due to random electron spin flips [1]. This shift termed as the red shift. The red shift was observed in the photosynthetic reaction center of photosystem I (PS I) in a trehalose matrix. It was theoretically shown [2, 3] that, the spin echo signal modulation frequency in the ESEEM experiment can be lower than the dipole–dipole frequency. This is due to random spin flips during spin–lattice relaxation. This effect is analogous to the well-known decrease in the oscillation frequency of a pendulum due to friction.

In PS I the dipole–dipole interaction between the P_{700}^{+} cation-radical and the A_1^{-} anion-radical can be observed in an ESEEM signal. We observed that the ESEEM frequency was temperature-dependent. This dependence was explained by the red shift caused by the different relaxation times of the P_{700}^{+} and A_1^{-} radicals. The difference in relaxation times is due to the different environment of the radicals. The environment of the radical includes paramagnetic iron ions, which can decrease the relaxation time. We performed ESEEM studies on intact and modified PS I complexes lacking iron-sulfur clusters [4, 5]. The influence of iron-sulfur clusters on relaxation times and charge recombination processes in the reaction centers of PS I is of particular interest, and we continue research in this area.

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π -Topology, spin alignment, DEP generation and ESPT of photogenerated organic multi-spin π -systems

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Understanding multispin photoexcited systems and their excited-state dynamics is crucial for modern technological applications of organic radicals and related spin systems. We have systematically studied the multispin photoexcited states and excited-state dynamics of anthracene–radical-linked π -conjugated spin systems since 2000 [1–3]. After a short review of our systematic studies for the spin alignment and excited-state dynamics of photoexcited multi-spin π -radical systems [3], we will present the most recent results of anthracene–radical-linked π -conjugated spin systems (**OV2** and **IN2**) with an extended π -conjugated spin coupler [4]. Their multispin photoexcited states and ESPT were investigated using time-resolved electron spin resonance (TRESR), pulse ESR, and transient absorption measurements. Effective electron spin polarization transfer (ESPT) from the photoexcited state to the ground state was directly observed in **OV2** and **IN2**. Pulse ESR experiments showed that the decay time of dynamic electron spin polarization (DEP) and the characteristic time of DEP generation strongly depended on the spin-coupler between the triplet-state chromophore and the radical substituent [3]. This finding supports that DEP generation in the examined π -radical systems proceeds predominantly by a radical spin–orbit borrowing-enhanced intersystem crossing mechanism via a charge-transfer state [2,4].

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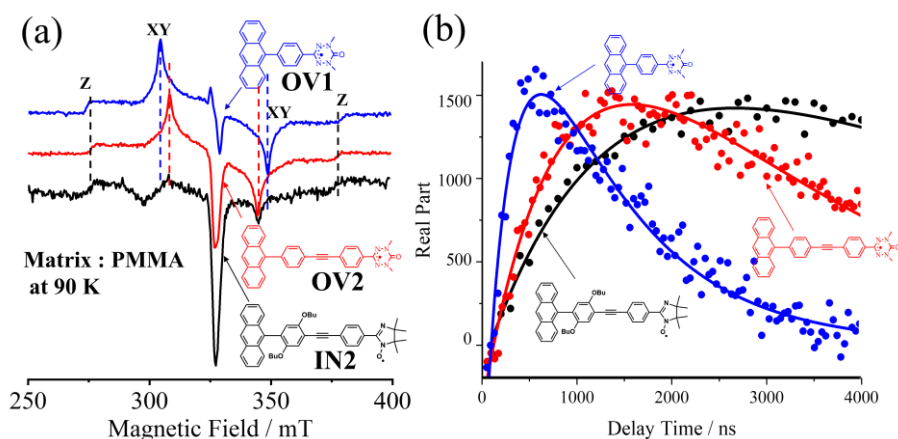


Fig. 1. Typical TRESR spectra (a) and DEP generation behaviors (b) of **OV1** (blue), **OV2** (red), and **IN2** (black) after the laser pulse excitation (DEP generation behaviors were measured by pulse ESR)

Dimerization of NO molecules as the initial stage of iron dinitrosyl complexes formation in animals and humans

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The main points of my report are as follows:

1. At micromolar concentrations, nitric oxide begins to dimerize, which ensures its rapid oxidation in animal and human tissues by the oxygen present therein, which is incorporated into NO dimers.

2. This oxidation can be competitively suppressed by weakly bound (“free”) iron, which is incorporated into NO dimers in place of oxygen, forming iron-dinitrosyl complexes.

3. Disproportionation of NO molecules in these complexes leads to their transformation into the nitrosonium cation (NO^+) and the nitroxide anion (NO^-), respectively. In an aqueous medium, the latter, after binding with a proton to form a nitroxide molecule, leaves the complex with the subsequent inclusion of a NO molecule in its place. As for NO^+ , its interaction with the hydroxyl anion is blocked by the transfer of electron density to it from the thiol sulfur atoms of thiol-containing ligands included in the iron-dinitrosyl complex with the formation of paramagnetic mononuclear dinitrosyl iron complexes (M-DNICs) with thiol-containing ligands, characterized by the d^7 electron configuration of iron.

4. M-DNICs, characterized by the resonance structure $[(\text{RS})_2\text{Fe}^{2+}(\text{NO})(\text{NO}^+)]^+$, are capable of acting in the body of animals and humans as donors of NO and NO^+ , characterized, respectively, by positive, regulatory and, conversely, - negative, cytotoxic action.

5. Numerous examples of this activity of DNICs will be given, including their ability to suppress the replication of the SARS-CoV-2 virus in Syrian hamsters and the proliferation of transplanted human Lewis sarcoma in mice.

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Multi-pulse protocols in EPR: From spectral diffusion suppression to quantum zeno analogy

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Multi-pulse protocols such as Carr–Purcell–Meiboom–Gill (CPMG) effectively suppress spectral diffusion arising from stochastic hyperfine modulation, thereby extending the electron spin echo decay. This prolongation is phenomenologically analogous to the quantum Zeno effect (QZE), wherein frequent unitary π -pulses interrupt coherent phase accumulation and suppress decoherence, even though they do not constitute projective measurements – an analogy justified within dynamical decoupling theory [1, 2].

A critical distinction must be made between two mechanisms that can extend echo signals: suppression of reversible T_2 dephasing via dynamical decoupling, which preserves coherence, and contamination by irreversible T_1 relaxation due to imperfect pulses, which artificially prolongs the signal while destroying true coherence. Only the former is relevant for quantum memory applications.

Consequently, multi-pulse experiments require distinguishing the apparent slowing of the echo envelope — which may arise from either Zeno-like suppression or T_1 contamination — from genuine phase coherence preservation. The CPMG protocol is a powerful tool for extending coherence times, but its interpretation demands careful consideration of pulse repetition rates, environmental correlation times, and the unavoidable mixing of relaxation channels. The QZE serves as a useful phenomenological analogy, provided its limits and distinction from projective measurements are clearly articulated.

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Broadband ESR spectrometer based on VNA and its application for FM materials

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The Ferromagnetic resonance (FMR) has been a traditional tool for studying the dynamic properties of magnetic materials [1]. This method allows one to determine the fundamental characteristics of a substance: the type of magnetic anisotropy, the anisotropy field, the effective magnetization, and the Gilbert damping parameter. However, classical spectrometers with cavity resonator have limitations in their operating frequency range and do not allow one to effectively study the local properties of samples under conditions as close as possible to the actual topology of integrated circuits. In recent years, significant advances in measurement technique and the development of vector network analyzers (VNA) have made it possible to perform FMR studies in a broadband format using planar transmission lines [2].

Three methods for recording the FMR spectrum are presented in this study: with a magnetic field sweep, a frequency sweep, and a modulated field sweep. The setup includes a VNA, coaxial cables, and a measuring cell based on a coplanar waveguide. A magnetic field of up to 8 kOe is generated by an electromagnet.

Obtaining a series of frequency spectra or a series of field spectra allows one to construct two-dimensional dispersion curves. To test the developed technique, experimental studies of thin epitaxial chromium dioxide (CrO₂) films grown on titanium dioxide (TiO₂) substrates were carried out. FMR spectra with both field and frequency sweep were successfully recorded for the samples. Dispersion curves were constructed based on the collected data set. Approximation of the obtained dependences using Kittel's formulas made it possible to unambiguously identify the magnetic anisotropy type of the CrO₂ films and confirm the presence of an easy axis of magnetization in the film plane [1]. The developed approach demonstrates the high efficiency of using a vector network analyzer for non-destructive testing of the parameters of magnetic materials intended for use in embedded electronic systems and in the design of modern integrated microwave circuits.

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Photoinduced spin dynamics in rigid chromophore–radical compounds

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Photoexcitation of rigid chromophore–radical compounds leads to spin dynamics governed by the interplay of initial intersystem crossing, subsequent doublet–quartet evolution, and spin relaxation. These processes determine the formation of non-equilibrium spin populations and their redistribution between spin sublevels of the metastable states observable by time-resolved EPR (TREPR) spectroscopy.

In these systems, the spectral properties are determined by the triplet zero-field splitting, exchange interaction, and Zeeman energy. Depending on the relationship between these terms, the TREPR spectra of rigid chromophore–radical compounds can be classified in-to weakly coupled, strongly coupled, and intermediate triplet–doublet regimes, including the D/J -dominant regime and the regime of anticrossings of doublet and quartet sublevels.

The presentation will discuss the systematics of spin-dynamic regimes in rigid chromophore–radical compounds based on their TREPR spectra and kinetic behavior.

Low-field NMR of ^{129}Xe at low temperatures: frequency and temperature dependences of spin-lattice relaxation in liquid and solid phases near triple point

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Nuclear magnetic resonance (NMR) of ^{129}Xe has proven to be an exceptional method for characterizing the structure of materials. Owing to its nuclear spin of $I = 1/2$, relatively high natural abundance (26.4%), and large electron cloud, ^{129}Xe serves as a versatile probe for investigating porous media and the diverse physical properties of nanostructures [1]. The ongoing relevance of ^{129}Xe research is further highlighted by its application in advanced fundamental physics; notably, within the Cosmic Axion Spin Precession Experiment (CASPER), ^{129}Xe is proposed as a highly sensitive medium for the detection of axion-like dark matter [2].

A large number of works are devoted to the study of hyperpolarized xenon in various media. However, there are few works that study xenon with a natural abundance composition and natural polarization in a liquid state.

To overcome the low signal magnitude caused by the small gyromagnetic ratio of ^{129}Xe and the use of a resistive magnet, a custom low-temperature high-Q NMR probe with tunable frequency was developed. Additionally, controlling the complex xenon phase diagram required integrating heaters and thermometers into the probe to ensure precise gas condensation and maintain a stable phase [3].

The frequency and temperature dependences of the spin-lattice relaxation time (T_1) of ^{129}Xe in both the liquid and solid phases were successfully measured using this optimized setup and a specialized pulse sequence combining saturation-recovery and Carr-Purcell-Meiboom-Gill (CPMG) methods. Notably, a distinct minimum in the T_1 relaxation time was observed in the frequency dependence for the liquid phase near 7.6 MHz.

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Infrared spectroscopy with the advantages of synchrotron radiation sources: global experience and prospects for the “IR-diagnostics” beamline at the skif facility

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Large-scale research infrastructures – often called “megascience” facilities – define the forefront of experimental capabilities in modern science. The fourth-generation synchrotron radiation facility “Siberian Circular Photon Source” (SKIF) [1], currently being developed within the Russian national project “Science and Universities”, will enable fundamentally new, high-level basic and applied research using synchrotron radiation beams in the Russian Federation.

While it is widely known that synchrotron radiation sources provide exceptionally high brightness in the X-ray range [2], this advantage is also retained in the infrared (IR) region [3]. For this reason, many synchrotron centres worldwide operate dedicated IR beamlines alongside their X-ray endstations [4]. A key feature of such beamlines is a specialized extraction and beamline optics system within the storage ring perimeter, optimized for efficient collection and transport of IR radiation, as well as the specific end-user equipment: Fourier-transform IR spectrometers, IR microscopes, and nano-IR setups.

This report presents the international experience in designing, building, and operating infrared beamlines at third- and fourth-generation synchrotron sources. A specific focus is placed on synchrotron-based frequency-domain THz-EPR spectroscopy, where the high brightness of synchrotron radiation in the far-IR (terahertz) range makes it possible to perform experiments on magnetically active compounds, including single-molecule magnets, that are hardly feasible with conventional thermal sources [5]. Based on this experience, we developed the concept of the “IR-diagnostics” beamline at the SKIF synchrotron radiation facility. Special attention is paid to the design of the IR-optimized extraction structure. Finally, the key fundamental and applied research tasks that will be addressed efficiently at the “IR-diagnostics” beamline are outlined, and the magnetic resonance community is invited to propose experiments and contribute to the research program of the beamline.

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Transferred hyperfine interactions in $\text{CaF}_2\text{:Pu}^{3+}$ according to ENDOR

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Experimental data obtained by ENDOR method [1] revealed that the interaction of Pu^{3+} 5f-electrons with fluorine nuclei in CaF_2 crystal differs significantly from the classical dipole-dipole interaction. There is a large isotropic electron-nucleus interaction with the A_s parameter, which was found to be negative. The reason for this anomalous phenomenon has not yet been explained.

In this work, we consider the effect of mixing the 5f- and 5d-electron wave functions of the Pu^{3+} ion with the 2s- and 2p-wave functions of fluorine on the values of the electron-nuclear double resonance (ENDOR) parameters A_s and A_p . Using the technique of irreducible tensor operators, we derive expressions for the spin Hamiltonian parameters of A_s and A_p via the hybridization parameters $\lambda_{fg} = s_{fg} + \gamma_{fg}$, $\lambda_{fr} = s_{fr} + \gamma_{fr}$ and $\lambda_{fs} = s_{fs} + \gamma_{fs}$. In addition to this generally accepted covalent approach, the virtual transfer processes of 2s- and 2p-electrons of fluorine into the empty 6d-shell of plutonium have been taken into account.

All overlap integrals were calculated on the Hartree-Fock wave functions of plutonium taken from [2], which were previously approximated by Gaussian-type orbital expansions. In the numerical evaluations of A_s and A_p , the covalency parameters γ_{5fg} , γ_{5fr} , $\gamma_{6d\sigma}$, $\gamma_{6d\pi}$ were assumed to be proportional to the overlap integrals s_{fg} , s_{fr} , s_{fs} , interaction with the A_s parameter, which was found to be negative. As it could be expected on the basis of transferred hyperfine interaction analysis, for rare-earth compounds (see, for example, [3]), the magnitude and sign of A_s for the Pu^{3+} ion in CaF_2 can be explained by virtual processes of transfer of 2s- and 2p-electrons of fluorine to the empty 6d-shell of plutonium. Moreover, using the experimental data of [1] we obtained the covalence parameters of 5f- and 6d-electrons of Pu^{3+} in CaF_2 .

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Quantum dynamics in Krylov space and operator growth: a study using multiple-quantum NMR

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Despite the enormous success of statistical mechanics in describing macroscopic behavior of the physical systems, the question of its relation to the underlying microscopic dynamics, have been the subject of debate since its foundations were laid. One of the most controversial issues is the reconciliation of the reversibility in time of most microscopic laws of nature and the apparent irreversibility of the laws of thermodynamics.

The emergence of statistical mechanics for isolated classical systems is due to chaotic dynamics and ergodicity. In quantum systems, however, the manifestation of ergodic behavior is an old mystery. Quantum mechanical evolution in time is local and unitary. Nevertheless, many quantum systems are effectively described by irreversible hydrodynamics. Understanding the ergodic (“thermolysis”) behavior that arises in this case, both at the conceptual and computational levels, is the central goal of theoretical research on quantum dynamics, the cornerstone of which is the “eigenstate thermalization hypothesis” [1].

However, in recent works, the focus has shifted from the study of eigenstates to the study of “operator growth” [2, 3]. The term introduced means that when considering the evolution over time in the Heisenberg representation, simple operators generically decay into an infinite “bath” of increasingly nonlocal operators. It is believed that the emergence of this dissipative behavior from unitary dynamics underlies thermalization, the decay of dynamic correlation functions, and the accuracy of hydrodynamics on a large scale. At the same time, as it turns out to be convenient to consider evolution not in the exponentially growing full Hilbert space, but in its subspace formed from the operators necessary to solve a specific problem.

Such a subspace is called the Krylov space, and its basis, formed from orthogonal operators, is the Krylov basis [2, 3]. Krylov subspace methods offer a powerful approach that makes it possible to identify the minimal subspace in which dynamics unfolds without having to fully diagonalize the Hamiltonian and explicitly store the quantum state. The method is named after A. N. Krylov, who made a deep and long-term contribution to applied mathematics, including innovative computational methods in linear algebra, which today bear his name and which inspired the creation of the concept of Krylov complexity [2], which is actively studied today.

Similar approaches, but under different names [4–6]: the recursive method, the method of continued fractions, the method of decomposition by orthogonal operators, etc. have been applied to calculations of spin time correlation functions in magnetic resonance. In particular, we applied them to explain the multiple-quantum (MQ) NMR spectra and the growth of clusters of dynamically correlated spins [7, 8].

In this report, based on the results of the theory we are developing [7, 8], we will show what contribution MQ NMR can make to solving global problems of irreversible quantum dynamics. We have determined:

1. The “Krylov complexity” introduced in [2] is equal to the second moment of the MQ spectrum or the average size of a cluster of dynamically correlated spins.
2. The type of dependence (linear, root, etc.) of the Lanczos coefficients on the number determines the type of dependence of the average cluster size on time, the shape of the MQ spectrum, and the dependence of the relaxation rates of the MQ spectrum components on their order [7, 8].
3. The dependence of the relaxation rates of the MQ spectrum components on their order allows us to judge the density of growing clusters of dynamically correlated spins [8].
4. “A universal operator growth hypothesis” proposed in work [2] finds support in NMR and MQ NMR experiments. The linear growth of the Lanczos coefficients from the number, the universality of which is asserted in the hypothesis, leads to an exponential growth of the second moment of the MQ spectrum with time, observed in experiments [7]. Such an increase in the coefficients corresponds to a rapid increase in the moments of the time spin correlation functions, leading to a divergence of the series in powers of time (moments) of these functions. The divergences of the series indicate the presence of singularities on the imaginary time axis, which lead to exponential wings of the spectra of correlation functions observed in NMR experiments [9].

Consequently, the MQ NMR method can be used to study quantum dynamics in Krylov space, measure Krylov complexity, study operator growth, measure the growth rate and shape (density) of growing clusters of dynamically correlated spins.

The work was carried out within the framework of the scientific topics of the State Assignment of the Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences and the State Assignment for the Semenov Institute of Chemical Physics of the Russian Academy of Sciences.

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Pulsed and steady-state thermal annealing of sapphire single crystal implanted with chromium ions: Optical and EPR studies

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Ruby crystal (an Al_2O_3 sapphire matrix doped with Cr^{3+} ions) has been used as an active medium for pulsed lasers operating at $\lambda = 0.694 \mu\text{m}$ since the 1960s. A pressing scientific and practical challenge is the creation of compact and integrated lasers based on $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ crystals and thin films, as well as various sensors sensitive to mechanical deformation, radiation dose, or temperature changes. These factors influence the position and intensity of the R-line of Cr^{3+} luminescence.

In this study, we investigated the doping of the near-surface region of a 0.5 mm-thick Al_2O_3 sapphire single crystal with Cr^{3+} ions using ion implantation with an ion energy of $E = 40 \text{ keV}$ and doses of $\Phi = 5 \times 10^{13} - 5 \times 10^{16} \text{ cm}^{-2}$. After implantation, the use of pulsed ion-beam treatment (PIBT) in melt mode ($T > 2000 \text{ }^\circ\text{C}$) was tested as an alternative to steady-state thermal annealing (TA) at $T = 1000 \text{ }^\circ\text{C}$ to obtain R-line luminescence at 300 K. This PIBT was carried out at the TEMP-4 pulsed accelerator with a powerful beam of C^+/H^+ ions with an energy of $E \approx 300 \text{ keV}$, an energy density of $W = 0.9 \text{ J/cm}^2$ and a pulse duration of $\tau \approx 100 \text{ ns}$. Modeling of the depth profile of Cr^{3+} ions in Al_2O_3 was carried out, which made it possible to estimate the concentration of chromium in the crystal (up to 2 at.% in a 50 nm layer) before annealing.

Comparative measurements of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ samples after PIBT and TA were conducted using optical transmission, Raman scattering, photoluminescence, and EPR. Despite the absence of characteristic Cr^{3+} absorption bands at 410 and 560 nm in the transmission spectra, the implanted samples exhibit similar luminescence intensities of the R_1 and R_2 lines ($0.69 \mu\text{m}$), which increases with implantation dose. The presence of red PL indicates the substitution of chromium ions for aluminum atoms in the sapphire crystal lattice.

The implanted samples were studied by EPR at 300 K on an Elexsys E580 spectrometer (Bruker) in the X- and Q-bands. A signal from chromium ions in the substitution position was detected in both bands for the samples with the implantation dose higher than $1 \times 10^{16} \text{ cm}^{-2}$. The spectroscopic parameters correspond to those of the chromium impurity ion in ruby.

Simulation of a specialized dual-frequency sensor for MRI 0.4 T

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The work is devoted to modeling the receiving and transmitting circuits of a small-sized specialized traumatological MRI with a magnetic field induction of 0.4 T. The receiving and transmitting system is designed to perform MRI scans sequentially at two frequencies in one session of the study facility.

The boundary conditions for the calculation: the working area for placing the receiving and transmitting circuits in the magnet along the Y and Z axes is 200 mm, along the X axis is 220 mm, selected for reasons of maximum filling factor and the size of the gap between the poles of the magnet.

For compactness of the entire structure, the receiving and transmitting system for each operating frequency is made in the form of a receiving and transmitting unit. An decoupling circuit is included in each circuit of this system [1] for efficient transmission of the excitation pulse energy and protection of the input elements of the preamp. The operating frequencies for the ^{129}Xe and ^1H cores in the 0.4 T field are 4.84 MHz and 17.5 MHz, respectively.

The outer circuit is based on a solenoid, and a saddle-shaped coil is used in the inner circuit. The axis of the receiving-transmitting circuit based on the solenoid is directed horizontally along the X-axis, and the axis of the saddle-shaped circuit is directed vertically along the Y-axis of the magnetic system.

It was carried out according to the state assignment of the Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center, Russian Academy of Sciences.

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Features of the search for an analytical solution of Bloch equations with nonlinear coefficients for describing the modulation technique for recording a nuclear magnetic resonance signal

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In the modern world, nuclear magnetic resonance (NMR) has found a wide range of applications in various fields of both scientific and industrial human activity [1]. A large number of NMR recording methods have been developed and implemented in various devices, ranging from stationary (high-resolution NMR) to mobile (portable NMR relaxometers) [1, 2]. The greatest challenges arise when recording NMR magnetic resonance signals from fluid flows with variable flow regimes over a wide range. One of the challenges when using such devices is characterizing the NMR signals recorded using modulation techniques. Recording NMR signals using modulation techniques offers undeniable advantages for applications involving weak fields or flowing liquids, both in NMR flowmeters and NMR magnetometers. Currently, only approximate solutions to the Bloch equations for describing NMR signals recorded using modulation techniques or numerical solutions exist. This creates difficulties in a number of research situations or when solving technical problems, such as those related to determining the longitudinal T_1 relaxation time [3]. This is important when using small-sized NMR relaxometers for rapid monitoring of condensed matter and flow state [1]. This paper proposes one solution to the Bloch equations to obtain an analytical solution without approximations.

Let us consider the system of Bloch equations in a rotating coordinate system [3], into which dispersion and absorption signals are introduced through the magnetization components M_x and M_y :

$$\begin{cases} \frac{du(t)}{dt} + \frac{v(t)}{T_1} + (W + \gamma H_m \sin(\omega_m t))v(t) = 0 \\ \frac{dv(t)}{dt} + \frac{v(t)}{T_2} - (W + \gamma H_m \sin(\omega_m t))u(t) + \gamma H_1 M_z(t) = 0 \\ \frac{dM_z(t)}{dt} + \frac{M_z(t)}{T_1} - \frac{M_0}{T_1} - \gamma H_1 v(t) = 0 \end{cases}$$

Let's rewrite the system in a different form:

$$\begin{cases} \dot{u}(t) + \frac{v(t)}{T_2} + (W + \gamma H_m \sin(\omega_m t))v(t) = 0 \\ \dot{v}(t) - (W + \gamma H_m \sin(\omega_m t))u(t) + \frac{v(t)}{T_2} + \gamma H_1 M_z(t) = 0 \\ \dot{M}_z(t) - \gamma H_1 v(t) + \frac{M_z(t)}{T_1} = \frac{M_0}{T_1} \end{cases}$$

Let's introduce the following notations:

$$x(t) = \begin{pmatrix} u(t) \\ v(t) \\ M_z(t) \end{pmatrix}, \quad A(t) = \begin{pmatrix} -\frac{1}{T_2} & -W - \gamma H_m \sin(\omega_m t) & 0 \\ W + \gamma H_m \sin(\omega_m t) & -\frac{1}{T_2} & -\gamma H_1 \\ 0 & \gamma H_1 & -\frac{1}{T_1} \end{pmatrix}, \quad f(t) = \begin{pmatrix} 0 \\ 0 \\ \frac{M_0}{T_1} \end{pmatrix}$$

Then the system will take the following form, taking into account the initial condition:

$$\dot{x}(t) + A(t)x(t) = f(t), \quad x(0) = x_0 = \begin{pmatrix} 0 \\ 0 \\ M_H \end{pmatrix}$$

General solution of the system:

$$x(t) = \exp\left(-\int_0^t A(s)ds\right)x_0 + \int_0^t \exp\left(\int_t^s A(k)dk\right)f(s)ds$$

Let's calculate the integrals:

$$B(t) = -\int_0^t A(s) ds = \begin{pmatrix} \frac{t}{T_2} & \frac{\gamma H_m}{\omega_m} (\cos(\omega_m t) - 1) - Wt & 0 \\ -\frac{\gamma H_m}{\omega_m} (\cos(\omega_m t) - 1) + Wt & \frac{t}{T_2} & -\gamma H_1 t \\ 0 & \gamma H_1 t & \frac{t}{T_1} \end{pmatrix}$$

$$C(s, t) = \int_t^s A(k) dk = \begin{pmatrix} \frac{s-t}{T_1} & -\frac{2H_m}{\omega_m} (\cos(\omega_m s)) - \cos(\omega_m t) & 0 \\ -\frac{2H_m}{\omega_m} (\cos(\omega_m s)) - \cos(\omega_m t) & 0 & -\frac{s-t}{T_1} \\ 0 & 0 & \gamma H_1 (s-t) \end{pmatrix}$$

To calculate matrix exponents, the matrices under study can be written in the following form:

$$D = \begin{pmatrix} a & b & 0 \\ -b & a & -c \\ 0 & c & d \end{pmatrix}$$

The final solution to the system is obtained by finding the Jordan form of the matrix above, then the initial functions under study are calculated using the following formulas:

$$u(t) = (A_3)_B M_H + \frac{M_0}{T_1} \int_0^t (A_3)_C ds$$

$$v(t) = (A_6)_B M_H + \frac{M_0}{T_1} \int_0^t (A_6)_C ds$$

$$M_z(t) = (A_9)_B M_H + \frac{M_0}{T_1} \int_0^t (A_9)_C ds$$

The coefficients $(A_i)_B$, $(A_i)_C$ are calculated in accordance with the considered cases depending on the values of the parameters.

The proposed new approach, unlike previously considered approaches, opens up the possibility of obtaining an analytical solution for dispersion, absorption, and magnetization components M_z . Analysis of the resulting relationships shows that $u(t)$, $v(t)$,

and $M_z(t)$ will be expressed solely in terms of H_1 , H_0 , H_m , and ω_m , as well as using T_1 and T_2 values. This will expand the potential for NMR applications in various fields using the above-mentioned instruments.

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EPR spectroscopy of rare earth ions in a CsCaF_3 crystal

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Rare-earth (RE) ions as impurity ions in dielectric crystals have been mainly studied in six- and eightfold coordinated positions. There are practically no studies of crystals in which both positions are present and possible for the localization. Therefore, it is certainly interesting to study RE ions in perovskite-type ABF_3 ($A = \text{Me}^+$, $B = \text{Me}^{2+}$) crystals.

Crystals of this structural type are convenient model systems. In such structures, it is possible to introduce an impurity ion into both a sixfold position and an unusual 12-fold position (Fig. 1). There are a number of works [1–5] where the probable localization of impurity RE ions in the 12-fold position was reported but the evidence was indirect. The study of Yb^{3+} ions in a cubic CsCaF_3 crystal using electron paramagnetic resonance (EPR) and optical spectroscopy demonstrated the observation of the Yb^{3+} ion in fluorite CaF_2 crystallites (the eightfold coordination) that are spontaneously organized in the CsCaF_3 crystal during the crystal synthesis [6]. However, previously [5] it was assumed that the impurity Yb^{3+} ion replaces the Cs^+ ion (the 12-fold position).

This work presents the results of a further experimental EPR study of RE ions in the cubic CsCaF_3 crystal confirming the existence of self-organizing CaF_2 crystallites.

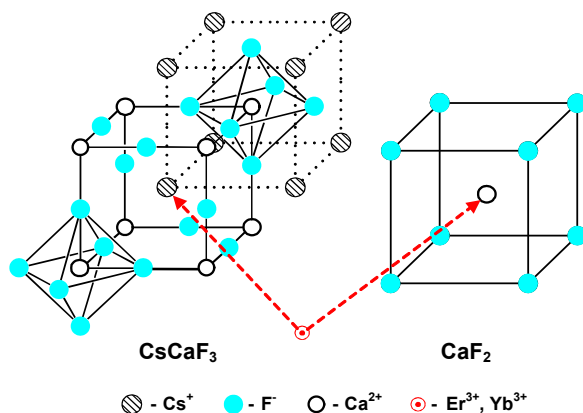


Fig. 1. Fragments of CsCaF_3 and CaF_2 crystal structures.

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Orientational motions of nitroxide molecules in glassy ethanol and dibutyl phthalate studied by CW and pulsed EPR

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Disordered molecular solids is a fairly wide class of substances of various origin – amorphous polymers, simple molecular glass-formers, technological materials for photonics and optoelectronics, pharmaceuticals, coating for the cells of quantum computers and others. Biological media in many respects also can be attributed to this kind of substances. However, there is still no generally accepted theoretical description of the structure and dynamics of these substances at the molecular level.

Among other experimental approaches, electron paramagnetic resonance (EPR) spectroscopy of spin probes and labels can be useful for studying the orientational motions of molecules in different environments. EPR can be applied in the traditional stationary continuous wave (CW) and pulsed (electron spin echo, ESE) versions. CW EPR spectra are sensitive to dynamic librations of molecules, ESE time kinetics allow detection of stochastic molecular reorientations.

Two systems were studied in this work: ethanol (with the addition of 5% v/v methanol for better glass formation upon cooling) and dibutyl phthalate. Stable nitroxide TEMPONE spin probe was dissolved in these substances at concentrations between 1 and 5 mol%. The measurements were performed in a wide temperature range around the glass transition temperature of these substances (~100 K for ethanol and ~180 K for dibutyl phthalate).

An analysis of the temperature dependences of the splitting of stationary EPR spectra allowed to reveal different temperature regimes for dynamic librations including their freezing due to quantum effects. ESE time kinetics showed the presence of two coexisting types of orientational molecular motions: small-amplitude stochastic librations and large-amplitude rotations.

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Magnetic properties of ludwigite $\text{Mn}_{0.53}\text{Mg}_{2.47}\text{BO}_5$ in the temperature range 300–570 K

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Ludwigites have a complex crystal structure with quasi-low-dimensional elements formed by metal-oxygen octahedra. Ludwigite unit cell contains four formula units, including divalent and trivalent (or divalent and tetravalent) cations distributed over four nonequivalent positions [1, 2]. Ludwigites with the structural formula $\text{Mn}_{0.53}\text{Mg}_{2.47}\text{BO}_5$ were studied by EPR measurements in the temperature range from 300 K to 570 K. Two lines were observed in the magnetic resonance spectrum: a broad line with a linewidth of about 6000–7000 Oe, and a second, intense exchange-narrowed line observed throughout the entire temperature range, confirming the presence of strong exchange interactions between the manganese magnetic ions. When approximating the spectrum shape, the broad line was assumed to have a resonant field of 3400 Oe that does not change with temperature. The linewidth ΔH of the narrow line was found to decrease monotonically with increasing temperature, from about 510 Oe at 300 K to approximately 260 Oe at 570 K (Fig. 1), which is typical behavior for exchange-coupled spin systems. The temperature dependence of the resonance field H_{res} shows non-monotonic behavior, with a pronounced minimum around 400–430 K, followed by a gradual increase up to 570 K (Fig. 2). Such behavior of H_{res} may indicate additional contributions to the magnetic anisotropy from magnetic clusters. The obtained results

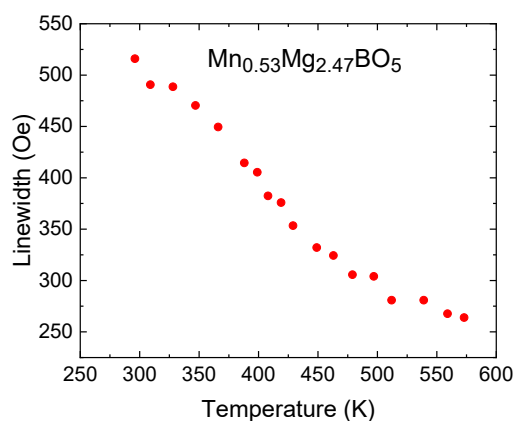


Fig. 1. Temperature dependence of the linewidth for $\text{Mn}_{0.53}\text{Mg}_{2.47}\text{BO}_5$.

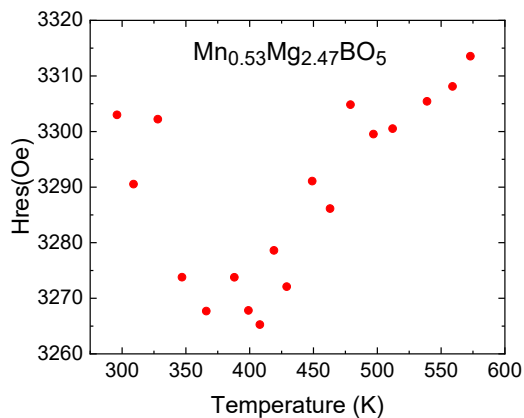


Fig. 2. Temperature dependence of the resonance field H_{res} for $\text{Mn}_{0.53}\text{Mg}_{2.47}\text{BO}_5$.

provide insight into the evolution of the local magnetic environment of Mn ions in the ludwigite structure upon heating from room temperature to 570 K. The temperature dependence of the magnetic susceptibility is also discussed.

This research was supported by the Russian Science Foundation (project no. 23-72-00047).

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Exchange and dipolar interactions in some photoexcited systems

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Chromophore-radical systems are promising platforms for molecular spintronics and quantum information science (QIS), where the nature of the spin-spin interaction governs their magnetic and photophysical properties. Understanding multispin photoexcited systems and their excited-state dynamics is crucial for modern technological applications of organic radicals and related spin systems. Upon photoexcitation of the chromophore, a molecular unit containing two spin centers is creating: the photogenerated chromophore triplet and the radical. The interplay between these spins is governed by their magnetic interactions, i.e. the isotropic exchange interaction (J) and the anisotropic dipole-dipole interaction (D), electronic Zeeman interactions and the ZFS interaction of the triplet state. These are primarily chromophores with covalently bound radicals; such systems have been intensively studied. They exhibit diverse properties depending on the strength of the exchange and dipole interactions between the unpaired electron of the radical and the photoexcited triplet states. Here, we also present an examples of a change in the sign of an exchange interaction in the systems with TEMPO radical attached to different positions of the perylene derivative [1]. One of these systems, which we have studied, is shown in the Fig. 1a. A significantly different situation is expected for systems in which the molecules of perylene and radical are linked by a sufficiently

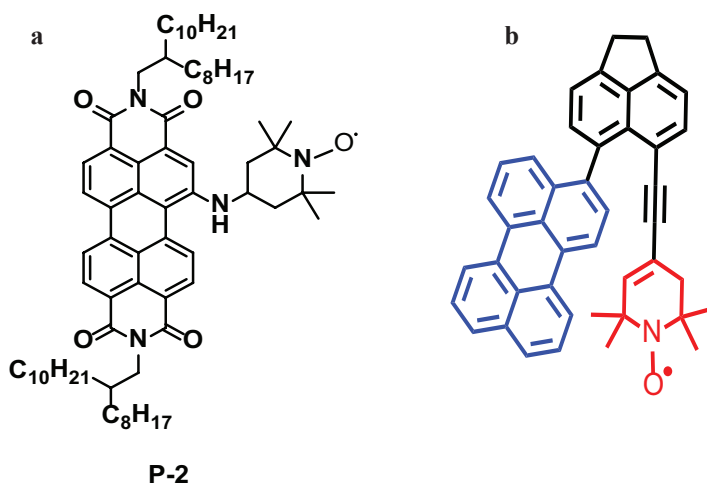


Fig. 1. Two types of molecular structures of perylene derivatives with TEMPO radical.

long U-shaped bridging fragment, which provides a three-dimensional spatially bound configuration. An example of such a system is shown in Fig. 1b.

While through bond exchange coupling is well studied in linear chromophore-radical systems, the role of direct through space coupling in controlling excited state dynamics remains less explored. Herein, we present the design, synthesis, and EPR investigation of two U-shaped perylene-bridge-nitroxide compounds using X-, Q-, and W-bands time-resolved EPR and pulse EPR at X-band. The values of the exchange interactions were determined on the basis of previously published theoretical considerations [2].

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Effect of quantum interference under simultaneous excitation of magnetic dipole and electric quadrupole resonance transitions

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Quantum interference of probability amplitudes of resonance transitions excited by electromagnetic waves between electron levels of ions and atoms can be caused by several physical effects. We observed for the first time new effect of quantum interference for magnetic dipole resonance transitions and electric quadrupole resonance transitions simultaneously excited between electron-nuclear levels of Cu^{2+} impurity ions in BaF_2 single crystal. [1].

In the crystal lattice of $\text{BaF}_2\text{Cu}^{2+}$ ions substitute Ba^{2+} ions as single ions (SI) and dimer associates (DA). Earlier these paramagnetic centers have been studied by EPR in details in [2]. Schematically, the magnetic field dependencies of the electron levels of the Cu^{2+} centers as shown in Fig. 1a. A significant difference between hyperfine and superhyperffine structures of the SI and DA EPR spectra allows one to determine the type of a paramagnetic center. Examples of the spectra recorded at different orientation of magnetic field are presented in Fig. 1b. It is clearly seen that low-field (DA-LF) and high-field (DA-HF) spectra of the DA differ in amplitude, and this difference depends dramatically on the magnetic field orientation. We believe that this phenomenon is due to the quantum interference of probability amplitudes of the magnetic dipole and electric quadrupole resonance transitions.

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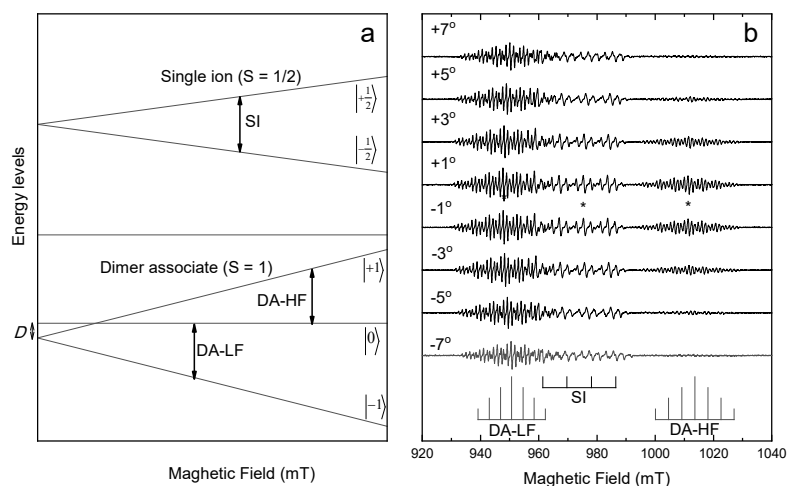


Fig. 1. **a** Electron level diagram of the SI Cu^{2+} with an effective spin of $S = 1/2$ and the DI ($S = 1$). The arrows indicate the resonance transitions observed in EPR spectroscopy; **b** EPR spectra of $^{63}\text{Cu}^{2+}$ impurity centers in BaF_2 recorded at different orientation of magnetic field.

