KAZAN (VOLGA REGION) FEDERAL UNIVERSITY

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ON THE 75-TH ANNIVERSARY OF MAGNETIC RESONANCE DISCOVERY

Pages in history. The development of radiospectroscopy at Kazan University

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KAZAN
2020

УДК 539.1
ББК 22.38.Г
A23, L25

Printed on the recommendation of the teaching commission
Institute of Physics, Kazan Federal University

Reviewers:
Doctor of Physical and Mathematical Sciences, Professor M.S. Tagirov
Candidate of Physical and Mathematical Sciences, Associate Professor
A.V. Dooglav

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A23, L25 **On the 75-th anniversary of magnetic resonance discovery. Pages in history. The development of radiospectroscopy at Kazan University**/ A.V. Aganov, A.L. Larionov. – Kazan: 2020. – 224 p.

Editors of English version – I.A. Larionov, A.V. Dooglav

This book is a brief overview of the development stages of two branches of magnetic resonance – electron paramagnetic and nuclear magnetic resonances (EPR and NMR), started with the first attempts to observe the resonant absorption of electromagnetic waves in paramagnets. It is described in more detail how this line of research was formed at Kazan University, in the USSR. All the most significant publications about the creation of an experimental EPR and NMR base at the University from the time when the first spectrometers were manufactured to today's developments are noted. A brief summary of the development of magnetic resonance research methods and their applications in a wide variety of fields of knowledge until 2010, when significant changes began in the system of the Higher School (Universities) of Russia and the Academy of Sciences, which left a deep imprint on the development of science in Russia as a whole, and on the development of one of its most important areas, "Magnetic resonance in materials science and in biomedical research" in particular is given. The main achievements of the University teams using these methods in their research in physics, chemistry, biology and medicine, oil and gas technologies, as well as for solving problems in various sectors of economy over the past decade, are presented. Current trends in the development of magnetic resonance methods in the world, the place of Russia, and the relative contribution of its leading teams are noted. Annexes 1 and 2 contain a list of Doctor of Science and Ph.D. theses made at Kazan University in this area, including dissertations, the performance or certification of which are related to Kazan University. Annex3 – Heritage.

CONTENTS

INTRODUCTION

A number of publications [1–5], including the results of the development of magnetic resonance over the first 25 years, are devoted to the discovery of the phenomenon of Electron Paramagnetic Resonance (EPR) in Kazan, at Kazan University, by Eugeniy Konstantinovich Zavoisky. A series of publications appeared on the eve of the celebration of the 100th anniversary of his birth, see e.g., [6–8].

These publications reflect some new details of this discovery, the view of contemporaries on its role in the formation of physical science in the postwar years in Kazan, and the scientific activity of E.K. Zavoisky after his departure in 1947 to Moscow. Almost all information is easier to find in the Internet search engines, so we will restrict ourselves to links to the main publications.

Over the past 10 years many changes have taken place in the life of the Russian scientific and educational community. Our University was also involved in the vortex of events. In 2010 Kazan University acquired the status of a Federal University with targeted funding for the "Development Program of the Kazan (Volga-Region) Federal University for 2010–2015". Its successful completion allowed the University to join on a competitive basis the new program "Global Competitiveness of Russian Universities in 2015–2020". It is known as the "Top–100" program for the right to become one of the 100 leading universities in the world. There was an urgent need to unite all the University groups working in the field of magnetic resonance into one "International Center of Magnetic Resonance at KFU" (http://kpfu.ru/physics/struktura/mezhdunarodnyj-centr-magnitnogo-rezonansa). Leading universities have also taken such a path, where magnetic resonance methods have been actively developed since the discovery of EPR and NMR, the appearance of the first publications that opened up the broadest scope for the use of these methods in the most diverse fields of science and technology (http://cmr.spbu.com/wp-content/uploads/Booklets/MR_laboratories_in_Russia_2015 - 2016.pdf).

On the eve of the 75th anniversary of the magnetic resonance discovery in the form of electron paramagnetic resonance, it was quite natural to again turn over the historical pages of the discovery, the details of which were described by S.A. Altshuler and B.M. Kozyrev – the participants of the work and the closest colleagues of S.A. Altshuler and B.M. Kozyrev [9, 10].

Founders of the Kazan Radiospectroscopy School
S.A. Altshuler, E.K. Zavoisky, B.M. Kozyrev

Indeed, the path to the discovery of magnetic resonance was long enough and was preceded by major scientific achievements:

1913: V.K. Arkadyev. The discovery and creation of the theory of the phenomenon of selective absorption of an alternating field energy in ferromagnets. Magnetic properties dependence of ferromagnets *vs* frequency of the external electromagnetic field of the *cm* range has been detected.

1922: O. Stern and V. Gerlach performed successful experiments on spatial quantization of the magnetic moment projection of an atom in a magnetic field H_0.

1922: A. Einstein and P. Ehrenfest published the results on quantum transitions between the magnetic sublevels of an atom affected by equilibrium radiation.

1923: Ya.G. Dorfman predicted the photomagnetic effect – the resonant absorption of electromagnetic waves by paramagnets. The attempt of Ya.G. Dorfman to transfer the idea of A. Einstein and P. Ehrenfest to quantum transitions between Zeeman levels of atoms in solids was criticized by E.K. Zavoisky ([5] p.210).

1932: I. Waller proposed and developed the quantum theory of paramagnetic relaxation due to the modulation of the spin-spin interaction by the atomic vibrations (Waller mechanism).

1936: C.J. Gorter and colleagues made the first unsuccessful attempt to observe the absorption of electromagnetic waves in paramagnets.

1937: work by I.I. Rabi to determine the nuclear magnetic moments in molecular beams, awarded in 1944 the Nobel Prize in Physics.

1938: H.B.G. Casimir and F.K. du Pre developed the phenomenological theory of paramagnetic relaxation and introduced the concept of the spin system temperature.

1939: R. Kronig and independently in 1939–1940 J.H. Van Vleck constructed the theory of spin-lattice relaxation due to the modulation of the crystal field by the lattice vibrations (Kronig–Van Vleck mechanism).

1940: L.W. Alvarez and F. Bloch measured the magnetic moment of the neutron.

1941: (May–June) E.K. Zavoisky noted in the measurement logbook the irregular observations of the proton magnetic resonance in aqueous solutions of paramagnetic salts. But no publications followed. The main reason was the lack of reproducibility of the observed results due to the inhomogeneity of the constant magnetic field created by a low-quality magnet [1].

1942: C.J. Gorter made another unsuccessful attempt to observe the absorption of electromagnetic waves in paramagnets, although the theory of paramagnetic relaxation due to the efforts of him and his colleagues, as well as other theorists, was constructed.

1944: E.K. Zavoisky made the discovery of paramagnetic resonance due to the magnetic moments of electrons {priority July 12, 1944 (J.Phys.USSR, 1945, 9, 211) – the beginning of the magnetic resonance era}. Doctor of Science Dissertation presented in December, 27, 1944 and defended January 30, 1945.

1945: Ya.I. Frenkel gave the first theoretical interpretation of the EPR.

1946: E.M. Purcell and F. Bloch discovered the phenomenon of paramagnetic resonance in atomic nuclei in condensed matter (NMR) (Phys. Rev. 1946), (Nobel Prize in Physics in 1952). In some publications, the NMR observation date is December, 1945.

E.M. Purcell

F. Bloch

1946–1947: J. Griffiths, E.K. Zavoisky – discovery of the ferromagnetic resonance.

1947–1948: N. Bloembergen, R.V. Pound and E.M. Purcell created the theory of NMR relaxation.

1950: H.G. Dehmelt and H. Krueger discovered the nuclear quadrupole resonance (NQR) due to transitions between the quadrupole energy levels of nuclei in crystals in the absence of an external magnetic field.

1951: M. Deutsch and coworkers determined the fine structure of the main energy level of the positronium.

1951: R. Poulis, C.J. Gorter *et al*. discovered the phenomenon of antiferromagnetic resonance.

1952–1955: S.A. Altshuler (KSU) predicted the phenomenon Acoustic Paramagnetic Resonance (APR) {priority June 12, 1952 (Dokl.AN SSSR, 1952, 85, 1235)} and constructed theory of APR, which was subsequently first discovered by W. Proctor *et al*. (USA, 1956).

S.A. Altshuler

The two main branches of magnetic resonance – EPR and NMR – developed relatively independently. In the works of Kazan scientists of the initial period they obtained the results that determined the main directions of the EPR development and its applications in various fields of science. These are described in detail in [1] and S.A. Altshuler and B.M. Kozyrev monographs [9, 10].

Below we give the links to the main results of the early period.

1944: S.A. Altshuler, E.K. Zavoisky, B.M. Kozyrev. A new method for studying the paramagnetic absorption has been proposed.

1945: E.K. Zavoisky. Paramagnetic relaxation in liquid solutions at perpendicular fields.

1945: E.K. Zavoisky. Magnetospin resonance in paramagnetics.

1946: E.K. Zavoisky. Magnetospin resonance in the region of the decimeter waves.

1946: E.K. Zavoisky. Report on EPR at high frequencies and on the prospects of EPR application.

1947: B.M. Kozyrev, S.G. Salikhov. The first observation of paramagnetic resonance in free radicals.

1947: E.K. Zavoisky. Determination of the magnetic and mechanical moments of atoms in solids.

1947: E.K. Zavoisky. Measurement of the magnetic susceptibility of paramagnets with the decimeter waves.

1947: S.A. Altshuler, E.K. Zavoisky, B.M. Kozyrev. On the theory of paramagnetic relaxation in perpendicular fields.

The first foreign publications, in fact, are devoted to the creation of the experimental techniques:

1947: R.L. Cummerow, D. Halliday, G.E. Moore. EPR in the microwave range (transmitted wave method).

1948: C.A. Whitmer, R.T. Weidner, J.S. Hsiang, P.R. Weiss. Microwave spectroscopy, operating with the principle of a T-bridge using a double bridge.

1950: T. England, E. Schneider. The first application of the superheterodyne method for observation of the paramagnetic resonance.

1953: B. Bleaney[1] and K.W. Stevens. The first studies of paramagnetic resonance spectra in the range of liguid hydrogen and liquid helium temperatures.

Domestic developments of the instrument base using which the experimental studies were performed are presented in the following works:

1954: N.N. Neprimerov. Observation of the plane rotation of the microwave polarization in the paramagnets.

1956: A.A. Manenkov, A.M. Prokhorov[2]. Microwave spectrometer with low-frequency modulation of the magnetic field (reflected wave method).

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[1] In 1992, B. Bleaney, one of the world's experts in the field of EPR, was elected as honorary professor of Kazan University.

[2] C.H. Townes, N.G. Basov and A.M. Prokhorov were awarded the Nobel Prize in Physics in 1964 “For fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle”. It should be noted that even today the magnetic resonance methods are actively used in the development of materials based on quantum technologies.

1959: A.G. Semenov and N.N. Bubnov. Magnetic spectrometer with double (high-frequency and low-frequency) modulation.

1959: V.I. Avvakumov, N.S. Garifyanov, B.M. Kozyrev, P.G. Tishkov. Construction of the resonator design allowing the measurements at elevated and lowered temperatures.

Full information on the development of experimental techniques in the early period can be found in the monographs:

C.J. Gorter. “Paramagnetic relaxation”. Elsevier Pub. Co; 1st edition 1947.

W. Gordy, W.V. Smith, and R.F. Trambarulo, “Microwave Spectroscopy”, John Wiley and Sons, New York, 1953.

M.W.P. Strandberg, “Microwave Spectroscopy”, Methuen and Co., Ltd., London, 1954.

1. MAGNETIC RESONANCE IN THE INITIAL PERIOD IN THE USSR

1.1. E.K. Zavoisky. The Magnetic Radiospectroscopy School at Kazan University

The publications of 1947 ended the Kazan period of work of E.K. Zavoysky in the field of magnetic resonance. He received an invitation from I.V. Kurchatov to work in Moscow on a new, at that time classified, subject area in the field of nuclear physics, nuclear energy in the Laboratory No.2. (Laboratory of measuring instruments of the USSR Academy of Sciences – LIPAN), subsequently transformed into the Institute of Atomic Energy of the USSR Academy of Sciences – now the National Research Center "Kurchatov Institute"[3]. According to Prof. N.M. Sergeyev (Moscow State University, NMR Lab.), "... he actually seemed to have disappeared from science" [11, p. 9]. This is the most likely reason that the EPR discovery was not awarded by the Nobel Prize: according to the Nobel Committee terms, a prize is awarded to the author of the discovery only if he/she continues to actively develop the method and is alive at the time of nomination[4]. In 1957, E.K. Zavoisky was awarded the Lenin Prize "For the discovery and study of electron paramagnetic resonance". In 1964 E.K. Zavoisky was elected as a full member of the USSR Academy of Sciences.

Another thing is important – today all over the world the discovery of magnetic resonance is associated with Kazan, with the name of E.K. Zavoisky. This becomes clear from his definition: *"Paramagnetic resonance is a set of phenomena associated with quantum transitions occurring between the energy levels of macroscopic systems under the influence*

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[3] In 1949, E.K. Zavoisky and others were awarded the Stalin Prize for their work on the creation of the atomic bomb.

[4] E.K. Zavoisky is the only member of the Institute of Atomic Energy who was nominated by I.V. Kurchatov for the Nobel Prize for the discovery of the EPR [12].

of an alternating magnetic field of resonant frequency. In this definition, we are talking about a combination of phenomena, because along with resonant paramagnetic absorption, resonant paramagnetic dispersion, resonant paramagnetic rotation, etc. are observed. In addition, it is emphasized here that phenomena are observed in macrosystems where spin-spin, spin-lattice, and similar interactions take place, which distinguishes paramagnetic resonance from resonant experiments by Rabi with molecular beams, Alvarez and Bloch with neutron beams etc." ([9], pp. 19–20). There is no a word about the nature of the spin (hence, the magnetic moment) – whether it is electronic or nuclear. Actually, this is emphasized in the titles of the first articles of E.K. Zavoisky "Magnetospin resonance in paramagnets". Paramagnetic resonance is considered as part of the magnetism theory. This explains the name of the Kazan school of radiospectroscopy in a broader sense: "Resonant properties of condensed matter".

A search for magnetic resonance in Kazan is reasonably connected with the names of S.A. Altshuler and B.M. Kozyrev – young colleagues of E.K. Zavoisky, who developed a highly sensitive method for measuring the energy absorption of a high-frequency (HF) magnetic field in the 1930s, based on a change in the HF generator parameters, called the grid current method by E.K. Zavoysky[5]. The actual starting year of the research can be considered 1934, when the decision of the People's Commissariat of Education of the Russian Soviet Federative Socialist Republic within the only physical department of the Physics and Mathematics Faculty of Kazan University after the initiative and direct participation of E.K. Zavoisky the ultra HF laboratory was created (in the prewar years, they attached great importance to the research of ultra HF radio waves). Its first employees were yesterday's graduate students, theoretical physicists S.A. Altshuler and A.V. Nesmelov, and chemist B.M. Kozyrev.

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[5] An autodyne generator based on the grid current method proposed and first applied by E.K. Zavoisky, in the postwar years was successfully used by researchers to observe NMR on protons of water in systems of simple composition.

The first task formulated by E.K. Zavoisky, S.A. Altshuler and B.M. Kozyrev in the field of magnetic radiospectroscopy in 1940 was to detect the resonant magnetic absorption by protons.

The main question that faced E.K. Zavoisky was as follows: whether the relaxation mechanisms of the magnetic moments of the nuclei are effective enough to ensure the outflow of energy into the heat reservoir? There were no experimental estimates of nuclear magnetic relaxation rates at that time.

A rough theoretical estimate indicated an extremely ineffective relaxation and gave practically no hope to observe the effect expected. Close collaboration of the brilliant experimenter E.K. Zavoisky and his young colleagues: S.A. Altshuler – an expert in the field of nuclear physics (he defended his Ph.D. thesis in the nuclear physics area under the supervision of I.E. Tamm[6] in 1936) and B.M. Kozyrev – an expert in the field of physical chemistry, was very successful. In May–June 1941, E.K. Zavoisky together with S.A. Altshuler and B.M. Kozyrev repeatedly observed the proton magnetic resonance. However, they failed to achieve reliable reproducibility of the results. As it was found out later, the reason for this was the inhomogeneity of the magnetic field created by a low-quality magnet. Therefore, in the paper [S.A. Altshuler, E.K. Zavoisky, B.M. Kozyrev. JETP. 1944. V.14. p.407.] the authors limited themselves and just mentioned their goal to detect the resonant absorption of energy of an oscillating magnetic field by atomic nuclei in a constant transverse magnetic field by a much more sensitive method compared with the calorimetric method of C.J. Gorter. But the war began... The work on the detection of resonant absorption of electromagnetic radiation in paramagnets was resumed only in 1943. After the recommendation of Ya.I. Frenkel (a corresponding member of the USSR Academy of Sciences, who during the war years

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[6] P.A. Cherenkov, I.M. Frank and I.E. Tamm were awarded with the Nobel Prize in Physics in 1958 “For discovery and interpretation of the Vavilov-Cherenkov effect”.

(1941-1945) worked at Kazan University[7], from March 1943 he headed the Department of Theoretical and Experimental Physics, temporarily unified departments of General, Experimental, and Theoretical Physics, and at the same time an employee of the Leningrad Physical-Technical Institute of the USSR Academy of Sciences), E.K. Zavoisky continued his studies of paramagnetic absorption due to energy transitions between the electronic energy levels of undiluted paramagnetic salts of manganese, chromium and copper, which led him to the discovery of electron paramagnetic resonance (EPR).

On June 23, 1970, the Committee on Inventions and Discoveries of the USSR Ministers Council recorded the discovery of E.K. Zavoysky "The electron paramagnetic resonance phenomenon", with a priority of July 12, 1944, No. 85 in the USSR Public Register.

After the recommendation of Ya.I. Frenkel in 1945 the Kazan branch of the USSR Academy of Sciences was organized, which included the Kazan Physical-Technical Institute (the Kazan E.K. Zavoisky Physical-Technical Institute (KPhTI) of the Kazan Scientific Center of the Russian Academy of Sciences)[8], where E.K. Zavoisky worked as head of the radiospectroscopy department until 1947.

At Kazan University, the formation of the magnetic radiospectroscopy school was under the supervision of S.A. Altshuler (after his death, this direction was headed by B.I. Kochelaev), and at KPhTI – B.M. Kozyrev.

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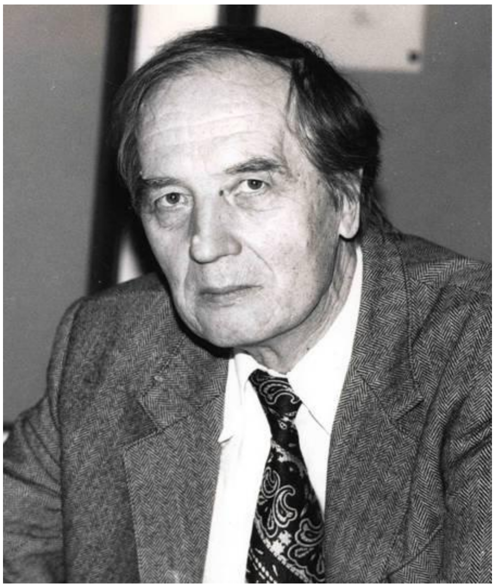
[7] In the war period the physical branch of the USSR Academy of Sciences was evacuated to Kazan, and the researchers live and work in Kazan University. That was highly beneficial for physics research in the University [13].

[8] All academic institutes of Kazan were part of the structure of the Kazan Branch of the USSR Academy of Sciences (KBAS USSR), which was transformed in 1990 into the Kazan Scientific Center of the USSR Academy of Sciences, renamed in 1992 into the Kazan Scientific Center of the Russian Academy of Sciences. Since 2019, the Kazan academic institutes have become part of the Federal Research Center of the Kazan Scientific Center of the Russian Academy of Sciences (FRC Kazan Scientific Center of RAS) as separate divisions with the previous names. Hereinafter, the names of institutions and units of the described period are given, often abbreviated. In this case, the abbreviation KPhTI is used.

A new page in the history of EPR, magnetic resonance in Kazan begins with the publications:

- S.A. Altshuler, E.K. Zavoisky, B.M. Kozyrev. On the theory of paramagnetic relaxation in perpendicular fields. JETP Letters. 1947. V.17. No.12. P.1122-1123. (The lineshape of paramagnetic absorption).


B.I. Kochelaev

- B.M. Kozyrev, S.G. Salikhov. Paramagnetic relaxation in pentaphenylcyclopentadienyl. Reports of the USSR Academy of Sciences. 1947. V.58. No.6. P.1023–1025 (The first observation of EPR in a free radical).
- S.A. Altshuler, B.M. Kozyrev, S.G. Salikhov. The effect of nuclear spin on resonant paramagnetic absorption in solutions of manganese and copper salts. Reports of the USSR Academy of Sciences. 1950. V. 71. No.5. P.855-857 (Discovery of the influence of the nuclear spin of a paramagnetic atom on the structure of the EPR line).
- S.A. Altshuler, V.Ya. Kurenev, S.G. Salikhov. Paramagnetic resonant absorption in crystalline powders of some compounds of rare-earth elements. Reports of the USSR Academy of Sciences. 1950. V. 70. No.2. P.201–204.

- S.A. Altshuler, V.Ya. Kurenev, S.G. Salikhov. Paramagnetic resonant absorption in metals. Reports of the USSR Academy of Sciences. 1952. V. 84. No.4. P. 677–679.

This was followed by work with the participation of N.N. Neprimerov, R.Sh. Nigmatullin[9], R.M. Valishev, V.I. Avvakumov, N.S. Garifyanov, P.G. Tishkov (1953-1959), K.A. Valiev[10], M.M. Zaripov, G.Ya. Glebashev, L.Ya. Shekun[11], Sh.Sh. Bashkirov, B.I. Kochelaev (1960) and others.

R.Sh. Nigmatullin

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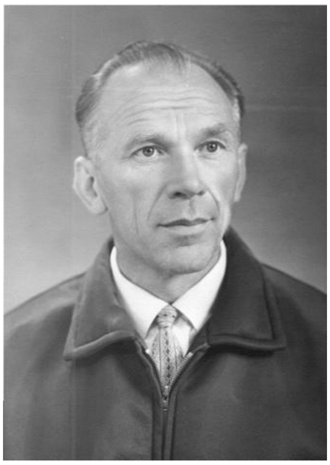
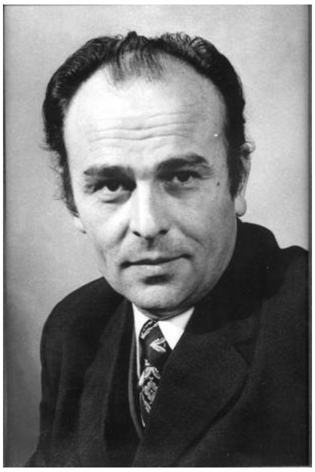
[9] Nigmatullin Rashid Shakirovich (1923–1991). A major national physicist. Doctor of physical and mathematical sciences, professor. He made a fundamental contribution to the creation of a new field of science - molecular electronics and founded a scientific school known in the country and abroad. The science manager and statesman – the Chairman of the Supreme Council of the TASSR (1971–1979), Rector of the Kazan Aviation Institute (now KNRTU–KAI), a participant of the Great Patriotic War (Second World War).