SECTION 2

MODERN
METHODS OF
MAGNETIC
RESONANCE

Seemiconductors: parameters and possible nature of CIDNP

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It is well known that the evolution of the spin density matrix should be described in terms of spin dynamics, diffusion, and recombination operators. Half a century ago, attention was drawn to the fact that the additivity-based approach for calculating singlet-triplet evolution – which implies additivity of the contributions of sequential radical pairs to chemically induced dynamic nuclear polarization (CIDNP) – is incorrect [1].

The present work describes a general approach for CIDNP calculations that is valid for arbitrary spin dynamics, diffusion, and (phenomenological) recombination operators. Here, the rates of chemical transformations of radical pairs are assumed to be constant. Using this approach we have obtained an explicit expression for the case of two radical pairs with reversible transformation. In particular, we have derived operator-free expressions for the case of irreversible transformation within two radical pairs that obey either Fickian diffusion or a two-site model of motion. Containing term proportional to the product of the singlet-triplet oscillation frequencies, these expressions clearly show the non-additivity of singlet-triplet evolution.

We have shown that our theory can incorporate one of the recently published [2] models of chirality-induced spin selectivity (CISS): taking this effect into account leads to the same problem with different spin-Hamiltonian. Whereas spin-spin interaction terms preserve their structure (changing effective parameters), effective magnetic fields in Zeeman terms have different orientations that are dependent on CISS. Therefore, it can be used to describe, for instance, charge transfer in deoxyribonucleic acid (DNA). A simple example demonstrates that the CISS effect leads to a decrease in the amplitude of the conventional singlet-triplet oscillations and to the emergence of much higher-frequency (higher by about three orders of magnitude than the conventional ones) singlet-triplet oscillations.

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Weighted least-squares approach to the weak-signal problem in orientational studies of graphene oxide membranes

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Electron paramagnetic resonance (EPR) spin probe spectroscopy is an effective technique for studying the orientational ordering of graphene oxide (GO) membranes. Quantitative interpretation of experimental spectra is based on numerical simulation, where spin-Hamiltonian parameters and orientational distribution functions are determined by minimizing the difference between experimental and simulated spectra. However, conventional least-squares fitting becomes inefficient when spectra contain components with significantly different intensities. In this case, the optimization process is dominated by the most intense spectral features, while weak signals carrying structural information are fitted with considerably lower accuracy.

In this work, a weighted least-squares approach for numerical analysis of EPR spectra has been developed and implemented. The method allows local weighting of selected spectral regions, increasing the contribution of weak signals to the objective function without modifying the underlying physical model. Both semi-automatic weight assignment, based on user-selected spectral regions, and an automatic procedure employing peak detection have been implemented. The latter enables efficient processing of large sets of experimental spectra.

The proposed approach was applied to the analysis of angular-dependent EPR spectra of nitroxide spin probes confined within graphene oxide membranes. The weighted fitting procedure significantly improved the agreement between experimental and simulated weak spectral features and enabled reliable modeling of room-temperature angular dependencies, which could not be accurately analyzed using the conventional least-

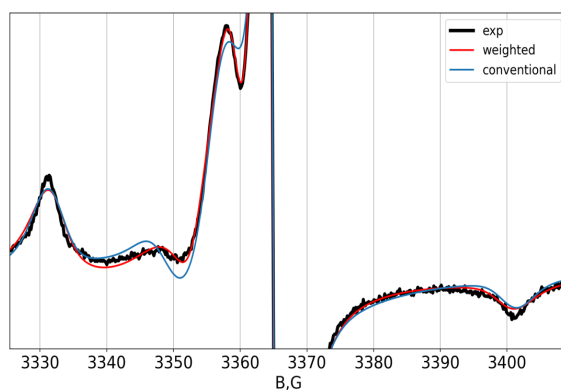


Fig 1. Modeling with conventional and weighted least squares approach.

squares approach. Furthermore, the noise floor of the fitting procedure was estimated using both baseline noise analysis and comparison of spectra recorded at equivalent sample orientations. The developed methodology provides a more reliable reconstruction of orientational distribution functions and extends the applicability of spin-probe EPR for structural characterization of graphene oxide membranes under ambient conditions.

This work was supported by the Russian Science Foundation (RSF), Grant No. 26-13-00023.

Dispersion shape of the EPR spectra lines of the impurity Gd^{3+} ions in the narrow-gap $\text{Pb}_{1-x}\text{Ag}_x\text{S}$ semiconductors: parameters and possible nature of the effect

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The studied mixed crystals of $\text{Pb}_{1-x}\text{Ag}_x\text{S}$ with gadolinium as a probe impurity were synthesized by the vertical Bridgman method. The main component of these crystals was galena, which belongs to the lead chalcogenide group of semiconductors (PbS , PbTe , and PbSe). While the other two semiconductors in this group have long been the focus of attention of many research groups, galena has remained virtually unnoticed. This position of galena was obviously associated with the high volatility of sulfur vapor at elevated temperatures. As a result, a large number of sulfur vacancies and defects associated with these vacancies arose in the volumes of grown galena crystals. Since each sulfur vacancy resulted in the appearance of two free electrons in the conduction band of the grown crystal, the typical conductivity type of this crystal turned out to be n -type. However, the physical properties of the grown PbS crystals turned out to be poorly reproducible.

It is known that a change in the conductivity type of galena can be achieved by introducing an acceptor impurity into its crystal lattice. Some of the acceptor ions will compensate for the influence of the donor ions. But if there are more acceptors than donors, an inversion of the conductivity type will occur in galena. This gives hope of achieving better reproduction of the results of the synthesis of alloyed galena.

As shown in work [1], silver can act as an acceptor impurity in galena. It is obvious that galena with two mutually compensating defects can demonstrate the realization of new, as yet unexplored phenomena. These expectations are based on the fact that galena and other crystals of the lead chalcogenide group are characterized by a number of features: ionic-covalent interatomic bonds with a small proportion of metallic component; narrow band gap ($0.2\div 0.4$ eV, increases with temperature); small effective masses of free charge carriers ($\sim 0.1m_e$) and the associated high mobility of charge carriers; a pronounced dependence of the band structure parameters on impurities: high values of dielectric constant; large spin-orbit interactions of free charge carriers; dipole instability of crystal lattices.

The aim of this work was to study changes in the crystal structure and dynamic properties of galena by doping it with an acceptor impurity of silver. EPR was chosen as the primary experimental method. Gadolinium was selected as the magnetic probe impurity. Three samples with the various concentrations of gadolinium were synthesized ($y_1 = 0.003$; $y_2 = 0.001$; $y_3 = 0.0002$).

The EPR spectra of the sample 1 showed seven broad fine structure lines of Gd^{3+} centers, indicating the presence of exchange interaction between these centers.

The EPR spectra of the sample 2 were more informative. Here, each of the seven lines of the fine structure of the Gd^{3+} centers had a rather complex shape. These lines could be imagined as the superposition of two completely different lines. One of the

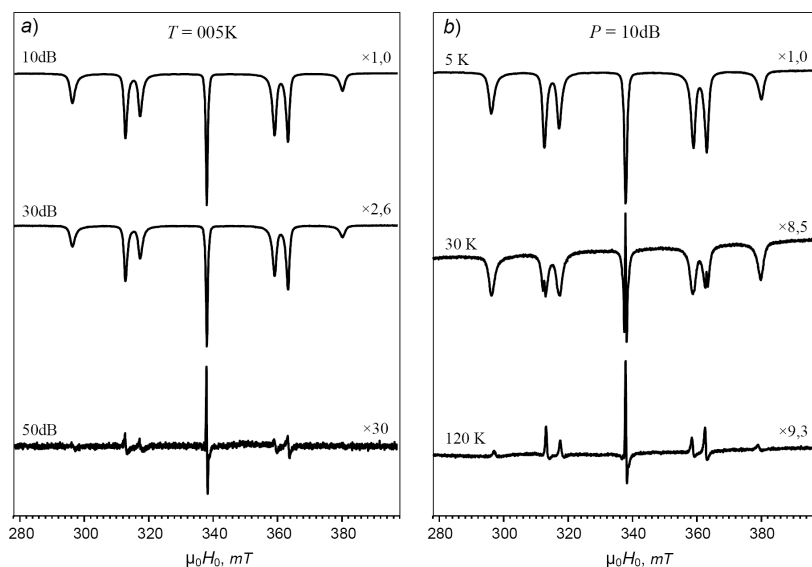


Fig. 1. Power and temperature dependencies in the intensities and shapes of EPR spectra lines of Gd^{3+} centers in the $\text{Pb}_{1-x}\text{Ag}_x\text{S}:\text{Gd}^{3+}$ arrow-band semiconductor ($x = 0.005$; $H \parallel \langle 001 \rangle$; $f_{\text{mw}} = 9.424$ GHz).

two components had a Dysonian shape. Another component of the line was shaped like an inverted bell. Here we will name such shapes as dispersion one. In the sample 2, the amplitudes of the line components were approximately the same. A saturation effect of each line component was observed. It was found the parameters of the saturation effect for each component were different.

In the EPR spectra of sample 3, the “inverted bell” component was predominant at high powers and low temperatures. The Dysonian-shaped component appeared only at very low electromagnetic wave powers in the resonator and at temperatures above 50 K. The power and temperature changes in the shape of the lines of the EPR spectra of Gd^{3+} centers in the sample 3 are shown in Figure 1.

The experimental facts obtained in the study will be discussed.

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Simulation of chirp pulse inversion performance in an inhomogeneous RF field

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In EPR experiment usually one has to cope up with challenge of increased spectral width with limited RF power. A simple hard pulse provides excitation or inversion over a limited range of resonance offsets that cannot be increased due to pulse power constraints. One solution to cope with this problem of bandwidth is use of adiabatic pulses. Adiabatic pulses are known to have increased bandwidths and high tolerance to spatial variations in RF field intensity [1-5].

Magnetization vector $\mathbf{M}$ of isolated spins can be described in the rotating frame by solution of Bloch equations without relaxation

$$\frac{d\mathbf{M}}{dt} = \left(\omega_1, 0, \frac{\partial\varphi}{\partial t} + \Delta\omega \right) \times \mathbf{M}$$

The simplest and most commonly used frequency sweep is a linear sweep defined by

$$\frac{\partial\varphi}{\partial t} = -C + at,$$

where $\Delta\omega = \omega_0 - \omega$, ω_0 is spins frequency distribution, ω_1 – adiabatic pulse amplitude, ω – pulse carrier frequency, a – constant sweep rate.

Simulations show that the maximum value of a for which populations are inverted adiabatically with $\Delta\omega = 0$ is given approximately by $a = 0.2\omega_1^2$. Simulation of spin inversion curves of resonance spin with

$\Delta\omega = 0$ was carried out depending on of the microwave pulse amplitude ω_1 . Deviations of ω_1 from its nominal value of ω_{10} arise experimentally from RF inhomogeneity and from miscalibration of the RF field. Calculations of the spin inversion curves from the parameter $\Delta\omega$ with averaging over the normal distribution of the parameter ω_1 were also carried out. The amplitude of the microwave pulses ω_1 was calculated by the following normal distribution

$$\omega_1 = \omega_{10} \text{Exp}[-\Delta\omega^2 / (2\pi\sigma^2)]$$

The Figure 1 shows the results of calculations for different values of σ the microwave pulse amplitude spread. Calculations performed for rectangle spectrum ω_0 . The carrier frequency ω of the microwave pulses corresponded to the center of the rectangle spectrum. Width of spectrum is $10\omega_{10}$. The calculations were carried out for several values of the inverting pulse duration t_p .

It is evident that near resonance ($\Delta\omega \approx 0$) at short durations ($\omega_{10}t_p < 8\pi$) of the inverting pulse, a good homogeneity of the field ω_1 is required ($\sigma \approx 0.01\omega_{10}$). For sufficiently long durations ($\omega_{10}t_p > 32\pi$) is sufficient to have the RF amplitude spread σ no more than $0.2\omega_{10}$.

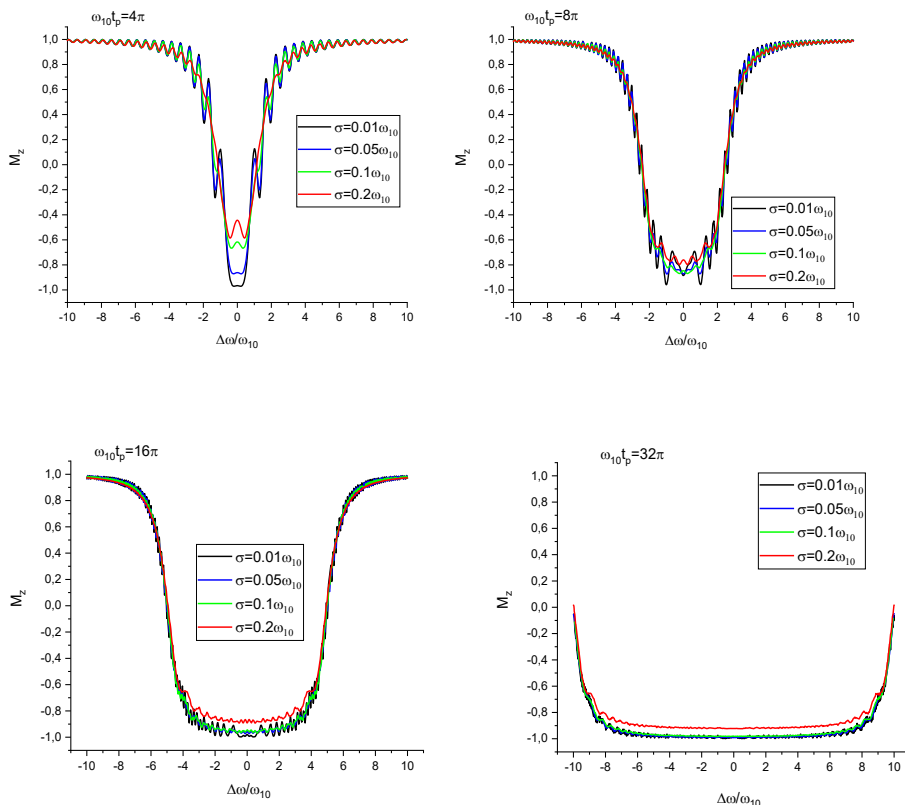


Fig. 1. Inversion curves for linear sweep pulses depending on $\Delta\omega$. The calculations were carried out for several pulse durations t_p and for different values of spatial spread σ of the microwave pulse amplitude.

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High-field EPR spectroscopy for measuring magnetic resonance parameters of heterospin complexes of Cu(II)

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The application of high magnetic fields (>10 T) is a promising approach in EPR spectroscopy, enabling the limitations inherent to conventional X- and Q-band techniques to be overcome [1]. One of them concerns spectral resolution, which is often insufficient to reveal the fine structure of the spectra of paramagnetic centers. For example, in heterospin complexes, where paramagnetic centers of different nature are coupled by exchange interaction, averaging of the individual g-tensors occurs, making their anisotropy weakly pronounced and difficult to distinguish in the spectrum. Increasing the operating frequency of EPR measurements leads to a proportional increase in the separation between resonance lines and, consequently, allows this anisotropy to be resolved.

At the same time, X- and Q-band EPR spectroscopy has several practical advantages. These methods are widely available, making the techniques accessible to many researchers. Additionally, within X- and Q-band EPR, spectra are commonly recorded as the first derivative of the absorption signal, making spectral features more pronounced. How much resolution is actually gained on going from X- and Q-band to the terahertz range is therefore worth establishing experimentally for a given class of compounds.

In this work, the EPR spectra of a series of heterospin complexes with the general formula $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]_2$ were characterized in the X-, Q-, and terahertz (100–576 GHz) frequency ranges. The compounds under study are exchange-coupled systems consisting of two types of paramagnetic centers: a nitroxide radical L^{R} with an isotropic g-tensor, and a Cu(II) ion with an anisotropic g-tensor. Such compounds exhibit spin-crossover-like magnetostructural transitions, which makes them promising for molecular electronics and data storage [2].

The dependence of spectral resolution on the measurement frequency was analyzed, and X- and Q-band EPR were compared with high-field EPR spectroscopy. The results show that a combination of several EPR frequency ranges gives a more complete characterization of exchange-coupled systems than any single frequency range alone.

This research was supported by the Ministry of Science and Innovation Policy of the Novosibirsk Region, Agreement No. 30-2025-000858, RSF project No. 25-13-20039.

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SECTION 3

LOW-DIMENSIONAL
SYSTEMS,
NANO-SYSTEMS
AND MOLECULAR
MAGNETS

Low-lying electronic energy levels correlate with faster electron spin lattice relaxation rates for lanthanide complexes in diverse coordination environments

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EPR spin-lattice relaxation rates were measured at about 4 to 10 K for seven lanthanide(III) ions bound to a phosphine oxide ligand (tris-(3,5-dimethoxyphenyl) phosphine oxide, OPR₃) that forms meridional pseudo-octahedral 6-coordinate complexes [1]. Samples were 10 mM in glassy solvents or 2% doped in diamagnetic hosts. These rates were compared with those for lanthanides in aqueous solution, bound to the protein lanmodulin which creates a 9-coordinate environment, and bound to the bio-inspired small-molecule chelator 3,4,3-LI-(1,2-HOPO) with 9-coordination [2]. Domination of relaxation by low-lying excited states with energies less than about 50 cm⁻¹ is proposed. For this wide range of geometries and ligands there are systematic patterns in the relaxation rates. The slowest rates were observed for Gd³⁺ and attributed to its very small zero field splittings. Of the other EPR active lanthanides, Tm³⁺ consistently has the slowest relaxation rates. For HOPO and lanmodulin complexes relaxation rates for Tb³⁺ and Er³⁺ are the fastest. At 4 K no echoes were observed for the complexes of Tb³⁺ and Er³⁺ complexes of OPR₃ which is attributed to very fast electron spin relaxation. Tb³⁺ and Er³⁺ have multiple low-lying excited states. Complexes of Yb³⁺, Nd³⁺, Ce³⁺, and Sm³⁺ have intermediate relaxation rates.

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ODMR based mapping of diamond and silicon carbide with nanometer resolution

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Optically addressable paramagnetic point defects or “spin centers” in diamond and silicon carbide are widely studied for applications in quantum information processing, quantum sensing, biological and medical imaging, telecommunications and spintronics. For their practical application, it is important to know their parameters and local environment, which can be determined by analyzing optically detected magnetic resonance (ODMR) spectra.

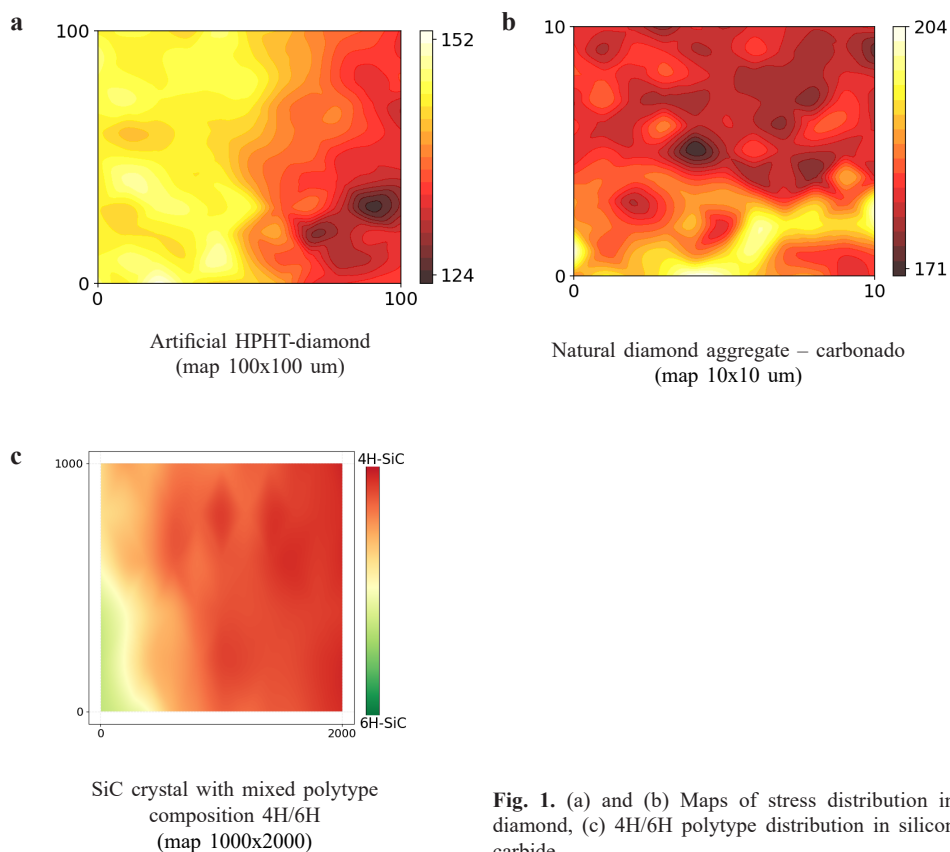


Fig. 1. (a) and (b) Maps of stress distribution in diamond, (c) 4H/6H polytype distribution in silicon carbide.

The photoluminescence and ODMR allow one to determine a wide range of diamond parameters, such as: nitrogen concentration (based on the intensity ratio of the satellite lines to the main line in the ODMR spectrum of NV centers), NV center concentration (based on the line intensity in the ODMR spectrum), the ratio of NV⁻ and NV⁰ centers (based on the intensity ratio of the corresponding lines in the PL spectrum), internal stresses (based on the splitting of the central line in the zero field ODMR spectrum), temperature (based on the zero-field splitting parameter D), and magnetic field (based on the line positions). For silicon carbide, the method also allows visually distinguishing between different polytypes (based on the spectra of photoluminescence and level anticrossings). Using a scanning confocal ODMR spectrometer developed in the Ioffe Institute based on a microscope from NT-MDT we could measure ODMR in every point on the sample surface and construct maps of different parameters. The construction of such maps requires the processing of a large volume of data - ODMR spectra, and a special program was created for this purpose.

An example is given in the Fig. 1, which shows map of stress distribution in two samples of diamond (a) and (b), and a map of 4H/6H polytype composition in a SiC single crystal irradiated with 2 MeV electrons. The value of stresses in diamond was determined from the splitting of the ODMR lines of NV defects in zero magnetic field, the polytype composition in SiC was determined based on photoluminescence spectra.

This work was supported by the Russian Science Foundation (project № 23-12-00152-II, <https://rscf.ru/project/23-12-00152-II>).

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Magnetic properties of PrF_3 nanoparticles

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PrF_3 is a dielectric Van Vleck paramagnet. The Pr^{3+} ion has a $4f^2$ electron structure. The ground state multiplet $^3\text{H}_4$ splits into nine singlets. The nucleus of this rare earth element has a nonzero nuclear spin of $5/2$, and compounds of this element exhibit nuclear magnetism. PrF_3 can be used to dynamically polarize the nuclear spins of ^3He [1].

PrF_3 nanoparticles measuring 20–50 nm were obtained by hydrothermal synthesis with coprecipitation from a colloidal solution. Structure, size, and morphology were monitored by X-ray diffraction analysis (Bruker D8 Advance Cu $\text{K}\alpha$, $\lambda = 1.5418 \text{ \AA}$) and transmission electron microscopy (Hitachi HT Exalens).

Helium-3, due to its nonzero nuclear spin of $1/2$ and its ability to remain liquid at low temperatures, is of great interest. ^3He has several advantages when used as a probe for studying porous media. The longitudinal relaxation times T_1 of liquid ^3He in bulk liquid are 1000 seconds, but can be shorter in a porous structure. Relaxation is also influenced by paramagnetic centers, which create local magnetic fields. In the case of paramagnetic particles, ^3He relaxation will also depend on the proximity of the paramagnetic particles to each other and their size. Studying these processes is crucial for understanding the relaxation mechanisms in such a system.

In this work, we investigated the NMR of ^{141}Pr and ^{19}F in PrF_3 nanoparticles and the NMR of He in contact with these particles. The measurements were performed on a laboratory-made NMR spectrometer [2]. The spectra and times of spin-lattice and spin-spin relaxation of ^{141}Pr in contact with liquid ^4He and ^3He were measured at frequencies of 6.63 MHz and 19.5 MHz. Magnetic coupling between the ^{141}Pr and ^3He nuclei was observed. The effect of PrF_3 powder on the longitudinal and transverse relaxation of ^3He nuclei in the adsorbed layer, in gas, liquid, and in a system with adsorbed ^4He (measurements at 1.5 K, fields up to 800 mT) was also studied. The relaxation mechanisms were analyzed, and a model describing them was proposed.

This work was financially supported by the Russian Science Foundation (Project No. 26-22-20044).

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³He NMR based measurement of the paramagnetic layer depth in LaF₃:Gd³⁺ delta doped nanoparticles

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The properties of core-shell nanoparticles depend on the concentration and location of paramagnetic impurities [1]. In this work low-temperature nuclear magnetic resonance (NMR) of adsorbed ³He was used to determine the location depth of a Gd³⁺-containing layer in LaF₃-based delta-doped nanoparticles.

Core-shell-shell nanoparticles were synthesized from pill-shaped LaF₃ cores coated with a 0.3 nm La_{1-x}Gd_xF₃ paramagnetic layer and an outer diamagnetic LaF₃ shell using colloidal precipitation method. The designed diamagnetic outer-shell thickness is 1.0 nm for the samples which have 5% and 30% Gd³⁺ containing in a paramagnetic shell and 0.5 nm for the 0.3% case.

Pulsed ³He (1.5–7 K) and ¹⁹F (1.5–70 K) NMR measurements were performed at 15–18 MHz. The ³He spin-lattice relaxation time was measured on the raw surface and after precoating with zero to three solid N₂ monolayers. Each layer increases the probe-to-surface distance by approximately 0.33 nm.

A finite-layer model of Gd³⁺-induced ³He spin-lattice relaxation was developed from the previous delta-layer model [2]. Fits of the relaxation-rate maxima (obtained from the temperature dependences) versus the number of N₂ layers by this relaxation model yielded location depths $d_0 = 0.7 \pm 0.2$ nm for the 5% Gd³⁺ sample with a designed

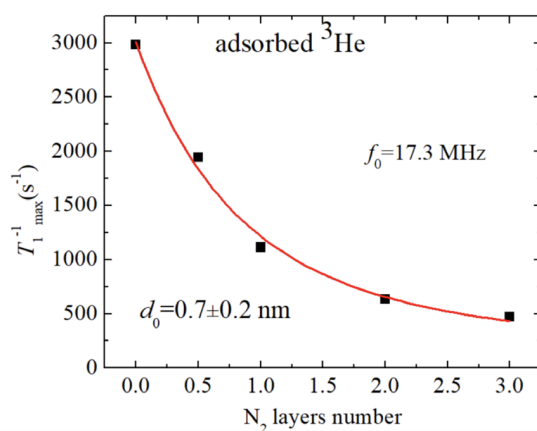


Fig. 1. Maximum ³He longitudinal relaxation rate versus the number of N₂ layers for the 5% Gd³⁺ LaF₃-La_{0.95}Gd_{0.05}F₃-LaF₃ sample. The solid line is the model fit.

1.0 nm outer shell and $d_0 = 0.28 \pm 0.03$ nm for the 0.3% sample with a designed 0.5 nm shell (Fig. 1).

The difference between designed and measured depths reveals shell-growth imperfections and demonstrates sensitivity to synthesis deviations. The 30% Gd^{3+} sample can't be measured because of very fast relaxation of ^3He . The ^{19}F relaxation is weakly sensitive to shell thickness and Gd^{3+} concentration because of the spin-diffusion barrier, whereas adsorbed ^3He is a sensitive probe for characterizing nonuniform magnetic nanoparticles and controlling their synthesis.

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Polarized neutron reflectometry in oscillating magnetic fields: resonant phenomena in low-dimensional magnetic systems

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Polarized neutron reflectometry (PNR) is a powerful method for studying magnetic and superconducting multilayer thin films and superlattices [1]. By measuring the four spin-dependent reflection channels, one can separate nuclear and magnetic contributions to the scattering-length density and reconstruct the magnetization depth profile with nanometer resolution [2, 3]. This technique has been successfully applied to investigate proximity effects in ferromagnet/superconductor systems, nontrivial magnetic ordering, and quasiperiodic Fibonacci structures [1–4].

The resonance method associated with spin neutron resonance is described in [5–7]. It involves the application of an oscillating magnetic field perpendicular to the static quantizing field. Evidence for neutron spin resonance in thin films has been found, and a spatial beam-splitting due to the exchange of an energy quantum $\hbar\omega$ between the oscillating field and the neutron has been observed [5]. This approach is also promising for studying other resonance phenomena using reflectometry with polarized neutrons: Josephson resonance, ferromagnetic resonance, inverse Faraday effect, nuclear magnetic resonance, etc.

At present, a working prototype for neutron reflectometric studies in an oscillating magnetic field has been developed at the REMUR spectrometer (IBR-2 reactor, Dubna). The field frequency is 10–30 MHz, the amplitude is 1–10 Oe. First measurements on an iron film show clear modulation of the polarized neutron reflection, confirming the feasibility of the method. A low-temperature system with ^4He pumping is being developed for operation in a highly uniform magnetic field created by a polar magnet with warm coils. This will enable time-resolved studies of domain-wall motion and vortex dynamics at cryogenic temperatures.

The combination of static-field PNR and RF-PNR is particularly valuable for investigating ferromagnetic-superconducting layered heterostructures and Fibonacci quasicrystals, where the interplay between magnetism and superconductivity leads to exotic phenomena such as triplet superconductivity, fractal superconductivity, and the paramagnetic Meissner effect [8–10]. Neutron-optical simulations for Fibonacci

sequences (orders F_6 – F_{12}) predict stable "quasi-Bragg" peaks and enhanced absorption, indicating that quasiperiodicity may stabilize long-range magnetic order even without translational invariance [11]. Our ongoing work focuses on experimental realization of these systems and on extending RF-PNR to study dynamic magnetic processes in low-dimensional structures.

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Modeling of the magnetic response of low-scaled spin structures

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Different modifications of carbon, such as fullerene arrays, have electrical, optical and mechanical properties that are valuable for practical applications [1]. The properties of these materials can be controlled by introducing metal cores into the shells or by depositing magnetic ions on the carbon surface. In addition, the described materials can find applications in the development of new systems for storing, processing and transmitting information using spin magnetic moments [2].

In our work we made direct calculations of Schrödinger equation with dipole-dipole interactions in magnetic field to see graphs of free induction decay of low-scaled spin systems. At our spectra graphs for random spherical spin structure we observed additional peaks (Fig. 1) which are close to zero and appear only in the rotating coordinate system (RCS) spectra for disordered structures (in the spectrum of a rectangular ordered structure we cannot see the same thing). Also there is no strong division of the main peak into several, as was the case with the ordered rectangular structure.

In this work we are conducting a theoretical analysis to understand the nature of additional peaks. In our work [3] we observed different random spin structures in rotating frame with dipole interaction and obtained additional peaks in their spectra. Also in [3] we made the analytical estimate of two interacting spins free conduction decay. In described analytical calculations [3] we did not find any low-frequency terms. Now we

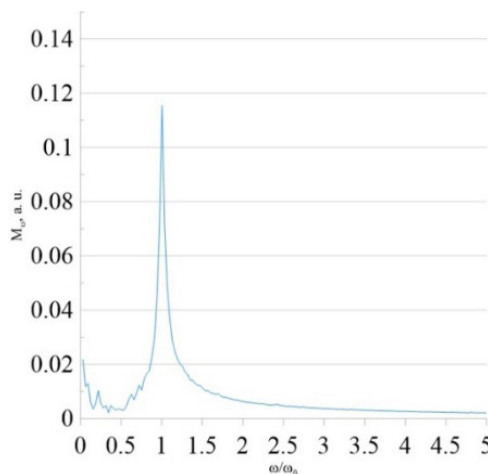


Fig. 1. Magnetization spectrum for a random spherical shell in RCS. Number of spins is 9, number of realizations is 100.

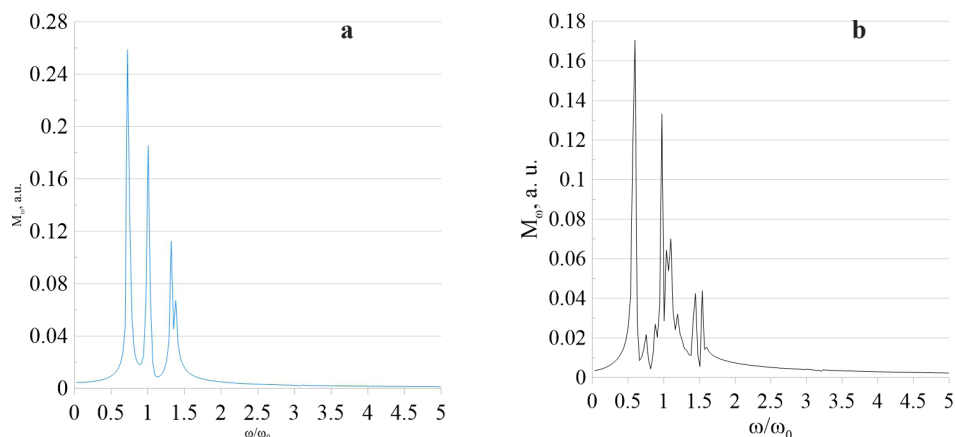


Fig. 2. Magnetization spectra for low-scaled spin chains in RCS. a – chain of 3 spins with two close spins and one distant spin; b - chain of 4 spins with three close spins and one distant spin.

assume that low-frequency dynamics can be found in higher dimensions and in this work we are considering other low-scaled theoretical models with higher number of spins and different arrangements in space.

Calculations of systems of three spin chains in RCS with different distances between particles showed us several clear peaks without the rise in zero on the spectra graph (Fig 2 a). A chain of four spins with three close spins and one distant spin in RCS shows a complicated structure of its spectra graph and also without the rise in zero (Fig 2 b).

In the work we want to study the fine structure of the spectra of our low-scaled spin models and understand the conditions for the appearance of low-frequency signals in some spectra.

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The influence of graphene oxide membranes architecture on their functional properties

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The selective permeability of graphene oxide membranes (GOM) makes them promising for the separation of various liquids and gases. The magnitude and selectivity of the GOM permeability are influenced by a variety of factors, among them there is inner membrane architecture, which includes alignment of individual oxidized graphene layers and ordering of layer-packages (lamellae). It has been demonstrated that more ordered membranes exhibit higher selective permeability for water and better separation properties toward low-molecular-weight organic impurities [1].

In the present work, the methods have been developed to quantitatively characterize the membrane structure at different length scales (Fig. 1). The spin probe method proves to be more sensitive to the nanoscale features of the layers ordering, whereas the numerical analysis of SEM images is more sensitive to the microscopic features of lamellae packing. The first correlations were also obtained between the architecture of graphene oxide membranes and their functional properties, including sorption and permeability for polar substances.

The work was supported by Russian Science Foundation № 26-13-00023

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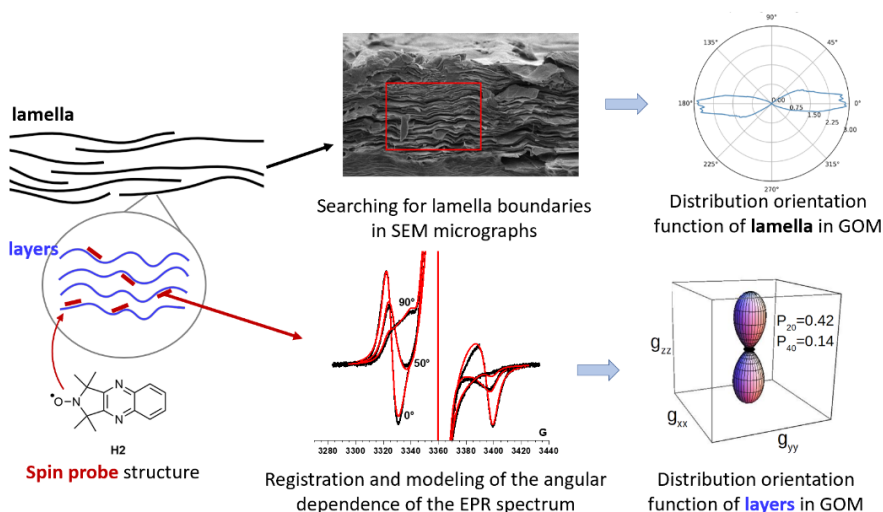


Fig. 1. Scheme for analyzing the architecture of graphene oxide membranes using numerical analysis of SEM micrographs (top) and the spin probe method (bottom).

^1H NMR monitoring of DyF_3 nanoparticle agglomeration

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Time-resolved ^1H NMR is a non-destructive method for probing the state of nanoparticle dispersions through the relaxation of the surrounding liquid. In colloidal systems containing paramagnetic DyF_3 nanoparticles, transverse relaxation is governed by water-surface interactions, molecular diffusion, and local magnetic-field inhomogeneities. Changes in particle organization therefore modify the effective interfacial area and the distribution of water environments. The aim of this work is to monitor the agglomeration of DyF_3 nanoparticles in aqueous dispersions using time-resolved ^1H transverse relaxation measurements.

After ultrasonic redispersion, the samples are studied as a function of time by the Carr-Purcell-Meiboom-Gill pulse sequence at a room temperature. The transverse magnetization decays are analyzed using regularized inverse Laplace transformation to obtain relaxation times distributions.

The measurements show non-monoexponential transverse magnetization decays and systematic time-dependent changes in the relaxation times distributions. The positions, widths, and relative amplitudes of the relaxation modes provide markers of the redistribution of water between environments associated with dispersed nanoparticles and agglomerates. In the investigated concentration and size range, the evolution of a longer relaxation times contribution is treated as an empirical marker of cluster formation, whereas the shorter relaxation times contribution is associated with the remaining dispersed fraction.

The study indicates that time-resolved ^1H NMR combined with relaxation-distribution analysis can provide non-destructive, time-resolved monitoring of DyF_3 nanoparticle agglomeration. The approach yields kinetic descriptors of cluster formation and can be applied to compare synthesis, post-treatment, and stabilization for dysprosium-based nanoparticles. This methodology is relevant to the characterization of magnetic nanomaterials and to the optimization of materials considered for high-field MRI applications [1, 2].

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

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Modeling of structural and magnetic properties of $\text{Gd}_{1-x}\text{R}_x\text{MO}_3$ compounds

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In this work, models of $\text{Gd}_{1-x}\text{R}_x\text{TiO}_3$ and $\text{Gd}_{1-x}\text{R}_x\text{FeO}_3$ compounds with different degrees of rare earth ion substitution were constructed and optimized. Calculations were performed in the MedeA environment using the VASP package. Lattice parameters and unit cell volumes were determined for ferrites and titanates. It has been established that a change in the nature of the R^{3+} ion leads to a regular change in the cell volume. The partial substitution of Gd^{3+} by R^{3+} also led to a decrease in the symmetry of the computational models.

Local spin and orbital magnetic moments were estimated for a number of rare-earth titanates, taking into account the spin-orbit interaction. It has been established that the main contribution to the magnetic moment is formed by the rare-earth sublattice, whereas the Ti sublattice in most cases partially compensates for this contribution. For heavy rare earth ions, the orbital component plays an essential role, therefore, consideration of the spin-orbit interaction is necessary to analyze the magnetic characteristics of such compounds.

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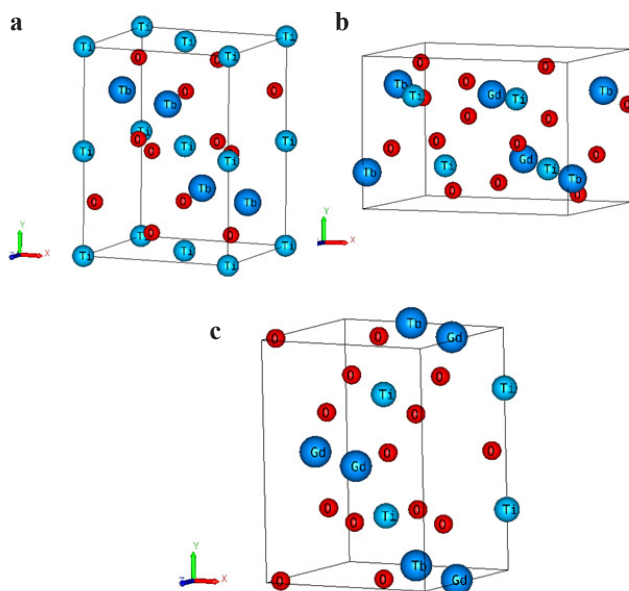


Fig. 1. Optimized structures of Tb-containing titanates with different degrees of substitution: **a** TbTiO_3 , $x = 1$, Pnma symmetry; **b** $\text{GdTbTi}_2\text{O}_6$, $x = 0.5$, $\text{Pmc}2_1$ symmetry; **c** $\text{Gd}_3\text{TbTi}_4\text{O}_{12}$, $x = 0.25$, Pm symmetry

Dependence of the ferromagnetic–paramagnetic transition temperature on microwire size in $\text{Co}_{83}\text{Fe}_7\text{C}_1\text{Si}_7\text{B}_2$ and $\text{Fe}_{45}\text{Co}_{30}\text{Si}_{10}\text{B}_{15}$

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Thin ferromagnetic glass-coated metallic microwires of compositions $\text{Co}_{83}\text{Fe}_7\text{C}_1\text{Si}_7\text{B}_2$ (s1) and $\text{Fe}_{45}\text{Co}_{30}\text{Si}_{10}\text{B}_{15}$ (s2–s4) with different sizes were prepared by the Taylor–Ulitovsky method. They exhibit various magnetization reversal modes, including bistable, stepwise, and S-shaped behavior with enhanced coercivity [1]. Co-based microwires with near-zero magnetostriction show step-like hysteresis loops [2], whereas magnetostrictive microwires are highly sensitive to the d/D ratio [3]. The effects of post-processing on the magnetic properties of amorphous and nanocrystalline microwires, including the roles of magnetoelastic, induced, and magnetocrystalline anisotropies, have been extensively studied [4]. The influence of sample geometry (ρ -ratio) on the magnetic anisotropy field has also been demonstrated [5]. Using an EPR spectrometer (Varian-12, 9.48 GHz), first-derivative microwave absorption spectra were recorded up to ~ 770 K in magnetic fields up to 10 kOe. The microwire was positioned vertically in the center of

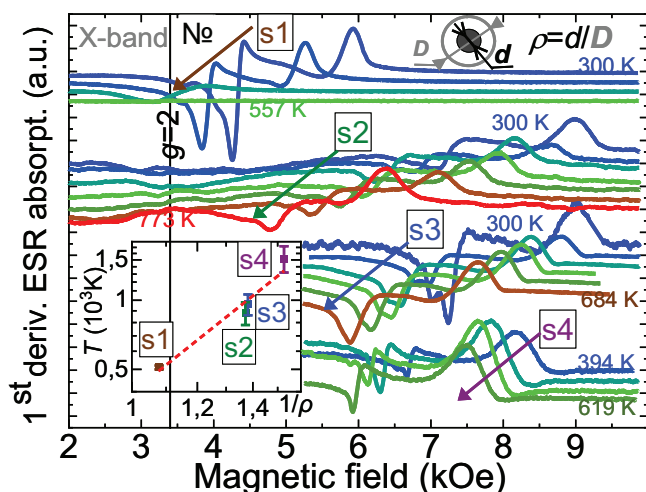


Fig. 1. EPR spectra of samples at different temperatures. Insert: Phase transition temperatures for micro-wires with different ratios of internal and external diameters.

a TE_{102} cavity, parallel to the microwave magnetic field. The spectra resemble those of powders and contain several lines associated with the g -tensor components (g_x , g_y , g_z) of ferromagnetic resonance. Above 510 K, the three resonance lines of $Co_{83}Fe_7C_1Si_7B_2$ ($\rho = 0.927$) merge into a single line, indicating a ferromagnetic–paramagnetic transition (Fig. 1). Using a similar power-law extrapolation, the transition temperatures of $Fe_{45}Co_{30}Si_{10}B_{15}$ microwires with different ρ values (0.729, 0.724, and 0.655) were estimated (inset to Fig. 1). The microwire size likely affects the dimensions of ferromagnetic regions and, consequently, the phase-transition temperature.

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Transition between transverse relaxation and regular spin dynamics in dipole chain

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The magnetization dynamics of classical linear dipole chains under constant external field is simulated numerically. The effect of initial longitudinal magnetization is considered for varying chain length. Total magnetization with its Fourier spectrum and local magnetization with spatial spectrum are analyzed.

If the average initial longitudinal magnetization μ_0^z is large, the signal exhibits regular behavior. Moreover, when $\mu_0^z \sim 0.9$, the travelling wave pattern is observed in magnetization map. There is a stable picture of independent waves propagating and reflecting from the chain ends with energy exchange between different spatial modes. So, here is a dynamics regime with synchronized phases of particle oscillations.

When μ_0^z is less than 0.30, the transverse relaxation becomes significant. In this case, the wave picture is broken, and dipole evolution seems to be independent. In continuum limit, this transition can be explained qualitatively by blocking of the travelling waves. Nevertheless, it is an open question whether the phases of individual particles are absolutely desynchronized or they just have zero mean with stable differences but remains in synchronization.

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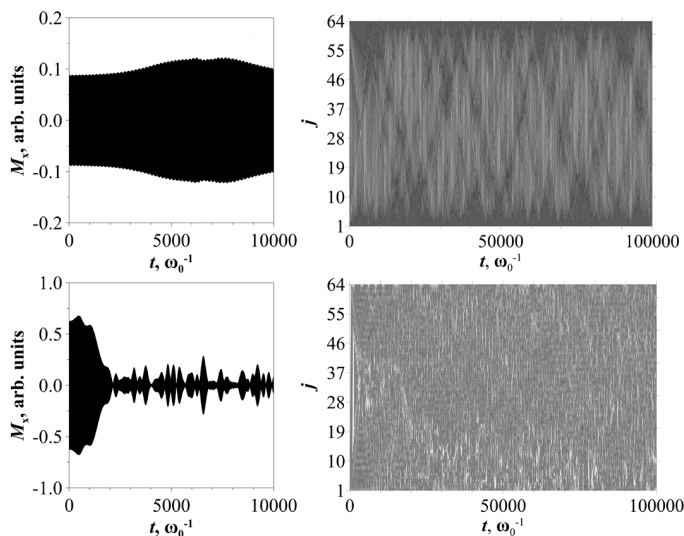


Fig. 1. Evolution of total and local transverse magnetization of linear spin chain with different initial longitudinal value: $\mu_0^z = 0.99$ (top), $\mu_0^z = 0.01$ (bottom).

Control of temperature dependence of coercive force in multilayer epitaxial films $\text{Pd}_{96-x}\text{Fe}_4\text{Co}_x$

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Ferromagnetic thin films, including gradient structures and systems with variable compositions, are being actively investigated in connection with the possibility of controlling their magnetic properties, in particular, the coercive force H_C and its temperature dependence $H_C(T)$ [1].

In the classical case of homogeneous ferromagnets, the coercive force typically decreases with increasing temperature. However, in gradient and compositionally inhomogeneous films, the behavior of $H_C(T)$ can deviate significantly from the classical one [1].

For example, in epitaxial Co–Ru films with a given Ru concentration profile, the temperature dependence of the coercive force can change substantially [2, 3]. In a specific temperature range, the coercive force may remain nearly constant, enabling the design of magnetic structures with tailored temperature stability of their properties.

In this paper, we study a series of single-layer and multilayer epitaxial ferromagnetic thin films based on a Pd–Fe alloy with a fixed iron content (4 at. %) and a variable concentration of cobalt. The Co concentration varies in the range $x = 0\text{--}4$ at. %, while the palladium content decreases from 96 to 92 at.%, which corresponds to the composition of $\text{Pd}_{96-x}\text{Fe}_4\text{Co}_x$.

The samples were grown by molecular beam epitaxy in an ultrahigh vacuum “SPECS” system on crystalline magnesium oxide (MgO) substrates. The growth process and surface quality were monitored in real time using low-energy electron diffraction (LEED). The final film thickness was controlled using a Bruker DektakXT stylus profilometer. The composition and its distribution were analyzed using an ultrahigh vacuum analytical module equipped with X-ray photoelectron spectroscopy. Magnetic and magnetotransport properties were measured using a Quantum Design PPMS-9 system in the temperature range of 5–400 K. This allows us to determine the nature of the magnetization reversal process and to assess the contributions of domain wall nucleation and pinning mechanisms to the formation of the coercive force.

The results obtained can be used in the development of multilayer and composite magnetic structures with a given temperature dependence of the coercive force. Varying the alloy composition and forming complex profiles make it possible to stabilize the coercive force over a wide temperature range or to realize its non-monotonic behavior, including growth in a given temperature range.

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Melting of the surface layer of the implanted GaAs and Si by the halogen incandescent lamps

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The aim of the work was to determine the effect of ion implantation (II) with Se^+ , In^+ , As^+ and B^+ ions and pulsed light heating (PLH) on the mechanism of formation of recrystallized relief periodic microstructures from the molten phase on the surface of a GaAs and Si plates [1].

GaAs and Si plates of the KEF brand with a crystallographic surface orientation of (001), (110)+7° and (111) as samples for the study were used. II by Se^+ ions with energy $E = 400$ keV and doses $D = 3.74 \times 10^{13} \text{ cm}^{-2}$, In^+ ions with energy $E = 40$ keV and doses $D = 5 \times 10^{16} \text{ cm}^{-2}$, As^+ ions with energy $E = 30$ keV and dose $D = 2 \times 10^{16} \text{ cm}^{-2}$, B^+ ions with energy $E = 40$ keV and a dose of $D = 6.25 \times 10^{15} \text{ cm}^{-2}$ were performed.

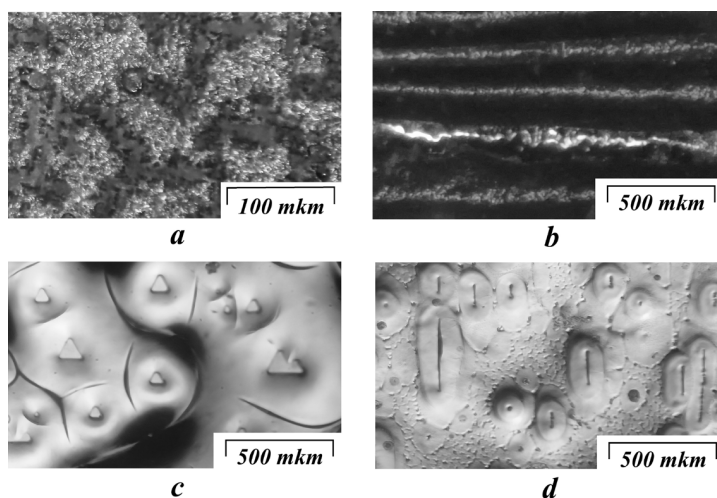


Fig. 1. Micrographs of the surface of II **a** GaAs(001) by Se^+ ions with energy $E = 400$ keV and doses $D = 3.74 \times 10^{13} \text{ cm}^{-2}$, **b** GaAs(110)+7° by In^+ ions with energy $E = 40$ keV and doses $D = 5 \times 10^{16} \text{ cm}^{-2}$, **c**– Si(111) by B^+ ions with energy $E = 40$ keV and a dose of $D = 6.25 \times 10^{15} \text{ cm}^{-2}$, and **d** Si(111) by In^+ and As^+ ions with every energy $E = 30$ keV and dose $D = 2 \times 10^{16} \text{ cm}^{-2}$ after PLH duration of $t = 6$ s.

The samples were PLH with pulses of second durations from halogen incandescent lamps on a Pulse-6 installation with a radiation power density of one lamp $W = 10 \text{ W} \cdot \text{cm}^{-2}$ with a pulse duration of 6 s (there are 22 lamps). The modified surfaces of the Si samples were analyzed using an MBS-9 optical microscope. The formed structures were recorded on a digital camera.

Influence of anions on the magnetic properties of mixed-valence heptanuclear iron complexes

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Polynuclear complexes hold promise for the creation of multifunctional materials whose magnetic properties are sensitive to light and heat. This work continues our investigation of the properties of the mixed-valence heptanuclear Fe(II)-Fe(III) cation $[\text{Fe(II)(CN)}_6\{\text{Fe(III)(L)}\}_6]^{2+}$ ($\text{L} = \text{N,N'-bis}[(2\text{-hydroxyphenyl)methylene}]\text{-4-azaheptane-1,7-diamine dianion}$) with various anions. As was previously established by magnetometry and CW-EPR methods, the replacement of the Cl^- anion with NCS^- leads to the manifestation of spin transition properties [1]. It has also been shown that the observation of the TR-EPR signal is due to a photoinduced transition from the high-spin to the low-spin state of Fe(III) [2]. This study focuses on newly synthesized complexes of the heptanuclear cation with the BF_4^- , PF_6^- , and NO_3^- anions.

The resulting compounds were characterized by UV-*vis* spectroscopy and powder XRD. Using the DFT method, probable geometric configurations of the complexes were calculated for two multiplicity (M) variants: $M = 31$, for which all six Fe(III) atoms have spin $S = 5/2$, and $M = 7$ ($S = 1/2$), for a low-spin state of the central Fe(II) atom.

The magnetic properties of the samples were studied using SQUID magnetometry, CW-, and TR- EPR. It was found that the nature of the anion not only influences the presence of a spin transition in the system but also determines the nature of the exchange interactions in the compounds.

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Observation of an unusual double quantum transition in the EPR spectrum

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The growing interest in molecular spin systems for quantum information processing and dynamic nuclear polarization demands a detailed understanding of multi-quantum coherence effects in coupled electron–nuclear ensembles. Here we report a previously unobserved spectral feature in the quantum dynamics of an $S = 1$ system, revealed by continuous-wave EPR. Along with the canonical triplet signal, an extra line appears at the spectrum center [1, 2]. Increasing the microwave power induces satellite lines not only near the main triplet transitions but also around this central component—a behavior not captured by standard spin-Hamiltonian models. We show that these satellites arise from hyperfine coupling to solvent protons. The central feature, however, is most intriguing: it corresponds to an unconventional double-quantum transition in which the two microwave quanta are absorbed with markedly different probabilities. This asymmetry originates from the fact that one quantum can only be absorbed if accompanied by a solvent proton spin flip. The observed effect offers a way to detect formally forbidden transitions and to probe local nuclear environments in related systems.

The work was supported by the ongoing funding of the FRC Kazan Scientific Center, Russian Academy of Sciences.

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Study of the magnetic properties of micro and nanosized DyF_3 powder

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Dysprosium fluoride DyF_3 is a dipolar ferromagnet with an easy axis of magnetization along the [010] axis of the crystal lattice [1]. The compound possesses unique properties, making it suitable for use as a high-field MRI contrast agent [2] and as an additive to Nd-Fe-B magnets to increase their coercivity [2].

DyF_3 powders with characteristic dimensions of $30 \text{ nm} \times 16 \text{ nm}$, $50 \text{ nm} \times 30 \text{ nm}$, $70 \text{ nm} \times 40 \text{ nm}$, and $220 \text{ nm} \times 150 \text{ nm}$ were synthesized hydrothermally via a chloride route. The 20 nm powder was prepared via a nitrate route, while the $7 \mu\text{m} \times 5 \mu\text{m}$ powder was obtained by crushing a single crystal. Control of the chemical composition and confirmation of crystallinity were carried out using X-ray phase analysis. Micrographs obtained using scanning and transmission electron microscopy were used to determine the shape and characteristic size of particles in the resulting powders.

In this work, the magnetization curves of the samples were measured in magnetic fields from 0 to 7 T at temperatures of 5, 10, 20, and 50 K. The energy spectrum was simulated using the exchange charge model. The saturation value of the magnetic moment in high magnetic fields varies with decreasing particle size. It is shown that the change in magnetization is caused by surface effects and clustering.

The temperature dependences of the heat capacity were measured in magnetic fields up to 9 T. The magnetic entropy change, heat capacity, relative cooling capacity, and adiabatic temperature change were calculated. It is shown that DyF_3 particles can be effective for magnetocaloric cooling at liquid hydrogen and liquid helium temperatures. The effect of particle size on the magnetocaloric properties of the DyF_3 powder was investigated, and the optimal size for practical application was identified.

We measured the rates of longitudinal and transverse relaxation of helium-3 nuclei in contact with DyF_3 (99.67%) and LaF_3 (0.33%) powder in the adsorbed layer, in the liquid bulk, and in the case of coating particles with a helium-4 layer depending on the temperature in the range 1.5–3 K in the fields of 173 and 505 mT. In the case of liquid helium-3, in the absence of helium-4 coating of particles, a two-component relaxation of the longitudinal and transverse magnetization is observed. A possible explanation for this phenomenon is proposed.

This work was supported by the Russian Science Foundation (Project No. 23-72-10039).

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Resonance response of finite two-dimensional ising-like ferromagnets

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Low-dimensional ferromagnets constitute a convenient model class for analysing the relation between microscopic exchange interactions and magnetic-resonance spectra. In contrast to infinite crystals, finite two-dimensional magnetic flakes have a discrete spectrum of spin excitations; their resonant response depends not only on exchange and anisotropy, but also on sample geometry, boundary coordination and size. This work considers a concrete finite-size problem: the calculation of magnon resonance modes in square and honeycomb Ising-like ferromagnetic flakes with open boundaries. The emphasis is placed on the finite-lattice splitting of resonance lines and on the shift of the lowest magnon gap caused by the Ising anisotropy.

The model Hamiltonian is taken in the form

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} (S_i^x S_j^x + S_i^y S_j^y + \Delta S_i^z S_j^z) - h \sum_i S_i^z, \quad J > 0, \quad \Delta > 1.$$

Here J is the ferromagnetic exchange constant, Δ is the easy-axis anisotropy parameter and h is the external static field. The finite systems are represented by a 20×20 square flake and by a honeycomb flake with the same number of spins, $N = 400$. The linear spin-wave approximation is obtained from the Holstein-Primakoff representation, $S_i^z = S - a_i^\dagger a_i$, $S_i^\pm \approx \sqrt{2S} a_i$. Keeping only quadratic terms gives the finite-dimensional magnon problem

$$\mathcal{H}_2 = E_0 + \sum_i A_i a_i^\dagger a_i - JS \sum_{\langle i,j \rangle} (a_i^\dagger a_j + a_j^\dagger a_i), \quad A_i = h + JS \Delta z_i,$$

where z_i is the local coordination number. Therefore, the resonance frequencies are the eigenvalues of the matrix $M_{ij} = A_i \delta_{ij} - JS \mathcal{A}_{ij}$, $M \psi_\alpha = \omega_\alpha \psi_\alpha$,

where $\mathcal{A}_{ij}$ is the adjacency matrix of the chosen finite lattice. The imaginary part of the model magnetic susceptibility is reconstructed as a set of broadened resonance lines,

$$\chi''(\omega) = \sum_\alpha I_\alpha \frac{\Gamma}{(\omega - \omega_\alpha)^2 + \Gamma^2}, \quad I_\alpha = \left| \sum_i \psi_\alpha(i) \right|^2.$$

The numerical data below were obtained for $S = 1/2$, $J = 1$, $h = 0.05J$ and $\Gamma = 0.02J$. For the square flake the calculated lowest frequencies are 0.050, 0.144, 0.414, 0.883, 1.550 at $\Delta = 1.00, 1.05, 1.20, 1.50, 2.00$, respectively. For the honeycomb flake the corresponding values are 0.050, 0.120, 0.301, 0.566, 0.899. Thus, increasing Δ opens a rapidly growing finite-size gap, while the honeycomb geometry

produces lower edge-influenced modes because of the reduced boundary coordination. The strongest resonance line is not always the lowest eigenmode; at large anisotropy the lowest mode becomes predominantly boundary-localized, whereas the main response is shifted to a more extended collective mode.

The finite-mode calculation was also checked against standard two-dimensional Ising finite-size scaling exponents $\beta = 1/8$, $\gamma = 7/4$ and $\nu = 1$. These values were used as a normalization benchmark for the size dependence of the computed susceptibility. The full size-dependent spectral data, together with the corresponding resonance-line intensity tables, will be reported in the full-length article; the representative gap and resonance curves are shown in Fig. 1.

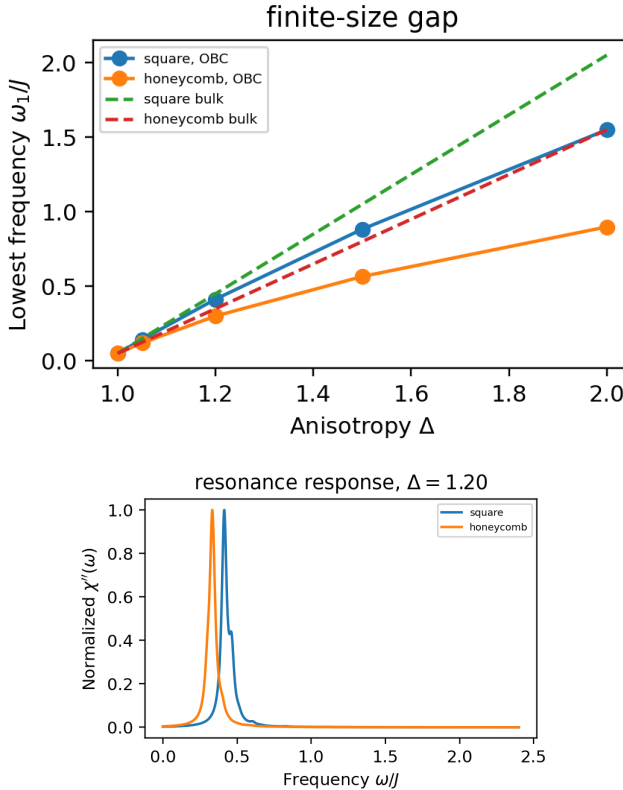


Fig. 1. Calculated finite-size magnon gap and model resonance response for square and honeycomb Ising-like ferromagnetic flakes with open boundaries. Parameters: $S = 1/2$, $J = 1$, $h = 0.05J$, $\Gamma = 0.02J$.

The proposed formulation separates the universal spin-wave part from the finite-geometry contribution encoded in the adjacency matrix. It provides a single operator framework for comparing different two-dimensional lattices and shows that the low-frequency resonance response is governed by local coordination, boundary geometry and Ising anisotropy. Thus these effects must be taken into account when interpreting magnetic-resonance spectra of nanoscale two-dimensional ferromagnets; the same framework can be compared with laboratory spectra by fitting J , Δ , h and Γ .

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Engineering electronic and magnetic behavior in functionalized MXene nanoclusters via first-principles calculations

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This study investigates the electronic and magnetic properties of edge-functionalized MXene clusters using first-principles calculations. Atomistic models of Cr_2C , Mo_2C , and W_2C MXene clusters functionalized with hydroxyl (-OH) and oxygen (-O) groups were constructed and systematically analyzed using density functional theory (DFT). The calculations reveal that both the transition-metal composition and surface functionalization strongly influence the structural stability, electronic band structure, density of states, bond energy, and spin polarization of the clusters. Furthermore, increasing cluster size and modifying the surface termination induce significant changes in the magnetic and electronic transport properties, highlighting the tunability of these materials for advanced spintronic, nanoelectronic, and catalytic applications. Comparison of the computational results with available experimental data demonstrates good agreement, supporting the reliability and practical relevance of the proposed models. Overall, this work provides valuable insight into the size- and functionalization-dependent behavior of MXene-based clusters and establishes a theoretical framework for the rational design of MXene nanostructures with tailored electronic and magnetic functionalities.

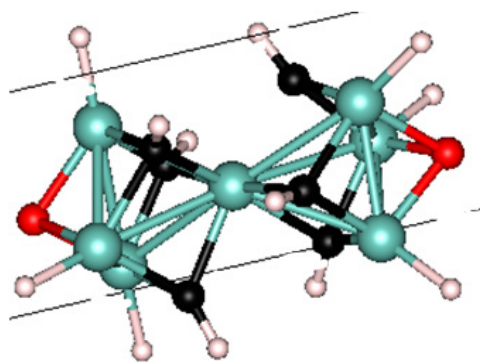


Fig. 1. The original structure of the $\text{Mo}_7\text{C}_6\text{O}_2\text{H}_{12}$ cluster. Mo is gray, C black, O is red, and H is pink.

Conditions of 180° switching of the quasiuniform magnetization in planar Ni particles by thermally induced magnetoelastic effect

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One of the tasks in straintronics [1] that currently being studied is to provide a 180° switch of the particles magnetization direction by inducing only uniaxial stresses in them. Since such the stress make an anisotropy axis, the desired switch cannot be achieved directly due to symmetry considerations. However, it can be achieved through serial rotations of the magnetization direction. Uniaxial stress can be created by varying the size of substrate. This can be done in controllable manner by varying the temperature of a single-crystal substrate, which has different thermal expansion coefficients along different crystal axes. Heating or cooling the sample relative to the particle formation temperature allow to compress or stretch them, i.e., allow to make an axis of magnetoelastic anisotropy in two mutually perpendicular directions. Certain single crystals, such as LiB_3O_5 (LBO), allow for significant particle deformation even with a small change in temperature [2].

In this study, the conditions for magnetization switch in planar square-shaped with concave sides particles of Ni deposited on LBO was investigated. Such particles can maintain a quasiuniform magnetization direction at large enough lateral sizes. The lateral size of a particle was defined as the side of the square into which the particle was inscribed. Concaveness of the sides (CS) was defined as the inverse ratio (taken as a percentage) of the particle's width at its narrowest point to the whole side. The simulation was performed for particles with CS of 24%, 32%, and 40%, and a height of 30 nm. A possibility of 180° magnetization switch was tested using the following algorithm: the initial equilibrium state of the particle without mechanical stress was calculated; the particle was compressed along a specific axis; stress was removed; the particle was stretched along the same axis; stress was removed. The magnitude of uniaxial stress was taken to be 320 MPa, which corresponded to a temperature variation of $\pm 20^\circ\text{C}$. The lateral sizes, CS, and the angle (α) between the initial magnetization direction and the uniaxial stress axis were found at which magnetization rotates by 180° (Table 1). The calculations shows that particles with CS 40% and with the lateral size range of 0.95-3.19 μm looks promising for further experimental studies.

Table 1. The range of lateral sizes of Ni particles at which 180° switch of the magnetization direction is observed, depending on the concavity degree and the α .

CS	$\alpha = 60^\circ$	$\alpha = 65^\circ$	$\alpha = 70^\circ$	$\alpha = 75^\circ$	$\alpha = 80^\circ$	$\alpha = 85^\circ$	$\alpha = 86^\circ$	$\alpha = 87^\circ$	$\alpha = 88^\circ$	$\alpha = 89^\circ$
24%	0.27-0.35	0.24-0.35	0.24-0.35	0.24-0.35	0.29-0.35	0.32-0.35	0.34			
32%			0.38-0.75	0.33-0.94	0.35-1.29	0.55-1.29	0.54-1.29	0.58-1.29	0.48-1.29	
40%			1.4	1.31-2.28	0.95-3.19	0.83-5.53	0.63-8	0.73-9	0.68-9	0.79-9

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Compositional structure influence on FMR properties of epitaxial $\text{Pd}_{1-x}\text{Fe}_x/\text{Pt}$ thin film bilayers

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A progress in microelectronics calls for novel approaches to the development of information storage devices characterized by low energy consumption and high switching rates. In this context, particular attention has been drawn to spintronics – a field that exploits not only the charge but also an intrinsic magnetic moment (spin) of the electron for information transmission and processing [1]. One of the actively developing fields is superconducting spintronics, which utilizes mutual influence of superconductors and ferromagnets in hybrid heterostructures. The implementation of superconducting spin valves requires ferromagnetic materials with a specific set of properties: a low Curie temperature, a small saturation magnetization, and a moderate coercive field. These requirements are satisfied by weak ferromagnets based on the $\text{Pd}_{1-x}\text{Fe}_x$ solid solution with an iron content of $x \leq 12$ at. % [2].

In the present work, single $\text{Pd}_{1-x}\text{Fe}_x$ films (20 nm) with $x = 10$ and 12 at. %, as well as their bilayers with platinum (12 nm) on top of these films, were synthesized by molecular beam epitaxy on $\text{MgO}(001)$ substrates [3]. The choice of platinum as the normal-metal layer is driven by its strong spin-orbit coupling and close lattice matching with $\text{Pd}_{1-x}\text{Fe}_x$ [4]. Both types of heterostructures were subjected to post-growth annealing: the $\text{Pd}_{0.9}\text{Fe}_{0.1}/\text{Pt}$ -800 sample at 800 °C and the $\text{Pd}_{0.88}\text{Fe}_{0.12}/\text{Pt}$ -600 sample at 600 °C, each for one hour.

X-ray diffraction study of the crystal structure revealed that, prior to annealing, both the $\text{Pd}_{0.9}\text{Fe}_{0.1}/\text{Pt}$ (Figure 1) and $\text{Pd}_{0.88}\text{Fe}_{0.12}/\text{Pt}$ heterostructures exhibited two angle-resolved (002)-type reflections originating from the Pt and Pd-Fe layers. The emergence of a single reflection at an intermediate angle between those of Pt and Pd-Fe after annealing at 800°C indicates a complete mutual dissolution of the two layers. In contrast, the characteristic shifts of the peak positions preserving two distinct reflections after annealing at 600°C can be naturally attributed to partial intermixing of layers at their interface. Evidently, this produces a composition gradient across that region. Phi-angle scans, together with the observation of sharp low-energy electron diffraction patterns, confirm that all samples are single-crystalline and exhibit «cube-on-cube» epitaxial relationships: $\text{Pd}_{1-x}\text{Fe}_x(001)[100] \parallel \text{MgO}(001)[100]$ and $\text{Pt}(001)[100] \parallel \text{Pd}_{1-x}\text{Fe}_x(001)[100]$.

Ferromagnetic resonance (FMR) measurements were performed at a temperature of 20 K using the Bruker ESP300 spectrometer operating in the X microwave band (~10 GHz). In the in-plane magnetic field configuration, a ~20 % broadening of the resonance line is observed for the heterostructure (Figure 2) compared to the single-layer thin film [5]. This broadening is attributed to an additional damping of the magnetization precession arising from the spin pumping effect. The shift of the heterostructure's

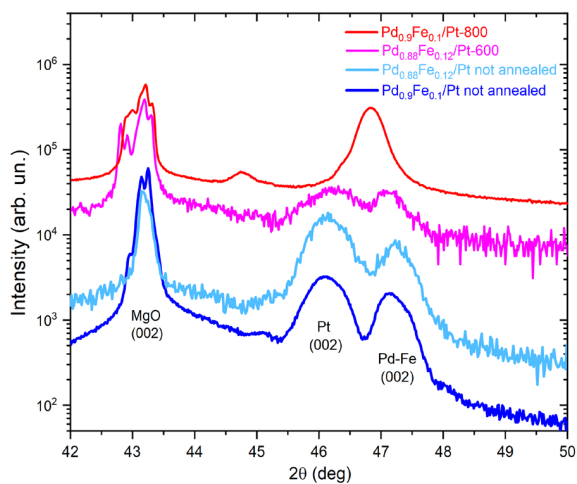


Fig. 1. θ - 2θ X-ray diffraction patterns recorded at $\varphi = 0^\circ$ and $\chi = 0^\circ$ for the following samples: $\text{Pd}_{0.9}\text{Fe}_{0.1}/\text{Pt}$ (blue line), $\text{Pd}_{0.88}\text{Fe}_{0.12}/\text{Pt}$ (cyan line), $\text{Pd}_{0.88}\text{Fe}_{0.12}/\text{Pt}$ -600 annealed at 600°C (violet line), and $\text{Pd}_{0.9}\text{Fe}_{0.1}/\text{Pt}$ -800 annealed at 800°C (red line).

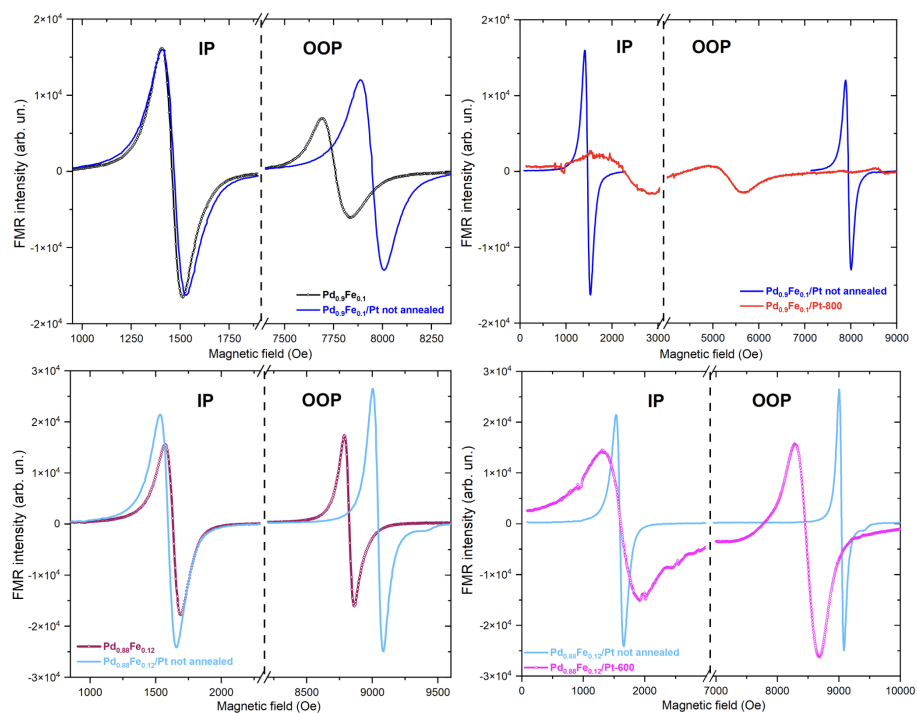


Fig. 2. Ferromagnetic resonance spectra measured with the static magnetic field applied in the in-plane (IP) and out-of-plane (OOP) configurations.

resonance line toward higher fields relative to that of the single film in the out-of-plane configuration is caused by an interfacial contribution to the magnetic anisotropy.

Annealing at 800°C resulted in a strong, 10 times, broadening of the resonance line and a reduction in the span between the resonance fields in the in-plane and out-of-plane configurations. The broadening stems from local inhomogeneities in the distribution of Pd and Pt atoms surrounding the Fe atoms, induced by the layer mixing. The reduction of the span is associated with a decrease in the saturation magnetization of the sample due to the dilution of the overall iron concentration. The line broadening induced by the annealing at 600°C was less pronounced (a factor of 5), and shifts of the resonance field were likewise smaller, which corroborates the conclusion that only partial intermixing of the two layers has occurred, accompanied by the formation of a gradient region.

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Synthesis and magnetic properties of dysprosium-doped lutetium titanates and lanthanum zirconates with pyrochlore structure

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Single-ion magnets (SIMs) are a type of compounds whose magnetic properties are determined by the presence of individual magnetic centres in an anisotropic local environment, rather than their interaction. At low temperatures SIMs can retain residual magnetization after the removal of an external magnetic field. At higher ones they demonstrate slow relaxation of magnetization. Such materials may find an application in spintronics and may be used as qubits in quantum computers. Inorganic SIMs are of particular interest because of their chemical, thermal, mechanical stability and practical convenience. The realisation of single-ion magnets with superior functional characteristics requires a high crystal field anisotropy of the magnetic ion [1]. For instance, in compounds with a pyrochlore structure with the general formula $A_2^{III}B_2^{IV}O_7$, the coordination environment of the trivalent ion at the A site is close to hexagonal-bipyramidal, corresponding to strong axial anisotropy. In particular, incorporation of Dy^{3+} ions into this site provides pronounced uniaxial magnetic anisotropy, as a result these compounds exhibit slow magnetization relaxation [2, 3]. In this work, dysprosium-substituted lutetium titanates and lanthanum zirconates with the pyrochlore structure and the general formulae $Lu_{2-x}Dy_xTi_2O_7$ and $La_{2-y}Dy_yZr_2O_7$, where $x = 0, 0.02, 0.1$ and $y = 0, 0.002, 0.02, 0.1$, were prepared by solid-state synthesis. Powder X-ray diffraction analysis confirmed that the pyrochlore phase is the predominant phase in all samples, with impurity fractions remaining minimal. A systematic increase in unit cell parameters for lutetium titanates and decrease for lanthanum zirconates with increasing dysprosium percentage was observed, indicating successful incorporation of Dy^{3+} ions into the crystal structure. The magnetic properties of the compounds were investigated via DC and AC magnetometry. A narrow-waist magnetic hysteresis loop was identified in both series for the first time, characterized by a zero-field pinched shape typical of single-ion magnets. DC magnetometry data indicate that all samples possess high values of magnetic anisotropy. AC magnetometry revealed the presence of slow magnetization relaxation. Two peaks are observed in the imaginary component of the frequency-dependent susceptibility at certain temperatures. The effective energy barriers for the Orbach process are approximately 200 and 500 cm^{-1} for lutetium titanates and lanthanum zirconates, respectively.

This work is financially supported by the Russian Science Foundation project No. 25-23-00892.

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The shape change of Neel's skyrmion as a result of an electric field

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The influence of an external electric field on the change in shape and on the magnetic properties of Néel skyrmions [1–3] in a thick film has been studied. The emergence of the Néel skyrmion in ferromagnetic insulators with Dzyaloshinskii-Moriya interaction [4, 5] has been considered within the framework of the phenomenological approach. The change in skyrmion properties under the influence of a homogeneous external electric field applied to the surface of a ferromagnet has been studied. The electric field was applied perpendicular to the surface of the ferromagnetic film. The Euler-Lagrange equation was written for the free energy of the ferromagnet. The solution of the equation has been found that corresponds to the minimum of the free energy.

An analytical solution of the Euler-Lagrange equation has been found for the ansatz proposed in [3]. This solution has the form of a three-dimensional skyrmion “tube” with a variable radius, whose shape depends on the direction of the electric field and the parameters of the ferromagnet. It was shown that the shape of the Néel skyrmion can be controlled by an external electric field.

The work was carried out at financial support from the government assignment of the FRC Kazan Scientific Center of RAS.

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^1H NMR study of acetonitrile fractions and relaxation in graphite oxide

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Graphite oxide (GO) is a promising material for membrane-based separation of polar liquids, but its development is limited by insufficient knowledge of molecular transport in the interlayer space. Using ^1H NMR spectroscopy, we have studied the molecular dynamics of acetonitrile intercalated in GO powder. Spectral analysis as a function of temperature and saturation level reveals two coexisting fractions of intercalated acetonitrile: a low-mobility fraction and a more mobile one. This two-phase behavior agrees well with independent EPR studies [1].

Relaxation measurements performed via various methods have provided estimates of correlation times for molecular motions, which vary with the degree of sample saturation and offer insight into the underlying relaxation mechanisms. The combination of NMR spectral and relaxation data demonstrates a complementary approach for probing molecular mobility in GO-based materials.

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Spin 1/2–3/2 crossover in a chain antiferromagnet Cs_2CoCl_4

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Cs_2CoCl_4 is a quasi-1D antiferromagnet with magnetic Co^{2+} ions carrying spin $S = 3/2$. The main exchange $J = 0.74$ K acts along the chains directed parallel to b -axis. The interchain exchange integral J' is an order of magnitude weaker [1, 2]. Remarkable feature of this material is strong single-ion anisotropy $D = 7$ K of the easy-plane type. This anisotropy results in separation of the upper spin doublet of Co^{2+} ion from the lower one and makes possible the use of a pseudospin $S = 1/2$ representation at low temperatures. As a result, strong easy-plane anisotropy of the effective exchange interaction and the renormalization of the g -factor should arise [3]. Thus spin system of Cs_2CoCl_4 should be equivalent to the set of weakly interacting strongly anisotropic chains of pseudospins $S = 1/2$ (the so-called XXZ chains). The quantum model of $s = 1/2$ XXZ antiferromagnetic chain is known to demonstrate remarkable collective ground states and excitations. There is a quantum critical spin liquid in zero field, long-range 1D-antiferromagnetic order in transverse field and restored spin liquid state before saturation. Collective excitations are of spinon-type [4]. Some of these features were detected experimentally [1, 3, 5].

The aim of this work is to check whether the crossover between spin-3/2 and pseudospin-1/2 really occurs. We observed the characteristic spectrum of spin-3/2 at the easy-plane crystal field anisotropy and followed the transformation of this spectrum into the spectrum of spin $S = 1/2$ with renormalized g -factor. We studied the spin dynamics at temperatures from 3 to 250 K in the wide frequency range 25–250 GHz and in the magnetic field applied along the a - and b -axes. $\mathbf{H} \parallel b$ is the only direction at which magnetic field lies within easy planes for all Co^{2+} ions. Local anisotropy axes of Co^{2+} ions have the same direction within each spin chain but alternates from one spin chain to another. Temperature evolution of 102 GHz ESR for $\mathbf{H} \parallel b$ is shown in Fig. 1a. It exhibits two modes A and B. The mode B is obviously thermally activated. This confirms the population of the upper spin doublet with heating. Energy levels calculated for single spin $S = 3/2$ with easy-plane anisotropy and corresponding frequency-field dependencies are shown by solid and dashed lines in Fig. 1c and Fig. 1b [6]. We notice good accordance of theory with experiment at $T = 15$ K with fitting parameters $D = 7.9$ K and $g = 2.15$. This correspondence and thermally activated intensity of B approve that at high-temperatures ($T \gtrsim D$) we deal with the system of paramagnetic spins $S = 3/2$ in a crystal field. At temperatures $T \lesssim 3$ K we observe g -factor of A mode $g_A = 3.3$. This value is in a good accordance with the theoretical expectation of pseudospin $S = 1/2$ g -factor $g_{1/2} = 4(I - 3J/2D)$ [3]. We also observe a small temperature shift of the resonance field of mode B towards lower fields (see Fig. 1a at heating presumably associated with an abrupt population growth of the upper Kramers doublet.