[10] Valiev Kamil Akhmetovich (1931–2010), an outstanding physicist and organizer of science, creator of domestic microelectronics, academician of the Academy of Sciences of the USSR and the Russian Academy of Sciences, director and head of the Physical-Technical Institute of the Russian Academy of Sciences, laureate of the Lenin Prize and Prizes of the Government of the Russian Federation. After defending his dissertation, he created the Department of Theoretical Physics at the Kazan Pedagogical Institute (now the Department of Computational Physics, Kazan Federal University).

[11] L.Ya. Shekun (1931–1967) – a specialist in the theory of EPR spectra of rare-earth ions in crystals, died prematurely in the prime of his scientific activity.


N.N. Neprimerov


K.A. Valiev


M.M. Zaripov


L.Ya. Shekun


Sh.Sh. Bashkirov

The history of the development of magnetic resonance at the KPhTI of Kazan Scientific Center of RAS is a separate topic, which is fully covered in the KPhTI publications (see, e.g., [4]). We only note that with a few exceptions, KPhTI employees are (and now are) graduates of Kazan University and actively cooperate with each other. After B.M. Kozyrev the work in the field of magnetic resonance at KPhTI was headed by M.M. Zaripov[12], Director of KPhTI (1972–1988) and part-time head of the Department of Quantum Electronics and Radiospectroscopy of Kazan

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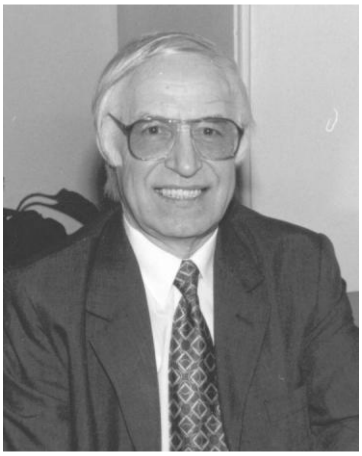
[12] M.M. Zaripov – Laureate of the USSR State Prize in Science and Technology in 1988 (as part of a group of authors) for the series of publications "The discovery of the phenomenon of pulsed oriented crystallization of solids (laser annealing)". Before moving to KPhTI he headed the department of radio quantum electronics and spectroscopy in the period 1963–1971.

University (1963–1971, Professor until 2011), and succeeding him as director K.M. Salikhov[13] (1988–2014), part-time head of the Department of Chemical Physics created by him at Kazan University (1989–2014).



K.M. Salikhov

B.A. Arbuzov had a special influence on the development of magnetic resonance applications in chemistry. B.A. Arbuzov is one of the first scientists in the USSR who appreciated the enormous opportunities for the development of science that physical methods of research can bring, and actively introduced them both at Kazan University and at the Institute of Organic and Physical Chemistry of the USSR Academy of Sciences[14] (subsequently, Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Center of RAS (IOPC)).

After the initiative of B.A. Arbuzov the Problem Laboratory for the study of the structure of organic compounds (PL SSOC) was created in 1957 at the Faculty of Chemistry of Kazan University. The formation of scientific groups in it (including high resolution NMR spectroscopy) was charged to Yu.Yu. Samitov, who was at the time of its creation the assistant professor of experimental and theoretical physics at the Faculty

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[13] K.M. Salikhov – Laureate of the Lenin Prize in 1986 (as part of a group of authors) for work on magnetic spin effects.

[14] Now –Arbuzov Institute of Organic and Physical Chemistry of FRC Kazan Scientific Center of RAS – separate structural unit of the Federal State Budgetary Institution of Science “Federal Research Center “Kazan Scientific Center of the Russian Academy of Sciences” (IOPC).

of Physics and Mathematics, then professor at the Department of Quantum Electronics and Radiospectroscopy (1969–1984) at the University’s Faculty of Physics, and in last years, professor at the Department of Organic Chemistry, Faculty of Chemistry.

In the early 1960s, the radiospectroscopy laboratory was organized by B.A. Arbuzov at the Institute of Organic and Physical Chemistry of the Academy of Sciences of the USSR (now A.E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Center of RAS). Yu.Yu. Samitov[15] was also in charge to assemble the research group.

Later it was headed by A.V. Ilyasov. Currently the group leader is Sh.K. Latypov [11]. The main results in the application of high-resolution NMR in chemistry obtained in joint research with the University will be noted below. The development steps of EPR in IOPC are described in the book [14].

B.A. Arbuzov

Yu.Yu. Samitov

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[15] Later, the students of Yu.Yu. Samitov organized a few NMR laboratories: in the Kazan Chemical-Technological Institute (now KNRTU), in the Institute of Chemical Industry Automation, Kazan State Veterinary Institute (now Kazan State Veterinary Academy), in Production Association “Nizhnekamskneftekhim” (Nizhnekamsk) and other organizations. However, during the years of perestroika, they were closed.

The second branch is the nuclear magnetic resonance. The fundamental papers that laid the foundations for the further development of NMR are given in a series of books of an early period [15–17]. The last two editions contain references to papers by national authors.

Below we give only the key publications in the field of NMR:

1949–1950: W. Knight, V. Dickinson, W. Proctor, H. Gutovsky *et al.*, reported the discovery of chemical shifts of magnetic nuclei.

1951: W. Proctor, H. Gutovsky, D. McCall, E. Andrew, C. Slichter *et al.*, observed multiplets in the NMR spectra due to indirect spin-spin interaction.

1950: E.L. Hahn developed the spin echo method.

1953: H. Gutovsky, D. McCall, and C. Slichter first observed the disappearance of spin-spin multiplets in the NMR spectra with temperature change due to proton exchange. This phenomenon is called chemical exchange, positional exchange. The first observations of chemical exchange in the EPR spectra are dated 1961.

1.2. The initial period of magnetic resonance development in the USSR and Kazan University

Naturally, in the USSR in the initial period, the EPR developed under the influence and with the participation of Kazan scientists. Following Kazan, scientific groups appear in Moscow and Leningrad:

1948: Physical Institute of the USSR Academy of Sciences (Lebedev Physical Institute). I.G. Shaposhnikov defended the doctoral dissertation at Lebedev Physical Institute. In 1944–1948 he worked as the assistant professor at Kazan University. In the following I.G. Shaposhnikov headed the research in the field of radiospectroscopy at Perm State University (since 1948 he was the head of the Theoretical Physics Department).

1956: A.A. Manenkov, A.M. Prokhorov. EPR spectrometer with the magnetic field modulation, operating with the reflected wave method. A.A. Manenkov (graduate of Kazan University in 1952, since 1953 an employee of the Lebedev Physical Institute, since 1983 an employee of the Institute of General Physics of the USSR Academy of Sciences, laureate of the USSR State Prize in 1976). Subsequently, he worked closely with the EPR spectroscopy group of Kazan University in the study of materials for quantum electronics – the most important area of EPR application in physical materials science both at that time and to this day. Confirmation of this is the fact that for a long time A.A. Manenkov, A.M. Prokhorov, and N.G. Basov used the EPR method to create materials for the first lasers.

1954–1957: Georgia, Tbilisi. T.I. Sanadze, G.R. Khutsishvili, L.L. Buishvili, M.D. Zviadadze *et al*. Mechanisms of dynamic polarization of nuclei in solids. Theory of nuclear spin diffusion (G.R. Khutsishvili). Phenomenological theories of relaxation and resonance phenomena in the nuclear subsystem of paramagnets (G.R. Khutsishvili). Solid effect.

1957: G.V. Skrotsky. In 1953–1964 he was the head of the theoretical physics department of the Ural Polytechnical Institute. Since 1964 he is the Head of the quantum electronics department in MIPT (Moscow Institute of Physics and Technology). Under his leadership the precision magnetometers were developed. He developed the theory of magnetic resonance phenomena, methods for its observation, *etc*. In 1959, he predicted the possibility of observing the so-called spontaneous resonance, experimentally observed later by E.B. Alexandrov, and then E.L. Hahn (USA). He was the organizer of all-Soviet Union schools in magnetic resonance, in holography and coherent optics.

1957: L.A. Blumenfeld, A.E. Kalmanson, Institute of Chemical Physics, Academy of Sciences of the USSR. L.A. Blumenfeld is the creator of the largest biophysical school in the USSR, head of the Laboratory of Physics of Biopolymers, Institute of Chemical Physics (USSR Academy of Sciences). In 1959 he founded the Department of Biophysics, Faculty of Physics, at M.V. Lomonosov Moscow State University. He was a Chairman of the Council on Radiospectroscopy at the USSR Academy of Sciences. Created the research direction of EPR in polymers.

1957: A.K. Chirkov, R.O. Matevosyan. EPR in free radicals. Ural Polytechnical Institute. In 1966, they created a laboratory of physical and physico-chemical methods for the study of organic compounds at the Institute of Chemistry of the Ural Branch of the USSR Academy of Sciences (since 1971 the Ural Scientific Center).

1958: V.V. Voevodsky, Yu.N. Molin, Yu.N. Tsvetkov, N.N. Bubnov, Siberian Branch of RAS, Institute of Chemical Kinetics and Combustion. Later V.V. Voevodsky became the one of the country's authority in the field of chemical physics. One of the domestic pioneers in the application of the radiospectroscopy methods in studies of the structure, properties and chemical transformations of free radicals in a variety of chemical processes.

1959: A.G. Semenov, N.N. Bubnov. EPR in the microwave range with double modulation of the magnetic field. INEOS of USSR Academy of Sciences (now A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS)). N.N. Bubnov became the leader of the group (1965–1992) and the laboratory (1992–2004) of EPR spectroscopy. He created the research direction “EPR in organic and organoelemental chemistry to study the structure and reactivity of radicals”.

NMR development steps:

1947: K.V. Vladimirsky for the first time in the USSR observed NMR signals (Reports of USSR Academy of Sciences, 58, 1625), LPI (Lebedev Physical Institute of the USSR Academy of Sciences). Thus, after Kazan University, the center of radiospectroscopy was formed at the Lebedev Physical Institute.

1950–1955: Moscow State University. S.D. Gvozdover and A.A. Magazinnik published the first article on NMR (JETP, 1950). The research direction of radiospectroscopy – NMR is being created at Moscow State University.

1950–1957: Start of work in the field of NMR at Kazan University. The first article by Yu.Yu. Samitov on proton relaxation (JETP, 1952). And his creation of a high-resolution NMR spectroscopy group after returning from Vietnam, to where he was sent to work after defending his Ph.D. thesis and where he met P.M. Borodin.

1952–1955: Creation of a radiospectroscopy school at Leningrad University. For the first time in the USSR, F.I. Skripov received an NMR signal in the Earth's magnetic field. P.M. Borodin created the first high-resolution NMR spectrometer in the USSR for fluorine–19 nuclei.

1954: B.M. Kozyrev and A.I. Rivkind (Kazan, KPhTI, Kazan Scientific Center of the USSR Academy of Sciences) published a paper on proton magnetic relaxation.

1958: N. Bloembergen, P.P. Sorokin. NMR of ^{133}Cs. (N. Bloembergen, P.P. Sorokin, Nuclear magnetic resonance in the cesium halides. // Phys.Rev. 1958. V.110, P.865–875).

The results of studies by the EPR method in the initial period are given in [9, 10], the links to the NMR work performed in the USSR – in monographs [16, 17]. The initial period of the radiospectroscopy development in the USSR was described in detail by A.V. Kessenikh – the representative of the first wave of NMR experts (from the group of S.D. Gvozdover) and the main historiographer of magnetic resonance studies in our country. There are sufficient grounds for believing that all of these groups proceed on the development of new fields of NMR radiospectroscopy independently and almost at the same time – in the early 1950s. [18, 19][16].

Therefore, we note only the most significant results achieved at Kazan University by the first generation of students of E.K. Zavoisky and S.A. Altshuler – the founders of the School of Radio Spectroscopy of Kazan University, who predetermined the development of radiospectroscopy and its various applications at Kazan University:

– Development of the classical theory of EPR in crystals (M.M. Zaripov);

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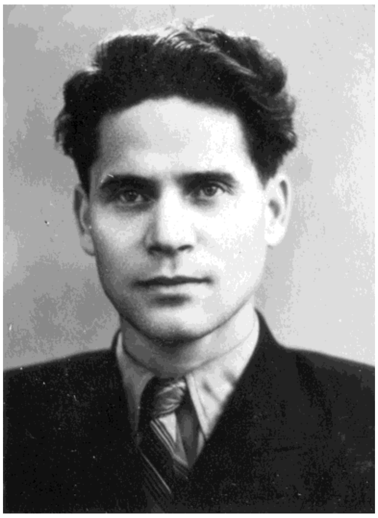
[16] The development of magnetic resonance (mainly NMR) in the initial period in the USSR, with personal memories, was described by A.V. Kessenikh in [19a, b].

– Development of the paramagnetic relaxation theory (Orbach – Aminov formula) (late 1960s – early 1970s);

– Fundamental work on the study of light super–scattering in paramagnets, the phenomena of a phonon avalanche (B.I. Kochelaev *et al.*, Late 1960s – early 1970s);

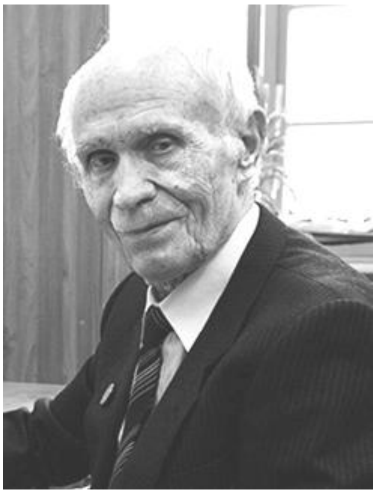


R.A. Dautov

A.I. Maklakov

A.A. Popel

V.M. Vinokurov



I.N. Pen’kov

– Creation of the fundamentals of the EPR theory in superconductors (B.I. Kochelaev *et al.*, Late 1970s – 1980s).

New research directions were created at Kazan Universiti and in the USSR (1959–1960):

– Yu.Yu. Samitov is one of the founders of high-resolution ^{1}H NMR spectroscopy in chemistry;

– R.A. Dautov was at the forefront of the development of the “spin echo” method in the country;

– A.I. Maklakov – created a research area – NMR relaxation in polymers;

– A.A. Popel developed a new physicochemical method (magnetic relaxation) of the analysis and study of inorganic substances;

– V.M. Vinokurov together with M.M. Zaripov introduced EPR into the practice of studying minerals;

– I.N. Penkov introduced the methods of nuclear quadrupole resonance in the study of the features of chemism and the structure of minerals.

2. DEVELOPMENT OF MAGNETIC RESONANCE AT KAZAN UNIVERSITY

2.1. Development of an experimental research base

For a long time experimental work at the University was carried out on original spectrometers created in the laboratories of Kazan University. Below are the main milestones of the achievements of KFU in the development of instrument engineering, which to a certain extent influenced the development of magnetic resonance in Kazan and in the whole country.

2.1.1. *EPR spectrometers*

With a few exceptions, EPR spectrometers were developed and manufactured in the laboratory of magnetic radiospectroscopy (MRS) (now named after its founder, S.A. Altshuler) of the Physical Faculty. At the end of the 1950s, the laboratory had at least one home-made X-band spectrometer (wavelength 3.2 cm), which was modernized in 1963 to make measurements at liquid helium temperature.

1960: The first electromagnets of their own construction and manufacture were created (Yu.E. Polsky, A.L. Bildyukevich and others). Later, when the needs of the MRS laboratory were met, more than ten magnets were manufactured and delivered to the laboratories of academic institutes and industrial research institutes.

1960–1961: Problem Laboratory for the study of the structure of organic compounds (PL SSOC) of the Faculty of Chemistry. EPR spectrometers of meter and 3 cm ranges (Yu.Yu. Samitov, A.V. Aganov, actually an employee and student of the Physical Faculty, respectively). But later EPR methods were not developed in the laboratory.

1962: The GS-2 helium liquefier was installed and put into operation (B.D. Pets, P.M. Goloburdov, F.S. Imamutdinov, E.I. Kirillov, *et al*.). A helium-3 refrigerator, manufactured by special order at the Kharkov Institute of Physics and Technology of the USSR Academy of Sciences, was also mounted and employed. NMR studies at temperatures below 1 K have begun (V.D. Korepanov, A.I. Chernitsyn, A.D. Shvets, E.I. Kirillov, V.M. Samsonov).

V.G. Stepanov developed an 8-mm range EPR spectrometer, which made it possible to perform studies at liquid helium temperature. The original design of the cryostat and resonator made it possible to change samples at 4 K, which allowed studies of several crystals in one helium fill. Much work on experimental spectroscopic studies of crystals and minerals on an 8-mm spectrometer was carried out by R.Yu. Abdulsabirov.

With liquid helium in the MRS laboratory, EPR studies of crystals doped by rare-earth ions were started.

1966: Spectrometers for measuring the spin-lattice relaxation time by the method of pulsed saturation were begun to build. Initially, at the frequencies of 9.5 GHz (I.N. Kurkin, A.N. Katyshev) and 36.0 GHz (A.A. Antipin[17]), and later – at 3 GHz (A.A. Antipin), 15 GHz (Yu.K. Chirkin) and 24 GHz (K.P. Chernov).

1969: Research began by the electron spin echo method (I.N. Kurkin),

1970: An EPR spectrometer-relaxometer operating in the 5 cm range was built (B.V. Soloviev). The studies of polymers began under the direction of B.G. Tarasov.

1970s: At the initiative of S.A. Altshuler a unique set of scientific and measuring instruments were built, which made it possible to study the nonequilibrium properties of paramagnetic ion crystals by traditional and newly developed EPR methods using electromagnetic, radio-frequency, optical, ultrasonic, pulsed magnetic and thermal fields (A.Kh. Khasanov, R.M. Valishev, A.V. Dooglav, F.S. Imamutdinov, Yu.G. Nazarov).

1971: V.I. Shlenkin had created an electronic spin echo EPR spectrometer with high technical characteristics.

1975–1985: A.A. Antipin in collaboration with colleagues from

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[17] A.A. Antipin, a talented experimenter, the leader of the group, died in 1989 after a serious illness, not having time to complete his doctoral dissertation.

State Optical Institute has built and installed laser EPR spectrometer.

This spectrometer has been successfully used to study crystals and glasses activated by rare-earth ions. The laboratory specimen of the spectrometer was taken as the basis for the manufacture of an experimental series of laser EPR spectrometers. Under the direction of A.A. Antipin the original 36 GHz electron spin echo spectrometer (avalanche-span diode as a source of microwave pulses) was designed and manufac tured, which at the time had no analogues in the world.

1980s: A.A. Antipin proposed and, together with the colleagues from the MRS laboratory, implemented a method of thermal pulses, which makes it possible to measure EPR on excited Stark sublevels (A.A. Antipin, R.M. Rakhmatullin, and Yu.K. Rosenzweig).

Since 1965, along with classical EPR spectroscopy, the method of electron nuclear double resonance (ENDOR, Yu.E. Polsky) has been developed. The ENDOR spectrometer was assembled, on which ENDOR on localized paramagnetic centers was first observed $CaF_2:V^{3+}$, (Yu.E. Polsky, Yu.F. Mitrofanov, M.L. Falin). A priority result is the detection of the phenomenon of triple electron-nuclear resonance on vanadium ions in fluorite crystals. When creating the experimental technique, an original spiral resonator was constructed, which was later described in classical textbooks on the EPR technique.

For special experiments (the study of spin kinetics and EPR spectra at low temperatures, experiments on the observation of a phonon avalanche, *etc*.), the following industrial spectrometers were modified:

1964: X, K, Q-range spectrometer from Jeol (Japan),

1966: X-band spectrometer from Thomson (France),

1971: X-band spectrometers RE-1301 (USSR),

1984: X-band spectrometer ESP300 from Bruker (Germany),

1986: X-band spectrometer-relaxometer IRES-1003 (USSR),

2007: X, W spectrometer of the Elexsys-680 range from Bruker (Germany),

2017: X-band spectrometer Labrador, Ekaterinburg (Russia).

2.1.2. *NMR spectrometers and relaxometers*

1958: A prototype of a pulsed nuclear magnetic resonance spectrometer was created to measure the proton relaxation times (NMR relaxometer). For the first time in the Soviet Union, a nuclear “spin echo” was observed (V.D. Korepanov, R.A. Dautov, V.M. Fadeev). Based on it, in 1960–1961 a serial instrument was developed for measuring the relaxation times of protons by the “spin echo” method (V.D. Korepanov, A.I. Chernitsyn). Relaxometers of this design were received by research institutes and factory laboratories, where they were used to study the physical and chemical properties of hydrogen-containing substances, and to control technological processes.

1959–1960: Yu.Yu. Samitov and his co-workers have built one of the first high-resolution ^{1}H NMR spectrometers in the USSR (NMR KSU–1). Simultaneously and independently, similar spectrometers were created at the Institute of Chemical Physics (V.F. Bystrov *et al.*) and at the Kazan Physical-Technical Institute of Kazan Scientific Center of the USSR Academy of Sciences (Yu.Ya. Shamonin and others). Publications dated 1961.

1959–1962: One of the first wide-line ^{1}H NMR spectrometers in the USSR was developed (Yu.Yu. Samitov, A.V. Aganov). (In the same years, a wide-line NMR spectrometer was created by A.S. Lundin and G.M. Mikhailov (Krasnoyarsk), publication 1960).

1963: A.I. Maklakov, G.G. Pimenov *et al*. The first proton relaxometer in the USSR for the study of polymers was created.

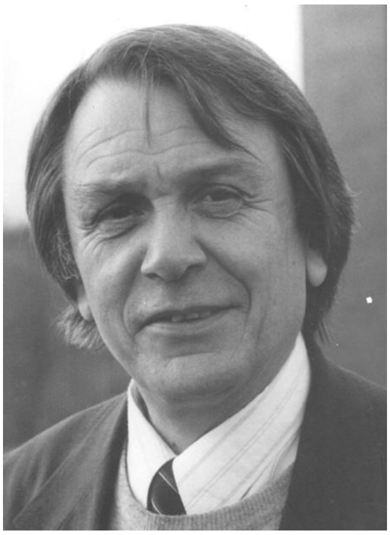
1962–1964: At the department of analytical chemistry A.V. Zakharov and Yu.I. Salnikov have built two proton NMR spectrometers for scientific and educational purposes using standard radio circuits. (One of them is still used in the special laboratory practicum for students of the Department of Inorganic Chemistry).