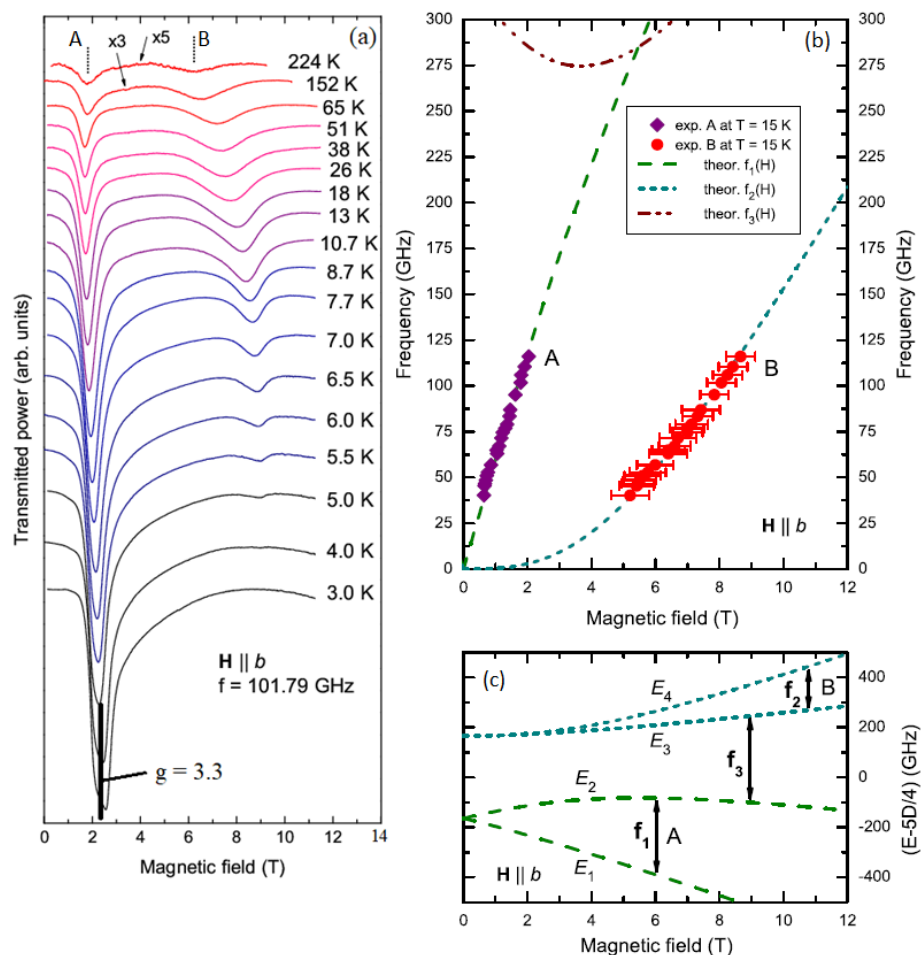


Fig. 1. **a** $f = 101.79$ GHz ESR records at different temperatures. **b** Frequency-field diagram taken for $T = 15$ K compared to the theory (solid and dashed lines) with $g = 2.15$ and $D = 7.9$ K. **c** Energy levels of single spin-3/2 with $g = 2.15$ and $D = 7.9$ K.

Thus we conclude that at lowering the temperature below 15 K a crossover from spin-3/2 to pseudospin-1/2 occurs in Cs_2CoCl_4 .

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Low temperature magnetism and g -factor anisotropy in the compound $\text{CaCuSi}_4\text{O}_{10}$

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Cuprorivaite $\text{CaCuSi}_4\text{O}_{10}$ is a synthesized quasi-two-dimensional layered copper silicate, which is the primary component of the ancient Egyptian Blue pigment and may serve as a model object for low-dimensional magnetism [1-3]. The compound crystallizes in a tetragonal symmetry (space group $P4/ncc$, No. 130). The local symmetry of the copper site is described by the D_{4h} point group, where the magnetic Cu^{2+} ($S = 1/2$) cations reside in a square planar oxygen environment.

In this work, the magnetic characteristics of the $\text{CaCuSi}_4\text{O}_{10}$ single crystal were investigated using ESR spectroscopy and static magnetometry. The ESR experiments were carried out with the help of spectrometer based on an Agilent network analyzer (GPI RAS) [4]. The sample was placed in a cylindrical cavity (TE_{011} mode) and tested at the microwave frequency of 60 GHz at $T < 40$ K (Fig.1). Static magnetization mea-

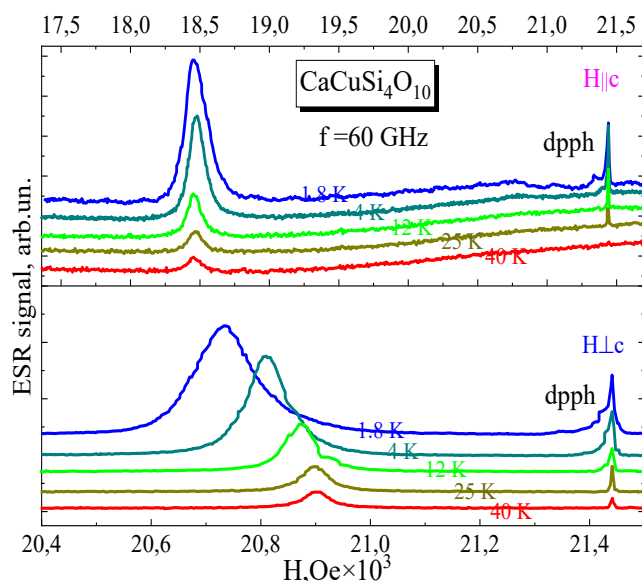


Fig. 1. Temperature evolution of the $\text{CaCuSi}_4\text{O}_{10}$ ESR spectrum for two directions of magnetic field. $H \perp c$ corresponds to the geometry when the applied magnetic field is parallel to lattice layers, $H \parallel c$ is the perpendicular geometry.

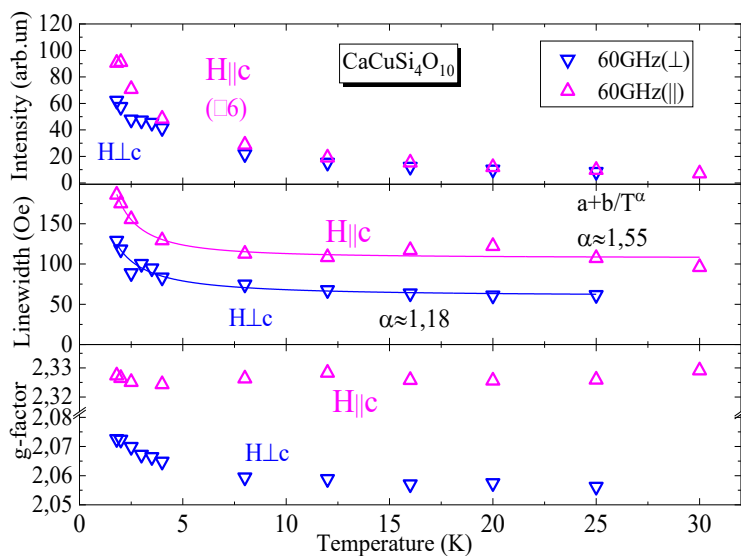


Fig. 2. Temperature dependencies of the ESR intensity, linewidths, and g-factors at $f = 60$ GHz.

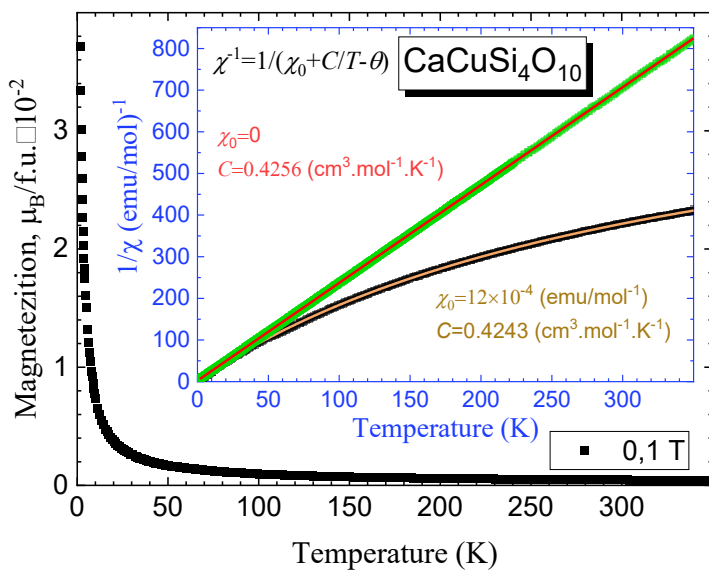


Fig. 3. Temperature dependence of the static magnetization at $H = 0.1$ T. Inset: black dots represent the inverse molar static magnetic susceptibility of the sample as a function of temperature; green dots show the data after subtracting the χ_0 contribution.

measurements were performed in magnetic fields ranging from 0 to 5 T and within a temperature range of 2–10 K using a Quantum Design SQUID MPMS XL5 magnetometer.

ESR spectrum of the $\text{CaCuSi}_4\text{O}_{10}$ single crystal depends on the direction of applied magnetic field that allows to study separately parallel (or longitudinal) and perpendicular (or transversal) ESR components (Fig. 1). The observed picture is in agreement with the presence of a unique Cu^{2+} paramagnetic centers with one unpaired 3d-electron and in the B_{1g} ground state of an apparent D_{4h} axial ligand field geometry [1]. Analysis of the angular dependencies of the ESR spectra revealed a pronounced axial anisotropy of the g -factor (Fig. 2), which is in good agreement with the literature data $2.32 < g_{\parallel} < 2.34$ and $2.055 < g_{\perp} < 2.08$ [1–3].

Interestingly, lowering of temperature results in substantial variation of perpendicular $g_{\perp}$ parameter, the parallel one staying almost constant (lower panel in Fig.2). The observed increase in the effective $g_{\perp}$ -factor may indicate the development of strong spin correlations due to the tiny changes in the ligand field geometry.

As the temperature decreases, a pronounced widening of the ESR linewidth was also observed (Fig. 2). This divergency, which can be fitted by the relation $a + b/T^{\alpha}$ with the exponents $\alpha_{\parallel} \approx 1.55$ and $\alpha_{\perp} \approx 1.18$ (Fig. 2), seems to be induced by enhancing spin relaxation processes to be more effective for parallel magnetic field.

The temperature dependence of the magnetic susceptibility $\chi(T)$ in the high-temperature region obeys strictly the Curie-Weiss law, taking into account the temperature-independent contribution χ_0 (Fig. 3). Paramagnetic Curie temperature $\theta \approx -1.01 \pm 0.07$ K was estimated from the linear fit of the $1/(\chi(T) - \chi_0)$ dependence. Low θ value indicate rather weak antiferromagnetic character of the intra-layer exchange interaction. The effective magnetic moment was found to be $\mu_{\text{eff}} \approx 1.84 \mu_B$. The obtained macroscopic value of μ_{eff} demonstrates an excellent agreement with the average value calculated from the g -tensor components of the ESR data $\mu_{\text{mean}} \approx 1.86 \mu_B$. At the same time, the different temperature evolution for the parallel and perpendicular components of g -factor as well as the enhancement of spin relaxation at low temperatures require detailed analysis of the origin of anomalous magnetic properties of this intriguing compound.

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Anisotropic magnetoresistance in magnetic tunnel junctions

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We study the influence of spin-orbit interaction (SOI) effects, induced by spin-polarized currents, on the tunneling anisotropic magnetoresistance (TAMR) in magnetic tunnel junctions (MTJs) of the type ferromagnetic metal/ δ -barrier/ferromagnetic metal (FM/ δ /FM). Analytical expressions for the currents and TAMR are derived within an approximation in which the dependence of the magnetoresistance on the magnetization orientation in the ferromagnets arises from interference between Rashba and Dresselhaus SOIs at the interfaces of the ferromagnetic metal and the δ -barrier. Additionally, we investigate the influence of SOI effects and magnetization orientation on TAMR in FM/SC/FM junctions, where SC is a semiconductor.

The conventional tunnel magnetoresistance (TMR) effect measures the difference between the conductivities of an MTJ in parallel and antiparallel configurations of the electrode magnetizations [1]. Here, we demonstrate that in FM/ δ /FM and FM/SC/FM heterostructures, conventional TMR becomes anisotropic due to SOI effects.

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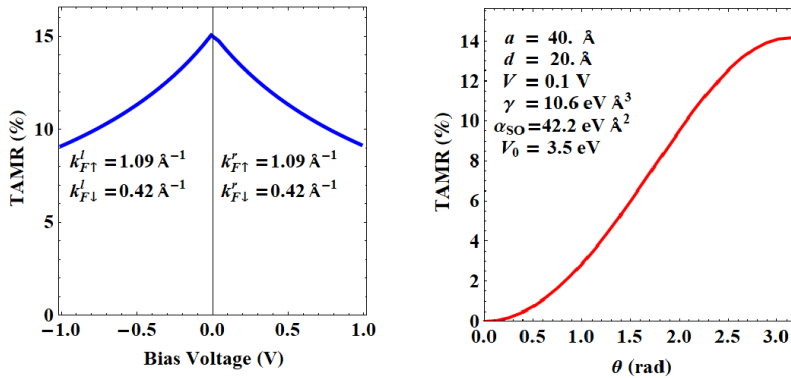


Fig. 1. Dependences of the TAMR on the applied voltage V and the angle θ between the magnetizations orientations of the ferromagnetic contacts. The magnetic orientation of the left (l) ferromagnet is specified relative to the crystallographic direction [110]. The graph panels show the heterostructure parameters: $k_{F,s}^{l(r)}$ are the absolute values of the Fermi wave vectors of the left (l) and right (r) ferromagnets ($s=\uparrow, \downarrow$ is the spin index of the conduction electron), a is the radius of the contact (barrier), d is the thickness of the δ -barrier, V_0 is the height of the δ -barrier (in energy units of eV), γ and α_{SO} are the phenomenological parameters of the Dresselhaus and Rashba SOIs, respectively [2].

SECTION 4

SPIN-BASED
INFORMATION
PROCESSING AND
OPTICAL
QUANTUM
TECHNOLOGIES

A selective pulse sequence for implementing associative memory on two qutrits via quantum annealing

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Quantum computing has evolved from a research topic [1] to a proposed approach for business applications [2]. Quantum artificial neural networks are not excluded either. One of the tasks for them is associative memory problem (the ability of a machine to remember and reproduce patterns). Previously, we proposed an algorithm for implementing the associative memory problem [3] using quantum annealing on qutrits (quantum system with three energy levels), and also considered alignment of the amplitudes of stored states mechanisms for improving pattern recognition [4]. In the proposed work, a simple example on two qutrits is considered, the experimental implementation of which is possible, for example, on NV centers in diamond [5], as well as on other physical systems. In the selected system [5], one of the qutrits is the nuclear spin ^{14}N $I=1$ and the another is the electronic state with $S=1$. This system is described by the following Hamiltonian:

$$H = D(S^z)^2 + \omega_e S^z + Q(I^z)^2 + \omega_n I^z + AS^z I^z, \quad (1)$$

where $D = 2.87$ GHz is the zero-field splitting. $Q = -4.95$ MHz is the quadrupole interaction constant. ω_e (ω_n) is the Zeiman frequency. $A = -2.16$ MHz is the hyperfine interaction constant.

Let's return to our algorithm. It is described by the following annealing Hamiltonian:

$$H(s) = sH_{mem} + s\Gamma H_{prob} + s(1-s)H_{help} + (1-s)H_0, \quad (2)$$

where $s = t/T$ is the annealing schedule. H_{mem} is memory Hamiltonian that creates a superposition of memorized states corresponding to stored patterns. H_{prob} is a recognition Hamiltonian that reduces the energy of the recognized level. H_{help} is a alignment Hamiltonian. At initial moment of time, system is prepared in the ground state of initial Hamiltonian H_0 – Hamiltonian of interaction with a transverse magnetic field. Then the Hamiltonian adiabatically changed in time (in the discrete-time approximation) to the final Hamiltonian, in the ground state of which we encode the solution of the problem [3, 4]. To implement the algorithm on a physical system, the interaction (2) in the evolution operator $\exp[-i\Delta t H(s)]$ should be expressed with interactions (1) (where Δt is the time discretization value). Effective Hamiltonian is implemented with rotation operators selective for transitions between the 9 levels of the system (1). Each such rotation operator is associated with a rectangular pulse described by the following Hamiltonian:

$$H_{pulse} = AS^z I^z + D(S^z)^2 + Q(I^z)^2 + (\omega_e - \omega_z)S^z + (\omega_n - \omega_z)I^z - \\ - \gamma_e \hbar_{pulse} (S^x \cos \varphi + S^y \sin \varphi) - \gamma_n \hbar_{pulse} (I^x \cos \varphi + I^y \sin \varphi), \quad (3)$$

where ω_z is frequency of attached RF (or MV) pulse, which determines the selectivity of the attached impulse: $\omega_{rf} = \omega^{k \leftrightarrow l} = E_k - E_l$ for the transition between levels k and l , γ_e (γ_n) are the gyromagnetic ratios of the electron and nucleus, respectively, h_{pulse} is the amplitude of the rotating field, and φ is the phase of the pulse. This Hamiltonian is substituted into the evolution operator $\exp[-it_{pulse}H_{pulse}]$ of selective rotation, where t_{pulse} is the pulse duration. To mitigate the phase shift error, t_{pulse} should be multiple $2\pi/\omega_e$, $2\pi/\omega_n$, $2\pi/Q$, $2\pi/D$. Therefore $t_{pulse} = (2\pi l)/\omega_n$, where l is an integer. The rotation angle is determined by the ratio: $\theta = \sqrt{2}\gamma h_{pulse}t_{pulse}$, from which the pulse amplitude is determined. We find the amplitudes and durations of rectangular RF and MV pulses in the control pulse sequence, and performed numerical simulation. Also we studied the dependence of the implementation fidelity on the parameters. We took NV center as two qutrits, but the results obtained will be useful for controlling quantum processors based on qutrits represented by other systems.

The study was supported by a grant from the Russian Science Foundation No. 25-22-00750, <https://rscf.ru/en/project/25-22-00750/>.

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Control of the states of quadrupole nuclei through hyperfine interaction with electrons

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Paramagnetic impurities (color centers) in a solid matrix, together with the nuclear spins surrounding them, are proposed as systems for processing quantum information [1]. For example, NV centers in diamond and ^{13}C , ^{14}N nuclei [1–4]. In this case, the hyperfine interaction with the electron spin, which is greater in magnitude than the dipole-dipole interaction, can be used to control nuclear spins [2, 4, 5]. This is especially important for quadrupole nuclei, which have small magnetic moments. Direct control of them would require large radiofrequency fields or long pulses.

The control through electrons of qutrits represented by quadrupole nuclei has not been studied and is performed in the presented work using two examples [6]: the SUM operator and the quantum Fourier transform (QFT) operator. The SUM operator is executed on two nuclei: a qutrit and a qubit. The QFT operator is executed on selected three states of the nine-level two-qutrit electron-nitrogen system of the NV center. Control is achieved through electrons. Two options are considered. 1) The hyperfine interaction contains only a longitudinal part, and two microwave magnetic fields transverse to hyperfine interaction are applied to the system – one on the electron and one on the nucleus. 2) The hyperfine interaction contains both longitudinal and transverse parts, and the microwave transverse magnetic field is applied only to the electron. To numerically find the parameters of the control fields implementing the selected logical operators, we used the GRAPE (gradient ascent pulse engineering) algorithm [6, 7]. A comparison of the efficiency of two control options with each other and with control by means of sequences of selective control pulses was performed. The obtained results will allow us to select the optimal parameters for the experimental implementation of the considered logical operators.

The study was supported by a grant from the Russian Science Foundation No. 25-22-00750, <https://rscf.ru/en/project/25-22-00750/>.

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SECTION 5

STRONGLY
CORRELATED
ELECTRON
SYSTEMS

Magnetic order in nabokoite family compounds

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Nabokoite family compounds $ACu_7(TeO_4)(SO_4)_5X$ (here alkali ion $A = K, Na, Rb, Cs$ and halogen ion $X = Cl, Br$) give shelter to the 2D copper ions' spin structure considered as a possible realization of a highly frustrated decorated square kagomé lattice [1, 2]. Frustration of exchange bonds in nabokoites causes drastic difference in Curie-Weiss temperature $\Theta \sim 150$ K and antiferromagnetic ordering temperature $T_N = 3...5$ K [2].

Antiferromagnetic order type in nabokoites depends on alkali ion. Antiferromagnetic resonance experiments reveal that light-alkali-ions nabokoites ($A = Na, K$) order non-collinearly, while magnetic ordering in heavy-alkali-ion nabokoites ($A = Cs, Rb$) follows convenient easy-axis collinear pattern. Temperature dependent studies of high-frequency dielectric [3] and magnetic properties demonstrate that non-trivial magnetic ordering in light-alkali-ion nabokoites is chosen as a result of several consecutive phase transitions: firstly, a dielectric (ferro-electric) transition takes place at much higher temperature (25–100 K) which presumably partially lifts magnetic frustration and thus pre-cooks oncoming magnetic ordering; and, secondly, magnetic order is formed in a two-step phase transition with $T_{N1} \approx 5.5$ K and $T_{N2} \approx 4$ K.

Antiferromagnetic resonance frequency-field dependence (which is the field dependence of $q = 0$ magnons' energy) in light-alkali-ion nabokoites features three zero-field gaps: two of them opens at the first transition temperature T_{N1} while the third (the smallest one) develops at the second transition at T_{N2} .

The sensitivity of the magnetic ordering type to the change of none-magnetic alkali ions can be qualitatively explained by a toy-model calculations of the magnetic properties of a pyramidal building block of the decorated square kagomé lattice. Depending on the ratio of the coupling constants the ground state of this toy model is either the direct product of the pyramid base singlet state and 'free' apical spin or the 'collective' $S = 1/2$ state of all five spins in pyramid vertices. Exchange coupling parameters values suggested by DFT calculations [4] are close to the crossover between these ground states. Thus fine-tuning of these exchange parameters by alkali ion substitution can trigger sharp change in the magnetic properties of the structural building block and hence to the change of the chosen collective ground state.

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High field ESR measurements of the interacting spin dimer systems

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In the interacting spin dimer systems KCuCl_3 and TlCuCl_3 , spin dimers, composed of two Cu^{2+} spins $S = 1/2$ form three-dimensional network. Reflecting the dimer structure, an energy gap between the spin singlet ground state and excited triplet states exists. In high magnetic fields, the energy gap is closed, and then the triplet excitation on a dimer, so-called magnon, is induced to the ground state, leading to the Bose-Einstein condensation of magnon which causes the magnetic order [1]. These compounds exhibit various magnetoelectric phenomena because of the coupling between spin and electric dipole. The high field ESR measurements revealed that the electric dipole transitions between the spin singlet and triplet states are observed in KCuCl_3 . The fluctuation of the electric dipole caused by the single-triplet transition leads to the observed electric dipole transition. In the magnetic-field-induced magnon BEC phase, the static electric polarization appears in the ground state and the magnetic excitation becomes both electric and magnetic dipole active, leading to the nonreciprocal response in ESR spectra in microwave and terahertz region. It was reported that the magnetic order in TlCuCl_3 occurs as the weak first order phase transition [2]. The high field ESR also provides useful insight into this phenomenon.

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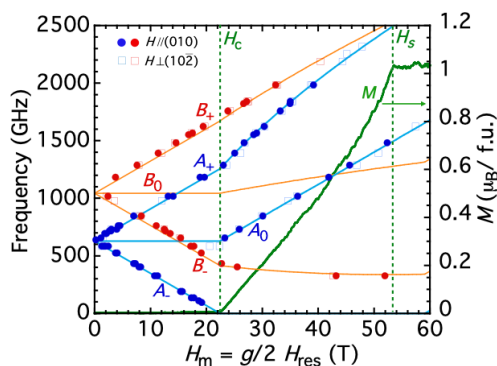


Fig. 1. Frequency-field diagram of the ESR signals in KCuCl_3 , observed in the magnetic field applied along the $[010]$.

Topological foundations of the scaling behavior of superconductors

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We consider the general universal scaling properties of superconductors. Scaling relationships lead to the identification of fundamental laws of nature and reveal the essence of superconductor physics. We analyze the scaling of the condensation energy. We show that the universal scaling is equally applicable to both conventional and uncommon superconductors. We also analyze experimental data demonstrating unique behavior of uncommon superconductors, which radically distinguishes them from conventional superconductors. We consider the differential resistance (or conductivity) collected under the application of magnetic field on the archetypical HF metal CeCoIn₅ that represents uncommon HF superconductor. We show that the observed scattering rate is explained by the occurrence of flat bands. We analyze experimental facts that reveal the same universal properties of both uncommon and conventional superconductors and theoretically explain these facts. We analyze the Homes' law and provide a theoretical explanation of its general scaling applicable to superconductors. Our theoretical results agree well with a body of diverse and seemingly unrelated experimental facts. They show that the topological fermion condensation quantum phase transition, generating flat bands, is an intrinsic property of strongly correlated Fermi systems and can be considered as a universal agent explaining the basic physics of strongly correlated Fermi systems. We demonstrate that these systems represent a new state of matter [1].

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A new permanent macroscopic coherent quantum state at room temperature

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Macroscopic quantum states such as superfluidity, superconductivity, and Bose-Einstein condensates (BECs) exist at low and ultra-low temperatures. We have successfully achieved a permanent coherent quantum state of magnons at room temperature. This is possible because magnons have very low mass and remain a gas at very high concentrations. Consequently, the conditions for the formation of BECs are met even at room temperature. However, BECs of quasiparticles typically arise under nonequilibrium conditions, with pulsed or continuous pumping of the quasiparticles. Therefore, their use in quantum devices remains problematic, since their quantum state—phase, frequency, and concentration—are determined by external excitations. Magnons decay into phonons and radio-frequency photons. Naturally, the quantum state of the condensate changes during this process. It leads to a broadening of the emission line due to spin-lattice relaxation of about 200 kHz under our experimental conditions.

We have developed a methodology for the formation of a permanent magnon BEC using the principle of boson amplification described earlier by R. Feynman [1]. We applied the principle of a self-oscillator. Using an antenna, we captured the BEC radio frequency signal, amplified it by three orders of magnitude, and fed it back to the sample. According to R. Feynman's theory, in the presence of a Bose condensate, new quasiparticles can only be excited in the quantum state of an existing Bose condensate. Therefore, under equilibrium conditions, the density and coherent state of magnons are permanently maintained. We were, apparently, the first to experimentally demonstrate the validity of Feynman's theory. We measured the BEC emission linewidth under self-oscillation conditions. It turned out that the RF emission line collapses by at least two orders of magnitude [2]. This means that the spin-lattice relaxation of magnons does not affect the BEC quantum state. In other words, the coherent quantum state of the BEC is permanently maintained. This opens the possibility of using this state in various quantum devices.

Moreover, we have obtained the conditions for switching between two BEC states with different frequencies under the same external magnetic field. The condition for quantizing these states is related to the change in phase shift in the feedback line. In other words, we have essentially obtained a prototype magnon qubit [3].

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Properties of ludwigite Cu_2MnBO_5

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The recovery of waste heat is becoming increasingly important for improving energy efficiency and reducing environmental impact. A promising approach is the direct conversion of heat into electricity via the Seebeck effect, which enables the use of thermoelectric generators in various applications, from industrial processes to automotive exhaust systems. Ludwigites, with their low carrier concentrations and polaron conductivity (featuring large effective masses) are ideal systems for investigating resonant thermopower contributions due to charge carrier interactions with optical and acoustic phonons.

We presented a combined analysis of magnetic resonance spectra for visualizing polarons, magnetization, and thermopower in Cu_2MnBO_5 ludwigite. Cu_2MnBO_5 compounds were grown by the flux technique [1]. According X-ray complex ludwigite Cu_2MnBO_5 has P21/c space group with $a = 3.146(5)$ Å, $b = 9.376(2)$ Å, $c = 12.02(3)$ Å, and $\beta = 92.238(6)$ at room temperature [2]. Ludwigites were studied via EPR measurements in the temperature range from 300 K to 570 K. Three lines were observed in the magnetic resonance spectrum in Cu_2MnBO_5 . The temperature dependencies of Seebeck coefficient demonstrates two peaks at two temperatures 522 and 558 K. Additionally, the EPR line from magnetic polarons was observed in magnetic resonance spectra near these temperatures.

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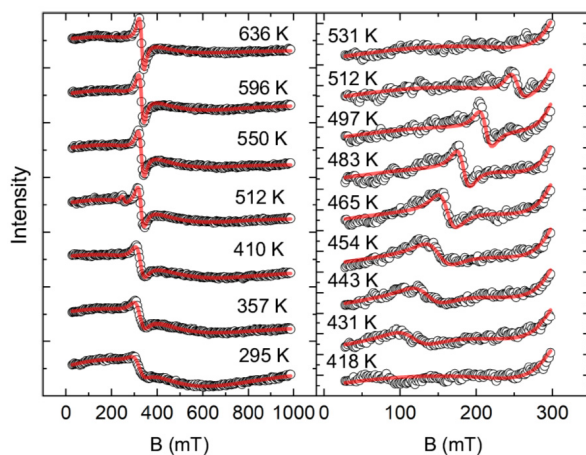


Fig. 1. The temperature dependence of EPR spectra in Cu_2MnBO_5

Electron paramagnetic resonance and magnetic oscillation modes described by semiclassical spin dynamics with combined relaxation term

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A semiclassical model of magnetization dynamics with a combined relaxation term, including Landau-Lifshitz and Gilbert contributions, is considered in a recent paper [1] and applied for the computation of the electron paramagnetic resonance (EPR) spectra. In the previous work [2] it was shown that in spite of the widely accepted similarity of the Landau-Lifshitz and Gilbert equations, they are based on essentially different relaxation mechanisms, which, in the real system, may appear simultaneously. It is shown that when both contributions have comparable amplitudes, varying the relaxation parameter α leads to a restructuring of the EPR spectrum (Fig. 1), emulating a magnetic transition with an abrupt change in the reduced resonance field $\omega_H/\omega = \gamma H/\omega$ and splitting of the absorption line into several spectral components [1]. Here ω is microwave frequency, γ is gyromagnetic ratio and H stands for magnetic field. These effects occur in a system describing a single magnetic oscillator with a constant gyromagnetic ratio γ and are caused exclusively by the peculiarities of magnetic relaxation in systems with significant damping, i.e., with $\gamma = \text{const}$ road EPR absorption lines. Such lines are characteristic of various strongly correlated electron systems, where magnetic fluctuations additionally contribute to line broadening. The suggested model is characterized by complicated magnetic oscillations that demonstrate the limited character of the classical interpretation of EPR as an eigen mode with the circular or

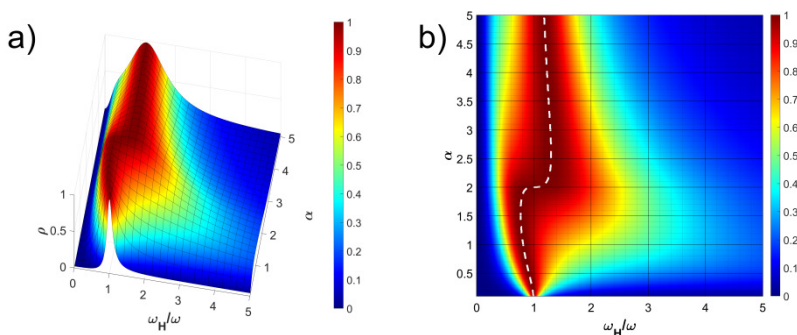


Fig. 1. Reduced EPR absorption power ρ as a function of reduced magnetic field $\omega_H/\omega = \gamma H/\omega$ and relaxation parameter α for equal mixing of relaxations in 3D graphics (panel a) and contour map (panel b). The dotted line in panel b shows the position of the EPR maximum.

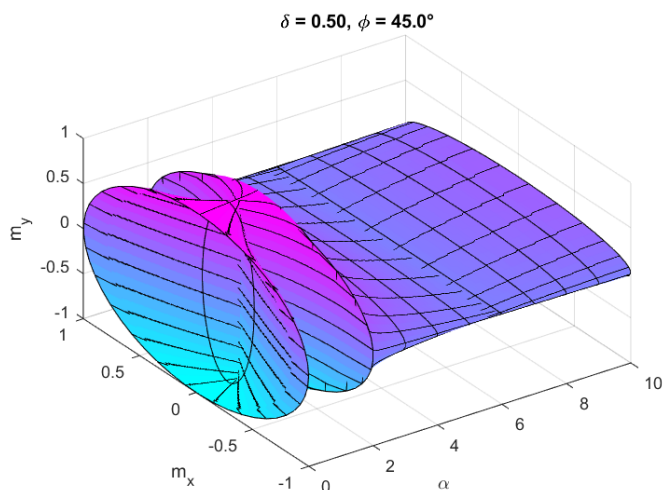


Fig. 2. The components of the oscillating magnetization at the EPR line maximum (dashed line in Fig. 1, panel b), depending on the relaxation parameter α .

elliptical polarization of dynamic magnetization [3]. When a steady magnetic field $\mathbf{H}$ is aligned along the z axis and Faraday geometry for EPR excitation is considered, the polarization of the oscillating magnetization vector $\mathbf{m} = \{m_x, m_y\}$ behaves in a non-trivial way, varying from elliptical to linear with an increase in the relaxation parameter α controlling the EPR line width (Fig. 2). This is a consequence of the fact that EPR is a case of a magnetic system with forced oscillations. Our simulation results show that the complex structure of EPR spectra in strongly correlated electron systems may be due to magnetic relaxation processes and, in general, may not be associated with the presence of several types of oscillating magnetic dipoles.

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Impact of manganese ions on magnetic and structural properties of cobalt containing ludwigites

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Oxyborates with formula $M_2M'BO_5$, where M is a divalent and M' is a trivalent metal ion, are classified as ludwigites. These compounds have four non-equivalent crystallographic positions per unit cell for aforementioned metal ions to occupy, resulting in the random distribution of magnetic ions, mixed valence of ions, strong electron correlations and unusual charge ordering. This feature leads to observation of unconventional magnetic properties in ludwigites [1, 2].

Ludwigites with structural formula of $Mn_xCo_{3-x}BO_5$ ($x = 0[3,4], 0.75, 1.2, 1.4, 1.8$) were studied via the magnetization, XRD and EPR measurements. Clear evolution in magnetic properties was observed for the compounds with different magnetic ions concentration. The compounds with low amount of manganese ions per unit cell (below 1.4) order at lower temperatures around 42 K into a spin-glass state, while compounds with high amount of Mn have a ferrimagnetic transition at 61K (Fig. 1). The analysis of the obtained effective magnetic moment suggests presence of Co^{2+} and Co^{3+} ions in both high- and low-spin states for all the compounds. Additionally, a correlation between manganese ion concentration and lattice volume was revealed (Fig. 2).

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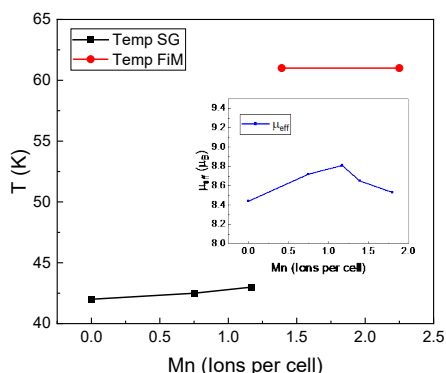


Fig. 1. Dependence of the transition temperature and magnetic moments from ions concentration

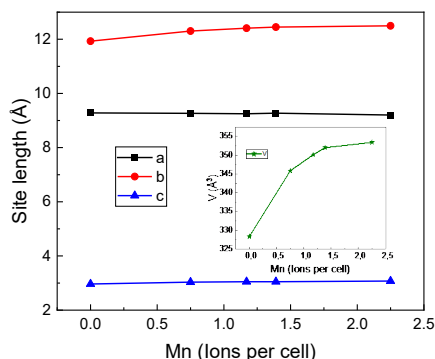


Fig. 2. Dependence of the crystallographic parameters and cell volume from ions concentration

Electron spin resonance probing of antiferromagnetic state in CeB_6

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Cerium hexaboride (CeB_6) is a unique system among cerium intermetallics in exhibiting electron spin resonance [1–3]. This provides a valuable scientific tool for both investigating exotic magnetic states in CeB_6 itself and for studying the nature of metamagnetic transitions characteristic of many rare-earth intermetallics. In this study, ESR measurements were performed for the first time in CeB_6 in the frequency range of 27–43 GHz for the [100] and [110] field directions. While the resonant behavior for $H \parallel [110]$ at all frequencies corresponds to the paramagnetic phase (Fig. 1), for $H \parallel [110]$, frequencies of 27 GHz and 33 GHz allow us to study the evolution of the resonance upon crossing the antiferromagnetic (AFM) phase boundary (Fig. 1). In the paramagnetic phase, the resonance line does not shift for both directions with decreasing temperature (the g -factor is in the range of $g = 1.4 \div 1.6$), while its intensity increases significantly. Upon transition to the AFM phase, the line intensity decreases, it broadens and becomes unobservable at $T < 2$ K. This behavior confirms the previously put forward assumption about the inhomogeneous nature of the magnetic structure in the antiferroquadrupole (AFQ) and AFM phases, caused by the effects of localization of the magnetic moments of Ce^{3+} [2]. The magnetization of CeB_6 in the AFQ and AFM phases was measured. The magnetic contribution of AFM ordered localized magnetic

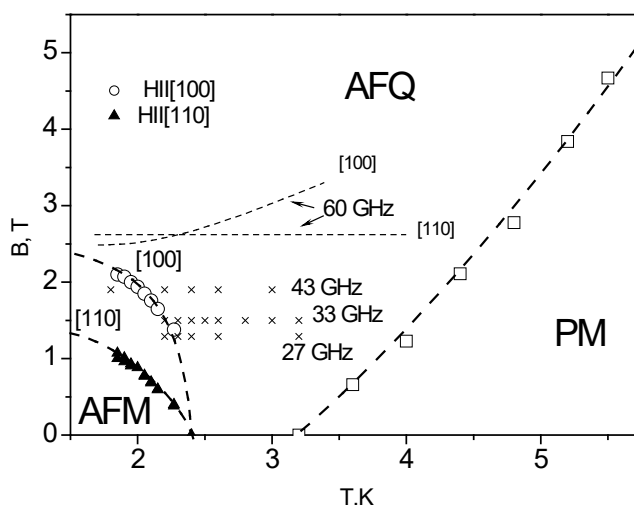


Fig. 1. Magnetic phase diagram of CeB_6 . PM – paramagnetic phase, AFQ – antiferroquadrupolar phase, AFM – antiferromagnetic phase.

moments was separated. Good agreement was demonstrated between the temperature dependence of this contribution and the dynamic magnetization obtained from the analysis of the ESR spectra constructed in units of magnetic permeability [2].

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Electron-polaron transition and high-temperature phonon drag in $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{Ti}_{0.3}\text{Mn}_{0.3}\text{O}_{3-\delta}$ perovskite

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Complex perovskite oxides with the general formula ABO_3 remain a focus of intensive research due to their diverse physical properties, including magnetism, ferroelectricity, and thermoelectricity, as well as the intricate interplay between them [1–3]. The ability to tailor these properties through targeted ionic substitution at the A- and B-sites of the structure offers promising avenues for designing materials with specific functional characteristics. Particular relevance lies in the co-doping of magnetic and non-magnetic ions at the B-site, which can significantly alter the magnetic order and enhance thermoelectric efficiency. In this context, compounds containing both magnetic manganese (Mn) and titanium (Ti) ions are of special interest, as their mixed valence states and complex electron interactions are key to understanding the mechanisms governing magnetic and electronic behavior.

The aim of the study is to establish the relationship between microscopic electron-magnetic changes and macroscopic anomalies of thermoelectric transport in highly substituted perovskite $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{Ti}_{0.3}\text{Mn}_{0.3}\text{O}_{3-\delta}$ over a wide temperature range.