1964–1966: Yu.Yu. Samitov, T.V. Zykova. Modification of the NMR-KSU-1 spectrometer to determine the chemical shifts of the phosphorus-31 nuclei, creation of a spectrometer for direct observation of resonance on phosphorus-31 nuclei (NMR-KSU-2, publication dated 1967. The device was made by the order of the Institute of Organic and Physical Chemistry Kazan Scientific Center of the USSR Academy of Sciences (IOPC). At the jubilee conference of the IOPC in 1966, the creation of a spectrometer for direct observation of the resonance of phosphorus-31 (S.G. Salikhov, Yu.A. Petrov, E.I. Loginova, the KPhTI scientists) based on a permanent magnet developed by Yu.Yu. Samitov, was reported.

1964–1966: a special ^{1}H high resolution NMR spectrometer (KSU-3 NMR, A.V. Aganov et al., “Instruments and experimental technique”, 1967), specialized for measurements of liquids at low temperatures (down to 123 K), was created.

In the same years, under the leadership of Yu.Yu. Samitov a ^{1}H NMR spectrometer (KSU-4) was created for one of the factories of Biysk.

1965: Autodyne low resolution NMR spectrometer (wide line NMR, 2–35 MHz) for measurements at cryogenic temperatures was built (M.A. Teplov).



M.A. Teplov

In the mid–1960s, the Department of Inorganic Chemistry of the Chemical Faculty (V.N. Kapustin, V.V. Vedernikov, V. Butorin, A.I. Khayarov and K.S. Saykin (Department of Radioelectronics of the Physics Faculty)) created a multi-nuclear relaxometer at frequencies 5 and 15 MHz, with the accumulator of signals.

1974: NMR spectrometer with a pulsed magnetic field gradient (PMFG) was built (V.D. Skirda, A.I. Maklakov *et al*.).

1978: Autodyne NMR spectrometer was built (50–320 MHz) – M.A. Teplov, M.S. Tagirov, A.A. Kudryashov.

1978: NMR spectrometer for studies at hydrostatic pressure up to 10 kbar, 4.2 K – M.S. Tagirov (totally 11 spectrometers for various purposes).

1980: Experiments at ultra-low temperatures were started. With the assistance of Academician P.L. Kapitsa and Head of the Laboratory of JINR B.S. Neganov, with the help of the specialists of the plant "Geliymash" R.G. Amamchan and S.N. Boldyrev, the scientific group of M.A. Teplov was able to install at MRS laboratory in 1980 the refrigerator for the dissolution of helium isotopes. Three years in total took M.A. Teplov with students (A.G. Volodin and M.S. Tagirov, and a little later V.V. Naletov) to bring this sophisticated technique to working condition and adapt it for NMR studies. With this facility many important results were obtained on stationary NMR at a temperature down to 50 mK.

In the 2000s, based on the Tesla BS 467A high-resolution NMR electromagnet, a multi-nuclear and multi-frequency (5, 10, 15, and 25 MHz) pulsed relaxometer with computer processing of NMR signals and their accumulation was made (A.I. Mukhtarov, Department of Inorganic Chemistry, A.M. Butlerov Chemical Institute).

With the advent of superconducting magnets (at the turn of the 1980s), the era of industrial devices of a new generation has come. Although few small magnets were made, the creation of big superconducting magnets in the laboratory was impossible. For this reason, further development of NMR spectrometers was aimed at modifying industrial instruments for conducting special experiments and creating specialized spectrometers for physical experiments; they do not stop at present.

2002: In the group of M.S. Tagirov (V.V. Naletov and D.I. Abubakirov) a bridge circuit of an NMR spectrometer for the frequency range 18–700 MHz for studying Van Vleck paramagnets in strong magnetic fields was created.

2011: A.V. Egorov created the digital NMR spectrometer with a frequency sweep. Unlike standard instruments, such a spectrometer allows one to study substances with a large value of nonresonant absorption (HTSC, magnetically ordered systems, *etc*.).

2013: In M.S. Tagirov's group (A.V. Klochkov, R.M. Rakhmatullin) a setup was created for observing stationary and pulsed NMR at frequencies of 500–600 MHz at helium temperatures. A number of interesting results on Bose-Einstein condensation in solid-state antiferromagnets were obtained at the facility.

2013: By the Joint group of scientists of the Departments of Quantum Electronics and Radiospectroscopy and the Department of Molecular Systems Physics of the Institute of Physics (M.S. Tagirov, I.R. Mukhamedshin, A.V. Egorov, G.V. Mamin, T.R. Safin, K.R. Safiullin, L.A. Batalova, V.D. Skirda, O.I. Gnezdilov, N.M. Azancheev, R.V. Arkhipov, A.V. Savinkov, B.I. Gizatullin, A.A. Ivanov, T.V. Shipunov, M.M. Doroginitskii, T.M. Salikhov, A.S. Aleksandrov) on the order of the oil industry, highly specialized ^{1}H NMR spectrometers were developed and created to determine distribution of oil and water in underground reservoirs (porosity), type of saturating fluid and its characteristics:

– nuclear magnetic logging tool YaMK1D (resonance frequency – 420 kHz, remoteness of the study area – 190 mm, the range of the measuring porosity 4–100%);

– mobile installation for core research NMR-Kern-8.1 (resonance frequency – 8.1 MHz, the range of measuring porosity 0.1–100%, diffusion measurement).

2014: A group of scientists (V.D. Skirda – supervisor, A.S. Aleksandrov, R.V. Arkhipov, A.A. Ivanov, O.I. Gnezdilov, M.R. Gafurov) created a pulsed NMR spectrometer for measurements of NMR spectra and relaxation characteristics of ^{1}H nuclei in a magnetic field of 100 G (400–500 kHz) with the possibility of pulsed pumping of EPR transitions at frequencies of 1–250 MHz.

2016: By the joint group of scientists of the Departments of Quantum Electronics and Radiospectroscopy and the Department of Molecular

Systems Physics of the Institute of Physics (M.S. Tagirov, A.V. Egorov, G.V. Mamin, A.V. Klochkov, E.M. Alakshin, T.R. Safin, K.R. Safiullin, M.Yu. Zakharov, V.D. Skirda, O.I. Gnezdilov, N.M. Azancheev, R.V. Arkhipov, A.V. Savinkov, B.I. Gizatullin, A.A. Ivanov, T.V. Shipunov, A.R. Lozovoy, A.S. Aleksandrov) significant improvements were made to the developed equipment (the dielectric and NMR characteristics of the fluid were recorded simultaneously, which makes it possible to determine the type of fluid with greater reliability). As a result, the following instruments were created:

– YaMK1T nuclear magnetic logging tool (resonance frequency – 700 kHz, remoteness of the study area – 190 mm, the range of the measuring porosity 2–100%);

– KMRK complex downbore nuclear magnetic logging tool (resonance frequencies – 460 and 700 kHz, remoteness of the research zones – 210 mm and 190 mm, the range of the measuring porosity 2–100%, module for measuring dielectric characteristics);

– mobile equipment for core research NMR-Kern-6.5 (resonance frequency – 6.5 MHz, the range of the measuring porosity 0.1–100%).

2018: By M.S. Tagirov group (G.A. Dolgorukov, V.V. Kuzmin, A.V. Bogaychuk, E.M. Alakshin, K.R. Safiullin, A.V. Klochkov) a setup was created for studying pulsed NMR of adsorbed liquid and gaseous ^{3}He at frequencies of 3–150 MHz.

2018: In the group of M.S.Tagirov (V.V. Kuzmin, A.V. Bogaychuk, A.V. Klochkov, K.R. Safiullin, E.M. Alakshin, I.K. Nekrasov) several setups were created: a pulsed multinuclear NMR spectrometer (temperature 1.5–4.2 K, magnetic fields up to 0.85 T, frequency range 3–150 MHz), adapted for the study of ^{3}He; unique digital multifunctional pulsed NMR spectrometer for operation in magnetic fields of 0–9 T, at frequencies of 5–500 MHz in the temperature range 1.65–300 K.

2.2. The main achievements of the school “Resonant properties of condensed matter” at Kazan University from the mid–1960s to 2005–2008

Work in the field of magnetic resonance was carried out in various fields in close collaboration with representatives of various departments of the University and other institutions of the city. These studies are described in a collective monograph [8]. Also, foreign partners took part in joint research.

On the eve of the 100th anniversary of E.K. Zavoisky and a little later they were described in cycles of works, summarizing the results of researchers. They were awarded by the State Prizes of the Republic of Tatarstan in the field of science of technology[18].

2.2.1. *Study of Van Vleck paramagnets*

2006: “Studies of Van Vleck paramagnets”: S.A. Altshuler (posthumously), M.A. Teplov (posthumously), M.M. Zaripov, B.Z. Malkin, L.K. Aminov, M.S. Tagirov, D.A. Tayurskii, A.V. Egorov.

The Van Vleck paramagnets are usually called the substances that in the ground electronic state have no magnetic moment, but whose paramagnetic susceptibility far exceeds the diamagnetic one. If diamagnetism is a manifestation of system energy quadratic in the external magnetic field, then the Van Vleck paramagnetism is a manifestation of terms linear in the field in the second order of perturbation theory. A variety of spectra of zero order determines a wide range of possible origins of the Van Vleck

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[18] These works cover an almost 40-year period of a large team of researchers. Therefore, here are excerpts from the abstracts of these work cycles, but without citation. More detailed information can be extracted from the original articles of the authors, which are quite simple to find in the Scopus database and Web of Science. In many cases, the contribution of colleagues who participated in this cycle of work can be determined from the list of dissertations presented in Annexes 1 and 2.

paramagnetism. A striking example of the Van Vleck paramagnets is crystals containing rare earth (RE) ions with unfilled 4f shells – Pr^{3+}, Eu^{3+}, Tb^{3+}, Ho^{3+}, and Tm^{3+}. The groung multiplet of these $^{2S+1}L_J$ ions is often split by the crystal field so that the lower levels are a singlet or nonmagnetic doublet, and the excited levels are separated from the ground level by intervals of the order of 10–400 cm^{-1}. The isotopes ^{141}Pr, ^{159}Tb, ^{165}Ho, ^{169}Tm have 100% abundance and a nonzero nuclear spin; therefore, the compounds of these elements possess not only electronic magnetism, but also nuclear magnetism. Paramagnetic (“chemical”) shifts of the NMR lines in such systems are, as a rule, highly anisotropic and reach enormous values up to hundreds. This leads to interesting features of the magnetic resonance of rare-earth (RE) nuclei, which makes it possible to classify it as a phenomenon intermediate between ordinary NMR and EPR.

From left to right: A.V. Egorov, D.A. Tayurskii, M.S. Tagirov,
M.Sh. Shaimiev, M.M. Zaripov, L.K. Aminov, B.Z. Malkin

These peculiarities have firstly been noted by S.A. Altshuler and, after his suggestion, M.M. Zaripov performed the calculations for NMR of the Van Vleck systems. NMR of RE ions in the singlet ground state was first discovered in 1967 by M.A. Teplov.

S.A. Altshuler also pointed on the promise of using the Van Vleck paramagnets to produce ultra-low temperatures. The implementation of this proposal by Andres and Bucher on the intermetallic RE compounds attracted the additional attention of physicists to this class of substances.

The pattern of Stark splitting of the main multiplet in a crystalline electric field, characteristic of rare-earth ions – a set of closely spaced levels with intervals of the order of 14–140 K – leads to a number of other features of rare-earth compounds, in particular, structural instabilities at low temperatures. These instabilities manifest themselves in the form of cooperative Jahn – Teller effects, in the form of giant magnetostriction of a number of crystals, anomalies of elastic constants (B.Z. Malkin), and finally in the form of peculiar field and temperature dependences of the EPR linewidth of impurity ions. Naturally, the NMR spectra and relaxation characteristics of the RE Van Vleck paramagnets bear the imprint of all rich physics of the materials under consideration, and the correct interpretation of the results of NMR studies thus has a wide physical interest.

The Hamiltonian of the Van Vleck ion includes the interaction with a crystalline electric field, electron Zeeman interaction, hyperfine interaction, and nuclear Zeeman interaction. If the nucleus spin is greater than 1/2, then it is also necessary to take into account the nuclear quadrupole interaction. At low temperatures and weak magnetic fields, one can use the second order of perturbation theory to calculate corrections to the ground state energy. The result is an effective nuclear Hamiltonian, the parameters of which (components of the effective gyromagnetic ratio) are usually highly anisotropic, and the effective moments can far exceed the moments of free nuclei. The latter circumstance was the basis for the use of the Van Vleck paramagnets for magnetic cooling. For example, for thulium ethylsulfate (axial symmetry), the components of the effective gyromagnetic ratio of ^{169}Tm nuclei differ by more than 50 times: 0.48 kHz/Oe and 26 kHz/Oe (longitudinal and transverse components). An experimental measurement of the parameters of the effective spin

Hamiltonian makes it possible to obtain information about the parameters of the interaction Hamiltonian with a crystalline electric field, which is completely impossible in the case of ordinary NMR.

The ground state of the Van Vleck ion can also be a nonmagnetic doublet, which is realized in the case of cubic symmetry. Such a resonance was first discovered on ^{165}Ho and ^{169}Tm nuclei in dielectric crystals with an elpasolite structure. A structural phase transition was detected in the Rb_2NaHoF_6 crystal.

At elevated temperatures, the regime of fast jumps between the states of the 4f shell is established in the crystals, and the nucleus experiences short-term effects of other hyperfine fields created by thermally excited electrons. Now, instead of one frequency of the nuclear spin precession, a frequency spectrum appears. With a fairly rapid change in the electronic states we will still observe one line, but this line will experience an additional shift.

The temperature-dependent shift of the resonance line is inextricably linked with the nuclear magnetic relaxation times and the line width. If at low temperatures the line width is determined mainly by collective interaction, then with increasing temperature the role of the intra-atomic electron-nuclear bond increases. The fluctuating hyperfine magnetic field at the nucleus usually has components perpendicular to the external magnetic field. The Fourier spectrum of these components contains components of resonant frequencies that induce transitions between nuclear energy levels, i.e. nuclear relaxation. There is a profound analogy between the situation considered here and the NMR phenomenon in liquids. The structure of the fluctuating hyperfine interaction Hamiltonian indicates the existence of a peculiar “scalar relaxation of the second kind”.

A theoretical analysis of the nuclei relaxation of rare-earth ions was carried out on the basis of the non-adiabatic theory of Redfield and Bloch-Wangness. For an arbitrary orientation of the external magnetic field relative to the crystal axes, the effective field at the nuclei of rare-earth ions changes both in magnitude and in direction. Thus, the use of adiabatic theory is excluded. The situation we are considering is reminiscent to “scalar relaxation of the second kind" in liquids, however, the specific behavior of the electronic moment of the rare-earth ion in crystalline electric and external magnetic fields requires a certain modification of the theory as applied to anisotropic systems. The experimental results give convincing evidence in favor of the theoretical model proposed by L.K. Aminov and opens up the possibility of extracting the value of the correlation time from the experiments – the only fitting parameter of the Redfield theory. The correlation times obtained in this way depend on the orientation of the external magnetic field. From this we can conclude that the lifetime of the Van Vleck ion in the excited state is determined mainly by interparticle interactions such as dipole-dipole, quadrupole-quadrupole, or via the phonon field.

The hyperfine field at the nuclei of rare-earth ions is modulated not only due to real transitions between electronic states, caused, for example, by dipole-dipole or electron-vibrational interactions of ions.

The lattice oscillations, perturbing the crystalline potential, thereby lead to a small change in the magnetization in each of the electronic states, including the ground singlet state. As a result of this, direct relaxation transitions between nuclear sublevels with emission or absorption of one phonon of the corresponding frequency become possible. The mechanism under consideration is very weak, however, it may turn out to be the only one at ultralow temperatures. The probability of a relaxation transition strongly depends on the magnetic field (~H^4). Studies of ^{169}Tm relaxation in thulium ethylsulfate at extremely low temperatures confirmed the presence of this type of dependence. In addition, it was possible to measure the spin diffusion coefficient of thulium nuclei in this Van Vleck paramagnet.

Giant magnetostriction was first detected in the Van Vleck dielectric crystal $LiTmF_4$. The forced magnetostriction of paramagnetic crystals is proportional to the magnetization and external magnetic field. In normal paramagnets with a magnetic ground state (effective spin 1/2), the magnetic moment is proportional to $\mathrm{th}(g\beta H/2kT)$; therefore, the quadratic growth of magnetostriction in the magnetic field in weak fields is replaced by a linear one under saturation conditions. In the Van Vleck paramagnets, the magnetic moment induced by an external field is proportional to $\beta H/\Delta$, where Δ is the energy of excited states in a crystalline field. In concentrated rare-earth normal paramagnets at helium temperatures in fields of few tens of kOe, magnetostriction reaches a huge magnitude of the order of 10^{-4}. It can be expected that if the excited Stark sublevel is close enough to the singlet ground state, the magnetostriction in the Van Vleck paramagnet can have the same order of magnitude in comparable fields as in a normal paramagnet. Indeed, the magnetostriction measured in the $LiTmF_4$ crystal was $-1.1 \cdot 10^{-3}$ in the magnetic field of 3 T.

The obtained data, both qualitatively and quantitatively, are consistent with the results of a theoretical analysis performed in the framework of ideas about the single-particle magnetostriction mechanism.

Thermal resistance at the solid – liquid helium-3 interface is one of the most interesting phenomena in ultra-low temperature physics. In 1981, Nobel Prize winner Prof. O.U. Richardson and colleagues, studying the relaxation of ^{3}He adsorbed on particles of a fluorocarbon polymer, have found the interaction between the nuclear spins of fluorine and helium-3. Using the Van Vleck paramagnets with strong anisotropy of magnetic properties, one can study the resonant interaction of nuclear spins at the ^{3}He – solid boundary. This kind of cross-relaxation between the nuclear spins of ^{169}Tm in thulium ethyl sulfate and the spins of liquid helium-3 was first discovered by A.V. Egorov et al. The time of longitudinal magnetic relaxation of helium-3 decreased substantially if the effective gyromagnetic ratio of ^{169}Tm nuclei became equal to the gyromagnetic ratio of helium-3 nuclei (3.243 kHz/Oe). To do this, it is enough to apply the external field at an angle of 7.05° to the crystallographic axis c of the crystal. Subsequently, the relaxation of helium-3 in contact with oriented powders of the Van Vleck paramagnets was studied.

Many high-temperature superconductors include the Van Vleck ions. The study of these compounds by the magnetic resonance method of the nuclei of the Van Vleck ions makes it possible to obtain information inaccessible to “ordinary” NMR. The first high-temperature superconductor in which the “amplified” ^{141}Pr NMR was detected is the electronic superconductor

$Pr_{1.85}Ce_{0.15}CuO_{4-y}$. Then, ^{169}Tm NMR was used to study the high-temperature superconductor $TmBa_2Cu_3O_{6.92}$. The measured parameters of the spin Hamiltonian made it possible to clarify the parameters of the Hamiltonian of the crystal electric field in these compounds. It was found that the effective gyromagnetic ratios strongly depend on the local oxygen environment, and, therefore, can be used to study the structural and phase separation of HTSCs.

In magnetic fields above 5 T, when the Zeeman energy of the Van Vleck ion becomes comparable with the distances between the energy levels of the Stark structure, the perturbation theory usually used in calculations of the magnetic characteristics of the Van Vleck ion becomes inapplicable and the problem arises of studying the influence of external magnetic field on the state of the Van Vleck paramagnetic ion. Strong magnetic fields should change both the energy intervals between the levels of the Stark structure and the form of the corresponding wave functions. The latter can lead to qualitatively new effects, since strong mixing of the wave functions within the main multiplet changes the selection rules for resonant transitions. The theory of the electron-nuclear system in dielectric Van Vleck paramagnets was created by D.A. Tayurskii. Experimental results of M.S. Tagirov and collaborators in the study of NMR in the Van Vleck paramagnets in strong magnetic fields and at low temperatures are consistent with theory.

Systems with high polarization of nuclear spins are the objects of intensive research, both in elementary particle physics and in solid state physics. Compared to the “brute force” method (strong magnetic fields and ultra-low temperatures), dynamic nuclear polarization (DNP) methods are more efficient. One of the DNP methods – the so-called “solid effect” – is based on the transfer of polarization from impurity paramagnetic centers to the nuclear spin system. M.S. Tagirov and D.A. Tayurskii proposed a modification of this method using the dielectric Van Vleck paramagnets in which the Van Vleck ions are located at the sites of the regular crystal lattice and act as paramagnetic centers during the transfer of polarization to nuclei.

2.2.2. *Study of the nature of nanoscale properties of superconductors by magnetic resonance methods*

2007: "Study of the nature of nanoscale properties of superconductors by magnetic resonance methods": I.A. Garifullin (KPhTI of Kazan Scientific Center of RAS), N.N. Garifyanov (KPhTI of Kazan Scientific Center of RAS), A.V. Dooglav (KFU), M.V. Eremin (KFU), B.I. Kochelaev (KFU), L.R. Tagirov (KFU), G.B. Teitelbaum (KPhTI of Kazan Scientific Center of RAS), E.G. Kharakhashyan (KPhTI of Kazan Scientific Center of RAS) (posthumously).

From left to right: L.R. Tagirov, M.V. Eremin, I.A. Garifullin, G.B. Teitelbaum, M.Sh. Shaimiev, B.I. Kochelaev, N.N. Garifyanov, A.V. Dooglav

Superconducting materials are the basis of high technology and energy in the near future. Physicists have always been interested in their amazing merit, with special interest in their local properties. The analysis of local properties is coupled with the use of “point” methods, with magnetic resonance in a special place. However, for many years, the application of this powerful method to the study of the superconducting state was considered impossible. The fact is that in this state the electrons are coupled in pairs with zero spin (magnetic moment), and the presence of a spin is a necessary condition for observing paramagnetic resonance. In addition, the superconductors of the first type completely eject an external magnetic field from themselves, which makes resonance impossible with magnetic ions especially introduced as a probe. Superconductors of the second type “let in” a magnetic field in the form of an Abrikosov vortex lattice, which is distributed so inhomogeneously that spins located in different places of the sample resonate at different frequencies. This should “spread” the observed total signal, making it unobservable. However, under conditions when the magnetic field distribution is periodic, it becomes possible to “collect” signals from spins located at the extreme points of this distribution. In 1972, E.G. Kharakhashyan and his collaborators just managed to carry out a similar experiment and for the first time use the EPR method to study superconductivity.