The synthesis of polycrystalline powder of $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{Ti}_{0.3}\text{Mn}_{0.3}\text{O}_{3-\delta}$ has been carried out via the solid-state route using precursor materials including CaCO_3 ($\geq 99\%$), SrCO_3 ($\geq 99\%$), TiO_2 ($\geq 99\%$), and Mn_2O_3 ($\geq 99\%$). Xray diffraction analysis revealed that the synthesized sample is singlephase and crystallizes in the orthorhombic space group $Pnma$ with unitcell parameters $a = 5.40308 \text{ \AA}$, $b = 7.63460 \text{ \AA}$, and $c = 5.39910 \text{ \AA}$.

In this work, the high-temperature thermoelectric properties and electronic transport mechanisms of the heavily substituted perovskite $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{Ti}_{0.3}\text{Mn}_{0.3}\text{O}_{3-\delta}$ were investigated

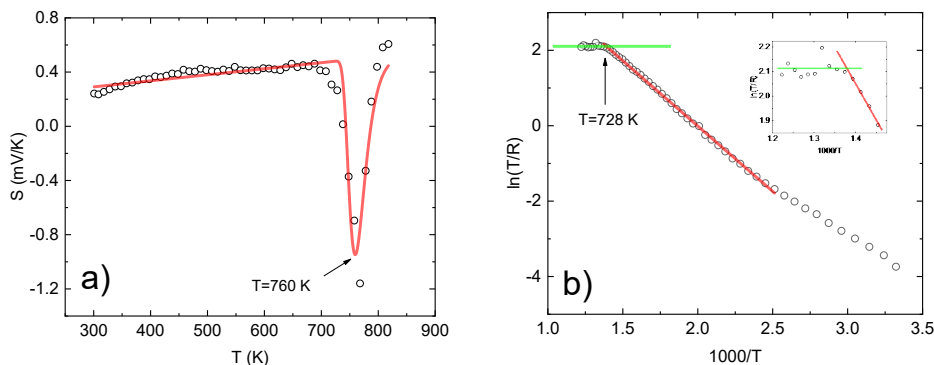


Fig. 1. **a** Temperature dependence of the Seebeck coefficient $S(T)$: circles denote the experimental data, and the solid line shows the fit using the phonondrag formula. **b** Temperature dependence of the electrical conductivity $\sigma(T)$, plotted in Arrhenius coordinates

using electron paramagnetic resonance spectroscopy, along with measurements of the Seebeck coefficient (S) and electrical conductivity (σ).

ESR measurements were performed using a Varian E12 spectrometer equipped with a Bruker EP 4114 XT high-temperature resonator with a TE011 resonant mode. Temperature dependence measurements in range of 290–786 K were performed in the X-band with a frequency of 9.4 GHz and a magnetic field range of 0–1 T.

A prominent anomalous “inverted” peak in $S(T)$ is observed at $T_m = 760$ K (Fig. 1a). Approximation of the temperature dependence by the Weibull function

$$S(T) = S_0 + \alpha T + S_{ph}(T),$$

where the phonondrag contribution is given by the expression proposed in [5]:

$$S_{ph}(T) = A \left(\frac{T_m}{T} \right)^{a-1} \exp \left(-\frac{a-1}{a} \left[\left(\frac{T_m}{T} \right)^a - 1 \right] \right),$$

reveals that this anomaly originates from the hightemperature phonondrag effect. The modelling yields highfrequency phonon wavenumbers in the range 1100–1700 cm^{-1} , which correspond to twophonon optical overtones activated by severe structural disorder [6].

To elucidate the microscopic origin of this transport anomaly, a systematic analysis of the temperature dependences of $\sigma(T)$ (Fig. 1b) and EPR parameters was performed. Up to the critical crossover temperature $T = 728$ K, the macroscopic electrical conductivity is perfectly described by the smallpolaron hopping model:

$$\sigma = \frac{A}{T} \exp \left(-\frac{\Delta E}{k_B T} \right)$$

with an activation energy $\Delta E = 298 \pm 2$ meV. Above this temperature, the Arrhenius plot exhibits a distinct plateau, indicating polaron delocalisation.

The hightemperature EPR parameters provide direct thermodynamic evidence for the underlying electronic reconstruction. Above $T = 651$ K, the inverse integral intensity $1/\text{int}$ abruptly deviates from the linear Curie–Weiss behaviour, reflecting changes in the effective magnetic moment of the manganese ions. Concurrently, the lineshape asymmetry parameter α begins to increase monotonically, signalling the transformation of the signal into a Dysonian line due to the appearance of mobile carriers. This selfconsistent sequence of events demonstrates that the thermal destruction of localised small polarons at $T > 651$ K generates a dense flux of conduction electrons (ntype), which subsequently drag highfrequency optical phonons, ultimately leading to the macroscopic Seebeck peak at 760 K.

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The effect of a superconducting spin valve in a Py/Pb/Py heterostructure with oxidized interfaces

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In work presents the results of a comprehensive study of the properties of a superconducting spin valve based on a three-layer Py/Pb/Py heterostructure with artificially oxidized superconductor/ferromagnetic interfaces. The effect of a superconducting spin valve is investigated, which consists in the dependence of the critical temperature of the transition of a heterostructure to a superconducting state on the mutual orientation of the magnetization of ferromagnetic permafrost layers at different thicknesses of the superconducting layer. It is found that with a Pb layer thickness of 100 nm, the maximum change in transition temperature when switching the mutual orientation of the magnetizations from antiparallel to perpendicular in an external magnetic field of 1 kOe is on the order of 0.1 K. At the same time, the classical effect of a superconducting spin valve was not observed in the studied structures, however, contrary to theoretical expectations for symmetrical systems, a triplet effect was recorded in the experiment, which indicates the imperfection of the interface and the specifics of Py oxidation due to its increased resistance to oxidation. It is shown that modification of the transparency of the superconductor/ferromagnetic interfaces by creating oxidized interfaces contributes to a significant increase in the critical temperature compared with samples without such interlayers.

The results obtained confirm the prospects of the method proposed by the authors for preparing structures of superconducting spin valves with oxidized interfaces [1] and demonstrate that the introduction of additional thin insulating layers between superconducting and ferromagnetic elements of the heterostructure opens up new opportunities for purposefully improving the characteristics of superconducting spin valves and increasing their functioning efficiency. It is worth noting that, according to classical concepts, the maximum spin valve effect is expected for structures with perfectly transparent metal interfaces, however, our data, consistent with the results of recent studies [1], indicate that significant values of the SSV effect can be achieved in systems with controllably variable boundary transparency, which expands the technological horizons of design such devices.

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ESR investigation of magnetic inhomogeneities in the pentaborate $\text{GdMnB}_5\text{O}_{10}$

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Pentaborates constitute a large class of borate compounds characterized by unique physicochemical properties, including nonlinear optical effects, ionic conductivity, and catalytic activity. Although significant progress has been made in studying the optical properties of pentaborates, their magnetic characteristics remain insufficiently explored. Previous studies reported a novel pentaborate compound $\text{GdMnB}_5\text{O}_{10}$ containing two magnetic cations (Mn^{2+} and Ce^{3+}). The present work investigates the magnetic properties of the $\text{GdMnB}_5\text{O}_{10}$ compound.

Electron spin resonance (ESR) spectra of the $\text{GdMnB}_5\text{O}_{10}$ samples were measured using an ER 200 SRC (EMX/plus) spectrometer (Bruker, Germany) at a frequency of 9.4 GHz (X-band) in the temperature range from 115 K to room temperature in steps of 5 K, and on an Eleksys E580 spectrometer (Bruker, Germany) at a frequency of 33.6 GHz (Q-band) in the temperature range from 100 K to room temperature in steps of 30 K. A polycrystalline sample of $\text{GdMnB}_5\text{O}_{10}$ was thoroughly ground into powder before the experiments to exclude orientation dependences of the ESR spectra. Fig. 1 shows representative well-resolved ESR spectra obtained at 115 K (X-band) and 120 K (Q-band). The absorption spectra exhibit a complex multicomponent structure that is well described by the sum of three asymmetric Lorentzian lines (solid curves in Fig. 1). The fitting results and spectral decomposition into individual components are presented in the same figure.

The ESR spectrum is dominated by Line 1, which arises from the presence of paramagnetic Mn^{2+} ($S = 5/2$) and Gd^{3+} ($S = 7/2$) ions in the crystal lattice. The Mn^{2+}

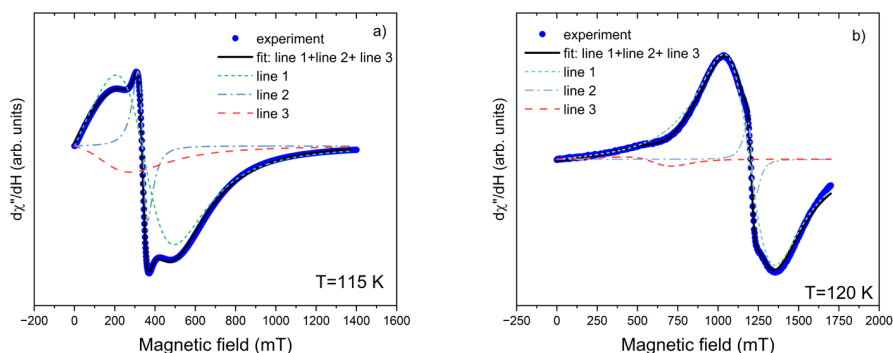


Fig. 1. Typical electron spin resonance spectra in $\text{GdMnB}_5\text{O}_{10}$ polycrystalline sample at two different temperatures: (a) X-band, (b) Q-band; details of the spectra decomposition are given in the text. Solid fit curve corresponds to the sum of three field derivatives represented by Eq. (1).

contribution exhibits a resonance field $H_{\text{res}} \approx 330\text{--}340$ mT with a g -factor of ~ 2.0 , while Gd^{3+} produces a signal in a similar field range ($H_{\text{res}} \approx 330\text{--}340$ mT), but with a slightly lower g -factor ($g \approx 1.97\text{--}2.00$).

The lack of fine structure in the ESR spectra suggests strong exchange interactions between spins, which collapse hyperfine splittings into a single line – a hallmark of magnetically concentrated systems. Notably, the Gd^{3+} spectral lines exhibit significantly broader linewidths than those of Mn^{2+} at room temperature. This difference persists despite both ions having nominally quenched orbital angular momentum ($L = 0$, ^{3+}Gd : $4f^7$, ^{2+}Mn : $3d^5$). The enhanced broadening in Gd^{3+} arises from its high spin ($S = 7/2$), which generates pronounced zero-field splitting (ZFS). Even small local symmetry distortions create distributed ZFS parameters across crystallographic sites, leading to severe inhomogeneous broadening of the Gd^{3+} resonance.

The ESR spectrum reveals two additional low-intensity signals (Lines 2 and 3) alongside the dominant resonance. Line 2 exhibits $g \approx 2$, whereas line 3 displays g -values in the range of $3.7\text{--}3.8$. These features may suggest the existence of crystalline defects or magnetically correlated domains arising from mixed-valence magnetic centers or other forms of magnetic disorder.

Spin nematicity in the Eu ternary pnictides: the ESR viewpoint

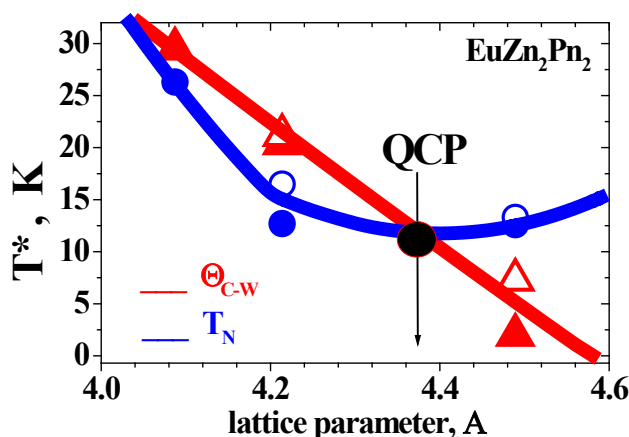
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In the past decade, compounds possessing subtle features of their crystal structure, which imply specific magnetic order and spatiotemporal structure of the electronic state, have attracted increasing attention. These features do not always give rise to local spectacular phenomena, but collective effects distinguish certain classes of materials of fundamental interest and the potential for new, previously unknown applications. Well-known examples of such materials include superconductors and topological materials. The latter illustrates how the discovered features of the electronic structure of graphene (Dirac spectrum, topological protection of electronic states) have given to discovery of a broad class of 3-D topological layered materials, in particular, Dirac and Weyl semimetals. More recently, magnetic layered systems have attracted attention as spin nematics [1], which exist in a specific region of the T-H diagram [2–6]. We are talking about intermetallic 1-2-2 pnictides. The intermetallic pnictides AMe_2Pn_2 (A = rare earth; Me = transition metal; Pn = P, As, Sb, Bi) (1-2-2 compounds) crystallize in the trigonal CaAl_2Si_2 -type structure (space group $\text{P}\bar{3}\text{m1}$) or the tetragonal ThCr_2Si_2 -type structure (space group I4/mmm) and exhibit a rich variety of magnetic and transport phenomena. The AMe_2Pn_2 family with the trigonal CaAl_2Si_2 structure is similar to the better known tetragonal ThCr_2Si_2 structure in which the cations on the A-site form layers interspersed with Me_2Pn_2 -layers, where the Me^{2+} -ions sit in the center of an Pn_4 tetrahedron. The way of packing this layers distinguishes between the ThCr_2Si_2 - and CaAl_2Si_2 - type structures. In such structures, on the one hand, the intimate relationship between the cation's valence and magnetic states determines the compound's diverse of magnetic properties. On the other hand, the network of valence bonds, which ensures the stability of the crystal lattice and determines its symmetry, is a network of orbitals on which valence electrons are localized, is find on the stability edge beyond which another type of crystal lattice is realized. Low electron density, ambiguity of the crystal structure, and the overlap of the valence band with the conduction band underlie the extremely wide variety of magnetic and electronic properties associated with localized distortions of the crystal structure of these compounds.

We have studied the magnetic properties of compounds EuMe_2Pn_2 (Me = Zn, Cd, Fe; Pn = P, As, Sb) by ESR. At the temperature decreasing well before the antiferromagnetic order we have observed an increasing of lineswidth and a decreasing of the resonance fields, which in our case is very good described by the Landau theory of magnetic fluctuations. However, the paramagnetic temperature $\theta_{\text{c-w}}$ obtained from the temperature dependence of the ESR signal intensity, has the positive sign. We believe that such behaviour of $\theta_{\text{c-w}}$ is connected with the proximity to quantum critical point and with the relevant instability of magnetic and crystal structures (instability Me_2Pn_2 -layers, competition between nonmagnetic $4f^6$ and magnetic $4f^7$ states of Eu). We also consider that the magnetic properties of studied compounds are due to the



instability of the CaAl_2Si_2 -type structures (similar compounds with bismuth and nitrogen are unknown), the interplay of spin and valence fluctuations (nonmagnetic $4f^6$ and magnetic $4f^7$ states of Eu), and the differences of interactions in comparison with pnictides with the ThCr_2Si_2 – type structure. Also Eu -ions have nonintegral valence, g-factor substantially not equal 2.0 and spins are stacked in layers by various means. We conclude that the valence instability can lead to a new type of magnetic behavior and, consequently, to the possible existence of new magnetic (nematic) A-phases and quantum phase transitions in a specific class of compounds.

Comparison of the behavior of the Curie temperature and the Neel temperature with changing of the composition of these compounds indicates on the presence of quantum critical point in these ternary systems. With the increase in lattice constant and change of the concentration of free electrons, the transition temperature into the nematic A-phase became less than the Neel temperature ($T_A \sim \theta_{c-w} < T_N$) and the situation returns to the normal case. Thus, a quantum phase transition takes place in the EuMe_2Pn_2 ternary systems.

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Critical temperature of thin superconducting films within the proximity-effect theory in the dirty limit

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For a thin metallic film, the superconducting transition temperature T_c can be significantly different from the bulk value T_{cs} , while the way T_c scales with film thickness d_s depends qualitatively on the material. For most superconductors (Mo, Bi, TiN, Nb, NbN) T_c decreases as the film becomes thinner, whereas for aluminium T_c increases with decreasing d_s [1–4]. We propose a single framework that reproduces both trends. Following Cooper's approach [5], films are modeled as three-layer $S_b/S/S_b$ structures. The central layer S of thickness d_s has the bulk parameters, while two symmetric near-boundary layers S_b of thickness d_b possess their own superconducting coupling constant.

The film is treated as a proximity superconducting system described by the quasiclassical (Usadel) equations of superconductivity in the dirty limit [6], with Kupriyanov–Lukichev boundary conditions at the internal S_b/S interfaces [7] and absence of pair flux at the outer surfaces. Averaging the Usadel functions over each layer and substituting them into the self-consistency equation yields a homogeneous linear system for the order parameters Δ_s and Δ_{sb} . The condition for a non-trivial solution leads to an algebraic equation for the film T_c , which we solve numerically. Rather than using the coupling constant of the boundary layers, we employ the corresponding critical temperature $T_{cs}^{(b)}$. The two classes of behaviour correspond to different boundary-layer parameters: $T_{cs}^{(b)} = 0$, where the boundary region acts as a normal metal and suppresses T_c , and $T_{cs}^{(b)} > T_{cs}$, which causes the critical temperature of the film to increase.

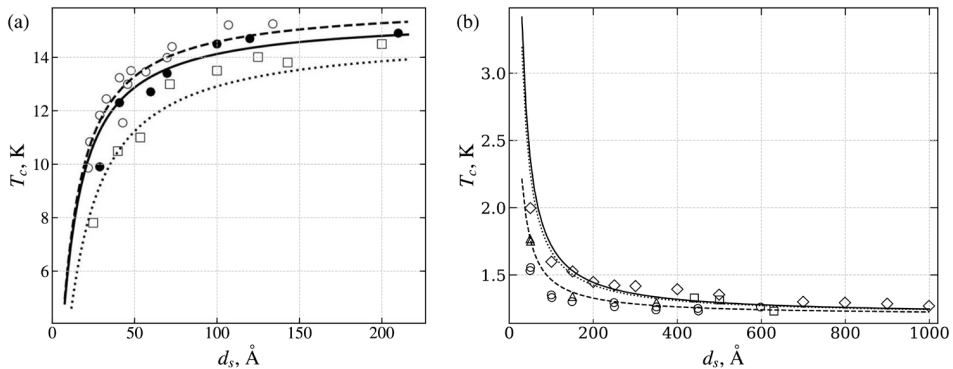


Fig. 1. Critical temperature T_c as a function of film thickness d_s : experimental data (symbols) and the present model (lines). (a) NbN ($\bullet$, solid line, $d_b = 0.8$ Å [1], ($\circ$, dashed line, $d_b = 0.8$ Å [2], ($\square$, dotted line, $d_b = 1.2$ Å [3]; (b) aluminium films on GaAs and Al_2O_3 substrates [4] ($T_{cs} = 1.2$ K, $T_{cs}^{(b)} = 3.9$ K, $\zeta_s = 100$ nm, $d_b = 0.7$ – 1.3 nm).

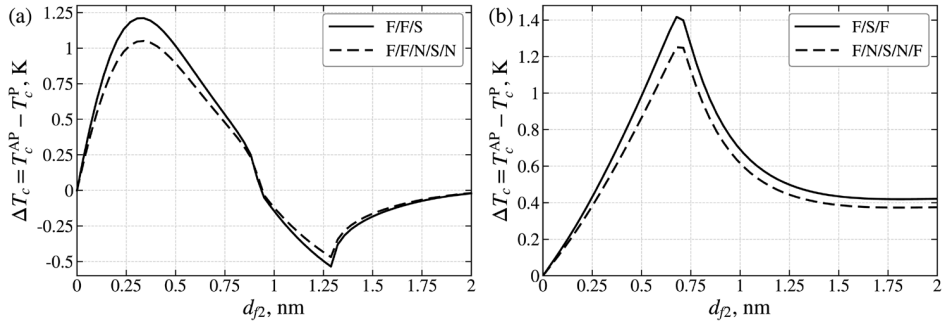


Fig. 2. Theoretical estimations for the spin-valve effect $\Delta T_c = T_c^{\text{AP}} - T_c^{\text{P}}$ versus the thickness of the second ferromagnetic layer d_{F2} without (solid line) and with (dashed line) normal-metal boundary layers: **a** F/F/S $\rightarrow$ F/F/N/S/N; **b** F/S/F $\rightarrow$ F/N/S/N/F.

With the bulk critical temperature and coherence length ξ_s taken from the literature, the only fitting parameter is the boundary-layer thickness d_b . The model provides a theoretical description of measured $T_c(d_s)$ for three NbN series grown on different substrates, with d_b on the angstrom scale. (see Fig. 1a) [1,2,3]. For aluminium we take $T_{\text{cs}}^{(b)} = 3.9$ K, the critical temperature reported for Al/Al₂O₃ core-shell metamaterials [8]. We used it to describe the anomalous increase of T_c observed experimentally [4] (Fig. 1b). Boundary-layer thickness $d_b \approx 0.7\text{--}1.3$ nm is comparable to the native Al₂O₃ thickness.

The same boundary-layer construction extends to multilayer heterostructures. Applied to superconducting spin valves, the F/S/F [9,10] and F/F/S [11, 12] structures become F/N/S/N/F and F/F/N/S/N once normal-metal (N) boundary layers are introduced at the S/F interfaces. The near-boundary layers reduce the magnitude of the spin-valve effect $\Delta T_c = T_c^{\text{AP}} - T_c^{\text{P}}$ by about 10–15 %, while preserving its qualitative form (Fig. 2). The two structures behave differently: in the F/F/S valve the effect changes sign: direct ($\Delta T_c > 0$) for a thin second ferromagnetic layer and inverse ($\Delta T_c < 0$) for a thick one, whereas in F/S/F it stays positive throughout. Adding the N layers lowers the theoretical estimations for the extrema (for F/F/S the maximum drops from 1.21 to 1.05 K and the minimum from -0.55 to -0.47 K).

Note that the experimental values of ΔT_c remain significantly lower than the theoretical predictions [12], but the boundary effects should be taken into account when quantitatively comparing theory with experiment for real superconducting heterostructures.

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Magnetisation and magnetic resonance in relaxor ferroelectrics with double perovskite structure $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbCo}_{1/3}\text{Nb}_{2/3}\text{O}_3$

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Multiferroics are a class of solids in which polar and magnetic ordering can coexist and interact with each other. The electrical and magnetic properties of these materials arise from their composition and crystal structure. The strong magneto-optical effect, manifested as a significant rotation of the plane of polarization with changes in magnetization, is of great interest for both fundamental and applied research.

Our research objects were relaxor ferroelectrics with a double perovskite structure - $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbCo}_{1/3}\text{Nb}_{2/3}\text{O}_3$. [1,2] This report presents the results of experimental studies of temperature-dependent magnetic resonance spectra of $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PNN) and $\text{PbCo}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PCN) crystals in the X-band microwave range (9.5 GHz) over a temperature range of 10–110 K. Several features of the temperature evolution are shown. Temperature dependences of magnetization were measured for $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbCo}_{1/3}\text{Nb}_{2/3}\text{O}_3$ crystals during heating in zero magnetic field (ZFC), with an applied magnetic field of 1000 Oe (FCW), and during cooling in an applied magnetic field (FCC).

The PCN crystal exhibits a set of observations indicating the presence of ferromagnetic fractions. The inverse magnetic susceptibility shows a “downturn,” and a signal appears/disappears in the low-field magnetic resonance region at temperatures of 60–70 K. Furthermore, a divergence is observed in the magnetization curves measured after field cooling (FC) and zero-field cooling (ZFC) at temperatures below 22 K. This phenomenon indicates magnetic irreversibilities (manifestation of open hysteresis loops in magnetization reversal curves). In the double perovskite PNN, the “downturn” in the inverse susceptibility begins at 210 K, also indicating the growth of ferromagnetic correlations in the system. In the magnetic resonance spectra, two temperature ranges can be distinguished: 10–110 K and 170–200 K, with a smooth transformation from one form to the other in the range of 110–170 K.

We detected a ferromagnetic component in the PCN crystal, which appears in a magnetic field region separate from the paramagnetic component. Identifying the ferromagnetic component in the PNN crystal is more difficult. In both cases, the inverse magnetization shows a downturn, indicating a transition of the double perovskite from the paramagnetic phase to increasing ferromagnetic correlations. However, while the transition in PCN is clearly manifested at $T \sim 60\text{--}70$ K, in PNN the linear dependence first changes slope and only later bends. Most likely, Ni^{2+} ions are more sensitive to polarization than Co^{2+} ions, and the relaxor ferroelectric nature is more clearly manifested in PNN.

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Processing and analysis of the electron paramagnetic resonance line shape in the noncentrosymmetric magnet $\text{Mn}_{1-x}\text{Rh}_x\text{Si}$

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$\text{Mn}_{1-x}\text{Rh}_x\text{Si}$ is a noncentrosymmetric B20 magnet in which Rh substitution leads to a strong increase of the Curie temperature and to a nonuniform magnetic response [1]. For the polycrystalline samples studied here ($x = 0.10$ and 0.15), the EPR spectra are broad, asymmetric and strongly temperature dependent. Such a line shape cannot be reliably interpreted by a single Lorentzian-type resonance.

A natural but problematic approach is to approximate the spectrum by several independent isotropic components. In the present system this approach may not be physically justified unless each line is assigned to a separate magnetic subsystem. Trial fits with two isotropic lines reduced the numerical error, but the resulting component parameters were effective averages rather than physically reliable characteristics of separate magnetic subsystems. Therefore, the processing procedure requires a different approach, in which the complicated EPR line shape is treated primarily as a powder-averaged anisotropic response of a metallic polycrystalline sample.

The experimental EPR signal was recorded in the X band in derivative mode, $d\chi''/dH$. Before fitting, the $d\chi''/dH$ was numerically integrated over magnetic field to reconstruct the dynamic magnetic susceptibility. The model was then compared with the absorption spectrum $\chi''(H)$. For a fixed temperature the fitted EPR response may be written as:

$$A_{\text{model}}(H, T) = C(T) + S(T)H + A_{\text{powder}}(H, T) + A_{\text{iso}}(H, T). \quad (1)$$

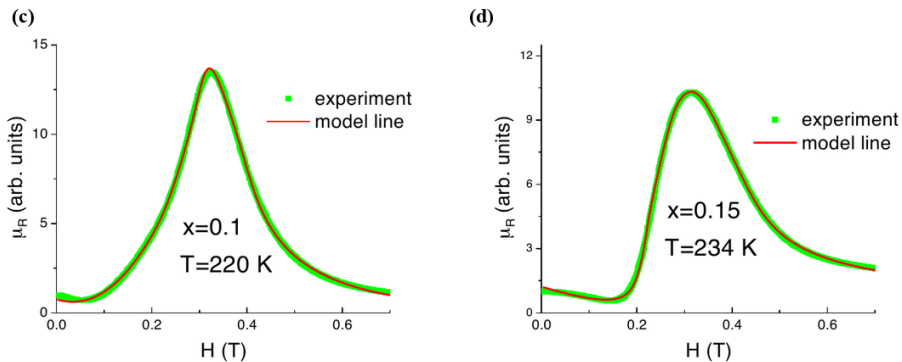


Fig. 1. Reconstructed EPR absorption spectra and fits: (c) $\text{Mn}_{0.90}\text{Rh}_{0.10}\text{Si}$, 220 K; (d) $\text{Mn}_{0.85}\text{Rh}_{0.15}\text{Si}$, 234 K.

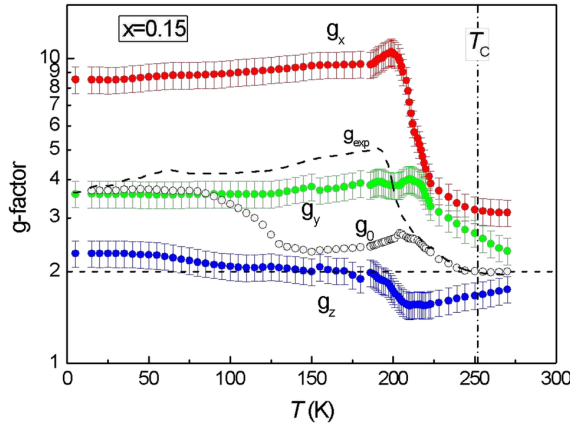


Fig. 2. Anisotropic effective g-tensor components for $\text{Mn}_{0.85}\text{Rh}_{0.15}\text{Si}$.

In Equation (1) the linear term describes the residual baseline. The main contribution, A_{powder} , represents an anisotropic powder line [2]. For a crystallite orientation defined by direction cosines l_x, l_y, l_z , the effective g factor and line width ΔH are written as:

$$\begin{aligned} g^2 &= g_x^2 l_x^2 + g_y^2 l_y^2 + g_z^2 l_z^2, \\ \Delta H^2 &= \Delta H_x^2 l_x^2 + \Delta H_y^2 l_y^2 + \Delta H_z^2 l_z^2. \end{aligned} \quad (2)$$

In further calculations we used the Landau-Lifshitz (LL) equation for magnetization dynamics. The local gyromagnetic ratio and damping constant were calculated as $\gamma(\theta, \varphi) = \gamma_e g(\theta, \varphi)$ and $\alpha(\theta, \varphi) = \Delta H(\theta, \varphi) \gamma(\theta, \varphi) / (2\pi f)$. The local magnetic response of a crystallite was obtained from the linearized LL equation. The resulting powder line was derived by averaging over random crystallite orientations [2]:

$$A_{\text{powder}} = \iint I(\theta, \varphi) A_{\text{loc}}[H, \gamma(\theta, \varphi), \alpha(\theta, \varphi)] \sin \theta \, d\theta d\varphi. \quad (3)$$

The isotropic term in Equation (1) may model the case of several magnetic phases, as may occur in $\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ samples [1]. The isotropic contribution was included in the model only when it improved the information criteria [3, 4]:

$$AIC = n \ln(RSS/n) + 2k, \quad BIC = n \ln(RSS/n) + k \ln n. \quad (4)$$

For $\text{Mn}_{0.85}\text{Rh}_{0.15}\text{Si}$ the two-component model was favored at all 69 temperatures (median $\Delta AIC \approx -2845$, $\Delta BIC \approx -2832$). For $\text{Mn}_{0.90}\text{Rh}_{0.10}\text{Si}$, the additional isotropic term was selected only for a minority of temperature points..

Local identifiability was analyzed using the scaled sensitivity matrix [5]:

$$\tilde{J}_i = \partial f(H_i, \theta) / \partial \theta_j \cdot \theta_j^{\text{scale}}, \quad \tilde{J} = U \Sigma V^T. \quad (5)$$

With $C_m = \sum_{k \leq m} \sigma_k^2 / \sum_k \sigma_k^2$, three SVD modes account for about 99% of the sensitivity and six for 99.99%, indicating sloppy multiparameter geometry [6].

The effective g -tensor and anisotropic linewidths are locally identifiable; several intensity parameters are auxiliary. Perturbed reoptimization gave a median absorption-maximum shift of 0 mT and FWHM/area changes below 0.2%. Thus, the $\text{Mn}_{1-x}\text{Rh}_x\text{Si}$ case demonstrates that the proposed approach provides a mathematically justified method for multiparameter fitting of powder EPR spectra.

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Fabrication of photomasks using combined photo- and scanning probe lithography techniques

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Measuring the critical current in “normal metal/superconductor” heterostructures requires achieving high current density and ensuring current uniformity (vortex suppression). This is feasible when such heterostructures are of micron scale.

One common method for producing such structures is photolithography, which enables the formation of micro- and nanometer-sized features with high precision. However, the fabrication of a high-quality photomask entails substantial financial costs. Consequently, we opted to independently develop and fabricate test photomasks – both for lift-off photolithography and etch-based patterning techniques.

Quartz glass, transparent in the UV range (suitable for mercury lamps), was chosen as the base for the photomasks. Copper, 100 nm thick, served as the opaque material. The entire photomask was coated with a 10 nm thick layer of silicon nitride (Si_3N_4) to protect the copper layer from oxidation by atmospheric oxygen. A 10 μm -wide stripe connecting the contact pads was formed in one of two ways: by shading using a 10 μm -diameter wire or by exposure through a photo slit. Subsequent refinement of the stripe geometry was performed using scanning probe lithography.

Two masks were fabricated, inverted relative to each other. The first type of mask is used for the etching method: the desired structure is deposited on the substrate and then covered with a layer of PMMA; the sample is subsequently exposed through the mask and developed (the exposed PMMA is removed), after which the unprotected areas of the structure are etched in acid, and the remaining PMMA is stripped. The second type of mask is used for lift-off photolithography: a layer of PMMA is deposited on the substrate, the sample is exposed through the mask and developed, after which the desired structure is deposited onto the surface; the resulting sample is placed in a solvent (chlorobenzene), which dissolves away the unexposed PMMA along with the structure deposited on these areas (the lift-off process).

In the upcoming phase of the research, we intend to fabricate multiple series of samples employing various methods. Upon successful fabrication of the target metal/superconductor heterostructures, the next steps will include either manufacturing custom masks or commissioning an industrial-grade photomask.

SECTION 6

CHEMICAL AND
BIOLOGICAL
SYSTEMS

Water molecules and biologically active substances in RBC on NMR data

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Molecular and ion exchange in cell membranes plays a crucial role in metabolic processes in living systems. One of the key characteristics of biological membranes is their selective permeability, the nature of which can be understood by studying the mechanisms of biomembrane function.

Currently, active research is underway on the permeability of biological membranes for water molecules and biologically active substances using a range of physicochemical methods, including luminescence, osmotic, indicator, chemical, and others. However, these methods are indirect and do not directly measure the parameters characterizing molecular diffusion.

Erythrocytes are of interest for studying molecular exchange processes, therefore RBCs are the main component of blood and play a key role in shaping its rheological parameters. Erythrocyte membranes also share the general principles of biological membrane organization.

To solve the problems described above, it is necessary to employ physical methods for studying structure and dynamics at the molecular level. In this regard, the pulsed field gradient NMR (PFG NMR) method deserves special attention, as it allows for direct quantitative assessment of molecular diffusion without damaging biological systems. The uniqueness of this method lies in its ability to measure partial self-diffusion coefficients and the populations of diffusant molecules in heterogeneous systems, including biological cells.

The PFG NMR method provided information on the self-diffusion of water molecules and pentasubstituted derivatives of fullerene C_{60} with attached residues of 3-mercaptopropanesulfonic acid $C_{60}[S(CH_2)_3SO_3Na]_5H$ (1), mercaptopropionic acid $C_{60}[S(CH_2)_2COOK]_5H$ (2), proline $C_{60}[N(CH_2)_3CHCOOK]_5Cl$ (3) in a suspension of erythrocytes [1-5].

It was shown that with an increase in temperature from 5 to 35°C, the permeability P of the erythrocyte membrane for water molecules changes from $0.3 \cdot 10^{-5}$ to $0.5 \cdot 10^{-5}$ m/s. The activation energy of self-diffusion was calculated, the value of which was $E_D = 24.1 \pm 1.9$ kJ/mol. The lifetime τ of a water molecule inside the cell was also estimated, which was 20 ± 2 ms.

For C_{60} fullerene derivatives, data characterizing their interaction with the erythrocyte membrane were obtained using the PFG NMR method (Table 1). The partial self-diffusion coefficients D_s of C_{60} fullerene derivative molecules in erythrocytes were determined. It was established that in erythrocyte suspensions, C_{60} fullerene derivative molecules exist as isolated and associated molecules in the aqueous phase or bound to

Table 1. Self-diffusion coefficients D_s , populations p and lifetimes τ of molecules of fullerene C_{60} derivatives in erythrocytes.

Substance	$D_s \cdot 10^{-12} \text{ m}^2/\text{s}$	p	τ, ms
1	5.5 ± 0.8	0.33	440 ± 70
2	5.0 ± 1.0	0.13	470 ± 70
3	6.0 ± 1.0	0.06	1200 ± 300

the cell membrane. The exchange time of C_{60} fullerene derivatives molecules between the erythrocyte membrane and the aqueous solution was estimated.

Suspensions of isolated erythrocytes and erythrocytes aggregated into structures of the “coin columns” type were studied. It has been suggested that there is an uneven distribution of membrane permeability characteristics over the surface of a human erythrocyte cell, which is in principle consistent with recent work by Hoffman (2016, 2018), which demonstrates the effects of an inhomogeneous density distribution over the cytoskeleton of the membrane. According to our data, the permeability of the erythrocyte cell is mainly controlled by the permeability of the membrane along the perimeter of the biconcave disc, which probably enables red blood cells to perform metabolic functions, both in isolated and aggregated states.

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Comprehensive use of NMR methods in studying microstructure and molecular mobility in ionic liquid systems

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One of the main directions of the scientific activity in the laboratory of quantum magnetic phenomena at the Saint Petersburg State University is a study of peculiarities of the microstructure and molecular mobility in electrolyte/ionic solutions which are very interesting objects due to their important role in physical, chemical, biological and technological processes. The main experimental method is nuclear magnetic resonance (NMR): spectra, relaxation, diffusometry. The computer simulation methods (modelling of molecular dynamics and quantum chemistry) were applied to interpret NMR data. A brief overview of these studies is offered in the presentation (here a few references are given as examples).

The unique capabilities of NMR spectroscopy are based on the facts that (i) the theory of the NMR phenomenon has been developed to the highest level; (ii) each chemical element has at least one nuclear isotope with a magnetic moment, that determines the universality of the method.

It should be underlined that there are no direct analogues of NMR-relaxation processes among the physical phenomena which define spectra in infrared, visible and higher frequency spectroscopies. The NMR-relaxation processes are governed by the interaction of nuclei with fluctuating internal magnetic or inhomogeneous electric fields in the media, and their investigation gives unique information associated with the understanding of character and velocity of the molecular thermal motion.

NMR method for the investigation of diffusion processes should be considered as the best one among modern experimental techniques, since this method is non-contact and non-destructive, does not require the insertion of any material marker, and allows selective measurements of diffusion coefficients of components.

In the 1960s–1980s, the author with colleagues carried out a large series of studies of aqueous solutions of strong electrolytes, the results of which were published during this period in Russian-language journals, but later they were reflected in the article Ref. [1]. In this article a method, developed for determining microstructural parameters of diamagnetic aqueous solutions from NMR relaxation data, is presented. Based on measurements of the concentration and temperature dependences of the spin-lattice relaxation rates of the ^1H and ^2H nuclei in aqueous solutions, the coordination numbers (n) of more than 20 ions and the reorientation times (τ_c) of water molecules in different substructures of the solutions were determined. As a result, some rules of the hydration-shell forming have been defined:

1) The monatomic ions are surrounded by highly symmetrical shells: for the first layers n_1 is equal to 4, 6, 8 (but not 3, 5 or 7). The symmetry of hydration shells of monatomic ions is also discussed in the work Ref. [2] in which the NMR-relaxation of quadrupole nuclei of monatomic ions was studied. The polyatomic ions form their hydration shells in accordance with the number of possible intermolecular bonds (this

was not included *a priori* in the model). The developed approach was also applied in the study of the hydration shell of the CH_2 group in solutions of ω -amino acids [3].

2) An analysis of the parameter τ_c for different substructures makes it possible to quantify the molecular mobility in different substructures of a solution. It should be emphasized that the coordination numbers of ions and the reorientation times of water molecules were obtained in one experiment, but from independent data (see the details in Ref. [1]).

3) Investigations of the temperature dependence of the relaxation rates show that the nearest vicinity of the ions keeps its geometry over a wide temperature range. However, it has been found that the Cl^- and Br^- anions change the microstructure of their hydration shells in the narrow temperature range near 35°C [4]. The hypothesis was formulated that this effect for the Cl^- anion, which is noticeably present in living organisms, could be responsible for the thermoregulation of warm-blooded animals.

Investigations of concentrated salt solutions of interest for electrochemistry.

Electrolyte solution is a key component of energy storage devices, including Li-ion batteries (LIBs). Currently, the electrolyte of devices usually consist of salt solutions in non-aqueous organic solvents. During the last decade the ultra-concentrated, so-called “water-in-salt” systems have been proposed as new electrolytes for water-based LIBs. The bulk physico-chemical characteristics of these solutions (viscosity, electrical conductivity) are, generally, well studied, but there are insufficient data on the local mobility of ions and solvent molecules. The NMR allows one to measure diffusion coefficients for each component in a solution using a single method. The example of such studies is the work [4] in which the main experimental method is NMR diffusometry. The additional important information on the local mobility can be obtained from the NMR relaxation measurements.