Following the first observation of resonance in superconductors, the Kazan group launched large-scale studies of various types of superconductors of the second type in fierce temporary competition with several groups from Los Angeles, San Diego, West Berlin, Geneva, Jerusalem and San Paulo. Nevertheless, thanks to fruitful cooperation with the P.L. Kapitsa Institute for Physical Problems of the USSR Academy of Sciences, B.I. Kochelaev (KFU), E.G. Kharakhashyan and I.A. Garifullin (KPhTI) have succeded to carry out the key experiments that gained international recognition. Namely, the phenomenon of the “electron bottleneck” in the superconducting phase was first studied and its theory was constructed (B.I. Kochelaev, L.R. Tagirov). The essence of the phenomenon is that when the resonant frequencies of the embedded localized moments (for example, gadolinium) and the conduction electrons coincide, their mutual connection is stronger than the interaction of each of them with a lattice (thermostat). The localized moments and electrons are first combined into one system (coupled oscillations of the magnetizations of both subsystems arise), then the combined system relaxes to the lattice by spin-lattice relaxation of conduction electrons (recall that at liquid helium temperatures the spin-lattice relaxation of localized spins can be neglected). Thus, the electronic bottleneck allows to see what is impossible to observe directly.

When studying the EPR on erbium ions in superconducting lanthanum, a sharp narrowing of the resonance line was found immediately below the temperature of the superconducting transition (I.A. Garifullin, B.I. Kochelaev, E.G. Kharakhashyan), which contradicted the idea that the resonance line should be broaden. This seemingly particular phenomenon led to the study of two-particle spin-spin interactions in the superconducting phase and the actual experimental proof of the appearance of a new, super-long-range exchange interaction in the superconducting phase (B.I. Kochelaev, L.R. Tagirov). The physical reason for the appearance of this new interaction can be explained as follows: the Cooper pair in a superconductor is a coherent formation (quasiparticle), which is rigid in size of the order of the coherence length of the superconductor, reaching hundreds of interatomic distances. If perturbation is applied to one side of this rigid object, for example, with the help of a localized magnetic moment, then it will “respond” on the opposite side, at a distance of the coherence length. Thus, the perturbation is transmitted through Cooper pairs from one localized moment to another, and an interaction is established between two spins separated by hundreds and thousands of angstroms from each other. The EPR theory of interacting localized moments, developed in Kazan, was able to explain both the narrowing of the line and the characteristic change in its shape during the superconducting transition (B.I. Kochelaev, L.R. Tagirov).

Immediately when the fact of modification of the exchange interaction in the superconducting phase was realized, the Kazan group successfully performed experiments to observe the magnetic ordering of localized moments in superconductors (I.A. Garifullin, E.G. Kharakhashyan, B.I. Kochelaev). The intrigue of the problem was as follows: since the mid-50s, after the work of Nobel laureate V.L. Ginzburg, the opinion was established that ferromagnetism and superconductivity are incompatible. Indeed, superconductivity is the union of electrons with opposite spins in the Cooper pairs. At the same time, ferromagnetism is the alignment of localized moments and the spins of conduction electrons magnetized by them parallel to each other with the achievement of the maximum magnetic moment. As a rule, a ferromagnetically ordered substance does not become superconducting at any temperature, and the appearance of ferromagnetism in a superconductor immediately destroys superconductivity, that is, these two long-range orders are antagonistic. The observation by the Kharakhashyan group of magnetic ordering with the preservation of superconductivity was an indication of a noncollinear magnetic order and, as it turned out later, a harbinger of worldwide studies of a wide class of superconducting triple and quaternary magnetic compounds, the result of which was a general understanding that magnetic and superconducting order can coexist, if their mutual adjustment occurs.

Further development of the method led to the fact that immediately after the discovery of high-temperature superconductors (HTSC), magnetic resonance was used to study their very unusual properties. In particular, a serious obstacle to the use of these materials is the fact that, despite the high temperatures of the transition to the superconducting state, the currents that they can transfer without electrical resistance are not very large. The explanation of this peculiarity was obtained after the first results on the observation of EPR in high-temperature oxides, which have revealed the natural heterogeneity of these materials (I.A. Garifullin, N.N. Garifyanov, B.I. Kochelaev, G.B. Teitelbaum). The fact is that a distinctive feature of such highly correlated electronic systems as superconducting metal oxides is their tendency to phase separation, which leads to the coexistence of magnetic and superconducting phases (see details below). This coexistence occurs at a microscopic scale and can be dynamic. In this case, superconductivity has a peculiar percolation character, and the distributions of magnetization and charge density are substantially inhomogeneous at very small scales. Questions remained open, such as the parameters of these distributions, the modes in which they exist, and their relationship with the nature of the superconductivity in these compounds.

To understand the properties of these systems, local ESR-related research methods such as NMR (nuclear magnetic resonance) and NQR (nuclear quadrupole resonance) are of particular importance. They make it possible to obtain “point” information on phases co-existing at nanoscale sizes, first of all, about the magnitude of the internal magnetic field and charge density at various nodes of the structure, and on the frequencies of charge and spin fluctuations. This series of works presents experimental and theoretical results obtained by team members in different years and reflecting consistent progress in solving these problems (A.V. Dooglav, M.V. Eremin).

In the process of studying high-temperature superconductors, it turned out that their unique superconducting parameters were surprisingly “tied” to their equally non-standard physical properties in the normal phase. The very normal phase of a substance located at the junction of metal, insulator, magnetic, and structural transitions is a challenge to the modern understanding of solid state physics. The fact is that the strong electron correlations characteristic of HTSC materials make traditional band schemes for describing insulators and metals inapplicable. The intensive development of the physics of such materials is associated both with the identification of new experimental facts that shed light on their nature, and with the construction of new theoretical models that can adequately describe them.

One of the unexpected and new in comparison with classical superconductors is the complete suppression of the superconducting transition when non-magnetic zinc (Zn) ions replace copper ions that are part of the structure of most of the known HTSC compounds. Using EPR, it was possible to prove that the mechanism of suppression of superconductivity by Zn ions is the destruction of superconducting pairs by local magnetic moments formed due to strong electronic correlations in the vicinity of zinc ions (G.B. Teitelbaum). These data stimulated a review of the results of previous studies on magnetic resonance in metal oxide systems – sodium tungsten bronzes (Na_xWO_3), which have properties of the normal phase similar to HTSC materials. A targeted search made it possible to establish the presence in the Na_xWO_3 bronze samples of a superconducting composition of low-frequency spin fluctuations of an antiferromagnetic nature, which are a characteristic attributed to high-temperature oxide superconductors. Further experiments with stoichiometry of the composition of the material made it possible to achieve high temperatures of the superconducting transition, comparable to those in HTSC materials. Thus, the important role of antiferromagnetic fluctuations in the HTSC phenomenon was demonstrated and, more broadly, the general physical properties of various classes of compounds exhibiting high-temperature superconductivity were revealed (N.N. Garifyanov, I.A. Garifullin).

The experimental data stimulated the development of physical models for describing both the normal and superconducting properties of HTSC materials. A theoretical model was proposed for the strongly correlated singlet conduction band in cuprates, which allowed: a) to calculate the dispersion law of quasiparticles in the conduction band; b) to explain the dependence of the energy of the superconducting gap on the wave vector; c) to give a possible explanation of the instability of the normal phase. The calculated renormalizations of the super-exchange interaction parameter of copper due to polaron effects made it possible to correctly interpret the data on NMR relaxation in HTSC materials (M.V. Eremin).

Another distinguishing feature of highly correlated electronic systems such as superconducting metal oxides is their tendency to phase separation, leading to the coexistence of magnetic, dielectric, and superconducting phases. In this case, superconductivity has a peculiar mesoscopic character, and the distributions of magnetization and charge density are substantially inhomogeneous. Studies of phase separation in metal oxides have led to a number of very interesting results (B.I. Kochelaev, G.B. Teitelbaum). Some of them relate to the properties of metal oxides at a low carrier density:

– A theoretical picture of the evolution of the magnetic and kinetic properties of superconducting cuprates upon their doping with carriers was developed, based on the possible appearance of topological spin excitations such as skyrmions;

– A model of the electronic phase separation of weakly doped cuprates into nanoscale metal and dielectric regions was constructed based on the strongly anisotropic interaction of three-spin polarons via the phonon field. Based on this theory, the temperature dependence of the intensity of the EPR signals from the metal and dielectric regions and its other characteristics were explained by the experiments of the group of the Nobel laureate Prof. K.A. Mueller.

The team members (B.I. Kochelaev, G.B. Teitelbaum, M.V. Eremin, A.V. Dooglav) performed a detailed analysis of microscopic phase separation in high-temperature superconductors in a wide range of carrier densities, which allowed:

– Using the NQR method, establish the amplitudes of the inhomogeneous distributions of the hole and spin densities of the stripe phase of the lanthanum-strontium metal oxides that arise when the carrier concentration is near 1/8, and understand the features of the appearance of bulk superconductivity when the stripe structure passes from static to dynamic mode;

– Based on the nature of the suppression of the NMR signal during the transition of the system to the stripe antiferromagnetic phase, find the frequency distribution of the magnetic fluctuations;

– Using EPR and NMR in a strong magnetic field to reveal the properties of dynamic phase separation in the superconducting state of $La_{2-x}Sr_xCuO_4$;

– On the basis of studying the low-temperature features of nuclear magnetic relaxation, find the first evidence of the stripe nature of charge fluctuations in the stoichiometric $YBa_2Cu_4O_8$ compound;

– Using data on nuclear spin relaxation, it was found that the pseudogap behavior of superconducting metal oxides that begins at temperatures significantly higher than the critical value is associated with the dynamic phase separation at microscale in metal and magnetic regions.

2.2.3. *The development of gradient NMR in research of structures and dynamics of complex molecular systems*

2008: "Development of gradient NMR in studies of the structure and dynamics of complex molecular systems": A.I. Maklakov, V.D. Skirda, G.G. Pimenov, N.F. Fatkullin, N.K. Dvoyashkin, V.A. Sevryugin (MarSU, Yoshkar-Ola), G.I. Vasiliev, A.V. Filippov.

From left to right: N.F. Fatkullin, A.I. Maklakov, V.D. Skirda, M.Sh. Shaimiev, G.G. Pimenov, G.I. Vasiliev, N.K. Dvoyashkin, V.A. Sevryugin

Nuclear magnetic resonance (NMR) belongs to the one of the most effective and dynamically developing research methods. The progress achieved in sensitivity, spectral resolution, and also in the use of complex multipulse techniques has allowed expanding the capabilities of the method in studies of molecules with a complex structure and dynamics. The development of techniques based on the use of a magnetic field gradient has further expanded the capabilities of the method. If at first nuclear magnetic resonance was associated as a method in which it was required to create a maximally uniform magnetic field, then in recent years, methods have been more actively developed in which the controlled magnetic field gradients are used. Moreover, if introduction of a magnetic field gradient in the high-resolution NMR only expands the possibilities of the method, the idea of spatial resolution in Magnetic Resonance Imaging (MRI) is completely based on the phase-frequency dependence of the signal on the coordinate of the spins in a spatially inhomogeneous magnetic field.

The relationship of the frequency of the NMR signal with the coordinates of the spins (molecules) in the space of an inhomogeneous magnetic field in the case of their random movement leads to irreversible phase dispersion, which can be detected by a simple change in the amplitude of the NMR signal in the spin echo technique. This effect was noticed much earlier than the publication of the principles of MRI tomography by Lautenbur (1971) and was actively used to study the processes of self-diffusion. A remarkable property of this NMR technique is that it allows one to obtain direct information about the movements of molecules in space, since the recorded phase dispersion in the linear gradient field is directly related to the dispersion of molecular displacements.

Thus, NMR with a magnetic field gradient (gradient NMR) – represents a very important direction in the development of nuclear magnetic resonance as a whole.

In self-diffusion measurements, as well as in MRI, the spatial resolution is determined by the magnitude of the magnetic field gradient. Initially, self-diffusion studies used a constant gradient over time, which could not be very high. In 1965, Steiskal and Tanner proposed a modification that opened up the possibility in principle of using substantially larger magnetic field gradient values in a pulsed mode. With the advent of this technique, hopes for a very quick and significant breakthrough naturally appeared. However, in reality, everything was not so simple. The creation of high-quality NMR equipment with a powerful pulsed gradient of the magnetic field is still a difficult task. Indeed, the requirements for the technical characteristics of the device consist of typical for NMR spectrometers (relaxometers) and a number of additional requirements associated with the use of pulsed gradient blocks. The main one is the requirement for the identity of the gradient pulses (**g**), which is hardened with increasing **g**. This is due to the fact that in experiments to study the translational mobility of molecules it is required to ensure not the relative stability of the magnetic field gradient amplitude, but the absolute one (!). There are a number of related problems: the need to exclude mechanical vibrations of the sensor; toughening the requirements for thermostatic control system; the problem of residual gradients associated with the magnetization of the magnet material and scattering fields, *etc*.

In 1973, at the Department of Molecular Physics of KSU at the initiative of A.I. Maklakov the work began on the creation of NMR equipment with a pulsed gradient of the magnetic field. At the beginning of 1974, the first result was obtained on the value of the magnetic field gradient – 1 T/m. (V.D. Skirda *et al.* See section 2.1). However, after a year and a half, this result was improved by more than an order of magnitude – 15 T/m. As the team managed to increase the resolution of the method, increasingly complex molecular systems became available for research. In 1980, an absolute record was reached for that time: 30 T/m. At that time, the best of the foreign installations in Leipzig was characterized by a gradient of 10 T/m. By 1994, a group of Kazan University (V.D. Skirda, V.I. Sundukov, D.Sh. Idiyatullin, V.A. Sevryugin, *et al.*) managed to overcome the 100 T/m value, and after 2 years – 200 T/m. In this case, the pulse power provided by the gradient block was more than 160 kW. For special studies (studying the semilocal translational mobility of polymer chains with molecular masses of more than 10^6 a.m.u.), a gradient coil with a reduced working volume (ampoule diameter 3 mm) was developed, in which at the same current power it was possible to obtain a value of 560 T/m.

It is worth noting that in 2001 publication (P. Galvosas *et. al.* // J. Magn. Res 151, (2001) P. 260–268), the ultra-high gradient of the magnetic field means the value 35 T/m, which is several times less than the result of the Kazan group. This indicates that the gradient NMR equipment in Kazan really has exceptional characteristics. Their achievement required the solution of a wide range of technical and methodological problems, including the development of special algorithms for processing primary experimental data, circuitry and design solutions. The developments at KSU are also distinguished by a small magnitude (10^{-5}–10^{-6}) of **g** instability, which made it possible to accumulate weak signals and, thereby, detect diffusion attenuation in a large dynamic range of signal amplitudes. To determine the gradient parameters, methods of absolute calibration of the **g** value were proposed, which are protected by several patents of the Russian Federation. Thus, the team of scientists and graduate students of KSU (V.D. Skirda, A.G. Stezhko, G.G. Pimenov, D.Sh. Idiyatullin, V.A. Sevryugin, V.I. Sundukov, N.V. Kashirin) back in the 90s of the past century, a complex of problems related to the creation of large (> 100 T/m) pulsed magnetic field gradients had successfully solved. This allowed the Kazan University group to become one of the world leaders in the field of gradient NMR.

Since the successful creation of gradient NMR equipment, the team of the Department of Molecular Physics of KSU has begun intensive studies of the mechanisms of translational mobility in various polymer systems, and then in other complex molecular objects. The uniqueness of the characteristics of the equipment, which was almost continuously improved, in many respects ensured the possibility of obtaining not less exceptional research results. These include:

– Experimental establishment of universal concentration and molecular-mass dependences of self-diffusion coefficients in melts and solutions of flexible chain linear polymers (V.D. Skirda, A.I. Maklakov, V.A. Sevryugin, G.I. Vasiliev) and then finding similar patterns separately for proteins (I.V. Nesmelova) and dendrimers (A.I. Sagidullin). The results obtained are not only of fundamental importance, indicating the possibility of describing the dynamic properties of the polymer chain by some universal function. From a practical point of view, such knowledge makes it possible to predict the quantitative characteristics of the translational mobility of macromolecules in solutions in the entire concentration region in the cases when the direct measurements (for example, for high molecular weight polymers at high concentrations) may not be possible;

– Obtaining the first experimental data (V.D. Skirda, A.I. Maklakov, M.M. Doroginitskii, I.R. Gafurov) on the mobility of polymer chain elements at scales comparable to the size of macromolecules, as well as in three-dimensional networks (gels). Moreover, the last result predetermined further possibilities of gradient NMR in the study of gelation processes in complex molecular systems. For the first time, the detailed studies of the gelation processes in the systems "gelatin-water", "agarose-water" and "cellulose triacetate-benzyl alcohol" has been performed (I.R. Gafurov, V.D. Skirda, A.I. Maklakov *et al.* // Polymer Science USSR – 1988. – V.30, Iss. 7. – P. 1644–1645; Polymer Science USSR – 1989. – V.31. – P. 292–300). Based on the results of these studies, conclusions were drawn about the mechanisms of gelation, the properties of the so-called sol and gel fractions. The most specific features in the behavior of the translational mobility of solvent and polymer molecules that were characteristic of gel-forming molecular systems were established. Subsequently, the accumulated experience and methodology were applied (I.Yu. Aslanyan, V.D. Skirda, A.R. Khokhlov *et al.* // Macromolecular Chemistry and Physics. – 1999. – V. 200 (9). – P. 2152–2159) to the study of an even more complex molecular system: polymethacrylic acid hydrogel under the conditions of collapse caused by the presence of the third component – linear polyethylene glycol (PEG). It was the results of these works that made it possible, in cooperation with "Kvart" company (2012–2014), to quickly and effectively solve the problem of creating high-quality water-swellable packers of domestic production. It should be noted that the level of research on gel-forming systems, achieved by the university team more than thirty years ago, is still unsurpassed;

– A detailed study of the form of diffusion decay in polymer melts and solutions in a large dynamic range of the signal amplitude and its dependence on the diffusion time. On the basis of these, as well as a number of other experimental data, including the study of binary mixtures of homopolymers, a concept was formulated (V.D. Skirda) according to which the translational mobility of macromolecules is carried out cooperatively by random supramolecular clusters formed due to interchain linkages. It must be said that the experimental results on the dependence of the diffusion decay form in polymer melts on the diffusion time obtained by the team back in the 80s have not yet been repeated in any laboratory, although an indirect confirmation of their reliability has been obtained. The fact is that at the time when these studies were carried out, the model of the so-called reptation mechanism of self-diffusion of macromolecules, proposed by the Nobel laureate P. de Gennes, virtually dominated overwhelmingly in polymer science. The indicated results of the team did not fit into the framework of this model and in fact were the first important experimental evidence of the limitations of this model approach. Only in later decades enough experimental material has been accumulated in the world to understand this fact. Currently the work of Fatkullin and Schweitzer based on the formalism of the Zwanzig-Mori projection operators method is developing a new approach that assumes a significant role of long-range intermolecular correlations. In 2006, it was theoretically shown that the implementation of the reptation mechanism in the mobility of the polymer chain is unlikely from the general thermodynamic positions (N.F. Fatkullin, R. Kimmich // Macromol. Symp. 237 (2006) 69–72);

– It was shown (G.G. Pimenov, V.A. Sevryugin and others) that in the diluted polymer solutions the concentration dependences of the self-diffusion coefficients of macromolecules are described by exponential dependences of the polymer concentration. An explanation of this result is given;

– For the first time by the gradient NMR method (A.I. Maklakov, N.K. Dvoyashkin, V.D. Skirda, R.R. Valiullin, A.V. Uryadov) the studies of systems with phase transformations both in volume and in introduced into a porous and nanoporous medium were done. Patterns specific to these systems in the behavior of partial coefficients of self-diffusion and populations of system components are established. It has been established that gradient NMR makes it possible to more accurately determine the boundary of the phase transition, since it is sensitive to the phase state of the system at scales comparable to the mean square displacement of molecules during diffusion.

Significant results include methodological developments. First of all, they concern the development of the basics of applying the gradient NMR to multiphase molecular systems and to exchange systems. It should be noted that the authors group was actually the first (back in 1987) who drew attention to the need for a joint analysis of relaxation data and self-diffusion data in the study of multiphase systems. Much later (2002), this idea was developed in the works of the M. Hurlimann group, in which, on the basis of the developed two-dimensional Laplace transform technique, it was proposed to present data on self-diffusion coefficients and relaxation times in the form of two-dimensional maps.

The developments in the field of interphase exchange research are of particular importance. The classical approach proposed by Pfeiffer and Karger is based on a methodology in which it is a priori assumed that the distribution functions of lifetimes in phases are exponential. The authors of the series of works considered for the first time the general case in which no restrictions were imposed on the distribution function of lifetimes in phases. The most interesting results of the proposed approach were manifested in the conditions of intermediate exchange. So, it turned out that even for a two-phase system (“phases” “a” and “b”), the form of diffusion attenuation is described by a continuous spectrum of self-diffusion coefficients. The main and most optimistic result is that the extreme values of this spectrum are always completely uniquely determined by the values of the true self-diffusion coefficients D_{sa} and D_{sb} in the exchanging phases, and the populations p_a and p_b of these components are decreasing functions of the diffusion time t_d, from the analysis of which the form of the distribution function of lifetimes in phases can be directly determined. In the description of the work cycle this approach is demonstrated by the example of studying proton exchange in aqueous saccharide solutions.

The significance of taking into account the features of nuclear magnetic relaxation in gradient NMR is especially high when testing the molecular system for interphase exchange. Several specialized pulse sequences to solve this problem were proposed (V.D. Skirda, V.A. Sevryugin, G.G. Pimenov).

The study of the self-diffusion of molecules in inhomogeneous media is undoubtedly the most important for the possible applications of gradient NMR. The team (A.I. Maklakov, N.K. Dvoyashkin, A.M. Khakimov, V.D. Skirda, G.G. Pimenov, R.R. Valiullin, and others) performed a significant amount of research in this area, covering both the task of studying the characteristics of the porous medium itself, and the task of determining the state and dynamics of molecules in a porous media. The complexity of the study of self-diffusion in porous media is primarily determined by the uncertainty in the structure of the porous medium itself. For different research regimes (short-time, intermediate, long-time), as a rule, separate independent approaches and techniques are developed with the aim of obtaining information about the porous medium. A team of authors (V.D. Skirda, R.R. Valiullin, A.I. Maklakov and others) developed a universal approach. In particular, to separate the effects of constraints and permeability, an expression was found that allows one to obtain information on the size of the constraints (characteristics of the porous medium) by a complete analysis of the entire dependence of the self-diffusion coefficients on diffusion time, which includes all three main regimes. The proposed approach is universal in its applicability: it allows one to obtain correct data on the size of constraints (pore size, cells, *etc*.) even in cases where the molecular system is only partially located in a porous medium.

The team of authors (A.I. Maklakov, V.D. Skirda, N.K. Dvoyashkin, R.R. Valiullin) actually has priority in detecting and then in a detailed study of the gas-liquid exchange processes in porous media with a highly developed surface. In particular, similar effects are found in studies (by N.K. Dvoyashkin, A.I. Maklakov) of oils in cores and in model porous media. Using the hexane-kaolinite system as an example, an attempt was first made (A.V. Uryadov, V.D. Skida, A.I. Maklakov) to experimentally establish the form of the distribution function of the lifetimes in the liquid phase. It was shown that the form of this function is very sensitive to the magnitude of the interaction of the liquid with the surface, which, when the porous medium is not completely saturated with liquid, determines the nature of its distribution over the porous space.