Ionic liquids (ILs) are compounds consisting entirely of ions, but in contrast to “classical” salts they are liquids at the room temperature or close to it. The first ILs were synthesized more than 100 years ago, but they have become the object of intensive research only in the last 2-3 decades. ILs have unique properties such as low vapor pressure, high boiling point, high thermal stability, and, besides, possess the ability to dissolve a wide range of chemical species. They have also been suggested as non-aqueous electrolytes for electrochemical applications, energy storage and conversion, super- or ultra-capacitors. Various aspects of the molecular “architecture” and molecular mobility in topical ionic liquids have been studied by laboratory scientists using various NMR techniques (spectroscopy, relaxometry, and diffusometry). The problem of the state of water at low content in some ILs has been widely discussed in the literature. In particular, the concept of “water pockets” was introduced by Japanese researchers in 2014–2015. We gave a critical review of existing models of the microstructure of the “IL – water” mixtures and proved a new model of the structure for systems such as “[bmim] $^+$ A $^-$ – H_2O ” [5].

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Applications of EPR spectroscopy to heterojunction photocatalysts

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The search for stable and efficient photocatalysts capable of converting solar energy into useful chemicals such as H_2 and others is a topical area in the development of new renewable energy sources. Developing optimal photocatalysts for each specific case requires a thorough understanding of the nature and properties of the active catalytic sites and reaction mechanisms. Electron paramagnetic resonance (EPR) spectroscopy has become an important tool in such studies over the past decades.

Various heterojunction photocatalysts are currently being actively studied. In a recent study, using modern EPR techniques, we conducted a detailed study of charge transfer in heterojunction photocatalysts consisting of TAPA (tris(4-aminophenyl)amine)-PDA (terephthaldicarboxaldehyde) and $ZnIn_2S_4$ (TP/ZIS) [1]. The use of continuous wave (CW) and pulse EPR allowed us to identify stable radical defects localized near the surface and accessible to water molecules. Furthermore, time-resolved EPR (TR EPR) allowed us to study the processes of photoinduced electron transfer from TP to ZIS, leading to the formation of spin-correlated radical pairs under the influence of light, indicating efficient separation of charge carriers and spatial transport within the S-scheme heterojunction. Another example of the application of EPR to heterojunction photocatalysts was the study of composites based on tungsten oxides and the ZnTCPP (meso-tetra(4-carboxyphenyl)porphyrin) chromophore [2]. The combination of CW and TR EPR allowed us to identify intermediate excited states and draw conclusions about electron transfer and side reactions in a series of ZnTCPP/ WO_3 photocatalysts. In general, although TR EPR is not currently a universal tool for studying heterojunction photocatalysts, it often provides useful additional information and contributes to a deeper understanding of the electron transfer reactions taking place.

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Structural reorganization of VO^{2+} complexes on the surface of TiO_2

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Studies of the structure, catalytic activity and mechanisms of titanium dioxide, TiO_2 , doped with metal ions action are described in thousands of articles and many books (see, e.g. in [1, 2]). At the same time, a question what is happening with metal complexes on the surface of modified TiO_2 was investigated much less. By this reason, this work presents our results for the samples of TiO_2 Hombicat UV 100 and Degussa P25, being modified with VO^{2+} ions, clarifying structural peculiarities and spatial organization of paramagnetic centers (PCs) on the surface of nanoparticles of corresponding VO- TiO_2 oxides. Modification of TiO_2 nanoparticles by VO^{2+} ions (aqueous solution of VOSO_4) led to formation several isolated and aggregated PCs VO- TiO_2 of various composition and structure identified using EPR spectroscopy. Isolated PCs are schematically shown in Fig. 1.

Analysis of concentration and kinetic changes in EPR spectra has demonstrated existence of dynamic transformations and transitions such as $\text{PCs}_{\text{aggregated}} \rightarrow \text{PCs}_{\text{isolated}}$ and $A \rightarrow B \rightarrow C$ characterizing different parameters of spin-Hamiltonian $A_{\parallel}$, $A_{\perp}$, $g_{\parallel}$, $g_{\perp}$. Sufficient differences in behavior of VO^{2+} complexes on the surface of Hombicat UV 100 and Degussa P25 particles has been observed. Details of the original software package for the computer simulation of complex superimposed EPR spectra and kinetic transformations of metal complexes are described in detail in Refs. [2, 3].

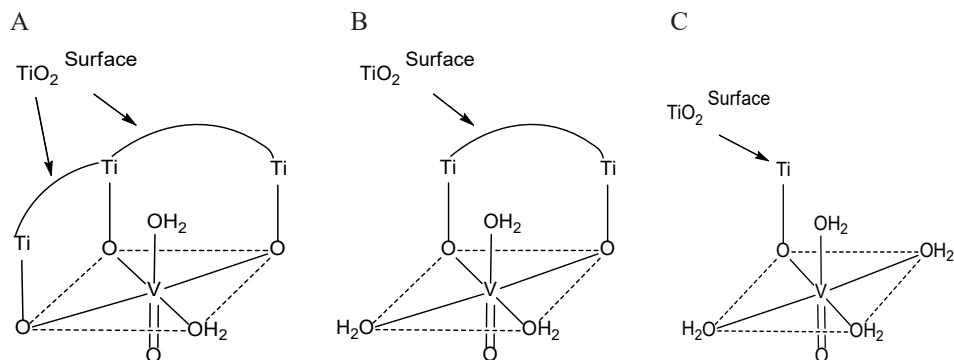


Fig. 1. Schematic structures of VO^{2+} complexes on the TiO_2 surface

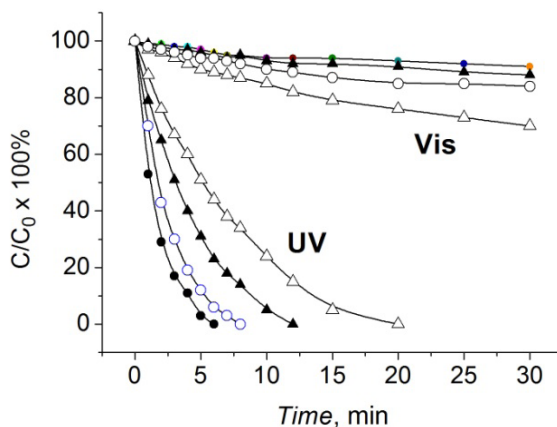


Fig. 2. Kinetic dependences Rhodamine RhB dye photodecomposition under UV or Vis light irradiation in the presence of photocatalysts Hombikat UV100 (bare, $\blacktriangle$, or VO-TiO₂, $\triangle$) TiO₂, and Degussa P25 ($\bullet$ bare) or VO-TiO₂, ($\circ$) TiO₂.

Photocatalytic peculiarities of VO-TiO₂ systems were studied on the example of models of the rhodamine dyes oxidation by air oxygen (Fig. 2). Heterogeneity of the metal complexes structure formed on the surface of the oxide catalysts and their possible transformations should be taken into account analyzing results of catalytic experiments.

This study was carried out as part of the state assignment on the topic “Interdisciplinary approaches to the creation and study of micro-/nanostructured systems” (Reg. No. 125012200595-8).

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Photoelectronic properties of optical sensor platforms based on anodic aluminum oxide

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Anodic aluminum oxide (AAO) is an ordered array of nanometer-sized pores and exhibits a number of unique properties, including controlled geometric parameters of the structure, large specific surface area, high thermal and chemical stability, mechanical strength and hardness, high adsorption capacity and, as a consequence, high sensitivity and selectivity with respect to biomolecules introduced into the AAO pores [1, 2]. Therefore, AAO is a promising material for the creation of optical sensor platforms for the detection of biomarkers [3]. The aim of this work was to develop optical biosensor platforms based on AAO and to study their photoelectronic properties depending on the synthesis conditions. The use of photoluminescence (PL) and electron paramagnetic resonance (EPR) methods makes it possible to establish PL mechanisms and obtain samples with a controlled concentration of spin centers (SC) and PL intensity.

To form optical biosensor platforms based on aluminum oxide, a two-stage anodization of aluminum substrates was used [4]. This method allows one to obtain a regular self-organized pore structure [4]. Aqueous solutions of organic etidronic (OEDP) and inorganic (sulfuric and selenic) acids were used as electrolytes for the synthesis of AAO. The obtained samples are designated as follows: AAO-Et, AAO-S, AAO-Se, respectively. Parameters such as electrolyte concentration and temperature, current density, and anodization voltage were varied during the synthesis. Rhodamine B was used as a test biomarker for testing the obtained sensor platforms; the application method for it is described in [6]. The PL spectra of the samples were measured under excitation with a helium-cadmium laser at a wavelength of 325 nm (photon energy of 3.8 eV). The radiation power was 10 mW, and the spot diameter was 1 mm. The PL signal was recorded using an MS750 grating monochromator (SOLAR TII) equipped with a CCD matrix. Analysis of defects with unpaired electrons (spin centers) was performed on a Bruker ELEXSYS-E500 electron paramagnetic resonance (EPR) spectrometer in the range of 10–300 K. A standard ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ single crystal) with a known number of spin centers was used to estimate their concentration.

The pore diameter of all synthesized samples was in the range of tens of nanometers according to electron microscopy data. All samples exhibited an EPR signal, which was a single symmetrical line with a g -factor of 2.0024 ± 0.0003 , which is consistent with their amorphous structure according to X-ray diffraction data. According to the literature, such a signal is due to oxygen vacancies in the oxide structure (F^+ centers) [5]. In addition, $\text{O}_2\text{-Al-Se-O}^*$ SC with orthorhombic symmetry were found in AAO-Se ($g_1 = 2.022 \pm 0.0003$, $g_2 = 2.015 \pm 0.0003$, $g_3 = 2.0075 \pm 0.0003$). The observation of an anisotropic EPR signal in amorphous alumina can be explained by the location of $\text{O}_2\text{-Al-Se-O}^*$ SC in the near-surface region of the samples along the entire length of

ordered (parallel to each other) nanopores. This hypothesis is confirmed by etching the near-surface layer: the longer the etching time, the lower the concentration of these SC. At elevated synthesis temperatures (approximately 25 °C and above), Se-O_x and S-O_x SC ($g = 2.0735 \pm 0.0003$) were detected in AAO-Se and AAO-S, respectively. The concentrations of F⁺ SC varied in the range from $8 \cdot 10^{15}$ to $2 \cdot 10^{17} \text{ g}^{-1}$ depending on the electrolyte composition and synthesis parameters, the concentrations of Se-O_x and S-O_x SC varied in the range from 10^{16} to $6 \cdot 10^{18} \text{ g}^{-1}$, for O₂-Al-Se-O* SC: $10^{16} - 10^{17} \text{ g}^{-1}$ (at synthesis temperatures in the range of 5–25 °C). Anodization at temperatures of 40 °C or annealing of AAO in air at 200–500 °C led to a sharp decrease in the concentrations of all SC. This indicates their localization in the near-surface region of the pores. EPR measurements were performed over a wide temperature range of 10–300 K. No new SC were detected at low temperatures. When applying the rhodamine B dye to the AAO surface, no change in the SC concentration was detected, indicating the absence of interaction between the SC and rhodamine molecules. The intrinsic PL of AAO-Se and AAO-S was at the background level; therefore, only the PL of the dye itself was recorded on these samples with rhodamine. The AAO-Se and AAO-S samples had high sensitivity: at a rhodamine concentration of 10^{-7} M , a sufficiently intense PL was observed. The AAO-Et samples were characterized by intrinsic intense PL, consisting of two PL bands with maxima at $\lambda_1 \approx 450 \text{ nm}$ and $\lambda_2 \approx 600 \text{ nm}$. Changes in the intensity of the first PL band (with variations in the synthesis conditions) correlate with changes in the F⁺ SC concentrations. Thus, PL at λ_1 occurs on F⁺. PL intensity at λ_2 does not correlate with F⁺ concentration, it is probably due to radiative recombination of electrons at non-paramagnetic centers. The PL of rhodamine ($\lambda_r \approx 580 \text{ nm}$) overlaps with the intrinsic PL of AAO, complicating the analysis of the PL spectra and requiring computer modeling. The AAO-Et optical platforms also demonstrated high sensitivity: PL was observed at a rhodamine concentration of 10^{-8} M .

These results have important practical implications, demonstrating the potential of using sensor platforms based on non-luminescent AAO, formed in electrolytes based on selenic and sulfuric acids, for studying the photoluminescence of biomarkers in nanopores. The study was supported by the Russian Science Foundation (RSF), grant No.24-19-00402, <https://rscf.ru/project/24-19-00402/>.

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Structural characterization of conformationally heterogeneous biomolecular complexes with photoactive ligands by pulsed dipolar EPR spectroscopy

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Photoactive ligands, including porphyrin photosensitizers, are relevant to photodynamic therapy and often form heterogeneous complexes with nucleic acids and proteins. Such complexes may include several binding sites and undergo ligand- or light-induced structural rearrangements, which complicates their characterization.

We used pulsed dipolar EPR to describe these systems through nanometer-scale distance distributions. The approach combines site-directed spin labeling, nitroxide–nitroxide DEER/PELDOR, and ReLaserIMD/LaserIMD, where the photoexcited triplet state of a bound porphyrin serves as one of the paramagnetic centers. The experimental distributions were analyzed together with spin-label conformer modeling, docking, and molecular dynamics simulations.

In human telomeric HTel-22 G-quadruplex complexes with cationic porphyrins [1], DEER revealed bimodal nitroxide–nitroxide distance distributions, consistent with coexisting G4 conformations. ReLaserIMD provided direct nitroxide–porphyrin distances and helped localize the photoligand on the DNA scaffold. After photoirradiation, longer distances appeared in both DEER and ReLaserIMD, indicating light-induced G-quadruplex unfolding, while singly labeled samples showed formation of dimeric species [1].

For the AS1411 aptamer bound to C3Py, ligand binding enhanced long-wavelength absorption. EPR showed that DNA-bound C3Py acquires features of a partially J-aggregate-like state. Dipolar EPR further indicated that C3Py shifts the AS1411 ensemble from monomeric G-quadruplex forms toward dimeric DNA structures.

The same concept was applied to human serum albumin complexes with porphyrin photosensitizers [2]. LaserIMD distances between a nitroxide label at Cys34 and photoexcited porphyrins were used to filter blind docking results. This EPR-guided analysis revealed multisite photosensitizer binding, including sites outside the commonly assumed albumin pockets [2].

Thus, pulsed dipolar EPR provides experimental distance restraints for localizing photoactive ligands and describing structural rearrangements in heterogeneous biomolecular complexes.

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EPR study of graphite oxides with different oxidation levels

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Graphite oxide (GO) is a promising material for membrane technologies due to its ability to intercalate polar liquids. However, the mechanism of a substance transport through the material, which is mainly determined by the mobility of the substance within nanoscale interlayer galleries, remains unclear. NMR spectroscopy has been successfully employed to characterize the molecular dynamics of liquids intercalated into the inter-plane space of GO [1]. Interpretation of NMR data in such systems requires accounting for the contribution of the GO matrix itself, including its intrinsic paramagnetic centers, which can affect the relaxation parameters and spectral line shapes of intercalated liquids. This work presents a comparative EPR study of four powdered GO samples differing in synthesis history and oxidational level (C/O ratio). For each sample, saturation of the intrinsic EPR signal was estimated in order to make correlations with the C/O ratio via the amount of oxidized and non-oxidized galleries in the materials. The temperature dependence of the EPR signal integral intensity was analyzed to determine the dominant type of spin centers (localized spins vs. conduction electrons). The obtained data correlated with the synthesis conditions of the samples will be subsequently used for correct separation of the contributions from the GO matrix and intercalated liquids in ¹H NMR spectra.

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MRI investigation of the development of bird embryos

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The conducted exploratory MRI studies have shown the possibility of noninvasive visualization of avian embryogenesis, with differentiation of incubation egg structures at an early stage, and systems and organs comparable to anatomical studies at a later stage. The MRI method makes it possible to determine the boundaries and sizes of embryo structures by contrasting T1W and T2W images.

The measurements were performed on an MRI with a field of 0.4 T, using a conformal sensor with a maximum fill factor [1].

A paper devoted to determining the viability of farm bird embryos at the early stages. The work is devoted to determining the viability of farm bird embryos at the early stages of ontogenesis. This is an important economic task, since up to 20% of incubated eggs do not develop and must be rejected. Currently, this problem is solved by ovoscopy or acoustics, but such methods provide information at a rather late stage. There are studies that show that NMR studies of eggs make it possible to determine the viability of embryos at earlier stages, and there is even a connection with the sex of the embryo, the determination of which is also important when breeding meat or egg-bearing breeds of birds.

We conducted an experiment with daily acquisition of MRI images of chicken eggs and their NMR relaxation parameters during incubation for 21 days. During the measurements, tomograms of sections with contrast in T1 weighted (T1W) images and T2 weighted (T2W) images, as well as relaxation drops in T1 and T2, were obtained. The measurement results were processed by decomposing the declines into two or three exponents using the regression method. MRI studies of the development of chicken embryos were performed in comparison with the method of anatomical hatching of eggs.

It was carried out according to the state assignment of the Zavoiisky Physical-Technical Institute, FRC Kazan Scientific Center, Russian Academy of Sciences.

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EPR study of nitric monoxide content in the brain of rats after combined brain and spinal cord injury

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Nitric oxide (NO) is an inorganic gas, which acts as a signaling molecule in most animal and plant tissues [1]. This small mobile reactive molecule is soluble in water and lipid membranes, so after synthesis it immediately diffuses into the surrounding space. Despite the fact that its lifetime in biological tissues is short, its mobility allows it to spread over significant distances between cells without difficulty. It is known that NO regulates cell metabolism and physiological functions of the body [2, 3]. It is widely distributed in the nervous [4, 5] and cardiovascular [6, 7] systems. Since NO is a chemically highly reactive free radical capable of acting as both an oxidizer and a reducer [8], an assumption arises about its diverse effects in biological tissues. Of great interest is the participation of NO in the mechanisms of development of various pathological conditions of the body [9]. The functional role of endogenous NO in the processes occurring during damage to the nervous system is controversial and remains insufficiently studied [2, 3]. It is fundamentally important to consider that the coordinated functioning of the NO system is disrupted during the development of hypoxia, cerebral ischemia, and other pathological processes [10, 11].

Traumatic brain injury is a major public health and social problem in every country. In nearly 60% of cases, death is caused by brain damage [12]. There is evidence that NO plays a key role in the cascade of secondary injuries [10, 13]. Therefore, we conducted a study of NO content in rat brain tissue 24 hours and 7 days after combined brain and spinal cord injury.

EPR spectroscopy was used to study the dynamics of NO content in the brain of rats after modeling combined brain and spinal cord injuries. The intensity of NO production by EPR spectroscopy was measured using the spin trap method [2, 14], which is based on the reaction of NO with a spin trap. The complex of Fe²⁺ with diethyldithiocarbamate (DETC) was used for capture NO with generating a stable ternary complex (DETC)₂-Fe²⁺-NO in animal tissue. These complexes are characterized by an easily recognizable EPR spectra with a g-factor value of g = 2.035–2.040 and a triplet hyperfine structure [2, 14, 15]. The measurements of spectra of complex of biological samples (DETC)₂-Fe²⁺-NO and Cu²⁺-(DETC)₂ were made using a Bruker X-band (9.5320 GHz) EMX/plus spectrometer.

It was shown that NO levels in the injured area (frontal lobes) significantly decreased after 24 hours. In the contralateral region of the brain, the decrease in NO levels relative to the control group was not significant. Seven days after the injury, a significant decrease in NO production in the injured area of the brain persisted, and a significant, but non-significant, decrease in NO production was also observed in the uninjured region of the brain.

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Comparative analysis of paramagnetic centers in nanosized anodic aluminum oxide synthesized in organic and inorganic acids and subjected to additional etching and annealing

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Currently, one of the promising areas in the field of nanotechnology is the development of optical biosensors characterized by high sensitivity and selectivity [1]. One of the materials actively used to create such biosensors is nanostructured anodic aluminum oxide (nano- Al_2O_3) [2, 3]. Its main advantages are the simplicity and low cost of synthesis, the absence of contacts, and fast response. It is known that paramagnetic centers (defects) in nanosized metal oxides play an important role in the physicochemical processes occurring in these materials [4]. The nature of spin centers in nano- Al_2O_3 , depending on the synthesis conditions, remains controversial. Therefore, the main goal of this work was to conduct a systematic comparative analysis of the type, concentration of paramagnetic centers (PCs), and their properties depending on the synthesis conditions and post-processing of nano- Al_2O_3 .

Synthesis of nano- Al_2O_3 was carried out by anodic oxidation in dilute solutions of various acids for comparison: oxalic, OEDP, sulfuric and selenic acids. As our studies have shown, the following acid concentration in the electrolyte is optimal: 0.45 M $(\text{COOH})_2$, 0.3 M OEDP, 1.5 M H_2SeO_4 , 1.5 M H_2SO_4 . The temperature varied in the range of 5–40 °C. We will designate the samples in accordance with the acids used for synthesis: nano- Al_2O_3 - H_2SeO_4 , nano- Al_2O_3 - H_2SO_4 , nano- Al_2O_3 - $(\text{COOH})_2$, nano- Al_2O_3 -OEDP. Analysis of paramagnetic centers was performed on a Bruker ELEXSYS-E500 electron paramagnetic resonance (EPR) spectrometer in the range of 10–300 K.

Oxygen vacancies (F^+ centers) were detected in nano- Al_2O_3 - $(\text{COOH})_2$ and nano- Al_2O_3 -OEDP. When the synthesis temperature varied from 5 to 40 °C, the concentration (N_s) of F^+ centers varied non-monotonically ($N_s^{\min} = 2 \cdot 10^{17}$, $N_s^{\max} = 3.4 \cdot 10^{17} \text{ g}^{-1}$) for nano- Al_2O_3 - $(\text{COOH})_2$ and ($N_s^{\min} = 3 \cdot 10^{16}$, $N_s^{\max} = 1.6 \cdot 10^{17} \text{ g}^{-1}$) for nano- Al_2O_3 -OEDP. In the samples synthesized in selenic acid, oxygen radicals were detected in addition to F^+ . The $N_s(\text{F}^+)$ value was approximately 10^{16} g^{-1} in nano- Al_2O_3 - H_2SeO_4 and nano- Al_2O_3 - H_2SO_4 ; $N_s(\text{oxygen radicals}) = 10^{17} \text{ g}^{-1}$ in nano- Al_2O_3 - H_2SeO_4 . With the increase of synthesis temperature to 25 °C in nano- Al_2O_3 - H_2SeO_4 , nano- Al_2O_3 - H_2SO_4 new PCs were found, which are fragments of selenic and sulfuric acids: SeOx ($3.2 \cdot 10^{16} \text{ g}^{-1}$) and SOx ($4.8 \cdot 10^{16} \text{ g}^{-1}$), respectively. With the increase of synthesis temperature to 40 °C the concentration of all PCs sharply decreased by more than an order of magnitude, which is caused by etching of the surface layer at elevated synthesis temperatures in nano- Al_2O_3 - H_2SeO_4 , nano- Al_2O_3 - H_2SO_4 . The effect of post-treatments (etching in an acid used for the synthesis and annealing in air at temperatures ranging from 200–500 °C) on the type and concentration of PCs in nano- Al_2O_3 was studied. It was found that, during etching, as well as during synthesis at elevated temperatures, SeOx and SOx -type PCs appear in nano- Al_2O_3 - H_2SeO_4 and nano- Al_2O_3 - H_2SO_4 , the concentration of which depends

non-monotonically on the etching time. During annealing, with increasing annealing temperature, the PC concentration in all the samples studied decreases, likely due to interaction with oxygen molecules. During etching and annealing of nano- Al_2O_3 -OEDP samples, a non-monotonic dependence of the F^+ center concentration on the etching time and annealing temperature was observed, which can be explained by multi-stage interactions with electrolyte molecules during etching and oxygen molecules during annealing in air.

The obtained data allows us to resolve the discrepancies existing in the literature and can be used to create optical biosensors based on nano- Al_2O_3 with controlled type and concentration of PC. The study was supported by the Russian Science Foundation (RSF), grant No.24-19-00402, <https://rscf.ru/project/24-19-00402/>.

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Disentanglement of intra- and inter-molecular pathways of photoinduced electron transfer in biomimetic Trp-Pro_n-F dyads by time-resolved and field-cycling CIDNP

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Blue-light photoreception in living species is frequently conducted via flavoproteins – a non-covalent assembly of a protein and a flavin mononucleotide (FMN) or flavin adenine dinucleotide (FAD). Upon photoexcitation, the electron transfer from a suitable amino acid residue to flavin generates short-lived spin-correlated radical pairs (SCRPs) that participate in spin-correlated phenomena such as photochemically induced dynamic nuclear polarization (photo-CIDNP) [1, 2]. The photochemical transformations in such systems control biological signaling, subsequent electron transfer, and the secondary structure of proteins. A fundamental question for understanding the underlying photochemical transformations in such systems is whether intramolecular or intermolecular electron transfer dominates. These processes result in the predominant creation of either covalently linked radical pairs or free radicals. In recent work [3] we addressed this question via studying rigid and chemically tunable artificial constructs: the electron donor was a tryptophan residue (Trp), the electron acceptor was N10-(4-carboxyphenyl)-flavin (F), and the linker was made of $n = 3\text{--}12$ proline residues that were reported to adopt the polyproline II (PPII) helix in methanol, with well-characterized geometrical characteristics, making it a kind of “molecular ruler”.

In photo-CIDNP, the electron spin correlation is transferred partially to nuclei through electron–nuclear spin dynamics dictated by hyperfine interactions and the difference in g -factors of radicals. The classical radical pair mechanism (RPM) [4] is thought to operate effectively if dye and quencher radicals (formed as a result of intermolecular electron transfer) can separate in space, but if the relative mobility of SCRPs is restricted as in a molecular donor-acceptor compound studied here, then RPM is predicted to be ineffective. However, in biradicals generated via the intramolecular electron transfer the so-called J-mechanism of CIDNP could be very effective, for instance, see [5]. In this mechanism, the level-avoided crossing of the singlet $|s\rangle$ and $|t_+\rangle$ or $|t_-\rangle$ triplet terms occurs at a magnetic field such that the Zeeman splitting matches the zero-field singlet-triplet gap $2J_{\text{ex}}$ caused by the exchange interaction, the hyperfine coupling enables singlet-triplet transitions with the conservation of electron and nuclear spin projections, e.g., $|s, m\rangle \rightarrow |t_-, m+1\rangle$.

However, contrary to the *a priori* assumption of polyproline helix being a “molecular ruler”, experimental data showed the vast diversity of linker conformations for all studied dyads, with a tendency towards increased PPII helix population with increasing number of proline residues. In ^1H NMR spectra the conformational diversity manifests as satellite lines with distinct chemical shifts near the intense NMR signal of the main conformer. Time-resolved CIDNP data (Fig. 1, left) were measured on the NMR signals of the major conformer and then fitted within Fischer’s model [6] with the same electron transfer rate of 10^5 s^{-1} for all $n = 3\text{--}12$ polyproline dyads, while the

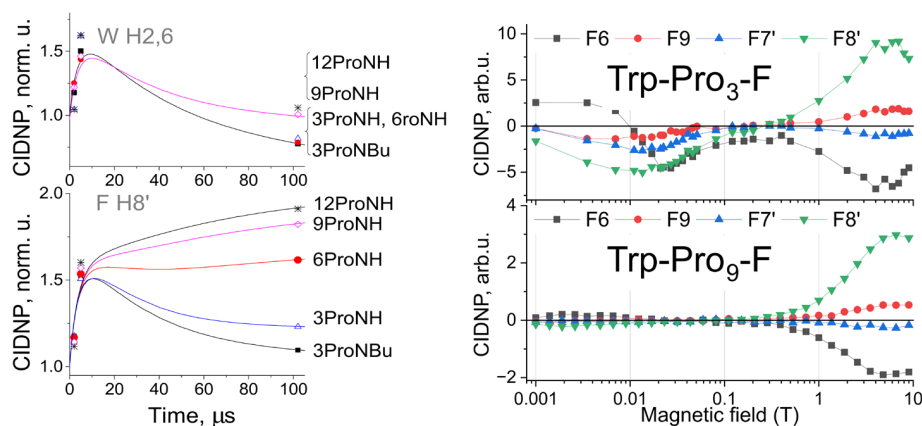


Fig. 1. Dots – experimental ^1H CIDNP data obtained with 0.2 mM of Trp-Pro_n-F in MeOD: Left column – time-resolved CIDNP data for W6/W2 (top) and F8' (bottom) protons for a series of $n = 3, 6, 9, 12$ dyads; Only three time points were measured due to the limited amount of available samples. Lines are showing simulation with Fischer's cyclic photoreaction model [6]. Right column – ^1H CIDNP field dependences of Trp-Pro₃-F (top) and Trp-Pro₉-F (bottom). The sizable ^1H CIDNP effect observed with Trp-Pro₃-F at the magnetic field 10–50 mT indicate the presence of photoinduced biradicals with the exchange coupling ca. 18 mT.

nuclear relaxation time $T_{1,N}$ decreased with increasing linker length. Both observations are typical of bimolecular reaction, thus revealing the predominance of intermolecular electron transfer as the source of CIDNP effect at high (> 1 T) magnetic field. Interestingly, at low field of 5–50 mT the satellite signals of minor conformers of $n = 3, 4$ polypyrroline dyads show much larger CIDNP enhancement than those of the major conformer, but only little or no CIDNP at high magnetic field. These are the characteristic features of the very effective J-mechanism of CIDNP generation in biradicals formed following intramolecular electron transfer. These data in combination with the magnetic field relaxation dispersion of dyad's protons allowed us to disentangle the dominant intramolecular electron transfer pathway in short $n = 3, 4$ dyads and intermolecular electron transfer pathway in longer $n = 6–12$ polypyrroline dyads. This work was supported by Russian Science Foundation, grant No 26-73-00264.

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NMR study of supramolecular drug delivery systems and drugs interaction with lipid membranes

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NMR spectroscopy is a powerful method sensitive to weak non-covalent intermolecular interactions. In our work we use various NMR techniques (T_2 relaxation and selective gradient NOESY) and molecular dynamics (MD) simulation to study drug-drug and drug-membrane interactions, as well as to prove the inclusion of drug molecules into supramolecular delivery systems. In particular, T_2 relaxation time is sensitive to the diffusional mobility of molecules and intermolecular interactions, so the changes in T_2 relaxation time are often considered as evidence of inclusion complex formation as well as self-association processes occurring in aqueous solutions. The intensities of cross-peaks in the NOESY spectrum are extremely sensitive to the distance between interacting protons. We can observe the appearance of cross-peaks in the NOESY spectrum if the distance between nuclei is less than 0.5 nm, thereby the arrangement of drug molecule in the lipid membrane or some delivery system could be determined.

Last years, these NMR techniques were applied to study inclusion complexes of some vitamins (A, E and D3) and carotenoids with cyclodextrins, micelles of glycyrrhizin, and model lipid membranes [1–4]. All these vitamins and carotenoids are known to be vital for human health. However, dietary sources alone cannot provide recommended level of these compounds due to their low solubility, stability and bioavailability. Recent advances in nanotechnology provide promising solutions of these problems through various encapsulation platforms. As an example, we have demonstrated the ability of glycyrrhizin to increase solubility and membrane permeability of various lipophilic drugs, and it was considered as the main physicochemical mechanisms for enhancing drug activity in complexes with glycyrrhizin.

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Analysis and simulation of EPR spectra of iron-doped bioactive glasses using the Czjzek distribution

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This report discusses the results of EPR studies of powders of 45S5 bioactive glasses doped with iron ions. The aim was to determine the magnetically inequivalent states of the iron ions, obtain data on the symmetry and strength of the crystal fields acting on them, and reveal signs of magnetic-nanoparticle formation as the iron precursor content increases. The EPR spectra were recorded on a JES-X330 spectrometer (JEOL, Japan) equipped with a DVT5 variable temperature unit. Spectral analysis was performed using a software package developed by the authors for simulating powder EPR spectra of paramagnetic ions.

For the quantitative description of the EPR spectrum of Fe^{3+} in a powder particle, the following spin Hamiltonian was chosen:

$$\hat{H} = g\beta(\mathbf{B}, \hat{\mathbf{S}}) + D \left(\hat{S}_z^2 - \frac{S(S+1)}{3} + \lambda (\hat{S}_x^2 - \hat{S}_y^2) \right),$$

where $\lambda = E/D$, the remaining parameters have their conventional meanings.

In the glass phase there is no long-range order, so the EPR spectra of the iron-doped powder were calculated assuming distributions of the fine-structure parameters D and λ . The weight w of each individual spectrum $f(B, D, \lambda)$ was given by the Czjzek distribution [1]:

$$w(D, \lambda) = \frac{1}{\sqrt{2\pi} \left(\frac{\sigma}{3}\right)^d} \left(\frac{D}{3}\right)^{d-1} [3\lambda(1-\lambda^2)] e^{-\frac{D^2(1+3\lambda^2)}{2\sigma^2}},$$

where σ is the parameter that determines the width of the distribution of D and λ , d is the number of independent components of the fine-structure tensor. The value $d = 5$ corresponds to the case of fully independent components, whereas smaller values may indicate the presence of correlations between the tensor components. Note that in this formula the range of λ , unlike in [1], corresponds to the inequality: $0 \leq \lambda < 1/3$.

The experimental EPR spectrum was fitted taking into account the distribution of the parameters D and λ , using the expression

$$F(B) = \int \int_{\lambda D} f(B, D, \lambda) \cdot w(D, \lambda) dD d\lambda.$$

Computer simulation of the EPR spectra of the powder doped with 1 wt.% iron ions showed that they are well described by the Czjzek distribution [1] for the parameters

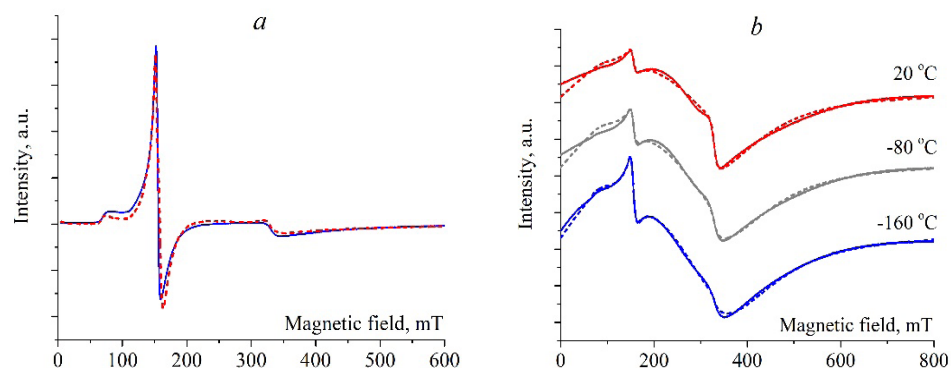


Fig. 1. Experimental (solid lines) and calculated (dashed lines) EPR spectra of powders of 45S5 bioactive glass doped with iron. (a) Sample doped with 1 wt.% iron ions; the fit was performed using the Czjzek distribution for the fine-structure parameters D and λ ; (b) Sample doped with 5 wt.% iron ions; the fit was performed using the sum of the contributions of the resonances of Fe^{3+} in the glass phase and in superparamagnetic particles.

D and λ in the glass phase (Fig. 1a). The value $d = 3$ obtained from this fit indicates short-range ordering associated with correlation of the fine-structure tensor components.

In the EPR spectrum of the powder doped with 5 wt.% iron ions (Fig. 1b), in addition to the signal characteristic of Fe^{3+} ions in the glass phase, there is a broad signal whose parameters are sensitive to temperature. As the temperature decreases, it broadens and shifts towards low fields, which is characteristic of the superparamagnetic resonance of an ensemble of magnetic nanoparticles. To describe its contribution to the spectrum, a model was used that takes into account the magnetocrystalline anisotropy, the particle shape anisotropy, the lognormal particle size distribution, and the Landau–Lifshitz lineshape [2]. Simulation of the spectra at various temperatures showed that they are well described by the sum of the contribution of Fe^{3+} ions in the glass phase and the varying contribution of superparamagnetic resonance.

Thus, the EPR data show that at low concentrations of the iron-containing precursor, the Fe^{3+} ions in the synthesis products are located predominantly in heterogeneous local crystal fields of the glass phase, as a result of which their spectra are described by a distribution of the fine-structure parameters D and λ . As the iron content increases, an additional broad temperature-dependent signal appears in the spectra, associated with resonance on superparamagnetic nanoparticles.

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Automated prediction of natural carbohydrate structure from 2D NMR data

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In carbohydrate chemistry and biology, NMR spectroscopy is a principal method for bioglycan research, but its applicability is hampered by the huge structural diversity and complexity of spectra. Semi-automatic primary structure elucidation approaches exist to generate all possible structural hypotheses and rank them according to the similarity between the simulated 1D spectra and the experimental data.

Within the framework of the Carbohydrate Structure Database glycoinformatic platform [1] and the GRASS NMR analyzer [2], we developed a structure predictor based on the simulation of 2D ^1H , ^{13}C HSQC NMR spectra and their comparison with unassigned experimental NMR data (Fig.1). A key achievement is the design of a similarity metric for two-dimensional spectra. To obtain this metric, the signals in the two spectra must be uniquely matched, which is a non-trivial challenge for 2D data. Our solution relies on the Sinkhorn optimal transport algorithm [3] adapted to the specific features of complex natural carbohydrates.

In contrast to neural-network approaches, the proposed tool provides not only predictive but also evidential power, enabling the user to trace each simulation down to referenceable literature data in the database. Its output is a list of the most probable primary structures ranked by simulation-to-experiment similarity.

The designed GRASS/HSQC service is freely available online at <http://csdb.glycoscience.ru/grass.html>. This work was funded by Russian Science Foundation grant 25-13-00008.

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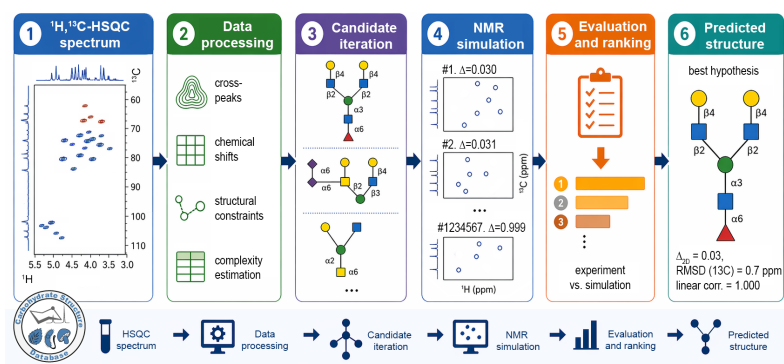


Fig. 1. The flowchart of HSQC-based glycan structure predictor.

2D noesy NMR spectroscopy study of mechanoactivated Ca and Mg gluconates

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Gluconates has found wide practical application in many fields. Its most important property is its use as a biologically active substance and medicinal product. It is known that the effectiveness of application of any drug depends on its solubility in aqueous media (in saliva, gastric juice). Many different methods are used to increase drug solubility, one of which is mechanochemical activation of substances [1].

One of the most important and frequently used methods for studying the structure of organic compounds in solutions is nuclear magnetic resonance. In this study, 2D NOESY NMR spectroscopy [2] was used to study the structural changes in calcium gluconate and magnesium gluconate molecules that occur after their mechanochemical activation. Both gluconates were dissolved at a concentration of 30 mmol/L in deuterated water. The resulting solutions were studied at room temperature by a Bruker Avance 400 NMR spectrometer. This study showed that 2D NOESY NMR spectra of both gluconates after mechanochemical activation differ from the spectra before mechanochemical activation.

NMR spectroscopy has already been used to study usual and mechanically activated calcium gluconate. However, in scientific researches involving the study of the spatial structure of molecules, 2D NOESY NMR spectroscopy is most often used. The intensity of cross-peaks in 2D NOESY NMR spectra depends strongly on the distances between hydrogen atoms in the molecules of the studied compounds (as $1/r^6$). If, after mechanochemical activation of calcium gluconate, small rotations of individual $-HCOH-$ or H_2COH- groups relative to each other in the gluconate ions of its molecules occur, this will lead to noticeable changes in the distances between hydrogen atoms and, consequently, to a significant change in the intensity of cross-peaks in 2D NOESY NMR spectra.

One of the reasons for the increased therapeutic efficacy of calcium gluconate after mechanochemical activation may be the conformational changes occurring in its molecular structure. Mechanochemical activation of calcium gluconate can lead to a bending of the chain structure of gluconate ions and a slight rotation of individual chemical groups relative to each other within the molecule. Associates formed in solutions of gluconic acid salts [3] may have different structures in their original and mechanoactivated states. This may be indicated by different degrees of line broadening from different proton groups.