By the example of studying the processes of self-diffusion in binary porous systems (zeolites, porous glass “Vycor” *etc*.), the effect of pseudo-limited diffusion was first discovered (V.D. Skirda, R.R. Valiullin, P.V. Kortunov), which was confirmed by computer simulation.

The possibilities of using the porous media as the conditions for testing the properties of the molecular system are shown. So, in one of the cases, macromolecules of different molecular weights were introduced into the porous medium and the molecular-mass dependence of the self-diffusion coefficients of the polymer in the bulk and in the porous medium was studied. From a comparative analysis of these two dependences, a very non-trivial conclusion was drawn that the mechanism of translational mobility of macromolecules in the melt is controlled by such a factor that is suppressed when the polymer is introduced into the constrained medium. This is a very important conclusion for understanding the mechanisms of complex translational mobility of linear macromolecules. Another example demonstrates (N.V. Kashirin, V.D. Skirda, I.V. Ovchinnikov) the possibility of detecting the effects of transition states in nematic fluids. These effects were recorded only when the liquid was introduced into the porous medium. This example demonstrates the potential of gradient NMR in studies of the subtle effects of self-organization of molecules.

Another methodical development of the authors of the cycle relates to the modification (A.V. Filippov) of the well-known cryoporometry method by including gradient NMR data in an additional analysis. It is shown that in this mode, the technique, called “NMR cryodiffusometry”, gives significantly richer information about the studied object.

For the first time, the gradient NMR method was used to study (A.I. Maklakov, R.S. Gimatdinov, D.Sh. Idiyatullin *et al.*) the processes of crystallization of polymers in solutions. The relation between the self-diffusion coefficient and the dynamic degree of crystallinity is established.

Also, the polymer-plasticizer systems were first investigated (A.I. Maklakov, N.M. Azancheev, G.G. Pimenov). The relationship between the value of the recorded coefficient of self-diffusion of the plasticizer molecules and the nature of its distribution in the polymer matrix is shown. A connection is established between the translational and rotational movements of the plasticizer molecules.

A study of the translational mobility of the molecular components of such a complex molecular system as residual oil in porous media made it possible for the first time to discover (N.K. Dvoyashkin, A.I. Maklakov) the phenomenon of selective adsorption of high molecular weight oil fractions on the pore surface. A method for determining the temperature at which all components of the residual oil acquire the properties of ordinary fluid liquids is proposed.

Biological systems are justifiably related to even more complex molecular systems. In addition to water (represented to the greatest extent), they contain tens of thousands of proteins, lipids, sugars, low molecular weight substances and ions. In addition, biological systems are also characterized by an extremely complex supramolecular structural organization. Despite the complexity of the objects, it is in them that the possibilities of NMR with large magnetic field gradients can manifest themselves.

This series of works includes studies concerning mainly two types of biosystems: solutions of biomolecules and membranes.

In aqueous solutions of amyloid Aβ peptides, the research task was reduced to the necessity of registering self-aggregation processes in order to detect early signs of Alzheimer's disease. The processes of fibrin self-organization were studied (A.R. Mutina, V.D. Skirda and *et al.*) in native human blood plasma. When studying biomembranes, the advantages of gradient NMR (A.V. Filippov, M.A. Rudakova) were maximally realized by using flat multilayers oriented on a substrate as an object of study. As a result, the following important results were obtained:

– It is shown that under aggregation conditions close to equilibrium, the dimers of protein molecules for lysozyme are, and for the amyloid peptide, they are not stable intermediates. Aggregation of Aβ peptides at low temperatures and exposure to ultrasound was studied;

– The self-diffusion of water in macroscopically oriented lipid multilayers was studied. A technique has been proposed for isolating the contribution corresponding to trans-layer self-diffusion of water. The trans-layered self-diffusion of water was studied depending on hydration, temperature, and biomembrane composition;

– For the first time, the dependences of the lateral lipid self-diffusion coefficients in bicomponent lipid model biomembranes were experimentally obtained depending on chain saturation, chain length, cholesterol concentration, and degree of hydration. The mechanism of the effect of cholesterol on the local mobility of a saturated and unsaturated chain has been established. The most unexpected were the results obtained for lipids with double bonds in the chain. In this case, regardless of the lipid, the effect of decreasing the mobility of molecules with an increase in the concentration of cholesterol dominates. This experimental result led biomembrane researchers to reexamine the existing ideas about the interaction of cholesterol with phospholipids.

In conclusion, we note the following – at the beginning of the work of this cycle there were no established theoretical concepts describing molecular motion, both in polymer systems and spatially inhomogeneous. Bridging a number of gaps in this area was the work of one of the team members (N.F. Fatkullin). He obtained the following results, which are of fundamental importance:

– It was first noted that the gradient NMR method is similar to the neutron scattering method. It is shown that the wave scattering vector $\vec{k}$ should be understood as $\vec{k} = \gamma\delta\vec{g}$, where γ is the gyromagnetic ratio and δ and $\vec{g}$ are the duration and amplitude of the magnetic field gradient. In explicit form this position was first formulated in a joint monograph (A.I. Maklakov, V.D. Skirda, N.F. Fatkullin, 1987). Since then, the language of wave vectors has become generally accepted in almost all works in this field of magnetic resonance;

– Based on the density matrix formalism, the theory of a spin echo with a pulsed gradient of the magnetic field in systems with dipole – dipole interactions is developed. It is shown that for systems with slow molecular movements, depending on the ratio of the characteristic times of the system, the amplitude of the spin echo contains information about either spin diffusion or self-diffusion of the particles under study;

– The theory of spin diffusion for concentrated polymer systems is constructed. It was shown that in polymer systems with a molecular mass exceeding a certain critical value, the spin diffusion coefficient is much larger than the self-diffusion coefficient of the macromolecules themselves and is characterized by a weak temperature and molecular weight dependences. Subsequently, the presence of the effect of spin diffusion in polymer melts was experimentally proved in joint studies with the University of Ulm (Germany);

– The interaction of the spin with a random magnetic field generated by the difference in the magnetic susceptibilities of components of spatially heterogeneous media was studied. Analytical expressions are obtained for the measured diffusion coefficient, the free induction decay and the spin-lattice relaxation time for the case of freely diffusing spin in a random Gaussian field. It is shown that, depending on the experimental conditions, the observed self-diffusion coefficient can be both greater and smaller than the true self-diffusion coefficient.

2.2.4. *High Resolution Nuclear Magnetic Resonanc in structural-dynamic studies of molecular systems*

2010: “High Resolution Nuclear Magnetic Resonance in Structural-Dynamic Studies of Molecular Systems”: A.V. Aganov, R.M. Aminova, V.V. Klochkov, Sh.K. Latypov (IOPC), A.A. Nafikova (IOPC), Yu.Yu. Samitov (posthumously), A.I. Khayarov.

This series of works covers a long period – from the first steps in the USSR of high-resolution NMR in chemistry to the time when this method became an integral part of structural, structural-dynamic, and kinetic studies.

From left to right: A.Yu. Samitova, A.I. Khayarov, A.A. Nafikova, M.Sh. Shaimiev, Sh.K. Latypov, A.V. Aganov, V.V. Klochkov, R.M. Aminova

In 1960–1965 Kazan State University was among the first in the USSR where under the leadership of Yu.Yu. Samitov a complex of high-resolution NMR spectrometers had been created (see section 2.1). At that time all of them had high characteristics, comparable with the first foreign spectrometers; the first results in the country of structural studies in chemistry by the ^{1}H, ^{31}P NMR methods (1960–1964) were published; the widespread implementation of NMR in chemical research practice began not only in Kazan, but also far beyond its borders.

Subsequently, by upgrading the spectrometers HA-100D (Varian, USA), WH-90 (Bruker, Germany), a unique complex was created for specialized NMR experiments, which made it possible to carry out experiments that are fundamentally important for all classes of studied organic and organophosphorus compounds, namely, it became possible to record the spectra of heteronuclear double resonance (^{1}H–{^{31}P^{tot}}), (^{1}H–{^{31}P^{sel}}), triple resonance spectra (^{1}H–{^{1}H^{tot}}{^{31}P^{tot}}), (^{1}H–{^{1}H^{sel}}{^{31}P^{tot}}) and (^{1}H–{^{1}H^{sel}}{^{31}P^{sel}}) with broadband or selective irradiation of phosphorus nuclei; facilities for carrying out experiments in the selective relaxation mode were created and the methodology of these experiments was developed, which made it possible to measure relaxation times T_1, T_2, $T_{1\rho}$ and carry out magnetization transfer experiments (according to the Forzen-Hoffman method which was modified); a new inertia-free system was developed, which allows one to vary the sample temperature in the range 123–423 K and stabilize it with an accuracy of ±0.2 K; temperature control was provided at the sample location in the NMR probe; the Bruker WH-90 spectrometer was adapted to measure the selective relaxation times T_1 and T_2 and to conduct studies at even lower temperatures (down to 113K for solutions), *etc*. (Yu.Yu. Samitov, A.V. Aganov, A.I. Khayarov, R.Kh. Sadykov, P.P. Chernov *et al*.).

In order to extract information about the spatial structure of the molecules based on the high resolution NMR spectroscopy:

– For the first time in the USSR (1960), quantum chemical methods and approaches began to develop for the theoretical interpretation of the magnetic resonance parameters of complex molecular systems;

– For the first time, methods of theoretical interpretation of the parameters of the NMR spectra were applied to establish the spatial structure of 1,3-sulfite and carbonate, a number of 1,3-dioxanes and 1,3-dioxolanes;

– A theoretical interpretation of the Proton Magnetic Resonance (PMR) spectra of ferrocene derivatives, unique for that time new “sandwich” compounds with an unusual electronic structure, is given;

– Quantum chemical calculations of the magnetic susceptibility anisotropy $\Delta\chi$ of cyclopropane and oxide three-membered rings were done for the first time, which were used to analyze the PMR spectra and establish the structure of stereoisomers of natural compounds, in particular, a number of bicyclic terpenes and their oxides (α- and β-oxides of Δ^3-karen, pinene, α- and β-forms of karanol-4 and karanon, bicyclo [3.1.0] and [4.1.0] hept-3-enes) (Yu.Yu. Samitov, R.M. Aminova *et al.*).

Subsequently, the calculated $\Delta\chi$ values were successfully used to establish the structure of many compounds containing cyclopropane or oxide fragments, and the theoretical values of the anisotropy of the diamagnetic susceptibility $\Delta\chi$ of various bonds (S–O, S=O, Se–O, Se=O, C–C, C–O, C=C, N–N) and the lone pair of electrons of the oxygen atom were used to analyze the structure of other classes of six-membered heterocyclic compounds such as selenites, 1,3-dithianes and dithiolans, oxazines, *etc*.

Based on calculations of the spin-dipole, orbital, and contact contributions to the spin-spin coupling constants, it was shown that the spin-spin interaction with the participation of the phosphorus nucleus is mainly determined by the Fermi contact mechanism, quantum-chemical calculations of the stereochemical dependences of the spin-spin interactions constants have been successfully used to establish the spatial structure of many molecules.

To develop more rigorous approaches for interpretation of the experimental NMR data as compared with methods based on taking into account magnetic anisotropic and electrical effects, R.M. Aminova and her students developed a theory of constants of nuclear magnetic shielding, as well as corresponding computer programs based on variational methods (direct variational methods and variational methods of perturbation theory).

It was found that the use of gauge-invariant atomic orbitals to describe the wave function of a molecule perturbed by a magnetic field and non-empirical wave functions of the ground state even in a simple basis of atomic orbitals allows calculating the proton magnetic shielding constants of molecules with good accuracy, while the results were successfully correlated with foreign literature data. The development of variational methods has led to the necessity of calculating a large array of integrals. This problem was successfully solved for the first time using the approximation of atomic orbitals by Gaussian functions.

Based on the developed methods for calculating the screening and magnetic susceptibility constants and the corresponding computer programs, the possibility of using localized molecular orbitals to successfully evaluate the contributions to chemical shifts from various localized fragments and bonds of the molecule was shown. This approach was used to establish the spatial structure of molecules based on the NMR spectra.

Diagrams of magnetic iso-screening lines convenient for practical applications were calculated in the vicinity of various bonds and lone electron pairs (C–C, C–H, C–N, C–O, P–C, O–O *etc*.). Numerous diagrams of isoscreening lines, as well as theoretically justified angular correlations of the spin-spin interaction constants, were subsequently widely used in the structural NMR analysis.

Theoretical estimates of chemical shifts turned out to be extremely useful when studying stereochemically non-rigid molecules by NMR methods for which a multicomponent conformational equilibrium takes place. For a number of derivatives of stereochemically nonrigid seven-membered 1,3,2-dioxaheterocycles, as well as their six-membered heteroanalogs, the observed NMR spectral regularities were generalized and theoretical interpretation was given based on the calculations of proton chemical shifts.

A theory has been developed (R.M. Aminova *et al.*) of the proton magnetic shielding constants and their changes under the influence of electric fields created by the polar groups of the molecule. Formulas were obtained that allow calculating more strictly the contributions to the chemical shifts of various bonds due to the electric influence of the polar groups of the molecule.

It has been established that electrical effects play a major role in the mechanism of molecular cluster formation, leading to the formation of supramolecular ensembles and nanostructures. The dependence of screening constants on the effect of electronic redistribution was studied for various associates of pyrimidine bases whose macromolecular derivatives are prone to significant intermolecular interactions and to the formation of well-ordered supramolecular structures. The magnetic screening constants of ^{1}H, ^{13}C nuclei were calculated taking into account electronic correlation in the framework of the modern DFT method, and the nontrivial nature of the changes in these magnetic resonance parameters in supramolecular systems was established.

To simulate the spatial structure of a molecule in a crystalline environment, as well as the structure of a molecule in solution:

- A method was developed for constructing large molecular clusters;
- An improved version of the program for calculations by molecular mechanics was developed, in which the periodicity of the crystal lattice was taken into account and more complex force fields were introduced to take into account the contributions of long-range interactions.

Modeling the crystal structure and quantum chemical calculations using the functional density method of the screening constants of ^{13}C nuclei made it possible to establish the most probable packing scheme of molecules in the crystal for a number of compounds and explain the reasons for the complicated structure of ^{13}C nucleus signals in the powder in comparison with the spectrum of this compound in solution. Quantum-chemical calculations of the screening constants of molecular clusters of a dissolved molecule surrounded by solvent molecules were carried out, which made it possible to establish the structure of the solvate shell (R.M. Aminova, A.A. Nafikova, A.V. Aganov, V.V. Klochkov, A.R. Yulmetov *et al.*).

Important results were obtained in the field of application of NMR to the study of chemical metabolic systems. A set of programs was created (V.V. Klochkov), which made it possible to analyze the line shape of the NMR signals in the entire temperature range of measurements, and experimental approaches were developed to determine the thermodynamic parameters (free activation energy ($\Delta G^{\neq}$) and equilibrium (ΔG_0); enthalpy of activation ($\Delta H^{\neq}$) and equilibrium (ΔH_0)), which characterize intramolecular rearrangements.

For the first time, a complete analysis of the problems that arise when using one-dimensional dynamic NMR to solve structural-dynamic problems in complex molecular systems, including the environmental factor, was carried out and methods for overcoming them were proposed. (A.V. Aganov, V.V. Klochkov). Using selective non-stationary methods of DNMR, a set of approaches has been developed for conducting unique DNMR experiments in the gas phase and solutions at extremely low temperatures. All this made it possible to expand the range of measured rate constants of chemical exchange and to study processes characterized by the thermodynamic activation parameters from 25 to 120 kJ/mol, which are limiting for high-resolution NMR spectroscopy. Based on the developed techniques in dynamic NMR spectroscopy, various molecular rearrangements in medium-sized heterocycles, penta- and hexacoordinated polyhedral structures, *etc.*, were discovered and described in detail. For the first time, conformational laws were established in various phase states: gas–solution (melt) – molecular crystal (A.V. Aganov, Sh.K. Latypov, A.A. Nafikova, A.I. Khayarov, A.R. Yulmetov *et al.*).

Using ^{1}H and ^{13}C NMR spectroscopy in the temperature range of solutions 133–293 K, the conformational composition of a large number of six-, eight-, and twelve-membered mono-substituted carbocycles; six-, seven-, eight-membered heterocycles (containing O and S) with a variation of atoms [C, P^{III}, P^{IV}, As^{III}, Sb^{III}, Se, S] in the second position was studied. The conformational composition of these compounds is described; at the same time, almost all known types of processes were observed for them, such as the exchange between energetically equivalent conformers such as chair – chair, twist – twist, twist-boat – twist-boat, boat – boat, boat – chair – boat – chair, and exchange processes between energetically nonequivalent conformers such as chair-a-chair-e, chair-twist, chair-e-boat-e, boat-e-chair-e, *etc*. A large array of data has been obtained (activation, equilibrium) characterizing these processes of chemical exchange in heterocyclic systems (A.V. Aganov, V.V. Klochkov *et al*.).

It was experimentally shown that, when analyzing the activation parameters of interconversion of cyclic molecules, the principle of additivity of the energy properties of a substituent can be applied, according to which the change in the chemical structure due to the introduction of one or another substituent entails a change in the activation parameters of the conformational transition by a value characteristic of this type of substitution.

An approach was proposed (V.V. Klochkov) for determining the proton distances in small organic molecules that fall under the condition of fast motion ($\omega_0\tau_c <<1$; τ_c is the correlation time, ω_0 is the resonance frequency of the nuclei), by a combination NMR NOESY experiment with data processing methods.

An expression is obtained that relates the cross-relaxation rate, the exchange rate constant, and the integrated intensities of cross- and diagonal peaks in the spectra of two-dimensional NMR spectroscopy (NOESY modification) for a system of two spins in the absence and presence of a scalar spin-spin interaction between them. An approach has been proposed for separating the contributions of cross-relaxation and chemical exchange, based on the analysis of temperature changes in the integrated intensities of cross-peaks between two magnetic nuclei (V.V. Klochkov, B.I. Khairutdinov *et al*.).

V.V. Klochkov and coworkers developed an approach for determining conformations of nanoscale molecules that are subject to fast motion dissolved in magnetically oriented lyotropic liquid crystal systems, which is based on the analysis of residual dipolar couplings (RDC) between ^{13}C and magnetic nuclei ^{1}H, separated by one chemical bond. Based on this approach, the spatial structure of nanoscale oligopeptides was determined: the Glu-Trp dipeptide, which is the main component of the drug; tripeptides Gly-Gly-Gly, Gly-Gly-His, Gly-Gly-Tyr, Glu-Cys-Gly, which are used as ligands in complexes with Cu (II) and are used as models of active centers of enzymes; tetrapeptide nAc-Ser-Phe-Val-Gly-OMe, a model oligopeptide in the study of intermolecular interactions of peptides with solvents.

A ^{2}H NMR spectroscopy method is proposed for determining the boundaries of the existence of a magnetically oriented lamellar L_α phase (in temperature – concentration plots) of micelle-forming compounds based on the quadrupole splitting of ^{2}H NMR signals of deuterated water. A lyotropic liquid crystal system of n-alkyl-poly (ethylene) glycol ($C_{12}E_5$), dimethyl sulfoxide and water is proposed and studied, which can be used to partially orient water-insoluble (or poorly soluble) organic or bioorganic molecules in water and determine the boundaries of magnetically-oriented lamellar L_α phase for this medium.

Sh.K. Latypov proposed a comprehensive approach based on the combined use of NMR correlation methods and quantum chemical estimates (*ab initio*) of chemical shifts (CS) to establish the chemical structure of organic compounds. The possibilities and limitations of this approach are systematically analyzed. The isomeric structure of a number of practically important compounds (quinoxalines, quinolinones, coumarins, fullerenes) was “directly” established. Theoretical foundations have also been developed for determining the absolute configuration of chiral molecules by NMR and the design of chiral derivatizing reagents (CDR). The main factors determining the reliability of this approach and the limits of its applicability are identified. The principles of rational design of CDR are formulated. New effective reagents for the analysis of secondary/primary alcohols, primary amines, and α-substituted carboxylic acids have been developed and experimentally tested. It was shown for the first time that the absolute configuration of secondary alcohols can be determined by synthesis and analysis of the NMR spectrum of only one of the diastereomers by comparing the ^{1}H NMR spectra at two temperatures. For the first time, a stereoscopic model was developed to determine the absolute configuration of secondary alcohols by chemical shifts of groups directly related to the chiral center of the reagent.

A.A. Nafikova (Musina) *et al.* studied the conformational and supramolecular structures of a number of macrocyclic derivatives of pyrimidine bases and found that for macrocycles with a certain spacer length, a “folded” structure is realized in solution, which is stabilized due to intramolecular hydrogen bonding. It was found that this intramolecular packing is destabilized upon protonation due to competition with intermolecular hydrogen bonds, which, in turn, leads to specific self-association, in which the acid counterion plays the role of a non-covalent bridge.

Methodological aspects of the combined use of relaxation and diffusion high resolution NMR methods to solve the structural problems of supramolecular systems are developed. The possibilities and limitations of the 2D DOSY method in these studies are shown. A number of individual/binary and multicomponent systems that are prone to association/self-association have been studied, and it has been shown that they can serve as models of various molecular devices (molecular capsule, two/three component molecular machine, pseudo-rotoxane, *etc.* (Sh.K. Latypov, A.V. Aganov and others).

The research results are summarized in five monographs. Among them is the unique “Atlas of NMR spectra of spatial isomers” (volumes 1, 2) (Yu.Yu. Samitov).

In these work cycles, the results of the long-term work of the teams created by the pioneers of magnetic resonance in the USSR and Kazan University on the topics that they formed at the dawn of magnetic resonance were summed up, and to a certain extent this is our tribute to their memory.

Until 1995, work in the field of magnetic resonance was carried out within the framework of the Main Scientific Research Direction (MSRD) of KSU (scientific school) “Resonant Properties of Condensed Matter” (headed by B.I. Kochelaev). In 1995, the MSRD “Biomedical Radiospectroscopy and Optics” stood out from it (headed by A.V. Aganov and V.D. Skirda). According to the MSRD “Resonant Properties of Condensed Matter” (headed by B.I. Kochelaev and A.V. Aganov), physical research continued, in which the teams of A.V. Aganov and V.D. Skirda took part. After a complete transition to project financing, these areas were adapted (formalized) to solve complex problems in the adopted strategic areas of the University’s development. In fact, in two of the four natural sciences directions of the Institute of Physics, all groups of magnetic resonance, or, to be precise, radiospectroscopy, take part.

1. Promising materials (structure and properties of new substances and materials, including that for quantum technologies. Coordinator – Prof. D.A. Tayurskii).

2. Studies of biomedical systems by physical methods. Coordinators – Prof. A.V. Aganov and Prof. V.D. Skirda.

3. In accordance with the requirements of the time, the research direction “Development of applications in various sectors of the economy (in the oil and gas, petrochemical, chemical, pharmaceutical, *etc*.)” was allocated. Almost all groups of magnetic resonance also participate in it. Below are the earlier main publications related to these areas, but not included in the given cycles of works directly related to the works of the last decade. The total number of publications is too large to be cited in a short article. Below are the only brief descriptions of the research results and only a part of the main publications. Naturally, these studies are based on magnetic resonance studies. However, studies on the resonance properties of condensed matter are also given, since they stimulate the development of magnetic resonance methods.

2.3. Theoretical and experimental studies in the field of magnetic resonance and related phenomena in the main scientific areas of the Institute of Physics of Kazan University of the modern period

2.3.1. *Research direction “Advanced materials – structure and properties of new substances and materials, including materials for quantum Technologies”*

The physics of strongly correlated systems is one of the hottest topics in condensed matter physics. The group headed by B.I. Kochelaev (S.I. Belov, A.M. Skvortsova, E.V. Shilova, A.S. Kutuzov, A.V. Vishina) together with foreign partners in this field, a large cycle of work has been carried out.

B.I. Kochelaev proposed the idea of using paramagnetic probes inside the CuO_2 planes to measure the magnetization relaxation rates in cuprate high-temperature superconductors, which was implemented in a joint study with a group of Professor B. Elschner at the University of Darmstadt (Germany) [20a, b]. Further research was carried out in collaboration with a group of Nobel Prize winner Professor K.A. Mueller from the University of Zurich (Switzerland) [21a–e]. This work led to an understanding of the nature of very fast spin relaxation of electrons and the development of a model explaining the observed phase separation into nanoscale metal and dielectric domains in CuO_2 planes [22a]. B.I. Kochelaev solved the long-standing problem of “unobservable EPR” in superconducting cuprates and showed that it is caused by a very fast spin-lattice relaxation of Cu ions at a rate significantly enhanced by the exchange coupling between them [22b].

B.I. Kochelayev proposed a new approach based on the idea of spin waves in media with topological excitations (skyrmions) [22c], and together with students (S.I. Belov, A.M. Skvortsova, A.S. Kutuzov) described from general grounds both the static and dynamic parameters of layered manganites, such as the spin coherence length, magnetic susceptibility, *etc*. Their cooperation with the experimental groups of Professor

H.-A. Krug von Nidda and Professor Alois Loidl from the University of Augsburg, as well as with the group of Dr. J. Sichelschmidt from Dresden, was extremely fruitful [22d–f]. The kinetics of electron spin in substances with giant magnetoresistance was studied by EPR, and the EPR spectra of compounds with heavy fermions below the Kondo temperature were studied. It was shown that the absence of the Slichter peak established in some superconductors by means of EPR measurements and the unexpected detection of the EPR signal in the Kondo lattice with heavy fermions below the Kondo temperature are the consequences of the formation of collective spin excitations of paramagnetic ions and conduction electrons.

Together with colleagues (S.L. Tsarevsky, Yu.N. Proshin, M.G. Khusainov) and graduate students from Yakutsk (E.P. Sharin, S.A. Efremova) the problem of the NMR shape line in second type superconductors was solved, including high-temperature superconductors, in oblique magnetic fields, taking into account changes in the inhomogeneity of the magnetic field of the vortex lattice and the skin effect near the surface of the superconductor. It was shown that NMR makes it possible to obtain more detailed information about the parameters of a superconductor, in particular, about its anisotropy parameter [22h–i].

In the field of magnetic resonance B.Z. Malkin[19] and co-workers studied coherent dynamics and relaxation of electronic and nuclear magnetic excitations, spin relaxation of implanted muons depending on the concentration of rare-earth impurity ions in oxide and fluoride crystals with scheelite structure taking into account cross relaxation, spin diffusion, and phonon bottleneck in spin-lattice relaxation [23a–f].

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[19] Boris Zalmanovich Malkin is better known as a theoretical physicist, expert in the field of optical spectroscopy of crystals (winner of the D.S. Rozhdestvensky Prize 2019 for the series of works “High-resolution spectroscopy of crystals containing rare-earth ions” https://media.kpfu.ru/news / professoru-kafedry-teoreticheskoy-fiziki-instituta-fiziki-malkinu-bz-prisudili-premiyu-ran-im, awarded the E.F. Gross medal (2016) and the S.I. Vavilov medal for outstanding achievements in the field of coherent spin dynamics excitations in crystals doped with rare-earth ions (2019).

He developed a microscopic theory of the anti-crossing of electron-nuclear sublevels in the spectra of rare-earth ions due to random deformations of the crystal lattice [24a–c] and a method for identifying the spectral characteristics of rare-earth ions in multicenter systems based on data from complex studies of optical and EPR spectra and inelastic neutron scattering spectra [24d].

In the works of M.V. Eremin [25a–g] and colleagues the results of ***studies of the EPR and NMR spectra of concentrated paramagnets*** are presented. An analysis is made of the temperature and angular dependences of the magnetic resonance lines. The parameters of anisotropic spin-spin interactions are determined.

As noted above, a large cycle of work on the study of magnetic resonance and relaxation in dielectric Van Vleck paramagnets in strong magnetic fields begun under the guidance of S.A. Altshuler and then continued by M.A. Teplov, who untimely passed away in the prime of his life (1998), was awarded the RT State Prize in the field of science and technology in 2006. This topic has been completed. In [26] one can find the necessary references to research in this area.

From the works of the early period, the ***study of spin kinetics in paramagnetic crystals at low and ultra-low temperatures*** should be noted (D.A. Tayurskii, B.I. Kochelaev). D.A. Tayurskii constructed the theory of magnetic resonance and spin relaxation in dielectric paramagnetic crystals at low and ultra-low temperatures, under conditions when the magnetic moment energy in an external field is of the same order or more than the thermal energy. Due to the strong thermodynamic coupling under these conditions, the dynamics of the electron-nuclear spin system acquires a complex nonlinear character, and the characteristic relaxation times depend exponentially on temperature [27a–e].

Magnetic relaxation of liquid helium-3 in limited geometry (D.A. Tayurskii, M.S. Tagirov, A.V. Klochkov, A.V. Egorov, V.V. Naletov, G.V. Mamin, E.M. Alakshin and R.R. Gazizulin, V.V. Kuzmin, K.R. Safiullin, A.N. Yudin). The most important results are published in [28a–j].

The mechanism and regularities of accelerated magnetic relaxation of the nuclear spins of liquid helium-3 under conditions of limited geometry – in nanopores of powder compounds, in nanocracks on crystalline surfaces, in aerogels, carbonizates, have been established. It was found that, in addition to the surface paramagnetic centers, the relaxation of the nuclear spins of liquid helium-3 is significantly affected by the modulation of the dipole–dipole interaction by the diffusion motion under conditions of very limited geometry, when only resonance modes of diffusion motion "survive". The complex of the results formed the basis of the cryoporometry method using liquid helium-3. It has been established that the surface paramagnetic centers in the studied carbonizates are highly concentrated, have an exchange-narrowed EPR line, and freely interact with ^{3}He nuclei located in the system. It is shown that there is a reliable magnetic coupling between the system of electronic spins of paramagnetic centers and the ^{3}He nuclear system. The EPR spectrum of the surface paramagnetic centers can be saturated. Based on the above data it was concluded that this system can be used to implement the ^{3}He dynamic polarization method.

Studies by NMR/NQR and muon spectroscopy of various phases of Na_xCoO_2 sodium cobaltates with different sodium contents, as well as the superconducting phase $Na_{0.35}CoO_2{\cdot}1.3H_2O$ with $T_C \sim 4K$. A large work has been performed by D.A. Tayurskii with co–workers (I.R. Mukhamedshin, A.V. Dooglav, *et al.*) in collaboration with foreign colleagues.

Six stable phases were identified in the phase diagram section with a sodium content of $0.65 < x < 0.9$, three of which transform into the magnetically ordered state at low temperatures. It was shown that in the phase with $x = 0.35$ and the superconducting phase, a single charge state of cobalt atoms and a lack of ordering of sodium atoms are observed. In all phases with sodium content $x > 0.45$, the ordering of sodium atoms is observed. Using NMR and NQR, the structure of the ordering of sodium atoms in the compounds $Na_{2/3}CoO_2$ and $Na_{0.77}CoO_2$ was determined. This ordering in $Na_{2/3}CoO_2$ leads to the charge separation of cobalt atoms in planes into two sublattices: a triangular lattice of nonmagnetic Co^{3+} and a kagome type lattice consisting of magnetic Co atoms with a charge state of 3.44+, for which an unusually large anisotropy of magnetic properties was experimentally discovered. This charge separation of cobalt atoms into the nonmagnetic Co^{3+} state and magnetic with a cobalt charge of ~ 3.5+ turned out to be characteristic for different phases of sodium cobaltates with $x > 0.55$, and differences in the ordering structure of sodium atoms cause differences in the magnetic properties of different phases. The most important results were published in [29a–l].

New methods for characterizing the magnetic properties of nanoparticles and nanoscale pores using ^{3}He NMR at low temperatures. (M.S. Tagirov, E.M. Alakshin, R.R. Gazizulin, T.R. Safin, A.V. Klochkov, V.V. Kuzmin, S.B. Orlinsky, G.V. Mamin, K.R. Safiullin *et al*.).

Using NMR methods, the effect of microwave irradiation on the restructuring of nanosized crystalline PrF_3 powders was found. A series of nanosized crystalline PrF_3 powders was synthesized in KFU [30a]. The spin kinetics of ^{3}He in contact with LaF_3 and PrF_3 nanosized powders with various crystallites sizes synthesized in KFU was studied. The channels of nuclear magnetic relaxation of ^{3}He were established. Peculiarities of the effect of cross-relaxation transfer of magnetization in the “^{3}He – nanosized PrF_3 powder" system were found [30b, c].

The study with non-linear magnetic resonance methods of Bose-Einstein condensation of magnons (headed by M.S. Tagirov, Yu.M. Bunkov). Group members: PhD’s R.R. Gazizulin, T.R. Safin, A.V. Klochkov, E.M. Alakshin, V.V. Kuzmin, S.B. Orlinskii, G.V. Mamin, K.R. Safiullin).

This phenomenon is a magnetic analogue of superfluidity and superconductivity, has great potential for use in various applications, from signal processing, quantum memory, supersensitive sensors, smart materials with controlled properties, to quantum computing. However, the application of the Bose-Einstein condensation phenomenon was previously limited to its observation only at record low temperatures. In the works of the group of M.S. Tagirov – Yu.M. Bunkov it was found that in two $CsMnF_3$

samples the free induction decay signals in the BEC state (Bose – Einstein condensation) of magnons after prolonged radio frequency pumping were significantly lengthened compared to the linear regime [31a, b]. Finally, Bose-Einstein condensation of magnons was found in yttrium ferrite garnet films at room temperature. This revolutionary discovery can be compared with the long-awaited discovery of superconductivity at room temperature, which opens up the possibility of its widespread use. The results are presented in [32a–i].

Magnetic systems of reduced dimensionality, ultra-thin magnetic films and magnetic heterostructures. In recent decades, these advantages of magnetic resonance as extraordinary sensitivity, the ability to act as a probe in multicomponent compounds and structures, the exceptional subtlety in the reaction to local environments and fields have made it possible to extend its applications to low-dimensional magnetic systems, ultra-thin magnetic films and magnetic heterostructures.

So, in a series of works by I.R. Mukhamedshin, D.A. Tayurskii, L.R. Tagirov [33a–f] and their colleagues a quasi-two-dimensional sodium cobaltates, quasi-one-dimensional triple iron chalcogenides and quasi-two-dimensional binary and mixed iron chalcogenides were studied, in which mutual correlation of magnetism and superconductivity completely non–coincidentally connected with low dimensionality of the lattice, and the compounds themselves are closely related to the high-temperature superconductors.

Ultra-thin film heterostructures. Modern nanotechnologies make it possible to operate with monolayers and nanometers of substances and compounds, combining synthetic nanostructured materials of them that are not found in nature. Moreover, they allow combining the antagonistic materials into layered structures, the new functional properties of which are due solely to the contacts of their components and the quantum-mechanical transparency of the layers themselves for quasiparticles that determine their properties. In most cases, these are ultra-thin-film heterostructures, for the construction of models of which the magnetic resonance methods as ferromagnetic resonance and nuclear magnetic resonance have proven to be very useful. Thus, L.R. Tagirov and his colleagues from KPhTI, Kazan Scientific Center, RAS, Gebze University of Technology, Turkey, University of Augsburg, Germany, and the Academy of Sciences of the Republic of Moldova investigated ultrathin films and thin-film heterostructures combining the antagonistic states of superconductors and ferromagnets, using which they demonstrated the reentrant superconductivity and functional property of a switch between the superconducting and normal states using a small magnetic field [34a–i].

Superconductivity in heterostructures. Note that the theoretical prediction of reentrant and periodically reentrant superconductivity in ferromagnet-superconductor (F/S) heterostructures was made by M.G. Khusainov and Yu.N. Proshin back in 1997 [35a]. A detailed analysis of this and other works on the proximity effect in F/S systems can be found in the highly cited review, the first in the world to appear on this topic, written by them together with academician of the RAS Yu.A. Izyumov (IMP UB RAS) [35b]. Among the later works of this theoretical group (Yu.N. Proshin, M.G. Khusainov, S.L. Tsarevsky, N.G. Fazleev, M.M. Khusainov, M.V. Avdeev, V.A. Tumanov) we note the work on the magnetic and transport properties of these systems [35c–i], including the effects of solitary reentrant superconductivity [35j, k] and the manifestations of the hidden pairwise interaction of electrons of a ferromagnet in contact with a superconductor [35l]. Thus, e.g., in cooperation with Yu.V. Goryunov, an experimenter at KPhTI, they investigated the superconducting and magnetic properties of the layered system (Fe/Cr/Fe)/V/Fe with a change in the thickness of the chromium interlayer, including the method of ferromagnetic resonance. It was shown that, with a change in the Cr interlayer thickness, nonmonotonic oscillations of the critical temperature T_c of a large-amplitude (more than 2 K!) arise, which was explained in the framework of the proximity effect theory by relating these oscillations to the features of the magnetic structure of the samples [35m].

SiCN ceramics doped with transition metal ions possesses superparamagnetic properties and is a very promising material for the creation of high-temperature magnetic sensors and pressure sensors [36a]. EPR and FMR methods can provide important information about the properties of SiCN ceramics and their magnetic derivatives, in conjunction with the study of their magnetic and electrical properties. Fruitful cooperation of S.I. Andronenko[20] and a group of experimenters from KFU (A.A. Rodionov, R.V. Yusupov, I. Gilmutdinov) with Prof. S.K. Misra (Misra, Sushil K.) from Concordia University (Montreal, Canada) on EPR and FMR study of SiCN ceramics and magnetic derivatives of SiCN is reported in [36b–d]. They are summarized in the chapter of the monograph [36e].

We also note the highly cited papers of this group devoted to the study of magnetic semiconductors $Zn_{1-x}Fe_xO$ [36f, b] and the Griffiths phase [36g] by the EPR method.

The work of I.A. Larionov, in part carried out jointly with foreign colleagues, presents ***studies of the dynamic spin response in high-temperature superconducting layered cuprates*** [37a–e]. Analytical expressions are obtained for dynamic spin susceptibilities by using the Mori-Zwanzig projection operator's technique in the paramagnetic state, in the doping region from a pure antiferromagnetic dielectric to an optimally doped (maximum T_c) high-temperature superconducting layered cuprates. The representation used correctly takes into account the role of all wave vectors of the Brillouin zone. Within the framework of a unified approach, the behavior of the experimentally observed spin-lattice

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[20] S.I. Andronenko, last 10 years senior scientist of Department of Theoretical Physics, KFU, defended his doctoral dissertation. Previously, he worked as a researcher at the Laboratory of Electronic Processes, created by V.A. Ioffe at the Institute of Silicate Chemistry, Academy of Sciences of the USSR (now RAS). Then for a long time he worked in a group of prof. Misra, S.K. (Misra, Sushil K.). V.A. Ioffe first began to use EPR (since 1960) to study defects (oxygen defects, vacancies, holes, and also paramagnetic impurity ions) in oxides and their effect on the electrical properties of oxides. V.A. Ioffe actively collaborated with S.A. Altshuler, A.A. Antipin, I.N. Kurkin *et al.* (MRS Laboratory at the Department of Quantum Electronics and Radiospectroscopy, KFU).

relaxation rates of copper $^{63}(1/T_1)$ and oxygen $^{17}(1/T_1)$ nuclei [37a, b], as well as experiments on inelastic neutron scattering, including the ω/T scaling of the imaginary part of the dynamic spin susceptibility, averaged over the Brillouin zone [37c], and the resonant inelastic X-ray scattering (RIXS) data [37d] are explained, which is achieved by taking into account the thermal damping of elementary excitations in the form of spin waves (paramagnons) in layered cuprates $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$ in the range of doping indices from 0 to optimal and temperatures above T_c.

It was also shown that the obtained damping value of elementary excitations in the form of spin waves (paramagnons) in the layered cuprates $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$ in the RIXS data analysis fundamentally depends on the analytical expressions used for the imaginary part of the dynamic spin susceptibilities [37d].

In the lightly doped superconducting $Y_{1-x}Ca_xBa_2Cu_3O_y$ phase, the divergence of $^{89}(1/T_1)$ with decreasing temperature is associated with a slowdown of excitations, possibly associated with the sliding motion of orbital currents or with the accompanying “freezing” of antiferromagnetically correlated spins [37e].

The development and application of magnetic resonance methods for the study of promising materials and nanostructures is presented in a series of works [38a–f], performed by a large group of experimenters (coordinating leaders M.S. Tagirov and S.B. Orlinskii).

The advantages of pulsed and high-frequency EPR/ENDOR methods are demonstrated for studying changes in the composition (doping) and functionalization of surfaces of a wide class of substances, (nano)crystals and thin films of the semiconductor, optical, biomedical, chemical industries: ZnO, AlN, SiC, Al_2O_3, and other various impurities, in order to determine the chemical composition and “purity” of nanoparticles, identify paramagnetic centers and establish their localization sites, which is extremely important for monitoring the processes of nanoparticle synthesis and their surfaces with a predetermined chemical composition and structure.

It was shown in [39a–f] that the use of high-field pulsed EPR and ENDOR methods allows one to separate signals from defects in the core of a nanodiamond and on its surface. In addition, in some cases it was possible to identify the chemical nature of these defects.

Spin manipulations for quantum computing. Co-workers of the Magnetic Resonance Laboratory (I.N. Kurkin, M.R. Gafurov, R.M. Rakhmatullin, S.B. Orlinskii, G.V. Mamin) and the Department of Theoretical Physics (E.I. Baibekov, B.Z. Malkin) together with foreign colleagues, has demonstrated the possibility of using the electronic states of impurity ions in crystals as a basis for elementary quantum logic cells – qubits [40a–g]. These states were controlled by pulsed EPR methods using the capabilities of commercial EPR spectrometers. In [40a] (see also [23c]) the performance of up to 10^4 consecutive single-qubit logical operations on the states of the Yb^{3+} ion in a $CaWO_4$ crystal has been demonstrated. The electronic spin nutations of impurity ions Cr^{5+} [40b], Nd^{3+} [40c], Gd^{3+} [40d], arising under the influence of a microwave pulse at the resonance frequency, were studied. The demonstration of spin nutations is a necessary step for the successful implementation of quantum computing algorithms using the electronic qubits. The processes of electron spin relaxation that occur directly during the action of a microwave field pulse on an ensemble of spins, as well as the contributions of various mechanisms to the attenuation of electron spin nutations, were theoretically studied in [40e–h]. It turned out that the decay times of spin nutations significantly differ from the values calculated using the mechanisms of phase relaxation (between microwave pulses) known in the literature. In [40e, i], the role of the nuclear ensemble in the relaxation of the electron spin in the presence of a resonant microwave field was studied using the example of the V_{15} molecular magnet and the spin marker, the TEMPO nitroxyl radical.

University staff S.B. Orlinskii and G.V. Mamin with partners from the A.F. Ioffe Physical–Technical Institute, Holland, and Germany (P.G. Baranov, J. Schmidt *et al.*) ***carried out an extensive research in the field of high-frequency EPR and ENDOR of modern materials.*** The main results are presented in publications [41a–n].

EPR in studies of the fundamental processes of photoinduced charge separation in organic electron-donor-acceptor systems. The development of energy sources based on the direct conversion of solar energy into electrical energy is currently the one of the highest priorities in the physics and chemistry of organic materials. The light-induced electron transfer in organic electron-donor-acceptor systems generates an anion/cation pair of radicals that are sufficiently stable at low temperatures up to ~ 130 K. Thus, these radicals are important objects for studying light-induced charge separation by EPR and its multi-resonance derivatives (double electron-electron resonance (DEER), electron-nuclear double resonance (ENDOR), triple electron-nuclear-nuclear resonance (TENNR), *etc*.). The main results of the collaboration of research groups of Kazan Federal University (A.V. Aganov, G.V. Mamin, S.B. Orlinskii, V.V. Klochkov, A.A. Konkin, M.R. Gafurov, V.G. Shtyrlin) and the Technical University of Ilmenau (Uwe Ritter, A.L. Konkin and others), mainly in the study of a number of new derivatives of fullerenes (electron acceptors) synthesized in TU-Ilmenau, are reported in [42a-h]. The technique of high-frequency EPR spectroscopy (94 GHz) made it possible to separate the spectra of radical anions and cations and to exclude an overlapping of their ^{1}H ENDOR spectra, but mainly the TRIPLE spectra. In this case, the use of multi-resonance methods of high-frequency (> 90 GHz) magnetic radiospectroscopy made it possible to significantly increase the resolution of the spectra of ligand hyperfine interactions (LHFI) in organic donor and acceptor ion radicals with unresolved LHFI in the EPR spectrum and made it possible to obtain a unique additional experimental information on the distribution and sign of electron spin density.

Spin relaxation of protons in polymer melts as a method of measuring the thermal displacements of segments of macromolecules in nano and mesoscopic spatial ranges. N.F. Fatkullin and colleagues showed that the anomalous nature of the diffusion of polymer segments at times shorter than the terminal relaxation of macromolecules in melts significantly affects the processes of proton spin relaxation. It turned out that at sufficiently low frequencies, comparable and lower than 100 MHz, the proton spin relaxation is determined mainly not by the magnetic dipole-dipole interactions of the nearest intramolecular proton pairs, but by the interactions of remote protons from various macromolecules. This effect has a frequency nature, which made it possible to measure the spatial displacements of polymer segments associated with thermal fluctuations in the range of 30 – 300 Å based on the frequency dependence of the spin-lattice relaxation rates and the time dependence of the initial decay of the FID, Hahn echo, and solid-state spin echo. These measurements are unachievable for other existing experimental methods (see [43a-h] and the literature cited there).