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Multinuclear ^1H and ^{31}P NMR characterization of hydrogen-bonded complexes of phosphine oxide

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Hydrogen bonding to the phosphoryl oxygen atom produces highly structured multinuclear NMR responses, offering a unique opportunity to dissect the interplay between individual and collective non-covalent interactions [1]. The pronounced sensitivity of the phosphoryl group to its surrounding environment arises from the high responsiveness of the ^{31}P nucleus [2], whose chemical shift undergoes substantial variations upon the formation of non-covalent interactions [3, 4]. Over the years, phosphine oxides have emerged as versatile ^{31}P NMR probes, enabling the characterization of Lewis acidity [5] as well as the assessment of Brønsted acidity [3]. Furthermore, computed ^{31}P chemical shifts have been widely employed as theoretical indicators of non-covalent interaction strength, providing a predictive framework that complements experimental observations [6, 7]. In this work, we present an extensive $^1\text{H}/^{31}\text{P}$ NMR investigation of hydrogen-bonded complexes formed between triphenylphosphine oxide (Ph_3PO) and twenty-four substituted phenols [1]. Low-temperature liquid-state NMR spectroscopy in a polar aprotic freonic medium ($\text{CDF}_3/\text{CDF}_2\text{Cl}$, 100 K) enables the resolution of distinct signals corresponding to both 1:1 and 1:2 complexes, allowing direct spectroscopic access to systems featuring one or two simultaneous $\text{O}-\text{H}\cdots\text{O}=\text{P}$ hydrogen bonds.

The ^1H NMR chemical shifts of the bridging OH protons span a broad range, reflecting systematic variations in hydrogen-bond strength across the phenol series. In contrast, the ^{31}P NMR chemical shift exhibits a cumulative downfield displacement that scales with the total hydrogen-bonding load on the phosphoryl oxygen. This dual-nucleus approach reveals a clear separation between local descriptors of individual hydrogen bonds (^1H shifts) and global descriptors of the entire hydrogen-bonding environment (^{31}P shifts).

A key outcome of this study is the direct experimental observation of anticooperativity in 1:2 complexes. When two phenol molecules simultaneously donate hydrogen bonds to the same $\text{P}=\text{O}$ acceptor, the strength of each individual $\text{O}-\text{H}\cdots\text{O}=\text{P}$ interaction decreases, as evidenced by the systematic upfield shift of the OH protons in 1:2 complexes relative to their 1:1 counterparts. This weakening is mirrored in the ^{31}P NMR data: although $\Delta\delta\text{P}$ increases upon formation of the second hydrogen bond, the increment is smaller than expected for two independent interactions, demonstrating that the two hydrogen bonds compete for the same electron density at the phosphoryl oxygen. Quantitatively, the anticooperative reduction in total binding strength is approximately 15–20%, consistent across both experimental NMR data and DFT calculations.

Complementary quantum-chemical calculations (PCM and explicit solvent molecules) reproduce the experimental geometries and NMR trends, and highlight the crucial role

of solvation. The computations show that Ph_3PO typically forms three hydrogen bonds in solution, with solvent molecules occupying the remaining coordination sites around the $\text{P}=\text{O}$ group, further modulating the observed NMR parameters.

Overall, this work demonstrates that multinuclear NMR spectroscopy provides a powerful framework for quantifying both individual hydrogen-bond strengths and collective effects such as anticooperativity, establishing ^{31}P NMR chemical shifts as a sensitive probe of total hydrogen-bonding load in phosphine oxide systems.

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Differences in the hydrodynamic radius of block and gradient copolymers in dilute solution

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Gradient copolymers emerged much later than classical copolymers and have been less studied [1–4]. Using Brownian dynamics [5] and a large-scale model, we conducted computer simulations of comparable block copolymers and gradient copolymers. Each chain contained the same number of hydrophobic and hydrophilic units. We studied block copolymers with 2, 4, and 8 blocks. In gradient copolymers, the comparable block contained 25% units with different chemical structures. Two homopolymers consisting of either completely hydrophobic (globule) or completely hydrophilic (helix) units were chosen as reference points.

We calculated the hydrodynamic radius in three ways: a) via translational diffusion, b) via rotational diffusion, and c) via the Kirkwood approximation. Since hydrodynamic interactions were not taken into account in the simulations, the first method cannot be quantitatively compared with the second. Therefore, in this study, we limited ourselves to a qualitative comparison.

For block copolymers, the hydrodynamic radius increases as the number of blocks in the copolymer decreases, while the total number of units remains constant. Gradient copolymers with 2, 4, and 8 blocks exhibited similar hydrodynamic radii, comparable to the 8-block block copolymer and significantly smaller than the 2- and 4-block block copolymers. In gradient copolymers, the interface between the hydrophilic and hydrophobic regions becomes more diffuse. The distribution of hydrophilic units shifts closer to the hydrophobic core and penetrates deeper into it. These structural changes explain the differences in relaxation properties between block and gradient copolymers. The obtained results are of interest for experimental studies of the relaxation properties of gradient copolymers and their practical applications.

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Features of the EPR spectra of serum ceruloplasmin in patients with undifferentiated connective tissue dysplasia

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Ceruloplasmin (CP) is a complex copper-containing protein, a ferroxidase, which contains 6 copper ions. The spatial organization of copper ions in CP is a complex system consisting of three types of centers. Three mononuclear “blue” copper centers (type I) accept electrons from substrates and transfer them to a trinuclear cluster (type II and III centers), the main catalytic center for oxygen reduction. Three type I copper ions and one type II Cu^{2+} ion are paramagnetic, while the type III center is a diamagnetic pair of two Cu^{2+} ions with a strong magnetic interaction between the two copper ions ($S = 0$).

One fairly common pathology is undifferentiated connective tissue dysplasia (UCTD), which is particularly associated with back pain. Laboratory tests for UCTD primarily include assessment of collagen metabolite levels in the blood or urine, as well as a blood chemistry panel to determine calcium, magnesium, and phosphorus levels. However, no studies have been conducted on CP levels in the blood of patients with this pathology. CP is not simply a transport protein; it is a critically important enzyme that maintains not only iron and copper balance but also provides antioxidant protection and is an important marker for a number of diseases.

In this study, serum samples from patients with UCTD associated with back pain were analyzed using the X-band EPR method at 80K. EPR spectra were recorded on a “Bruker EMX Plus” spectrometer at a frequency of ~ 9.38 GHz with a modulation frequency of 100 kHz, a modulation amplitude of 5 G, and a microwave power of 20 mW from samples of equal volume (0.15 ml).

Figure 1 shows the EPR spectra of blood serum recorded at 80 K for a control sample and two samples taken from patients with undifferentiated connective tissue disease. As can be seen from Figure 1, the spectrum represents the absorption lines of transferrin (Tf), an iron transporter, with $g_{\text{eff}} \sim 4.28$ and ceruloplasmin with $g \sim 2.05$. The signal with $g \sim 2.05$ represents the absorption lines of Cu^{2+} ions in type I and II centers. According to the literature, there are two types of type I centers with hyperfine splitting constants $I_a \sim 7.2$ mT and $I_b \sim 9$ mT and one type II center with $A_{\parallel} \sim 170$ mT. The obtained data showed that a number of patients with moderate severity of UCTD do not experience an increase in ceruloplasmin concentration compared to the control samples. At the same time, most patients show a significant increase in the signal intensity from Cu^{2+} -CP with a well-resolved hyperfine structure with $A_{\parallel} = 7.4$ mT. According to the study [1], for pairs of data compared using linear regression analysis of serum copper content, EPR *versus* atomic absorption spectroscopy, there is a high correlation: the correlation coefficient r^2 of 0.96 for human normal control (blood bank), and in the presence of pathology (in cancer patients with different tumor locations), the r^2 value varies from 0.55 to 0.87 (on average $r^2 \sim 0.80$).

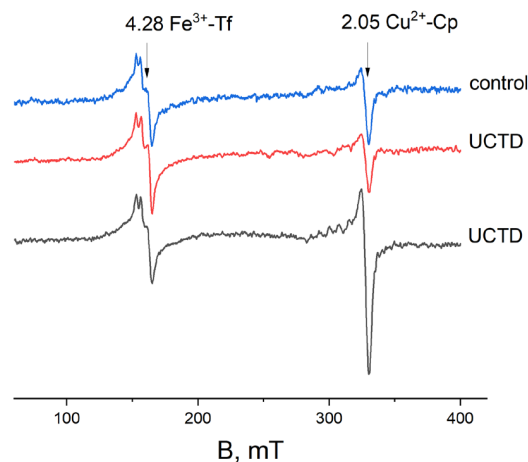


Fig. 1. X-band EPR spectra of blood serum, recorded and 80 K.

At this stage of the study, it can be stated that the observed increase in the concentration of CP in patients with undifferentiated connective tissue disease is associated, at least, with type I_a copper centers. The reasons for the increase in CP levels may be different, but it is very likely that it may be associated with the antioxidant defense system of the body, namely, the compensatory response to increased oxidative stress. The data obtained will certainly be interesting and will require further research.

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NMR spectroscopy of the interaction between 4,6-dinitro-7-chlorobenzofuroxan and an oligonucleotide

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The synthesis of new biologically active substances and the development of medicinal products based on them is one of the most important tasks of modern organic chemistry. Dinitro- and nitrobenzofuroxanes provide a convenient platform for the synthesis of a variety of organic compounds with potential biological activity. They have found application as antibacterial, antifungal and antiparasitic medicinal products in veterinary medicine and agriculture.

Currently, the development of therapies for cancer is a promising and highly sought-after area of research. To synthesize antitumor agents involved in the destruction of tumor cells, it is necessary to understand the mechanisms of intermolecular interactions between new (hetero)aromatic compounds and DNA. High-resolution NMR spectroscopy will enable the identification of structural features of the model molecule – a DNA fragment and benzofuroxane derivatives – as well as an assessment of their interactions.

To achieve this objective, control one-dimensional spectra of aqueous-organic solutions of the test sample, the model DNA molecule (an oligonucleotide) and a mixture of the test sample with the oligonucleotide were recorded using high-resolution NMR methods. A comparative analysis of the experimental data obtained suggests that an interaction exists between the benzofuroxanes and the oligonucleotide. For further qualitative analysis, homo- and hetero-nuclear two-dimensional spectra of the solutions were recorded, and a partial correlation of the NMR spectra was carried out for the subsequent construction of a computer-generated three-dimensional spatial model of the complex of 4,6-dinitro-7-chlorobenzofuroxan and the oligonucleotide.

Analysis of the anticancer potential of novel (hetero)aromatic derivatives using NMR spectroscopy and molecular modeling methods

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Cancer therapy is one of the priority challenges of modern science and medicine, including in the Russian Federation. The development of agents for the controlled destruction of cancer cells represents a pressing scientific task. A promising direction is the design of drugs whose mechanism of action is based on interaction with cancer cell proteins involved in key metabolic cellular processes. Intracellular redox homeostasis plays an important role in tumor initiation and progression and is closely associated with reactive oxygen species (ROS). This, in turn, triggers the conversion of ROS into reactive quinone methides, which damage DNA, lipids, and proteins and can ultimately result in tumor cell death. As part of the development of this field, a strategy has been proposed for creating anti-cancer agents based on the properties of phosphorus-containing sterically hindered phenols (SHPs). Experimental data obtained from studies of novel hybrid molecules combining SHPs with an activating phosphonate group at the benzylic position have demonstrated the ability to exhibit selective toxicity toward the tumor microenvironment. Accordingly, functionally substituted SHP derivatives may serve as a basis for the creation of therapeutic agents capable of switching from a protective action to targeted destruction.

This work presents the results of the assessment of the ability of the studied compounds to form complexes with a model DNA fragment, obtained using molecular modeling and NMR spectroscopy. Oligonucleotides 5'-GCG-TAG-CAT-GCG-3' and 5'-GCG-TTA-ACG-C-3' were used as research objects, along with the ligand's dimethyl (3,5-di-tert-butyl-4-oxocyclohexa-2,5-dienylidenemethyl)phosphonate and 4,6-dinitro-7-chlorobenzofuroxan.

Molecular dynamics simulations of the oligonucleotide 5'-GCG-TAG-CAT-GCG-3' in aqueous solvent were performed using the GROMACS software package. Binding energy parameters for the studied systems were determined by molecular docking based on the Lamarckian genetic algorithm (LGA), as implemented in AutoDock 4.3.

Analysis of the time dependence of the radius of gyration indicated a successful attainment of a thermodynamic equilibrium plateau for the 5'-GCG-TAG-CAT-GCG-3' oligonucleotide system. According to molecular docking data, the binding energy of dimethyl (3,5-di-tert-butyl-4-oxocyclohexa-2,5-dienylidenemethyl) phosphonate with the aforementioned oligonucleotide was -3.33 kcal/mol, whereas for the complex of 4,6-dinitro-7-chlorobenzofuroxan with the sequence 5'-GCG-TTA-ACG-C-3', this value reached -4.87 kcal/mol. The obtained values indicate a weak thermodynamic stability of the target complexes.

Is local mobility in lysine-based dendrigrafts similar to that in dendrimers or chains?

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To date, only a limited number of experimental and computational studies have investigated dendrigrafts [1]. Nevertheless, a theoretical framework for understanding NMR relaxation in these macromolecules remains absent. Proper interpretation of NMR relaxation data for dendritic macromolecules yields valuable insights into their key properties. We performed molecular dynamics simulations of first- and second-generation lysine-based dendrigrafts in water between 280 and 340 K. The orientational dynamics of CH₂ groups in both constructs were analyzed using the second-order orientational autocorrelation function and spin–lattice NMR relaxation times. The mobility patterns of terminal and side groups in both dendrigrafts are in qualitative agreement with earlier NMR measurements for the lysine-based dendrimer [2]. However, the inner segments of the second-generation dendrigraft behave differently from the inner segments observed in the dendrimer (by NMR) and from chains built from ϵ -lysine [3].

The average backbone end-to-end distance is comparable for the two dendrigrafts, but the second-generation species exhibits reduced fluctuations in this parameter. We also find that the dendrigrafts are essentially spherical. Their overall size, shape, and radial density distributions show no significant temperature dependence within the examined range. Compared with the lysine dendrimer, the dendrigrafts are more compact and possess a higher density, which leads to partial exclusion of solvent and counterions. Consequently, the macromolecules carry a higher effective charge and form more hydrogen bonds per amino-acid residue.

In relative coordinates, the density profile of the second-generation dendrigraft falls between those of the first-generation dendrigraft and the lysine-based dendrimer. Nevertheless, this rise in density alone cannot account for the observed differences in spin–lattice relaxation rates. The local mobility of second-generation lysine-based dendrigraft cannot be captured by a single-dominant-process approximation, which is usually applicable to linear polymer chains. Thus, the local mobility within the second-generation dendrigraft diverges from that of both dendrimers and linear polymers. These findings can serve to experimentally verify successful synthesis.

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Features of T_2 behavior of water in aqueous sugar solutions

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The determination of intermolecular interactions and the dynamics of hydration is one of the important tasks of biomolecular physics. An example of the simplest and most common biomolecule systems where hydration processes are carried out are aqueous solutions of saccharides. Currently, the mechanisms of hydration and intermolecular interactions in these systems are still being studied and supplemented [1, 2]. Important information about the patterns of molecular interaction can be obtained from studies of molecular mobility using the nuclear magnetic resonance method [3].

The purpose of the study is to determine the mechanisms of hydration of water molecules in systems of aqueous saccharide solutions based on NMR data. The study of the dynamics of molecules was carried out by determining the spin-lattice and spin-spin relaxation times at two ^1H resonance frequencies – 20 MHz and 400 MHz. The main objects of the study were aqueous solutions of D-xylose of different saccharide concentrations.

It has been shown that the presence of saccharide molecules leads to a significant decrease in the observed spin-spin relaxation time related to water molecules and hydroxyl groups of saccharide. It has been suggested that the effect of a significant reduction in the spin-spin relaxation time may be due to the chemical exchange of protons (water and -OH) between magnetically nonequivalent states in accordance with [4, 5]. It was further shown that an increase in the resonance frequency of an external magnetic field leads to an increase in the effect of proton exchange between water molecules and hydroxyl groups of saccharide. Using an example of an aqueous xylose solution of 15% (wt.), the characteristic exchange times were determined, which were 1.7 ms and 0.3 ms at 20 MHz and 400 MHz, respectively.

The work was carried out on the equipment of the Federal Center of Shared Facilities for physical and chemical research of substances and materials (FCSF) KFU Bruker AVANCE 400 MHz spectrometer optimized for microtomography, solid state and self-diffusion.

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2D NMR study of phthalazole

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In medicine, doctors treat bacterial infections by means of many different antibiotics [1]. Sulfonamides, which are sulfanilic acid amide derivatives, form extensive class of antibiotics [2]. The mechanism of action of sulfanilamide antibiotics is well known: they interfere with the biosynthesis of folic acid in bacterial cells by preventing the incorporation of para-aminobenzoic acid into the folic acid molecule [3]. Sulfonamides are used in the treatment of gastrointestinal infections, skin and soft tissue infections, genitourinary infections, respiratory tract infections, ENT infections, ophthalmic infections, etc. [1,3]. In combination with other antibiotics they are applied as adjunctive therapy in the treatment of brucellosis and malaria.

Phthalazole (also called phthalylsulfathiazole or sulfalidine) is a broad-spectrum sulfonamide antibiotic. Despite the fact that it was discovered in 1941, it is still used in medicine because it has proven useful in the treatment of intestinal infections [4]. It remains in the gastrointestinal tract, when it is taken orally, barely penetrating the intestinal wall. Due to this fact a very low concentrations of phthalazole are observed in the blood and other tissues of patients, resulting in very rare side effects [5, 6].

In order to study the various properties of sulfonamides, scientists use such methods as IR, UV and rotational spectroscopy, liquid chromatography, quantum chemical calculations. Phthalazole was also studied by IR [7, 8], UV [9] and Raman spectroscopy [8], X-ray diffraction [7]. One of the most important methods for studying the structure of organic substances in solutions is NMR. Many antibiotics, including sulfonamides, have been studied by NMR spectroscopy.

Phthalazole has been studied by 1D NMR [7, 10], but it has not been studied by 2D NMR. In this work, phthalazole was characterized by 2D COSY, NOESY, HSQC and HMBC NMR spectroscopy. For this purpose, phthalazole was dissolved at a maximum concentration in a mixture of deuterated acetone and deuterated dimethyl sulfoxide. All NMR spectra of this solution were recorded by a Bruker Avance 400 NMR spectrometer at room temperature.

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Observation of noise-like magnetic resonance fine structure in spectra of biological tissues

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Our long-term study of various biological tissues (both intact and pathological) by EPR spectroscopy allowed to accumulate some experimental facts of observation of the new type of spectra known as fine-structure (FS) spectra of ferromagnetic resonance (FMR).

This type of signals was discovered rather recently [1–3]. Before our studies, it had been observed only in synthetic samples in particular polycrystalline powders such as iron oxides (Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$) and other finely dispersed magnetic materials [1–4]. This type of signals consists of a set of multiple narrow lines called as "noise-like" lines in the electron magnetic resonance spectrum. It is observed over a wide range of magnetic fields H_{res} (from near-zero up to several thousand Oe) and is often accompanied by additional broad FMR line. Despite the noise-like appearance of the spectrum, narrow lines are reproducible upon repeated recording in the same orientation. A key feature of these signals is their strong orientation dependence. As is known from literature, fine-structure FMR signals are observed in dispersed ferromagnetics. The origin of these fine-structure signals is due to magnetic inter particle interactions within the dispersed magnetic material, which determine the spectral characteristics of the spectrum.

This study represents the first attempt to systematize and draw attention to the existence of this newly discovered type of signal in tissue samples obtained from living organisms. It should be noted that this type of signal may be characterized as rarely observed in biological systems and it still requires its physical and biological

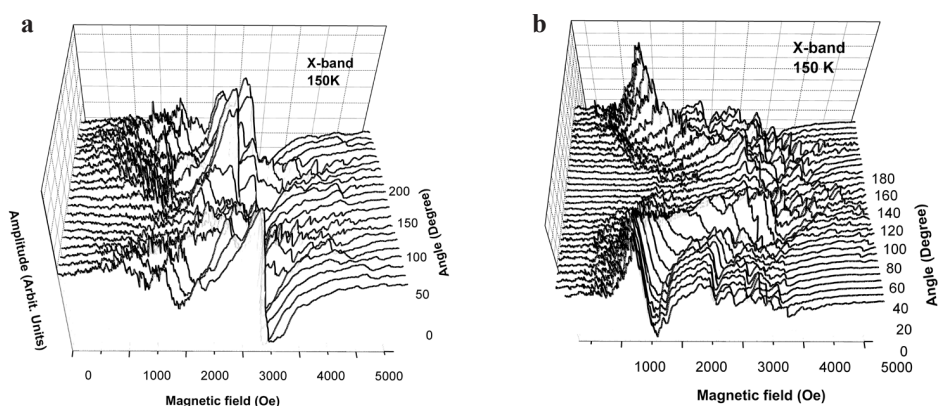


Fig. 1. The examples of angular dependences of noise like lines in electron magnetic resonance spectra of biological samples: **a** Rat muscle tissue after simulated microgravity model [5], **b** Non morphogenic callus cells of *Fagopirum tataricum* in the phase of intensive division [6].

interpretation. To date, we have observed such spectra in various types of biological samples: in pathological rat tissues (in model simulating microgravity consequences – antiorthostatic hypokinesia) [5], in snail tissues following long-term sensitization, in biopsy material of cervical tumor after radiotherapy and chemotherapy, and in samples of plant callus cells of *Fagopirum tataricum* in the phase of intensive division [6]. The lines we observed exhibited all the characteristics listed above, particularly a strong orientation dependence; the examples are shown in Fig. 1. In this study we obtained the new data about angular dependences and temperature dependences of FS FMR spectra in some tissues and their characteristics were determined. The difference between the maximum and minimum resonance field values in the angular dependence exceeds 1000 Oe. All EPR studies were performed using X-band Bruker-EMX and Bruker-ESR-300 spectrometers at a temperature of 150 K. Tissues or cell culture samples that we studied by EPR technique were either frozen in liquid nitrogen (77 K) or lyophilized (freeze-dried).

We have never observed such signals in the tissues of control animals, not subjected to any experimental influences, they are also unknown in any other studies of control tissues.

It can be hypothesized that in biological tissues and cells, this type of spectrum may arise from dipole-dipole interactions between naturally occurring iron oxide magnetic nanocrystals or nanoparticles, such as ferritins and magnetites/maghemites (which are well-documented in the scientific literature and formed naturally within living cells) when these particles are located close to each other.

It should be noted that biological tissues and cells are generally considered as diamagnetic materials. However, it is known that biomineralization processes occur in living systems, resulting in the formation of nanoscale crystalline particles. Iron oxide crystalline nanoparticles within these systems may correspond to a model of interacting magnetic nanoparticles embedded in a diamagnetic matrix; this can lead to interparticle interactions and, consequently, the appearance of noise like fine structure FMR signals in electron magnetic resonance spectra.

The obtained results support the development of methodology in EPR study of biological tissues and expand the application of electron magnetic resonance in investigation of biological and medical problems.

The study was carried out within the framework of the implementation of the topic of the state assignment for the Kazan Physical-Technical Institute of the Kazan Scientific Center of RAS.

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SECTION 7

DEFECTS
AND
SPIN QUBITS

Electron-nuclear interactions of V_B^- centers and ^{11}B shells in hexagonal boron nitride

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Boron vacancies (V_B^-) in hexagonal boron nitride (hBN) are promising solid-state spin defects for quantum technologies owing to their addressable triplet ground state. The nuclear environment of V_B^- is a potential resource for hybrid electron-nuclear quantum systems. [1, 2].

In the present study, the interaction of the V_B^- electron spin ($S = 1$) with surrounding ^{11}B nuclei ($I = 3/2$) was investigated by pulsed electron-nuclear double resonance (ENDOR) spectroscopy in the W-band. Analysis of the ENDOR spectra allowed several boron coordination shells (Fig.1), to be resolved and hyperfine (A_{xx}) and quadrupole (C_q) interaction parameters to be determined. Rabi oscillations were observed for selected ^{11}B nuclear transitions corresponding to a certain boron coordination shell, demonstrating coherent and selective manipulation of boron nuclear spin states.

These results indicate that ^{11}B nuclear spins coupled to the V_B^- center can serve as additional qubits for electron-nuclear registers.

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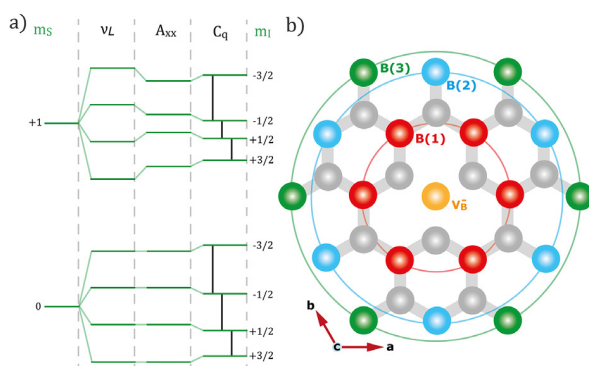


Fig. 1. a Energy-level diagram of the $V_B^- - ^{11}\text{B}$ system, showing the sequential lifting of degeneracy owing to the nuclear Zeeman (v_L), hyperfine (A_{xx}), and quadrupole (C_q) interactions. **b** hBN crystal lattice with the boron vacancy located at the center; three coordination shells of ^{11}B nuclei, B(1), B(2), and B(3), are highlighted by color.

Spin properties and electron-nuclear interactions of axial NV centers in 6H-SiC: spectroscopic and theoretical study

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Optically active spin defects in wide-bandgap semiconductors represent fundamental building blocks for scalable quantum technologies, including quantum communication networks, computing devices, and high-spatial-resolution sensors. Silicon carbide (SiC) has emerged as a highly promising, quantum-ready platform due to its well-established bulk growth techniques and the capacity to host a rich variety of spin-active defects with near-infrared emission, which is compatible with standard fiber-optic networks. The 6H-SiC polytype is particularly unique due to its complex stacking sequence, which provides three structurally inequivalent lattice sites for the formation of axially symmetric nitrogen-vacancy (NV⁻) centers: one hexagonal (*hh*) and two quasicubic (*k₁k₂* and *k₂k₁*) (Fig. 1a). While individual configurations have been partially studied, a unified, comparative analysis of all axial NV defects in 6H-SiC is essential for the rational design of hybrid spin-photon quantum architectures.

In this work, we present a comprehensive investigation of the spin, coherent, and microscopic properties of all three axial NV⁻ centers (*S* = 1) in isotopically purified 6H-²⁸SiC crystals (²⁸Si enrichment suppresses the nuclear spin bath, minimizing spin diffusion). The study synergistically combines high-frequency (94 GHz, W-band) and conventional X-band (9.6 GHz) pulsed electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) spectroscopy with advanced density functional theory (DFT) calculations (Quantum ESPRESSO, PBE functional, GIPAW module).

The pulsed EPR spectra clearly resolve the three distinct axially symmetric configurations via their characteristic zero-field splitting (ZFS) parameters: *D* ≈ 1331 MHz for the *hh* site, *D* ≈ 1358 MHz for the *k₁k₂* site, and *D* ≈ 1282 MHz for the *k₂k₁* site (Fig. 1b). High-resolution Mims ENDOR spectroscopy in the weak-coupling regime (W-band, *B*₀ = 3.4 T) allowed for the precise determination of the ¹⁴N hyperfine (*A*) and quadrupole (*Q*) interaction tensors (Fig. 1c). A striking result is the dramatic enhancement of the quadrupole coupling constant for the NV⁻ centers (*C*_q ≈ 2.43–2.53 MHz for all three axial sites) compared to an isolated substitutional nitrogen donor (*C*_q ≤ 10 kHz). This two-orders-of-magnitude increase unambiguously demonstrates that the neighboring silicon vacancy (*V*_{Si}) completely dominates the principal electric field gradient (*V*_{zz}) at the ¹⁴N nucleus, inducing a strong axial symmetry (asymmetry parameter *η* ≈ 0). Furthermore, the isotropic hyperfine coupling is small and negative (*A*_{iso} ≈ −1.1 to −1.2 MHz for all sites), indicating a highly delocalized electron spin density (≤0.2% at the ¹⁴N nucleus) and a core polarization mechanism mediated by the surrounding carbon sublattice.

Crucially, DFT calculations reveal a direct, quantitative correlation between the local crystal symmetry, spin density distribution, and the macroscopic phase coherence time

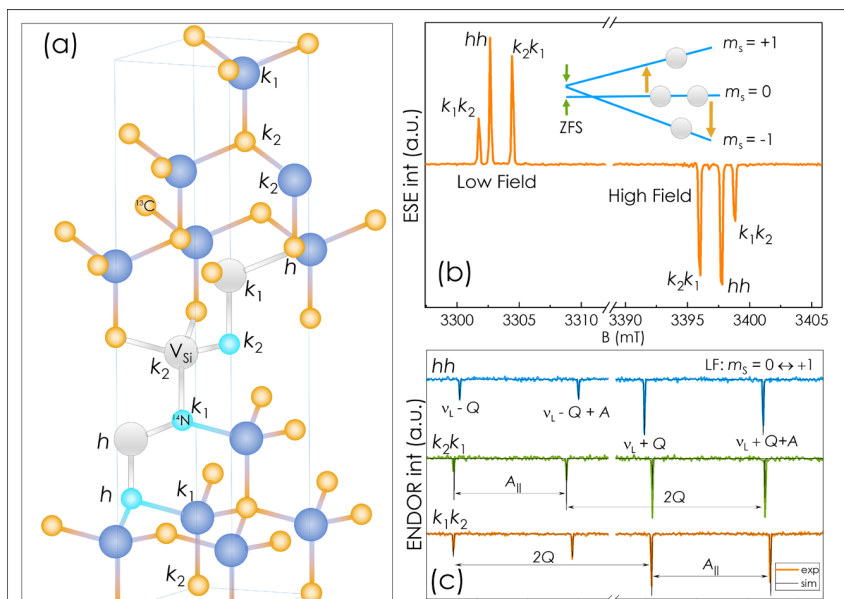


Fig. 1. **a** Crystal structure of 6H-SiC highlighting three axial NV⁻ center configurations: hexagonal hh, and quasicubic k₁k₂ and k₂k₁. **b** W-band (94 GHz) EPR spectrum showing low-field and high-field fine-structure components. The inset shows the spin level scheme with ZFS and optical spin polarization into the m_s = 0. **c** W-band ENDOR spectra (T = 150 K) recorded at the low-field fine-structure transition (m_s = 0 ↔ +1) for hh, k₁k₂ and k₂k₁ NV centers.

(T₂). The spin density is predominantly localized in the vacancy plane, perpendicular to the crystallographic c-axis. However, the hh configuration exhibits a more localized electron wave function and a significantly lower total magnetization per unit cell (1.03 μ_B) compared to the k₂k₁ configuration (1.49 μ_B). This ~45% reduction in spatial overlap with the surrounding nuclear spin bath weakens the magnetic dipole-dipole interactions, which are the primary source of decoherence. Consequently, this results in a ~13% increase in T₂ for the hh site (T₂ = 22.3 ± 0.1 μs) relative to the k₂k₁ site (T₂ = 19.8 ± 0.1 μs) at room temperature (297 K).

In conclusion, the combined spectroscopic and theoretical approach provides a complete microscopic picture of all axial NV centers in 6H-SiC. The established structure-property correlations enable the informed selection of specific NV configurations for targeted quantum applications: the hh site is optimal for applications requiring maximized coherence times (e.g., robust quantum memory), while the k-sites, with their distinct and well-resolved hyperfine parameters, are highly suitable for protocols requiring strong electron-nuclear spin coupling for the implementation of multi-level nuclear spin registers.

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Comprehensive studies of magnetic and optical spectroscopic properties of PbGa_2S_4 crystals doped by Ho^{3+} and Na^+ ions

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Lead thiogallate crystals (PbGa_2S_4) doped by trivalent lanthanides exhibit a narrow phonon spectrum and look are promising for design mid-IR lasers [1,2]. Trivalent lanthanides in these crystals substitute for the Pb^{2+} cation, resulting in the formation of several types of impurity centers. Co-doping of PbGa_2S_4 crystals with Na^+ ions allows partially overcome this problem. Of particular interest are crystals activated by Ho^{3+} ions, which exhibit a branched energy level structure with more than 10 laser channels from the visible to the IR range, realized through transitions between them [3].

$\text{PbGa}_2\text{S}_4:\text{Ho}(1.4\%)$, $\text{Na}(1.4\%)$ single crystals were grown from a stoichiometric composition in evacuated quartz ampoules by the Bridgman-Stockbarger technique. Samples with characteristic dimensions of $3 \times 4 \times 6 \text{ mm}^3$ with known directions of the crystallographic axes were cleaved from the grown crystals and oriented. EPR spectra were measured on a broadband EPR spectrometer ($1.2\text{--}28 \text{ cm}^{-1}$) [4] at liquid helium temperature in magnetic fields up to 0.9 T. Spectral-kinetic properties of samples in the visible and near IR ranges were carried out in the temperature range of 6–320 K on a Fluorolog-QM-75-22-C (Horiba) spectrofluorimeter. Fluorescence excitation was carried out by radiation from a Hamamatsu L2174-01 UXL75XE high-pressure xenon lamp.

EPR spectra are caused by resonant transitions between two singlet electron states in collinear polarizations of constant and alternating magnetic fields. Three intense EPR spectra were recorded, belonging to Ho^{3+} ions in three nonequivalent positions (Ho1, Ho2, and Ho3). Models for these impurity centers are discussed.

The fluorescence spectra of the samples excited in the $^5\text{I}_8\text{--}^5\text{G}_5$ and $^5\text{I}_8\text{--}^5\text{F}_4$ transition areas consist of multiple spectral lines due to transitions between the Stark components of the $^5\text{F}_3$, $^5\text{F}_4$, $^5\text{F}_5\text{--}^5\text{I}_j$, and $^5\text{S}_2\text{--}^5\text{I}_j$ manifolds, respectively, as well as transitions between components of the $^5\text{I}_j$ ones. A detailed interpretation of the observed spectra and Ho^{3+} ions energy structure is provided, which does not reveal the formation of optically nonequivalent types of Ho^{3+} centers.

The opportunity of using these crystals as active media for visible and IR lasers and for luminescence radiometry tasks are discussed.

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Research of oxygen vacancies in two types of α -SiO₂ (G2 fused silica and G3 natural silica) using EPR under γ -radiation

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Today, there are a large number of facilities in Russia and around the world where, in one way or another, there is interaction with radioactive elements: these may include nuclear power plants, radioactive waste disposal facilities, research facilities, or other large industrial sites. In other words, the factors that can lead to an increase in background radiation are on the rise [1]. For the normal operation of both specialized facilities and ordinary enterprises, reliable communication is required, based on fiber-optic lines. Ionizing radiation negatively affects the performance of the fiber, causing defects to form in its structure, which lead to a loss of the ability to transmit information. These defects are called radiation-induced color centers.

One of the most significant color centers that arises in the fiber, due to its structure as well as relaxation-related processes, is the E' center. This type of defect forms dark (opaque to radiation) spots in the fiber structure, ranging in size from 200 to 230 nm depending on the type of optical fiber material structure [2]. Currently available methods for cleaning fibers of radiation defects are limited in their application. The method we previously developed for cleaning optical fibers of color centers using ultraviolet laser radiation has a significant limitation related to distance (the length of the optical fiber) in its application; at distances exceeding several kilometers, it loses its effectiveness. There are currently no other methods for cleaning fibers of color centers. Hence, there is a need to develop other technologies that can reduce the negative effects of γ -radiation.

An important question that remains unanswered concerns the mechanisms underlying the formation of E' centers under irradiation. Various hypotheses have been proposed, such as the activation of one or more precursors simultaneously, leading to exponential defect growth [3]; activation of the undisturbed matrix, which correlates with defect growth without saturation [4, 5]; and, finally, the generation of E' centers followed by their transformation into other defects simultaneously with a reverse transformation to restore the initial structure. These processes are associated with a sublinear dependence of concentration on irradiation dose [6].

In this paper, we report the results of experimental studies on the generation and bleaching of E'-centers and weak satellite peaks induced by either coaxial irradiation or thermal treatment in selected α -SiO₂ variants. The generation of E'-centers was monitored using EPR measurements in each variant over a dose range from 1 to 500 kGy. Furthermore, Fourier spectroscopy (FTR) was employed in this work to investigate the influence of both water molecules and hydroxyl groups on the behavior of the EPR signal intensity. In conclusion, attempts were made to identify the potential

of one of the studied materials as a candidate for use as a radiation indicator or a means of radiation protection.

Two samples of pure silicon oxide were taken. Synthetic fused silicon oxide (G2), which contains 1 ppm of total cationic impurities, excluding hydrogen. This grade consists of ingots of pure material with Z-growth, from which 100 g was sampled and ground for use in EPR studies. The second sample, G3, consists of commercial natural sand from a deposit. The sample was washed with water, sieved to obtain grain fractions of 0.1–0.25 mm in size, and treated with deionized water to remove organic matter. After purification, the separated grains were soaked in a 6 mol/L hydrochloric acid solution for approximately 1 hour to remove any traces of contamination from the feldspar as well as from the outer layers of the grains. The samples were thoroughly washed with water and dried at 100 °C. Finally, any magnetic minerals in this sample were removed using a magnetic separator.

Following irradiation and subsequent heat treatment, measurements reveal an increase in the concentration of E' centers with increasing irradiation dose (1–500 kGy) for the sol-gel sample (no saturation effect is observed), i.e., it exhibits some radiation resistance. The precursors of the studied materials may possess a particular resistance to the formation of E' centers as a result of ionization, as in G2 and G3. It has been established that isothermal treatment of the samples can cause differences in EPR characteristics. The FTIR study clarifies the bonding system of constituent atoms and groups, such as Si, O, and OH, which sheds light on the expected intensity structure. These results indicate that the studied G2 and G3 samples are promising materials (reflective layer) for addressing radiation protection challenges in optical fibers.

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Spin dynamics and local structure in $\text{Pb}_{1-x}\text{Cu}_x\text{S:Mn/Gd}$ probed by pulsed EPR

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Magnetic semiconductors based on lead sulfide (PbS) doped with transition and rare-earth ions attract growing interest due to their potential in infrared optoelectronics, spintronics, and quantum sensing. PbS is a narrow-gap semiconductor ($E_g \approx 0.4$ eV at 300 K) with high dielectric constant and strong exciton confinement, making it an excellent matrix for impurity engineering. Doping with Cu^{2+} (d^9 , $S = 1/2$), Mn^{2+} (d^5 , $S = 5/2$), and Gd^{3+} ($4f^7$, $S = 7/2$) allows introducing local magnetic moments, tuning charge carrier concentration, and creating hyperfine-coupled spin ensembles. However, the complexity of multi-center systems leads to inhomogeneous broadening, overlapping EPR lines, and weak hyperfine interactions that remain unresolved in conventional continuous-wave EPR.

To overcome these limitations, we performed a comprehensive pulsed EPR study of a PbS single crystal co-doped with Mn, Cu, and Gd. Measurements were carried out using Elexsys E580 operating at X/Q-bands in the temperature range 5–60 K. Echo-detected EPR spectra reveal multiple resonances corresponding to Mn^{2+} and Gd^{3+} centers. Transverse relaxation kinetics are single exponential in all fields. Below 20 K, T_2 for Mn is longer than for Gd; above 20 K the trend reverses, suggesting temperature-dependent exchange coupling. Longitudinal relaxation exhibits a biexponential recovery with two distinct time scales (fast: $\sim 1\text{--}10$ μs , slow: $\sim 15\text{--}500$ μs), indicating two parallel spin-lattice relaxation channels, likely direct and Raman/Orbach processes. Three-pulse ESEEM unambiguously detects nuclear modulation frequencies at 1.6, 5, 7 MHz for Mn line and 2, 6–7 MHz for Gd line. These frequencies match the Larmor frequencies of ^{55}Mn , ^{63}Cu , and ^{207}Pb calculated for the experimental magnetic fields, proving the existence of weak hyperfine coupling between the electron spins and the ligand nuclei (sulfur, lead) as well as other dopant nuclei.

The combination of relaxation and ESEEM data demonstrates that pulsed EPR is essential for characterizing multi-ion paramagnetic systems in PbS. The measured T_1 and T_2 times (microsecond range at low temperature) and the identified nuclear frequencies provide a foundation for future quantum technology applications, such as spin qubits in semiconductor matrices and magnetic field sensors.

The work was supported by the ongoing funding of the FRC Kazan Scientific Center, Russian Academy of Sciences.