L.K. Aminov and colleagues systematized the results of observations and simulations of the ***superhyperfine (ligand hyperfine) structure (SHFS) of the EPR spectra of impurity ions of rare earths and uranium in dielectric crystals.*** Most attention was paid to the tetragonal double fluorides $LiRF_4$ (R = Y, Lu, Tm) [44a-d]. Various models of rare-earth paramagnetic centers in mixed crystals with fluorite structure have been studied [44e-i].

R.M. Aminova with co–workers have carried out the ***quantum chemical calculations of the structure and parameters of*** ^{1}H, ^{13}C, ^{31}P ***NMR spectra of molecules in solutions, crystals, and fragments of polybutadiene*** using combined methods of quantum chemistry and molecular mechanics. The calculation methods for the parameters of nuclear magnetic shielding in molecular clusters of a dissolved molecule with calcium ions have been developed [45a-d].

2.3.2. *Research direction "Research of biomedical systems by physical methods"*

High resolution NMR studies of the structure and properties of biomolecules, including drugs, and their interaction with cell membranes (leaders A.V. Aganov, V.V. Klochkov. Group members: K.S. Usachev, L.F. Galiullina, S.V. Efimov, A.R. Yulmetov, I.A. Khodov, I.Z. Rakhmatullin, D.S. Blokhin *et al*.).

This new research direction in the University in the field of high-resolution NMR spectroscopy research has started in 2005. The most important results are highlighted.

The spatial structure was established and atom coordinates were determined in the pdb format of peptides (Val-Ile-Lys-Lys-Ser-Thr-Ala-Leu-Leu-Gly decapeptide, beta-amyloid Aβ16–22, beta-amyloid Aβ10–35 (fragment of beta-amyloid Aβ1–40), in aqueous solution and in combination with model biological membranes (micelles, based on sodium dodecyl sulfate). The main results are presented in publications [46a–c]. The conformational composition was determined, the thermodynamic parameters of conformational equilibrium in chloroform solution were determined, and the spatial structure of minor conformer of cyclosporin CsA were described [46d].

The spatial structure and atomic coordinates were determined in pdb format for antimicrobial peptides (Protegrin-1 – Protegrin-5) in solution and in the of the complex peptide with the model cell membrane surface (micelles, based on DPC) [47a–c], the spatial structure and atomic coordinates in the pdb format of the complexes of pravastatin and simvastatin with models of the cell membrane surface (micelles, based on sodium dodecyl sulfate, SDS) were obtained [47d].

In [47e], the atomic coordinates (pdb format) of the spatial structure of RGD and AGDV peptides in solution and in the complex peptide – platelet + Integrin αIIbβ3 complex were determined.

The crystallographic and NMR structures of the N-terminal TERT domain (TEN domain) of the thermophilic yeast Hansenula polymorpha are presented and it has been shown that the central structural motif is preserved in evolutionarily different organisms [47f].

Translational mobility of lipids in model biomembranes (A.V. Filippov, M.A. Rudakova *et al.*). The NMR method with Pulsed Field Gradiemt (PFG NMR) was successfully used to study oriented lipid bilayers of various compositions in order to establish the characteristics of lateral diffusion of lipids, lateral phase separation and the influence of various salts and polymers on these processes [48a–g]. In particular, it was shown that a lipids mixture system of dioleoyl phosphatidilglycerol, sphingomyelin and cholesterol forms a lamellar liquid crystal phase, and in a certain range of temperatures and cholesterol concentrations the system is subdivided into two subphases. The effect of polyacrylic acid (PAA) on the phase state and lateral diffusion in bilayers of dimyristoyl-phosphatidylcholine (DMPC) was studied by ^{31}P NMR, ^{1}H PFG NMR and ^{1}H NOESY spectroscopy. The obtained experimental results indicate the formation of at least two types of lateral PAA-DMPC complexes. Moreover, the first is characterized by stoichiometry of 6-7 lipids per polymer and contains PAA molecules that are only partially adsorbed on the membrane [48d]. The second type of complexes has a lifetime of about 0.1 s. and is characterized by stoichiometry of about 28 lipids per polymer, which corresponds to the adsorption of the entire PAA molecule on the membrane.

Translational mobility and features of the supramolecular organization of proteins with an internal disordered structure (V.D. Skirda, D.L. Melnikova, I.V. Nesmelova). For the first time, with the help of NMR with pulsed field gradient (PFG NMR) the features of the translational mobility of molecules in aqueous solutions of α-casein and κ-casein, as typical representatives of a new class of proteins-proteins with disordered internal structure has been studied in detail. For the first time, the data were obtained on the characteristic lifetimes of molecules in a gel state and on the ratio of the fractions of protein molecules in a gel state and in a free state [49a, b].

The results obtained in this paper, on the one hand, supplement the current understanding of the mechanisms of action of the TCEP agent on the intra- and intermolecular disulfide bonds of protein molecules in concentrated solutions. On the other hand, the data obtained for concentrated solutions of β-casein and κ-casein indicate the ambiguity of the results of the use of these reducing molecular agents and indicate the need for more careful use in other studies.

Biomedical EPR applications. This research had started in the late 1990s as part of the project "Biomedical Optics and Radio Spectroscopy" of the Federal Program "Integration" (A.V. Aganov, N.I. Silkin, Yu.A. Chelyshev *et al*., see, e.g., [50a, b]). They received further development in the joint work of the group of N.I. Silkin, Inter-regional Clinic–Diagnostic Center (ICDC) and Kazan State Medical University (KSMU) (I.M. Ignatiev, R.N. Khairullin) [51a–e]. They showed that the atherosclerosis calcific plaque is an organomineral aggregate and hydroxyapatite plays a significant role in its formation. It was found that, depending on the composition and structure of the organomineral deposits, the spectroscopic and relaxation characteristics of the observed paramagnetic centers change. It has been demonstrated that the spectral and relaxation characteristics of the observed radicals (Mn^{2+} and CO^{2-}) correlate with the degree of calcification and stability of the atherosclerotic plaque and can serve for diagnostic purposes, to monitor the development and progress of atherosclerotic changes, and evaluate the effectiveness of the therapeutic effect.

Studies have been carried out and are ongoing by magnetic resonance methods and theoretical calculations of synthetic calcium phosphates doped with various impurities (micro and nanoscale powders and ceramics) in order to optimize their synthesis methods, improve their physicochemical, biological properties, quality control, post-synthetic processing and storage processes. The work is carried out jointly with Baikov Institute of Metallurgy and Material Science, RAS, Faculty of Chemistry and the Faculty of Materials Science of Moscow State University. These materials are used as implants for the replacement and regeneration of bone tissue, and are also model for studying the processes of pathological calcification [52a–g].

The history of ***magnetic resonance imaging (MRI)*** in Kazan and Tatarstan begins in the 80s and is based on the achievements of the Kazan EPR and NMR school. The initiators of this research direction were A.V. Ilyasov, head of the Laboratory of radiospectroscopy of the A.E. Arbuzov IOPC KSC RAS, and I.V. Klyushkin, head doctor of the Republican

Diagnostic Center No.2 (later RCH-2, now a University clinic of KFU). Thanks to their efforts, a Bruker Tomikon R28 clinical NMR tomograph with a magnetic field strength of 0.28 T was acquired in 1989 (at that time the third medical tomograph in the USSR). The history of acquiring a tomograph is detailed in [14].

From the first days an interdisciplinary team was created, which included NMR experts V.N. Zinin and K.A. Ilyasov, and on the part of the diagnostic doctors R.F. Bakhtiozin and I.R. Chuvashaev. V.N. Zinin had experience in creating, repairing and operating the NMR spectrometers, K.A. Ilyasov at that time knew the modern methods of pulsed NMR and two-dimensional NMR spectroscopy. R.F. Bakhtiozin was a recognized expert in the new (at that time) ultrasonic diagnostic method, and I.R. Chuvashaev was a successful oncologist-surgeon. Since March 1990, a stream of patients has begun. Active participation of the MRI team of the clinic in the tomograph installation subsequently allowed the most of the maintenance and repair works using our own resources to carry out. A great merit of the chief physician I.V. Klyushkin was that he was able to convince the direction of the Ministry of Health of the Republic of Tatarstan and the Government of the Republic of Tatarstan about the need to allocate a “methodological” day on the instrument. Despite the huge need for MRI studies and the queue of patients for examinations, the MRI team in the clinic had the opportunity to learn and practice new advanced techniques and methods for MRI diagnostics on the device. This yield the results – MRI examinations were carried out at a higher level with the maximum use of the device capabilities and MRI techniques available at that time, and new methods and approaches were developed. After 1.5 years, the team’s scientific report at the international conference on MRI in Berlin received the ISMRM Society Prize [53a], and the following year at the European MRI Conference in Rome the report was awarded the ESMRMB European Society Prize [53b]. Formation of the direction of the scientific research was the support in 1994 for the K.A. Ilyasov’ MRI Project by the Alexander von Humboldt Foundation and establishing contacts with Prof. Jürgen Hennig (University of Freiburg, Germany) was of great importance. This subsequently led to the development of fast MRI methods for diffusion and axonal tractography and MRI methods for measuring the local temperature in the human body, which was summarized in K.A. Ilyasov's doctoral dissertation (2011) (Annex 1). The most important results of that period are published in [53c–f].

The development of clinical applications, that begun in [53b], and result in a doctoral dissertation by R.F. Bakhtiozin in 1996, and the experience in MRI diagnostics of the musculoskeletal system and brain tumors was summarized in doctoral dissertations by I.V. Klyushkin (1996) and M.M. Ibatullin (2002), respectively. The most important results of that period are published in [53c–f].

The international conferences Modern Developments in MRI, held in Kazan in 1997, 2001, 2007, 2015 by the teams of MRI and KSU (KFU) with the support of the ISMRM and ESMRMB societies were of great importance for the development of clinical applications in MRI. A great help was provided by Prof. Jürgen Hennig. In 2014, the achievements of the clinic team in the development and implementation of MRI methods in clinical practice were awarded by the Tatarstan State Prize in the field of science and technology "Development and application of magnetic resonance imaging methods in medical diagnostics": R.F. Bakhtiozin (Moscow), K.A. Ilyasov (KFU), I.R. Chuvashaev, M.M. Ibatullin (Interreginal Clinic Diagnostic Center), N.A. Ilyasov (Kazan-Samara), I.V. Klyushkin, A.R. Abashev, K.J. Hennig (Germany).

From left to right: I.V. Klyushkin, K.A. Ilyasov, M.M. Ibatullin, R.F. Bakhtiozin, R.N. Minnikhanov, I.R. Chuvashaev, N.A. Ilyasov, A.R. Abashev

Currently, the development of clinical applications of MRI is continued by a group of Professor of Medical Physics Department, Institute of Physics, KFU, K.A. Ilyasov in close collaboration with the University Clinic and foreign colleagues. The results of recent years are published in [53g–j].

2.3.3. Research direction "Development of applications of physics in various sectors of the economy (in the oil and gas, petrochemical, chemical, pharmaceutical and others."

Work on orders of enterprises of real sectors of the economy in previous years was carried out very intensively. For a number of well-known reasons, their intensity dropped sharply during the so-called years of “perestroika”. In the last five years, they are mainly carried out as part of national programs. Currently, under the program “Eco-Oil - Global Energy and Resources for the Materials of the Future”, the Center of Excellence in the field of research and development of economical, environmentally friendly and energy-efficient technologies for hydrocarbon production and processing are in work with the participation of Institute of Physics (KFU) teams in a number of areas. The main objectives of the research:

- structure studies of the asphaltene complexes of oil disperse systems with a view to their further efficient processing and utilization;
- development of radio frequency and microwave techniques for the study of polymers, catalysts and oil disperse systems. They are carried out on an initiative basis.

Decoding the structure of oil and oil products by high resolution NMR spectroscopy (headed by V.V. Klochkov). The objectives of the project are the adaptation of modern high-resolution NMR spectroscopy methods to determine the composition of oil and oil products, as well as the determination of the NMR test signs of typical impurities present in these samples; analysis of oil samples from a number of oil fields, samples of viscous oils with a high content of aryl and naphthyl fragments and samples of numerous oil products, *etc*. The results are presented in [54a–c].

The study of the structural and dynamic properties of oil and the factors that determine its rheological characteristics (group of V.D. Skirda). Based on the results of joint research with Schlumberger Ltd. of heavy oil samples, methods to obtain information on the quantitative fraction of asphaltenes and crystallized paraffins by NMR were developed and patented [55a, b]. The developed technique turned out to be in demand, since it has significant advantages compared with GOST (National Russian Standard).

As a result of NMR studies of spin-spin relaxation in resin samples and in resin-asphaltene model systems, it was shown that only some of the resin molecules interact with asphaltenes and as a result change their characteristics, while for the other, large enough parts of the resin molecules, the structural-dynamic characteristics remain unchanged. Moreover, the ratio between these parts depends on the particle size of asphaltenes. A proportion of the component fraction of the recorded NMR signal with features characteristic of solid asphaltenes was found to depend on the particle size of asphaltenes.

A proportion of the fraction of the component recorded in the NMR signal with features characteristic of solid asphaltenes was found to depend on the particle size of asphaltenes.

Based on the results of the experimental data analysis and corresponding calculations, a hypothesis is formulated on the partial dissolution of asphaltene molecules in the model resin-asphaltene system.

The kinetic dependences of the solid-state component fraction in the NMR signal and the fraction of resin molecules in the state of interaction with asphaltenes were first obtained and characterized, which is evidence that the resin-asphaltene model system is in the nonequilibrium state at the initial stage. It is shown that resin molecules, interacting with asphaltene, do exist not only on the surface of asphaltene particles, but also in their volume. Based on the obtained experimental results, an addition to the existing model of resin-asphaltene aggregate is proposed.

To characterize the properties of asphaltene-resinous aggregates, the high information content of nuclear magnetic relaxation data extracted from NMR experiments in the range, which includes the range of spin-spin relaxation times typical for a solid, was demonstrated.

A technique has been developed that allows one to determine the relative fraction of resin molecules directly interacting with asphaltenes.

It was shown that the possibility of preliminary dissolution of asphaltenic formations with their subsequent aggregation in the resin is determined by the conditions of their separation from oil, as a result of which the structure of the obtained aggregates is different from the native one.

The possibility of establishing a correlation of NMR relaxation data with the degree of maturity of kerogen was demonstrated. This circumstance is important for the development of methodological recommendations for the analysis of core material selected in the course of the ongoing well logging [56a–d].

It should be noted that the fundamental research of the ^{3}He properties has found its practical application for the study of porous media. A method for measuring the porosity of materials, substances and minerals based on nuclear magnetic resonance of inert gases is proposed and patented. For the first time, the inverse Laplace transform was applied to the data of nuclear magnetic relaxation of ^{3}He, which made it possible to obtain the size distribution of pores [57].

Applications of EPR spectroscopy (headed by M.R. Gafurov). A "Method for determining the saturation factor of electronic transitions of a paramagnetic subsystem in matter" [57a] is proposed. The possibilities of using high-frequency EPR for studying the structure of in-situ asphaltenes, aggregation processes, catalytic transformations, determining the structures of vanadyl-porphyrin complexes and their changes with chemical or heat treatment are demonstrated. For the first time in the world, an English-language review was published on the application of high-frequency EPR methods for studying oil dispersed systems [58b]. The results of the work are also presented in the publications [58c–f].

3. NMR APPLICATIONS IN CHEMISTRY

In the previous section, the results of studies were presented, which concerned, first of all, the creation of an experimental base, the theory of magnetic resonance as applied to the solution of physical problems and the development of research methods and techniques carried out at the Department of Physics (Institute of Physics) of the University. The development of applied research was actively conducted at the Faculty of Chemistry and A.M. Butlerov Scientific Research Chemical Institute (now the A.M. Butlerov Chemical Institute) and the Department of Geology (now the Institute of Oil and Gas Technologies and Geology).

3.1. NMR in chemical research

At the A.M. Butlerov Chemical Institute the research is performed in several teams in numerous directions.

3.1.1. *High Resolution NMR Spectroscopy in Organic and Organoelemental Chemistry*

In the aforementioned series of publications jointly entitled “High Resolution Nuclear Magnetic Resonance in Structural and Dynamic Studies of Molecular Systems”, awarded by the RT State Prize for Science and Technology in 2010, the results of long-term work of the high-resolution NMR spectroscopy group together with the Departments of Organic and Organoelemental Chemistry, Problem Laboratories “Study of the structure of organic compounds” (SSOC) and “Chemistry of monomers and polymers” of the Faculty of Chemistry, A.M. Butlerov Scientific Research Chemical Institute and the laboratory of radiospectroscopy, A.E. Arbuzov IOPC of Kazan Center of Academy of Sciences of the USSR under the supervision of Prof. Yu.Yu. Samitov, A.V. Aganov, are summarized. This cycle of work included only the development and creation of an experimental base for high-resolution NMR spectroscopy, the development of the theoretical foundations of a number of techniques and the physical interpretation of research results. All work was carried out in close collaboration with the Faculty of Physics (Institute of Physics). After the premature death of Yu.Yu. Samitov this team was headed by Prof. A.V. Aganov, who organized in 2005 a high-resolution NMR laboratory for biomedical research at the Faculty of Physics (Institute of Physics) of KFU, being the dean (director) of this unit. Actually, this is a specialized bioNMR laboratory, functioning at the Department of Medical Physics, which stood out from the Department of General Physics of Instutite of Physics of KFU in 2015 (Head of Department A.V. Aganov). Currently, the laboratory is headed by V.V. Klochkov. Naturally, the traditional structural-dynamic studies by high-resolution NMR spectroscopy in chemistry continue.

At the Department of Organic Chemistry (Head I.S. Antipin), NMR spectroscopy is widely used to carry out scientific research, primarily to establish the structure of complex organic, organometallic, and supramolecular compounds using a wide range of modern NMR methods in close collaboration with NMR groups of Physics Institute of KFU and the Institute of Organic and Physical Chemistry FRC RAS.

Under the direction of I.S. Antipin and A.I. Konovalov, starting in the mid-nineties of the twentieth century, work is being carried out in the field of synthesis and supramolecular chemistry of macrocyclic compounds: meta- and para-cyclophanes [59a–e]. In particular, in the group of I.I. Stoikov studies are underway to model and develop approaches to the synthesis of receptors and nanoscale structures based on (thia)calix[4]arene, pillar[5]arene, as well as nanosized particles of silicon dioxide capable of molecular recognition of biologically significant substrates [59f–i]. The main direction of work of the scientific group of V.A. Burilov is a directed synthesis of new macrocyclic amphiphilic compounds on the p-tert-butylthiacalix[4]arene platform, capable of acting as “smart” surface-active substances capable for both self-association and binding to other molecules [59j–l]. For a series of works on supramolecular chemistry, calix[4]arenes in 2005 a team of authors (A.I. Konovalov, I.S. Antipin, A.R. Burilov, I.I. Stoikov, S.E. Solovieva

(IOPC), A.R. Mustafina (IOPC), L.Ya. Zakharova (IOPC), I.S. Ryzhkina (IOPC), A.T. Gubaidullin (IOPC)) was awarded the State Prize of the Republic of Tatarstan in the field of science and technology.

From left to right: A.I. Konovalov, I.S. Antipin, A.R. Burilov, A.T. Gubaidullin, A.R. Mustafina, M.Sh. Shaimiev, I.S. Ryzhkina, S.E. Solovieva, I.I. Stoikov

Scientists of the department conduct research on the synthesis of new carbo- and heterocyclic compounds, establish the structure and their application for biomedical purposes (biological activity, imaging of tumor tissues, *etc*.). Scientific group of A.R. Kurbangalieva is developing preparative methods of synthesis, studying the structure and properties of new chemically and biologically active derivatives of five-membered heterocycles of the 2(5H)-furanone and 3-pyrrolin-2-one series, as well as homo- and heterogeneous glyco-conjugates (molecular receptors) for selective recognition and visualization of target tumor cells and tissues in living organisms [60a–d]. The chemistry group of renewable natural raw materials (headed by V.F. Mironov, A.V. Nemtarev) is focused on the separation of biologically active components from plant materials with subsequent chemical modification of the most valuable of them in order to give the latter the necessary level of activity [60e].

^{31}P NMR is also widely used to control the course of reactions, especially in the case of unstable compounds, and also as a method for determining the coordination of phosphorus in establishing the structure of the obtained products. Under the leadership of Prof. F.Kh. Karataeva with the method of one- and two-dimensional ^{1}H and ^{13}C NMR spectroscopy and semi-empirical quantum-chemical calculations (AM1 method) the structure of hyperbranched polyesters of BOLTORN H_2O-OH and BOLTORN H_2O-OH polyols with maleic anhydride was studied for the first time. It is shown that polyols have a non-stereoregular structure, where two linear, as well as terminal and dendritic branches are pairwise approaching each other.

Three main types of hydrogen interactions (C=O...HO, OH...OH and C=O...HO...HO), which have both intramolecular and intermolecular character [61a, b], were revealed.

Equally actively the high-resolution NMR method was used at the Department of Elementorganic Compounds and the Problem Laboratory of the Chemistry of Monomers and Polymers. Structural–dynamic studies of polymers by NMR relaxation were started by G.G. Pimenov from the group of Prof. A.I. Maklakov in 1963, but did not receive development, at the chemical faculty.

High-resolution NMR spectroscopy studies (mainly ^{31}P NMR) were carried out from the first steps of applying NMR in chemistry in our country on the basis of the PL SSOC at the Department of Organic Chemistry and the Laboratory of RadioSpectroscopy of the Institute of Organic and Physical Chemistry of the Academy of Sciences (since the mid-1960s; now IOPC) under the supervision of Yu.Yu. Samitov and A.N. Pudovik. From PL SSOC, the work was supervised by F.Kh. Karataeva (now Professor of the Department of Organic Chemistry), from IOPC – by A.A. Nafikova (Musina) and T.A. Zyablikova. The work was carried out in various directions. At the initial stage, these were works on establishing the spatial structure of phosphorus-containing compounds and establishing NMR parameter–structure correlations. The most important results of this period are published in [62a–c].

The results of the active use of the NMR method in studying the reactivity of phosphorous–organic compounds (POC) are reflected in numerous original publications and reviews. The main results are presented in [63a–d].

One of these directions at the department was supervised by A.N. Pudovik, R.A. Cherkasov and M.G. Zimin, later by N.G. Zabirov – the study of POC with a non-rigid molecular skeleton, the intramolecular dynamics of which in solutions are determined by several varieties of reversible and irreversible rearrangements. Rearrangement schemes in these molecules are speculative, debatable in nature [64].

The use of ^{1}H, ^{13}C, and ^{31}P dynamic NMR methods in the study of N-(thio)phosphoryl(thio)amides of various structures in solutions made it possible to isolate several intramolecular processes with the determination of the spectral features of each of them and to reveal the exchange pattern [65a-f].