SECTION 8

MAGNETIC
RESONANCE
IMAGING AND
APPLICATIONS IN
MEDICAL PHYSICS
SYSTEMS

Mixed-valence heptanuclear iron complex as a potential MRI contrast agent

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Magnetic resonance imaging (MRI) is one of the most informative medical imaging techniques due to its high spatial resolution, absence of ionizing radiation, and excellent soft tissue contrast. However, in many clinical applications, the intrinsic contrast of biological tissues is insufficient, necessitating the use of contrast agents. Gadolinium-based compounds are currently the most widely used MRI contrast agents because of their large magnetic moments arising from multiple unpaired electrons. Nevertheless, recent studies have demonstrated that gadolinium-containing agents may accumulate in bone tissue and the brain and may increase the risk of nephrogenic systemic fibrosis. Consequently, considerable efforts are being devoted to the development of alternative contrast agents based on biocompatible transition metals, particularly iron and copper.

The subject of the present study is the mixed-valence heptanuclear iron complex $[\text{Fe(II)(CN)}_6\{\text{Fe(III)L}\}_6](\text{Cl})_2$, where L = dianion N,N'-bis(1-hydroxy-2-benzyliden)-1,7-diamino-4-azaheptane. The presence of six high-spin Fe(III) centers ($S = 5/2$) gives rise to a large total spin and magnetic moment, making this compound a promising candidate for MRI applications. Such magnetic properties suggest a significant effect of the complex on water proton relaxation processes. The structure of the complex was optimized using by density functional theory with the TPSS functional, def2-SVP basis set, and ZORA relativistic correction.

To evaluate the potential of the complex as an MRI contrast agent, colloidal solutions of the complex with dodecylphosphocholine were prepared at five different concentrations of the paramagnetic compound. The longitudinal (T_1) and transverse (T_2) relaxation times of water protons were measured by ^1H NMR spectroscopy using a Bruker Avance 500 spectrometer at 305 K. Based on the concentration dependence of the relaxation rates, the longitudinal (r_1) and transverse (r_2) relaxivities were determined, characterizing the effect of the complex on water proton relaxation processes. The obtained results indicate a pronounced effect of the investigated compound on transverse relaxation, suggesting that this heptanuclear iron complex may serve as a promising platform for the development of new iron-based negative MRI contrast agents.

Improving the structural correspondence of MRI studies using a modified TransMorph neural network

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Prostate cancer is one of the leading causes of death among the male population from oncological diseases. One of the reasons for high mortality is the difficulty of diagnosing the disease in the early stages of tumor development. The classic method of cancer detection is monitoring prostate-specific antigen (PSA). One of the options for helping in the analysis of MRI studies is the development of technological solutions based on Artificial Intelligence (AI) algorithms [1, 2].

When working with diagnostic radiology studies, especially with MRI and CT studies, a situation often arises when a specialist receives a deformed series of images. Deformations of CT and MRI studies often occur due to shifts in the patient's position relative to the positioning of the specialist or the urgency of the study, when it is not possible to perform the correct positioning. Such cases contribute to the fact that the output series contains rotations of the patient relative to the standard placement or unclear boundaries of internal structures due to random movements.

One solution to the problem of image deformation is the use of classical image registration algorithms. The main advantage of solutions of this kind is that they work based on clear and easily interpreted rules. The main disadvantage of this approach is the high cost of calculations and, therefore, the speed of their operation. An alternative solution to this problem is to use neural networks, which, after training, are capable of solving the DIR problem with good results, while gaining in image processing speed compared to classical algorithms.

In our study, we used the TransMorph architecture to solve the registration problem, but used the T2 and ADC series of each patient as the reference and bias series. The registration solution showed good results when testing the two series using the structural similarity metric (SSIM). To achieve better results, we decided to modify the original TransMorph architecture with a convolutional preprocessing unit for the transmitted data.

The study calculated the SSIM metric for the ADC and T2 series before processing by the TransMorph network, and between the resulting tensor after TransMorph and the T2 series for both the original and modified structures. The obtained data demonstrate an improvement in the SSIM metric when using the original and modified neural networks to solve the problem of registering two series.

Figures 1 and 2 show modified architectures of the TransMorph neural network, and result of SSIM (Structural Similarity Index Measure) metrics.

poster

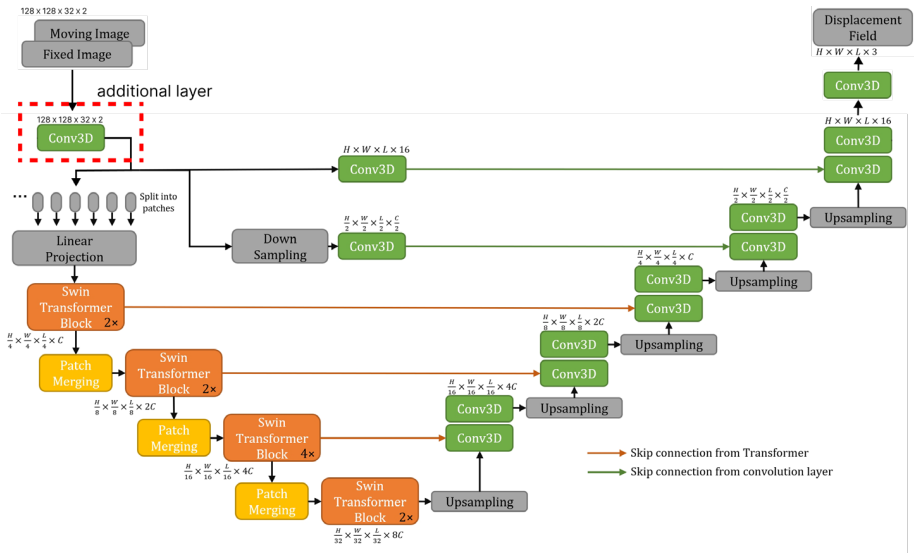


Fig. 1. Modified TransMorph architecture.

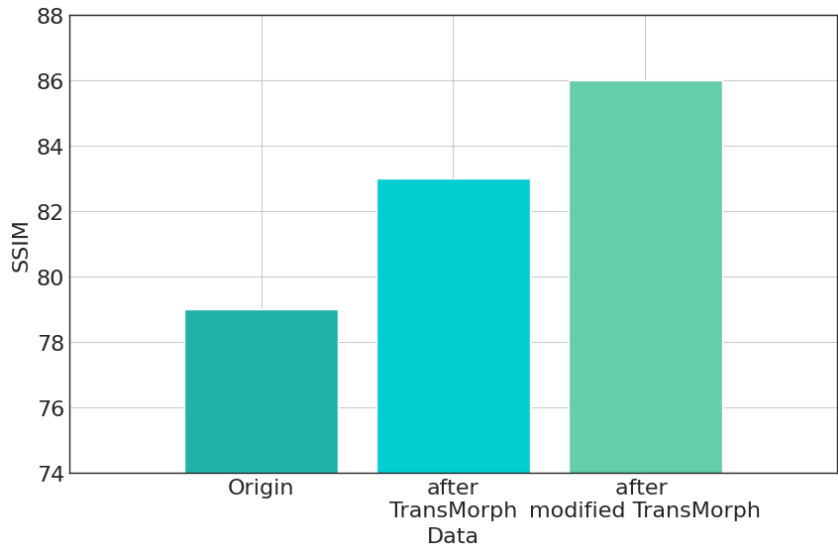


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Gradient pulse shaper for NMR or MRI installation

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NMR relaxometry devices use pulses of magnetic field gradients to measure self-diffusion, flow velocity, or spatial encoding when obtaining MRI images. They are formed when preset currents are passed through coils of a certain shape. Since the coils have a finite inductance, the current through them cannot change instantly with an instantaneous change in the control action, the rate of its change will be determined by the current stabilization device. In addition, the shape of the current pulse front may significantly depend on the amplitude of the change, since the control elements are in the key mode, outside the control range. This non-linearity creates indeterminacy in the integral pulse power and leads to a deterioration in the clarity of MRI images and errors in measuring diffusion and flow velocity. This makes it relevant to use control action shapers for gradient pulses.

We have developed a pulse generator with a preset rate of change of the control action signal, which allows the current stabilizer to remain in the control range for any signal change. The device diagram includes:

- An inverter for generating an initial signal of the opposite polarity,
- An integrator for forming linear shape edges,
- An analog multiplexer for switching the modes of forming edges and transmitting the levels of the original signal,
- Two comparators for detecting input signal changes and controlling the multiplexer.

In addition, the device includes a protection circuit that disables the output when a long-term input signal with an amplitude exceeding a set threshold is detected, which prevents emergencies in the event of malfunctions of the digital part of the NMR installation.

The development was carried out according to the state assignment of the Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center, Russian Academy of Sciences.

CTCF as a backbone-agnostic cascade plug-in for deformable 3D brain MRI registration

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Deformable registration aligns 3D medical images for atlas-based segmentation, longitudinal analysis, and label transfer, often through cascades that refine a displacement field from coarse to fine [1, 2]. Most cascades, however, are tied to one backbone: when refinement uses the backbone's internal features, resolution, or channels, changing the network forces a redesign. We study the Cascade Transformer for Coarse-to-Fine registration (CTCF) [3] as a backbone-agnostic plug-in whose levels exchange only images and displacement fields with the main module, so any backbone can be substituted directly. We address three questions: integrating heterogeneous backbones through one fixed interface, comparing the configurations on OASIS [4] and IXI [5], and deriving backbone-selection guidance under resource limits.

CTCF comprises a coarse quarter-resolution U-Net, the replaceable backbone, and a residual refiner driven by a normalized-cross-correlation error map between the warped moving and fixed images (Fig. 1); because the two cascade levels use no backbone-internal features, integrating a new network only means wrapping it behind a uniform forward interface.

We evaluate five backbones from three families spanning over two orders of magnitude in parameters: the CNN VoxelMorph [6], the large-kernel LKU-Net at two widths [7], and the state-space models MambaMorph [8] and VMambaMorph [9]. All are trained unsupervised for 100 epochs, the headline runs to 500, under the standard CTCF loss [3]. Accuracy is the mean Dice over anatomical labels; regularity uses each dataset's standard metric — SDlogJ on OASIS, fold fraction on IXI [10] — and is compared only within a dataset.

CTCF with SVF-integrated MambaMorph (11.9 M parameters) reaches Dice 0.831 on OASIS and 0.763 on IXI with near-zero folding (Table 1). Since the original CTCF [3] spans configurations differing from ours in backbone, operating resolution, and Level-3 settings, we read this not as a head-to-head Dice gain but as matching its accuracy at **25× fewer parameters** and an **order-of-magnitude lower fold rate**. Across the five-backbone sweep the cascade helps most where the backbone is weak — about +0.07 Dice to VoxelMorph but little to the 38 M LKU-Net-32, VMambaMorph tracking MambaMorph; Table 1 reports the three strongest, each extended to 500 epochs, alongside the heavyweight reference methods of [3]. The SVF refiner suppresses folding at negligible Dice cost.

CTCF thus acts as a genuine plug-in across CNN, large-kernel, and state-space backbones with no per-backbone engineering. The SVF MambaMorph configuration gives the best accuracy–regularity–efficiency balance; under tight resources a lightweight LKU-8 or VoxelMorph recovers most of the accuracy, while heavy backbones gain little from the cascade.

Table 1. Heavyweight reference methods [3] vs. compact CTCF cascades; all 500 epochs, unsupervised. The reference methods run their own non-full-resolution protocols [3]; UTSRMorph params are the OASIS-Large / IXI-Large variants. Best per column in bold.

Method	Params, M	OASIS Dice	SDlogJ	IXI Dice	Fold, %
Reference methods					
TransMorph-DCA	283.9	0.8145 ± 0.022	0.0805	0.7456 ± 0.028	1.153
UTSRMorph	421.5 / 152.2	0.8172 ± 0.023	0.1015	0.7602 ± 0.024	0.677
Original CTCF (Swin-DCA)	295.96	0.8208 ± 0.020	0.0797	0.7624 ± 0.023	0.561
CTCF cascades					
CTCF + LKU-8 SVF	6.69	0.8296 ± 0.022	0.0769	0.7629 ± 0.023	0.034
CTCF + VoxelMorph SVF	9.24	0.8279 ± 0.022	0.0774	0.7635 ± 0.023	0.016
CTCF + MambaMorph SVF	11.91	0.8314 ± 0.023	0.0775	0.7628 ± 0.023	0.036

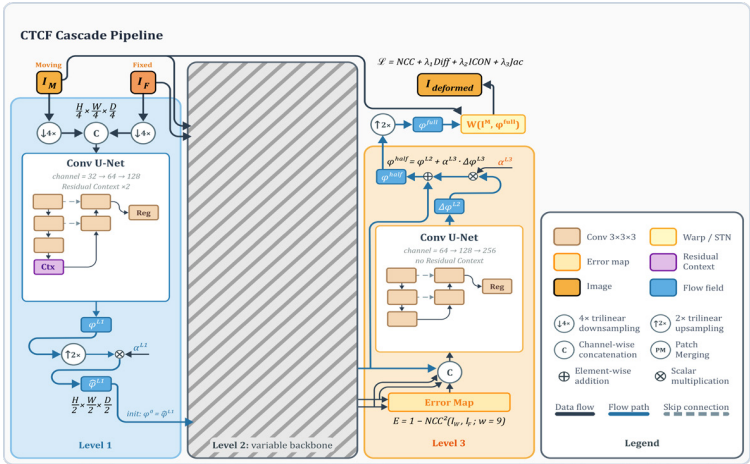


Fig. 1. CTCF cascade architecture. The replaceable Level-2 backbone — the plug-in point — is wrapped by a coarse Level-1 initializer and an NCC-error-driven Level-3 refiner.

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Computer simulation of hydroxyapatite doping with vanadium: search for thermodynamically stable configurations

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The development of biomaterials and bone implants is largely based on the use of hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which is highly relevant for regenerative medicine. HA does not cause inflammatory reactions and successfully integrates with bone tissue. A promising area of modification of HA properties is the introduction of transition metal impurities. Vanadium (V) doping increases the thermal stability of HA ceramics, gives it antibacterial properties, and also increases catalytic efficiency [1].

Despite its practical significance, the mechanisms of V-incorporation into the crystal lattice of HA have not been sufficiently studied [2]. Modeling of various variants of substitution of Ca atoms with vanadium was carried out within the framework of density functional theory (DFT). In this cell, four calcium atoms are located at the Ca(I) positions, where they are surrounded by nine oxygen atoms belonging to PO_4 tetrahedra. The remaining six calcium atoms Ca5–Ca10 are located in Ca(II) centers coordinated with seven oxygen atoms, one of which belongs to the hydroxyl group (OH^-) [3]. Calculations of the total energy of the system and the relative energies of defect formation (ΔE) were performed using the QuantumESPRESSO software package. The calculations employed the PBE (Perdew–Burke–Ernzerhof) exchange-correlation functional. The calculations revealed that the incorporation of vanadium in the form of vanadyl ion $\text{V}=\text{O}$ into the hexagonal hydroxyapatite lattice ($a = b = 0.943$ nm, $c = 0.688$ nm) is most thermodynamically favorable at the Ca7 and Ca8 crystallographic positions. These results provide a theoretical foundation for the targeted synthesis of vanadium-containing bioceramic materials with tailored functional properties and for the correct interpretation of the EPR/NMR structural and phase analysis data. The identified preferential sites are also crucial for interpreting EPR and NMR spectra of V-doped HA.

The work is supported by the grant FZSM-2026-0030 for Kazan federal University.

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SECTION 9

MÖSSBAUER
SPECTROSCOPY
AND ITS
APPLICATIONS

Increasing the efficiency of a special wireless communication system based on the stochastic gamma-ray flow

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Further development of wireless communications technology inevitably faces fundamental challenges related to the energy range (frequency) of photons used as information carriers. To further increase information recording density, transmission range, and noise immunity, it is necessary to move to increasingly higher frequency ranges, including X-ray and gamma-ray photon ranges [1]. The scientific problem of transmitting information using photons in these ranges, as well as the technical means for implementing nodes in such systems, is currently being actively developed [2, 3].

Most of these researches focuses on the use of X-ray photons. Gamma-ray photons, which are generated by radionuclides, on the one hand, have absolutely same properties. On the other hand, they also offer several advantages, including energy efficiency [4] and the possibility of coherent control of photons [5]. Indeed, advances in gamma optics in recent decades have enabled the development and experimental implementation of a method for wireless information transmission using gamma photon beams [6]. Moreover, ways to further improve the quality of information transmission using this method were shown [7, 8].

The main goal of the current study is to further improve the efficiency of the proposed method for transmitting information using the stochastic gamma-photon flow. We will demonstrate how the shape and magnitude of signals applied to a piezoelectric modulator which modulate the gamma-ray flow influence the temporal and frequency Mössbauer spectra. The data obtained will enable optimization of the shape of information signals whose application to the piezoelectric modulator will generate bursts in the gamma-photon beam of the highest intensity and shortest duration.

The work was carried out using a grant provided in 2026 by the Science and Technology Fund of the Republic of Tatarstan for the implementation of fundamental and applied scientific work in scientific and educational organizations, enterprises and organizations of the real sector of the economy of the Republic of Tatarstan.

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Nanoscale magnetic inhomogeneities in Fe–Al alloys with Ga and B additions: structure, stability, and temperature evolution

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Magnetic properties of iron aluminides underpin their growing relevance for spintronic, mechatronic and sensing applications. Polarized-neutron scattering studies of off-stoichiometric *B2*-type Fe–Al single crystals (34–43 at.% Al) have revealed nanoscale correlations of magnetic moments, indicative of incommensurate spin structures such as incommensurate spin-density waves or spiral spin waves [1]. The microscopic origin of these configurations remains controversial, and their unambiguous identification poses a substantial experimental challenge. A clear understanding of the mechanisms governing the formation and stability of magnetic inhomogeneities – particularly incommensurate spin-density and spiral spin waves – is essential for their prospective exploitation in functional devices.

This talk presents a comprehensive investigation of the complex magnetic structure of the binary alloy $\text{Fe}_{65}\text{Al}_{35}$ and related multi-component alloys alloyed with gallium or boron. To characterize the samples thoroughly we combined ^{57}Fe Mössbauer spectroscopy over a wide temperature range (3–624 K) and in external magnetic fields up to 5 T

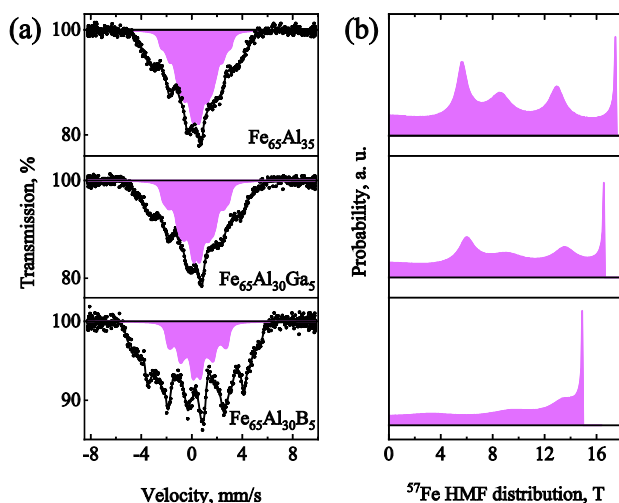


Fig. 1. a Mossbauer spectra of ordered $\text{Fe}_{65}\text{Al}_{35}$, $\text{Fe}_{65}\text{Al}_{30}\text{Ga}_5$, and $\text{Fe}_{65}\text{Al}_{30}\text{B}_5$ alloys; the shaded partial component of the spectra corresponds to ^{57}Fe nuclei associated with SSW-type magnetic ordering, with the distribution of the HMF shown in b.

with magnetometry, X-ray diffraction and elemental analysis. These experiments were complemented by rigorous ab-initio calculations of hyperfine parameters and magnetic moments using the WIEN2k package [2].

Our integrated experimental–theoretical approach has enabled us to determine how B and Ga additions influence the stability of the spin structure; refine the limits of its stability and chart their temperature evolution; estimate the characteristic length scales of the magnetic inhomogeneities.

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Combined Mössbauer effect and DFT studies of the hyperfine interactions and lattice dynamics in phosphafereocenes

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The discovery of ferrocene in the middle of past century was a milestone in organo-metallic chemistry due to its unique sandwich structure as well as chemical stability and reactivity [1]. This discovery became the starting point for the synthesis of a large number of sandwich compounds known today [2]. The isolobal substitution of CH- fragments in cyclopentadienyl rings, for instance, by nitrogen (azaferrocenes) or phosphorus (phosphafereocenes) atoms allows to obtain new supramolecular complexes and coordination polymers with multidimensional topologies and mixed σ/π coordinations, which are not characteristic of classical ferrocene derivatives [3-5].

This work presents the results of Mössbauer effect studies of hyperfine interactions in the 80-295 K temperature range in the series of phosphafereocenes differing in the number of phosphorus atoms. The obtained hyperfine parameters were compared with the values calculated using *Orca* software in the different levels of theory. Quantum chemical calculations were performed using pure DFT and the Hartree-Fock exchange functionals as well as hybrid ones with the different level of Hartree-Fock exchange fraction. Combined Mössbauer effect and DFT studies of hyperfine interactions allow us to determine the effect of phosphorus substitution in ferrocene on the molecular orbitals (MOs), especially, on the character, energy, and population of frontier MOs.

The lattice dynamics of these phosphafereocenes were studied accounting both intra- and intermolecular vibrations. The intramolecular vibrations were calculated within the quantum chemical calculations. The intermolecular vibrations were approximated by the Debye model, and the effective Debye temperature were estimated by fitting of temperature dependence of the Lamb-Mössbauer factor. The obtained Fe weighted vibrational density of states was also used for the fitting of the temperature dependence of center shift values of doublet in Mössbauer spectrum. Small linear contribution in the center shift was found that was related with the charge delocalization due to thermal expansion of molecules.

This research was funded by the grant of the Russian Science Foundation, grant number 26-13-20031.

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SECTION 10

RELATED
PHENOMENA

Magnetic hysteresis of paramagnetic LiDyF_4 : a magnetocaloric model

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Lithium tetrafluorides of heavy rare-earth elements, LiREF_4 ($\text{RE} = \text{Gd-Yb}$) attract interest as model objects in physics of dipolar magnets. Among them, LiDyF_4 is an antiferromagnet, magnetic moments of Dy^{3+} ions align in the (001) plane, $T_N = 610(15)$ mK; crystal structure belongs to the $I4_1/a$ symmetry of CaWO_4 scheelite mineral [1, 2].

Previously, we have observed a magnetic hysteresis effect in crystalline samples (a micro-sized polycrystalline powder and a single crystal) in the temperature range of 2–10 K [3]. Present work develops a magnetocaloric approach [4] to describe this exotic phenomenon, involving the exchange-charge framework for calculations of magnetic properties [1, 3] and *ab initio* simulations of lattice thermodynamics within the density functional theory framework [5], achieving both qualitative and quantitative agreement for the LiDyF_4 single-crystal magnetization data collected in the magnetic field applied along its [100] axis as well as for the magnetometry of the powder polycrystalline sample.

The financial support of the Russian Science Foundation (grant No. 22-12-00259-II) is gratefully acknowledged.

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Entropy: a perspective based on NMR relaxation times

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Thermodynamic properties (mostly activation energy) have long been evaluated using NMR relaxation times [1, 2] due to their sensitivity simplifies to $1/T_2 \approx M_2\tau_c$. Contrary to the expected behavior, an increase in τ_c does not cause a continuous to molecular dynamics. In addition to the motional contribution, relaxation times are also influenced by structural factors, typically quantified by the second moment (M_2) of the spectral line. Within the classical Bloembergen-Purcell-Pound (BPP) theory [3], which is actually valid for isotropic liquids but yet extensively used even for the constrained molecular systems, with internal dynamics characterized by a single correlation time τ_c , both M_2 (mostly structural component, that describes the inhomogeneous line broadening) and τ_c (dynamics, responsible for the homogeneous line broadening/narrowing) contribute to the expression for the spin-spin relaxation rate. For solids ($\omega_0\tau_c \gg 1$), the formula shortening of T_2 – indeed, the T_2 curve reaches a plateau, often denoted as the “bottom line” of the relaxation time T_{2stat} [3]. This value inversely reflects the static Van-Vleck dipolar coupling that is no longer averaged out by molecular motion. In this rigid limit the NMR line generally is not characterized by a Lorentzian shape but rather with the Gaussian or more complex patterns (combination of Pake, Abragam, etc.) and in common case can be described by only a relaxation time only approximately.

The proportionality of $T_2 \approx \frac{1}{M_2\tau_c} \cong T_{2stat} \frac{T_{2stat}}{\tau_c}$, with $a = 2$ for the Gaussian spectral line, leads to the following expression:

$$w = \frac{T_{2stat}}{\tau_c} + 1 = \frac{T_2}{T_{2stat}}, \quad (1)$$

and finally reassembles the equation for transverse relaxation rate with the terms for slow and fast motions:

$$\frac{1}{T_2} \approx \left[T_{2stat} \left[\frac{T_{2stat}}{\tau_c} + 1 \right] \right]^{-1} + \frac{1}{3T_{2stat}^2} \left[\frac{5\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2\tau_c^2} \right]. \quad (2)$$

The introduced value $w = [T_{2stat}/\tau_c + 1]$ can approximately be considered as a number of changes/positions which a single molecule occupies within the period of T_{2stat} (a few tens of microseconds) that can be referred as an NMR observation window:

$$w = \frac{T_{2stat}}{\tau_c} + 1 = \frac{T_2}{T_{2stat}}. \quad (3)$$

For the T_2 of liquids on the order of seconds and short τ_c , this number of such *microstates* can reach huge values, while in rigid solids with the correlation time of the same order as T_{2stat} , w tends to 1.

Adopting the classical definition of entropy via the Boltzmann formula to w , it's easy to come to the proportionality between the *dynamic* entropy and logarithm of the .

$$S_{dyn_NMR} \propto \ln(w) = \ln \frac{T_2}{T_{2stat}} . \quad (4)$$

Notably, similar conclusions can be derived from several other approaches, including the average thermodynamic molecular velocity, diffusion or free volumes in solids; the last links T_2 to the configurational entropy. Furthermore, this trend is experimentally demonstrated by examples of T_2 dependences on elastic deformation of rubbers, temperature change in liquids, and variation of nanoparticles concentration in suspensions.

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Conducting and superconducting films with local electric field on interphases

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Study of interface states of heterostructures and proximity effects has attracted continued interest in condensed matter physics [1-4]. We investigate the features of conductivity and superconducting properties of the heterostructures consisting of metallic or superconducting films deposited on a ferroelectric substrate or deposited on substrate which can possibility to change a charge on the interface between the film and substrate. In the first case the local electric field comes from bound charge of ferroelectric, and in the second case the local electric field comes from charged interface boundary. These problems have in common that in both cases the influence of the local electric fields on the conducting and superconducting properties of the heterostructures. And in both cases the main effects are associated with the screening of these fields by the free carriers, and the change of the carrier concentration due to this screening. In these cases of conducting or superconducting heterostructures, the change in the behavior of the order parameter is associated with the sign of the bound charge on the interface with the ferroelectric, and therefore similar behavior can be obtained by applying a field or creating charged layers in the interface region with the superconductor. Both problems are solved within the framework of simple, phenomenological approach in the theory of phase transitions.

The work was performed with the financial support from the government assignment for the FRC of the Kazan Scientific Center of RAS.

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Electron spin resonance and magnetic properties of ZnO and Cu-doped ZnO: Effect As³⁺/As⁵⁺ treatment

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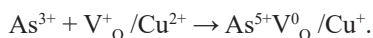
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Arsenic contamination of water is a serious environmental problem caused by anthropogenic and natural activities. Arsenic enters waterways and soils through the use of pesticides, mine drainage, and geothermal discharges. Adsorption is often used to remove arsenic, and mixed metal oxide composites such as ZnO, CuO, and TiO₂ are particularly effective, capable of removing both forms of arsenic (As³⁺ and As⁵⁺). Pre-oxidation of As³⁺ to As⁵⁺ followed by adsorption is a key step in removing arsenic from water. In our previous work [1], we proposed a possible mechanism of arsenic adsorption on ZnO and Zn_{0.95}Cu_{0.05}O samples, in which oxygen vacancies play a key role. In this work, we look deeper into the adsorption process using the electron spin resonance (ESR) method, since the mechanism may not be limited to oxygen vacancies alone.

We investigated the ESR spectra of ZnO and copper-doped Zn_{1-x}Cu_xO ($x = 0.025, 0.05$) samples in their initial form and after sorption in As³⁺/As⁵⁺ solutions. All spectra, including those of pure ZnO, consist of two components: a single narrow absorption line of Lorentzian shape (line 1) and a low-field broad absorption line of complex shape (line 2). Line 1 was observed in all samples, including pure ZnO, except for the copper-doped sample after sorption in As³⁺ solution, Zn_{0.95}Cu_{0.05}O/As³⁺. As shown earlier, this signal is associated with singly charged oxygen vacancies. For the other samples, its linewidth ($\Delta H = 0.3$ mT) and position ($g = 2.002$) do not depend on the method of subsequent treatment.

The main focus of our previous work [1] was the investigation of the possible impact of As³⁺/As⁵⁺ sorption on the physical properties of Zn_{1-x}Cu_xO samples. According to [1], sorption from all solutions (As³⁺/As⁵⁺) significantly affects the ESR spectra. However, regarding the oxygen vacancy, only the sorption of As³⁺ leads to the disappearance of line 1. This suggests that in the case of photosorption, the oxidation of As³⁺ involves vacancies directly associated with Cu, since in other cases line 1 remains unchanged. Based on the obtained experimental results, we conclude that the following reaction scheme occurs on the surface of the Zn_{0.95}Cu_{0.05}O sample in an As³⁺ solution [1]:



In addition to vacancies (line 1), the low-field ESR signal (line 2) is also attributed to intrinsic defects (located in the ZnO lattice both in the bulk and on the surface). In copper-doped samples the intensity of the low-field ESR signal increases with increasing copper concentration. Given the presence of defects in the initial sample, it is most likely that the ESR signal in the Zn_{1-x}Cu_xO samples arises from Cu²⁺-V_O⁺ and Cu²⁺-V_O²⁺ centers (or other pair defects), or from two coexisting magnetic sublattices Cu²⁺ and V_O⁺ (or V_O²⁺, etc.) whose magnetic centers interact with each other. As

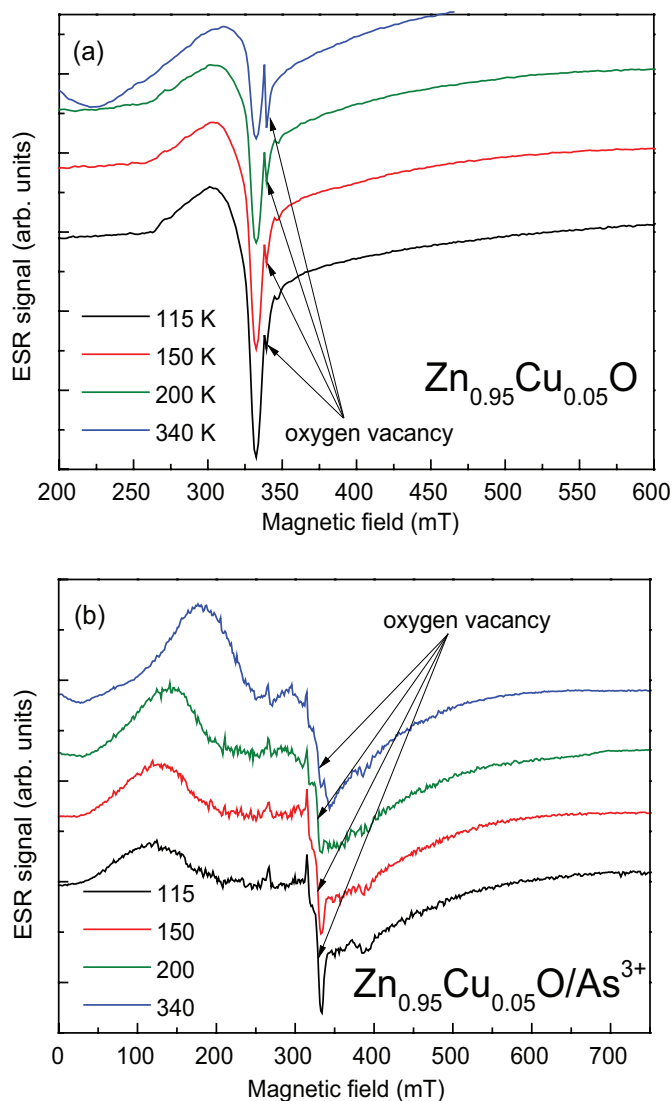


Fig. 1. Electron spin resonance spectra of: (a) $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$; (b) $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}/\text{As}^{3+}$

shown in Fig. 1, line 2 exhibits a pronounced temperature dependence and a complex shape composed of several components, which requires detailed interpretation. To clarify the nature of line 2, detailed temperature-dependent ESR studies were carried out. In addition, magnetic properties are planned to be studied by vibrating sample magnetometry (VSM).

High-entropy perovskite-like oxide $(\text{BaCaSrLaNa})_{0.2}\text{FeO}_3$: Synthesis, EPR and magnetometry measurements

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High-entropy oxides (HEO) with perovskite structure ABO_3 are oxides, where an atomic site (A or B) is occupied by more than 5 elements in equimolar ratios. Such modifications of the structure results in an unusual magnetic properties and spin states [1].

In this work, we report the synthesis and EPR study of $\text{Ba}_{0.2}\text{Ca}_{0.2}\text{Sr}_{0.2}\text{La}_{0.2}\text{Na}_{0.2}\text{FeO}_3$ (BSCLNF) HEO with perovskite-like structure. This compound was synthesized by solid-state reaction method. We used analytical grade reagents such as BaCO_3 , CaCO_3 , SrCO_3 , Na_2CO_3 , La_2O_3 and Fe_2O_3 (all are >99% purity), which was mixed in planetary ball mill at 350 rpm for 6 hours. Then we calcined mixed powders in air for 3 hours at $T = 1050^\circ\text{C}$ and pressed calcined powders with $P = 470$ MPa into pellet with 14mm in diameter for sintering at $T = 1100^\circ\text{C}$ for 12 hours.

Temperature dependence of CW EPR measurements at X-band for $\text{Ba}_{0.2}\text{Ca}_{0.2}\text{Sr}_{0.2}\text{La}_{0.2}\text{Na}_{0.2}\text{FeO}_3$ powder from sintered pellet is shown in figure 1. The model fit parameters such as linewidth, g -factor and their temperature dependencies are discussed within the context of ferromagnetic cluster formation.

Field cooling and zero field cooling magnetization measurements at $H = 1$ kOe has showed the existence of ferromagnetic phase transition at approximately $T = 73$ K (Fig. 2). Paramagnetic region of the magnetization curve is fitted by Curie-Weiss law

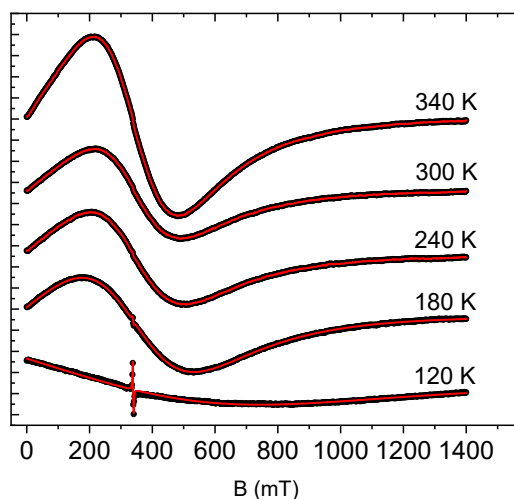


Fig. 1. Temperature dependence of EPR spectra of sintered BSCLNF sample. Black dots are experimental points; red line is the model fit.

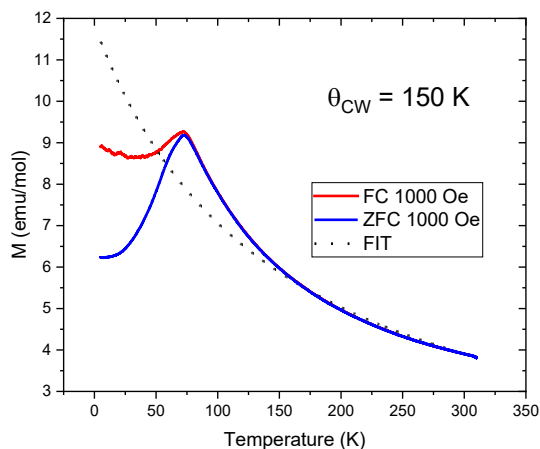


Fig. 2. Temperature dependence of magnetization measured in field-cooling (red) and zero field-cooling (blue) regime. Paramagnetic region of the curve is fitted by Curie–Weiss law with $\theta_{CW} = 150$ K/

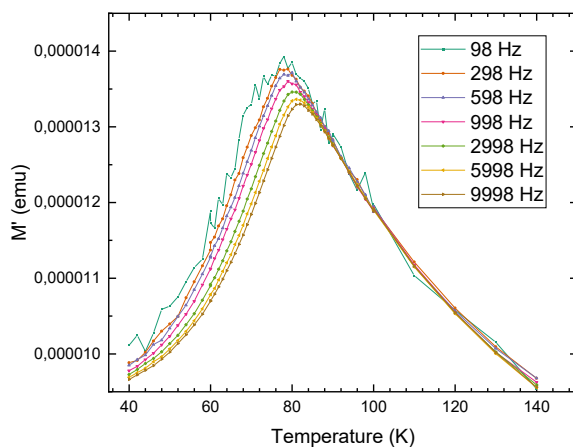


Fig. 3. Temperature dependence of the real part of magnetization M' , measured at different magnetic field oscillation frequencies.

$M = C/(T + \theta_{CW})$, where $\theta_{CW} = 150$ K. Positive value of θ_{CW} suggest the ferromagnetic exchange behavior.

From the AC magnetization measurements (Fig. 3), the Mydosh parameter was obtained $\Omega = (T_2 - T_1)/T_2(\lg(f_2) - \lg(f_1)) \approx 0.0244$ K⁻¹. This value suggests that the sample's magnetic structure is between canonical and cluster spin-glass.

Prospects for the use of LiHoF₄ microparticles in LIR² thermometry

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Today, thermometry based on the temperature-dependent luminescence of micro- and nanoparticles of various substances is a well-established field of research. However, the vast majority of methods and materials allow for the detection of temperature changes of at least 10 K. In this paper, we investigate a relatively new method which, in theory, enables much greater thermal sensitivity to be achieved [1].

LIR thermometry involves observing the luminescence of a material at two wavelengths, λ_1^{lum} and λ_2^{lum} , corresponding to transitions from two thermalised excited states, 2 and 3 (see Fig. 1a), as the temperature changes.

In this paper, we investigate LIR² Boltzmann thermometry, which was proposed recently [4]. The methodology remains the same, but the system is excited at different wavelengths corresponding to transitions between two thermalised states, 1 and 2. In theory, this allows for the convolution of two exponential functions simultaneously. In the case of LiHoF₄ microparticles, one corresponds to LIR for the excitation of the system at wavelengths $\lambda_1^{\text{ex}} = 447$ nm and $\lambda_2^{\text{ex}} = 457$ nm, and the other to its luminescence at wavelengths $\lambda_1^{\text{lum}} = 658$ nm and $\lambda_2^{\text{lum}} = 640$ nm (Fig. 1b).

Our work demonstrates the potential of the promising LIR² technique, which enables an increase in the sensitivity of any existing LIR sensors. Furthermore, we show that LiHoF₄ nanoparticles exhibit high thermal sensitivity and are suitable for use in luminescent Boltzmann thermometry.

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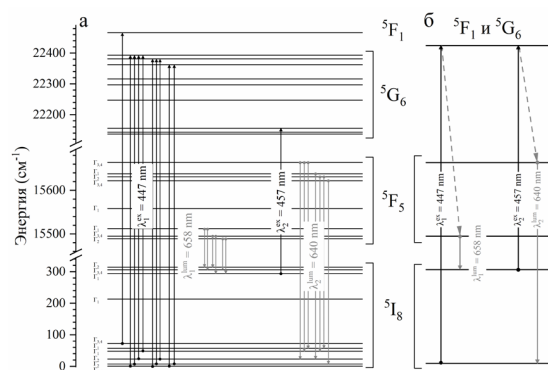


Fig. 1. Interpretation of the observed radiative transitions in LiHoF₄ nanoparticles (based on [2, 3]), which were used to implement the Boltzmann LIR and LIR² thermometry methods

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