A series of research performed in one of the modern areas – the synthesis of physiologically active substances, was awarded by the State Prize of the Republic of Tatarstan in the field of science and technology in 2015: “Directed synthesis of physiologically active substances for medicine and veterinary medicine based on the biomimetic approach”. (V.I. Galkin, I.V. Galkina, S.N. Egorova (KSMU), M.Kh. Lutfullin (Kazan Veterinary Academy), L.M. Yusupova (KNRTU), O.K. Pozdeev (KSMA) O.I. Gnezdilov (KFU–KPhTI), M.P. Shulaeva (KSMA)).

From left to right: O.K. Pozdeev, V.I. Galkin, O.I. Gnezdilov,
I.V. Galkina, R.N. Minnikhanov, S.N. Egorova, M.Kh. Lutfullin,
M.P. Shulaeva, L.M. Yusupova

3.1.2. ***NMR relaxation methods in inorganic chemistry***

This area of NMR applications is developed at the Department of Inorganic Chemistry. At the turn of the 1960s – 1970s, as already noted in the Introduction, A.A. Popel on the basis of the first relaxometer, created in the USSR in 1958 at the Faculty of Physics of KSU by R.A. Dautov, V.M. Fadeev, and V.D. Korepanov, developed a new physicochemical method for the analysis and investigation of inorganic substances, which he called the magnetic relaxation method [66a].

Further, the method was developed and implemented into the chemical research by A.A. Popel together with E.D. Grazhdannikov [64b, c], and then by A.V. Zakharov, Z.A. Saprykova and Yu.I. Salnikov using relaxometers created according to standard schemes in the laboratory of A.A. Popel. The publications of the early period are summarized in [66d-e].

Since 1977 the Laboratory of Coordination Compounds is also successfully working at the Faculty of Chemistry. The main focus of its research is the study of the thermodynamics and kinetics of the formation of complex coordination compounds of metals using a set of physicochemical methods (primarily NMR and EPR); study of their useful physicochemical and biological properties. It was headed by A.A. Popel, Z.A. Saprykova, Yu.I. Salnikov, A.V. Zakharov (currently V.G. Shtyrlin). A.N. Glebov, F.V. Devyatov, V.V. Chevela *et al.* also took part in the studies. The results are summarized in [67a–c].

Since 1988, under the leadership of R.R. Amirov (Head of the Department of Inorganic Chemistry since 2012) using the NMR relaxation method, systematic studies of aqueous dispersions of various nano-objects (surfactant solutions, macrocycles, metal oxide nanoparticles, graphene oxide, *etc.*) are carried out. Since 2004, together with A.E. Arbuzov IOPC (A.R. Mustafina, R.R. Zairov, A.S. Stepanov, S.V. Fedorenko, and others) the magnetic relaxation characteristics of nanoscale complexes of gadolinium (III) and nanoparticles of iron oxides in lipid, silicate and polymer shells are studied. The results of the studies allow to propose the prototypes of new contrast agents for the magnetic resonance imaging. Their results are summarized in [68a], and the latter are presented in [68b].

Since 2016, aqueous dispersions of graphene oxide and magnetite nanoparticles as potential sensors in biology and medicine are studied [68c].

3.2. Magnetic resonance in geology

3.2.1. *EPR and NMR in studies of the structure and properties of minerals*

At the Faculty of Geology (now the Institute of Geology and Oil and Gas Technologies, IGOGT), implementation of modern physical methods for studying the minerals dates back to the second half of the 1950s. Implementation was carried out in two directions. The initiators of one of them, “Applications of EPR and NMR in studies of the structure and properties of natural minerals,” were S.A. Altshuler and Head of the Department of Mineralogy Leonid Mikhailovich Miropolsky. The geologist, Associate Professor Vladimir Mikhailovich Vinokurov and physicist Associate Professor Maksut Mukhametzyanovich Zaripov were charged to head this new research direction. Their young colleagues V.G. Stepanov (KSU) and N.R. Yafaev (KPhTI, USSR Academy of Sciences) appeared in the group. Naturally, at the beginning of the work, the main method was the EPR method, and the first samples were minerals from the collection of the geological museum of KSU[21].

The first publications are dated 1959–1961 [69a–e].

The results of the initial period were summarized in [69f] and in the doctoral dissertation of V.M. Vinokurov “Magnetic properties of minerals” (1966). (see Annex 1).

Since the early 1970s, other physical methods have been actively implemented. The main approaches and results were described in the monograph [67f].

In 1989, on the basis of several laboratories V.M. Vinokurov created the research laboratory “Physics of Minerals and Their Analogs”, and after his initiative a group was created at the All-Union Institute of Non–metallic Materials (Kazan, headed by V.F. Krutikov). The group's tasks included the creation and implementation of EPR, NMR and gamma resonance techniques in technological mineralogy, which are actively used in the technological department of the institute, and three doctoral dissertations were defended at Kazan State University (V.F. Krutikov, V.A. Grevtsev, F.M. Bulatov, and see Appendix 1).

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[21] Probably, the minerals from the museum’s collection served as test samples for other researchers thanks to the courtesy of V.M. Vinokurov. For many of them the crystallographic data were already known. At least one of the authors was provided with gypsum single crystals (“larkspur”) for testing the methods on a broad-line NMR spectrometer in the early 1960s [see 11].

For a rather long time, EPR was the main method for studying minerals. Somewhat later, NMR methods began to be applied. G.R. Bulka, N.M. Khasanova, I.M. Nizamutdinov, A.A. Galeev and others took part in it [70a–d]. To a large extent the research solved the physical problems.

At the turn of 1970-1980 these trends intensified. Another group of physicists joined the research (R.A. Dautov, V.D. Shchepkin, D.I. Weinstein), who introduced a rather complicated method – pulse double nuclear-nuclear resonance in the study of impurity crystals [71a–d].

Studies of crystals using NMR and optical spectroscopy methods that begun in 1977 [72] had no further active development.

The use of NMR methods in the exploration and production of oil and bitumen dates back to the 1970s [73a, b]. Work in this area today is being carried out with the direct participation of the research teams of the Institute of Physics as was already noted in the previous section.

3.2.2. *NQR and NGR (Mössbauer effect) methods in mineralogy*

This area of radiospectroscopic studies at the Faculty of Geology was created by I.N. Pen’kov in close collaboration with I.A. Safin (KPhTI Kazan Branch of USSR Acandemy of Sciences) in 1961. It was also a pioneering work in the USSR on the use of nuclear quadrupole resonance (NQR) methods in mineralogy, the first of which was published in 1962 [74a]. They were devoted to determining the parameters of the NQR spectra of natural minerals in stibnite, prustite, pyrargyrite, stephanite, and bournonite, etc, and generalized in the paper [74b] and, subsequently, in the doctoral dissertation of I.N. Pen’kov (V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry of USSR Academy of Sciences, 1970) (see Annex 1).

It showed the capabilities of the method as a fine tool in studying the real electronic and crystal structures, the lattice dynamics of minerals, which are associated with fundamental properties and natural typomorphism, for the first time described an alternative mechanism for the involvement of structural impurities in minerals associated with an anomalously high reaction ability of a crystalline substance at polymorphic transformation (phase transition). This cycle of research is completed by the study of the nature of small structural impurities in some As, Sb, and Bi chalcogenides [74c].

In 1976, I.N. Pen’kov organized the NQR spectroscopy laboratory at the department he headed, where the studies were carried out together with R.R. Abdullin, V.P. Kalchev, N.V. Togulev. In the following year, a series of publications appeared [75a, b etc.]. This 10-year cycle of NQR studies ends with studies of the crystal chemistry, electronic structure, and lattice dynamics of copper-containing minerals [75d, e].

This period includes the work on the use of nuclear gamma resonance (NGR) (Mössbauer) spectroscopy in mineralogy, which began in collaboration with the Solid State Physics department of the physical faculty of KSU, which actually started under the direction of Sh.Sh. Bashkirov, who was a pioneer in the USSR in the field of nuclear gamma–resonance, and the physics school of Mössbauer spectroscopy was already formed as one of the branches of the Kazan school of radiospectroscopy. The first publications were devoted to the NGR of Sn^{119}, Fe^{57} in franckeite and cylindrite [76a] and the cation distribution in natural chrome-spylene compounds [76b].

Summarizing the 25-year cycle research of the NQR group of the Department, it should be noted that for the first time more than 60 minerals of different classes and their artificial analogues were investigated. The results obtained are of interest for modern (genetic) mineralogy, crystal chemistry, geochemistry, and materials science.

After a long break, the research of minerals with NQR was resumed in the 2000s with the participation of a fairly large group of researchers from the Faculty of Physics (A.V. Dooglav, R.R. Gainov, I.R. Mukhamedshin, F.G. Vagizov and others). This collaboration turned out to be very fruitful, as evidenced by publications in rating journals of both physical and mineralogical profiles [77a–d]. In these publications the physical and physicochemical aspects were dominated. These studies had a complex nature, and other methods began to be involved, first of all, NMR, which had already shown at that time its effectiveness in a wide variety of areas, in combination with NQR, supersensitive magnetometry (SQUID) and *ab initio* theoretical calculations [77d, e]. One of the latest areas of joint research was at the junction of three scientific fields at once - condensed matter physics, biomineralogy, and nanodiagnostics: the possibilities of diagnostics by the NQR method of ultra- and nanodispersed particles of binary copper sulfides formed during the life of bacteria in organic residues (in particular wooden fragments) were studied [77g]. Together with scientists from Australia, the possibility of using NQR and NGR methods for the express analysis of copper ores was considered [77h].

4. MAGNETIC RESONANCE TODAY

EPR and NMR are of the same nature. But there is a significant difference between them, which, ultimately, predetermined the dynamics of their development and their effect on numerous areas of science and technology.

EPR has a higher resonance frequency (about 2000 times) and, therefore, a higher sensitivity. The requirements for uniformity and stability of the magnetic field are not as high as in NMR. At the turn of the 1940s – 1950s the experimental installation could be assembled with industrial units, for example, radar installations, which were transferred to civilian organizations after the Second World War (unfortunately, in our country the signature stamp "top secret" was removed much later than abroad). In addition, the real prospects for the development of NMR and its applications were revealed about five years later. In the first decade after the discovery of EPR, these factors together have led to higher rates of EPR studies than NMR studies. The situation did not change much after the advent of industrial EPR and NMR spectrometers in the second half of the 1950s. Spectrometers created in laboratories were quite competitive in comparison with industrial ones. The main advantage of NMR – the possibility of direct observation of the signal of the magnetic nuclei of atoms of chemical elements (which are practically all elements of the D.I. Mendeleev Periodic Table of Elements) – was realized much later as a result of the creation of R. Ernst and colleagues at the turn of 1960–1970 the method of pulsed NMR spectroscopy with Fourier transform[22]. The next stage in the development of NMR is associated with the development of methods for decoding the NMR spectra

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[22] R. Ernst. 1991 Nobel Prize in Chemistry "For contribution to the development of high resolution nuclear magnetic resonance (NMR) spectroscopy methodology".

of macrobiomolecules by K. Wüthrich[23]. This research was also awarded by the Nobel Prize.

Today there are about a thousand varieties of NMR methods for solving the structural and dynamic problems in a wide variety of molecular systems. The experimental technique became more complicated and its construction became not only impossible for laboratory specialists, but also for most equipment manufacturing companies for magnetic resonance[24]. Obvious advantages had teams that had equipment with a full set of operating options. In this regard, domestic laboratories were clearly in a losing position and, of course, this circumstance restrained the pace of research, especially in Russian universities. This problem is covered in sufficient detail in the publications cited above. The strategic line of any method is to increase sensitivity and resolution. In magnetic resonance this means necessity to obtain high homogeneous magnetic fields (realized in magnets with superconducting solenoids) and hence the higher working frequencies of the spectrometer. In NMR spectroscopy an operating frequency of 1.1 GHz has already been achieved. The operating frequencies of modern EPR spectrometers are just starting from 9.4 GHz (spectrometers with a frequency of 256 GHz have been launched for serial production, spectrometers with higher frequencies have been developed). Creation of electronic components in the radio frequency range is much simpler compared with that in the microwave range. Therefore, the variations of the techniques in technical terms in the NMR spectroscopy are much wider. There is one more circumstance. Nuclear spin labels of various types exist in the vast majority of compounds. Electronic spin labels are available in a limited class of compounds. Often they need to be injected. Further,

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[23] K. Wüthrich. 2002 Nobel Prize in Chemistry “For the Development of Nuclear Magnetic Resonance Spectroscopy for Determining the Three-Dimensional Structure of Macromolecules in Solutions”.

[24] Two manufacturers of NMR and EPR spectrometers remained virtually in this market: Bruker (Germany) and Jeol (Japan) with a shorter line of instruments. The number of manufacturers of MRI scanners is much wider.

the EPR spectra are not as informative as the NMR ones. Their interpretation is carried out by comparing theoretically calculated spectra with experimental spectra at the present time also. NMR spectra contain many lines. There are tens of thousands of them in biological macromolecules. The stage of comparing the theoretical and experimental spectra has long passed. Decryption algorithms are developed and automated. But there is a wide range of problems that cannot be solved by NMR methods, but are accessible by EPR methods, and vice versa. The time scales of these methods differ by three orders of magnitude. They complement each other when solving complex problems. An industrial spectrometer with a magnetic field of 9.4 T has already been created, that corresponds to the EPR resonance frequency of 263 GHz and 400 MHz proton NMR. Zavoisky observed EPR at a frequency of 10 MHz, i.e. the operating frequency of modern EPR spectrometers is about four orders of magnitude higher (10^4), which corresponds to an increase in sensitivity of about 100 million (10^8) times. The spectrometer allows recording both NMR and EPR signals with interchangeable sensors.

Magnetic resonance methods are applicable in research in physics, chemistry, biology, medicine, geophysics, *etc.*, in the field of creating new materials and substances for numerous purposes, but also in many areas of production. In addition to the already mentioned role of EPR in the creation of materials for quantum electronics (physical materials science) in the first post-war years (S.A. Altshuler, A.A. Manenkov, A.M. Prokhorov), one can give an example of creation of superconducting materials on the basis of discovery of high temperature superconductivity (HTSC) in ceramic materials by K.A. Müller[25], an employee of the physical department of the IBM Zurich office, which forerunner was the study of perovskites by EPR [78a, b]. For many years starting in 1986, as noted

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[25] K.A. Muller (jointly with G. Bednortz) awarded the Nobel Prize in Physics in 1987 “For their important break-through in the discovery of superconductivity in ceramic materials”.

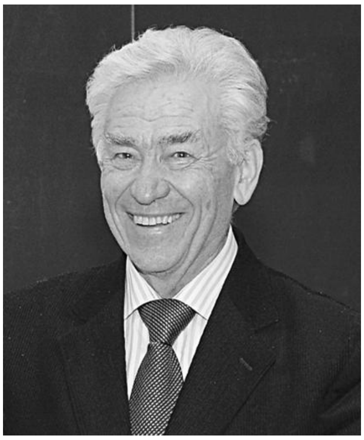
above, the fruitful collaboration of K.A. Müller and B.I. Kochelaev in the field of studying the properties of HTSC materials by EPR was estabished.

In a number of industries, for example, in the pharmaceutical industry, in laboratories working in large international research programs (for example, to establish the structure of proteins), several dozen NMR spectrometers are in line. The creation of a huge industry of high-tech production of spectrometers for magnetic resonance and tomography is directly related to the scientific developments and needs of competing economies of countries – world leaders. Therefore, in the list of the largest world centers where magnetic resonance methods are used, not all are the scientific or educational centers. The total number of spectrometers in the laboratories of these countries totals thousands of units. In general, the availability of equipment of a large number of large foreign centers is about an order of magnitude higher than the equipment of the best Russian academic and university centers (there are practically no laboratories in scientific-production and similar organizations, and only single spectrometers were used in the laboratories of some large enterprises as an analytical tool). The involvement of magnetic resonance methods in solving the production problems is earlier and today is carried out using the experimental base of laboratories of the institutes of the Academy of Sciences and universities.

As already noted above, in accordance with the general development trends of the magnetic resonance, the ICMR (International Center for Magnetic Resonance) of KFU and its research area were formulated. R.Z. Sagdeev, Academician of the RAS (ITC SB RAS), and Prof. H. Alloul (France) are the consulting professors of ICMR. Prof. A.V. Aganov is the head of the Center.

Honorary Doctor of KFU R.Z. Sagdeev

Honorary Doctor of KFU H. Alloul (France)



A.V. Aganov

The experimental work is structured as follows. Main methods of magnetic resonance:

– High-resolution NMR (V.V. Klochkov);

– PFG NMR, diffusofometry, micro- and minitomography (V.D. Skirda);

– Multinuclear resonance (M.S. Tagirov);

– MRI of a human (K.A. Ilyasov (based on a university clinic));

– EPR spectroscopy (S.B. Orlinskii);

– Development of competitive equipment by the application fields (co-ordinators: V.D. Skirda, M.S. Tagirov).

In addition, the experimental bases are used for work:

– The experimental base of the Federal Center for Collective Use of Physical and Chemical Research of Substances and Materials (head of the experimental research department S.I. Nikitin);

– Center for Quantum Technologies (head D.A. Tayurskii).

V.V. Klochkov

V.D. Skirda

M.S. Tagirov

K.A. Ilyasov

S.B. Orlinskii

D.A. Tayurskii

S.I. Nikitin

Experimentalists are fruitfully collaborating with theorists: Professors B.I. Kochelaev, L.K. Aminov, M.V. Eremin, B.Z. Malkin, L.R. Tagirov, D.A. Tayurskii, N.F. Fatkullin.

Today it’s quite simple to track the development of any research area, for example, using an international database of publications indexed in a database, such as Scopus or Web of Sience.

It is quite natural to ask a question, what are the trends and rates of research using magnetic resonance methods in the world, and in Russia? What place does Kazan University take in the world of magnetic resonance? The general idea of the pace of development of magnetic resonance and its applications in the world is given by the graphs presented in Figs. 1–19.

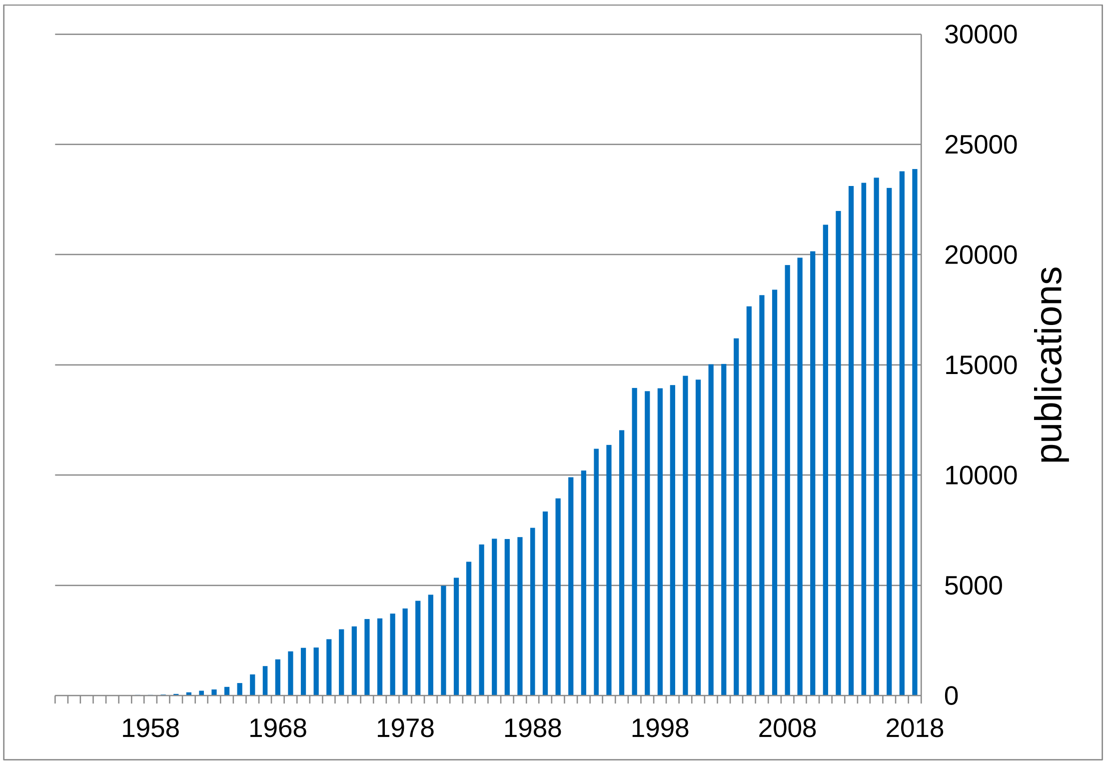


Fig. 1. Trend in the development of magnetic resonance and its applications in all areas of research (hereinafter throughout the world without tomography) (Scopus Keywords: “NMR”, “ESR”, “EPR”)

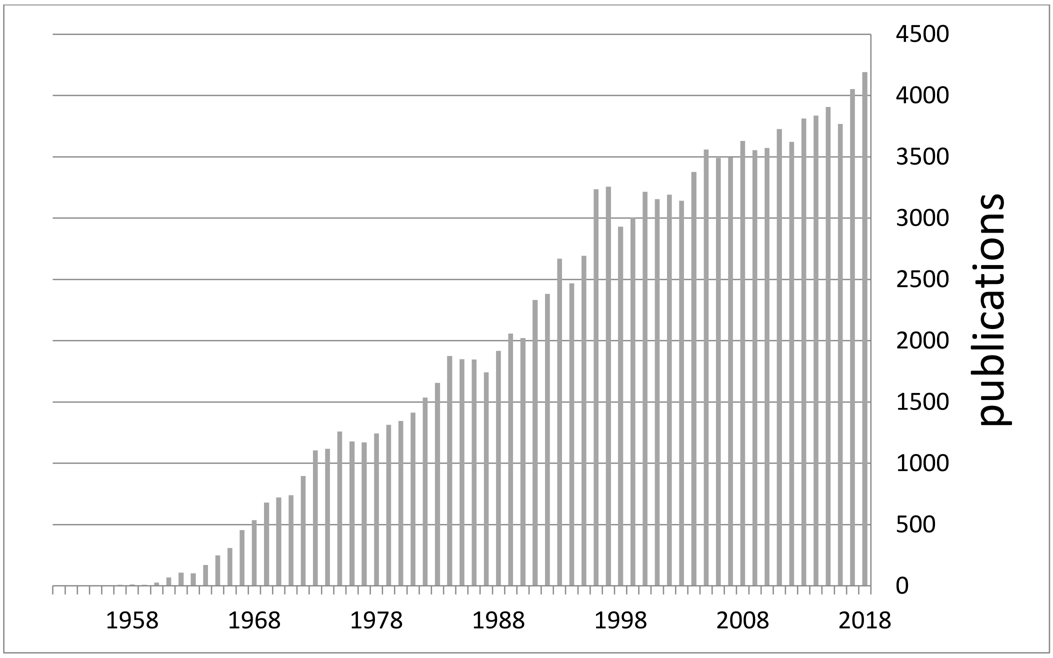


Fig. 2. Trend in the development of the EPR and its applications in all areas of research (Scopus Keywords: “ESR”, “EPR”)

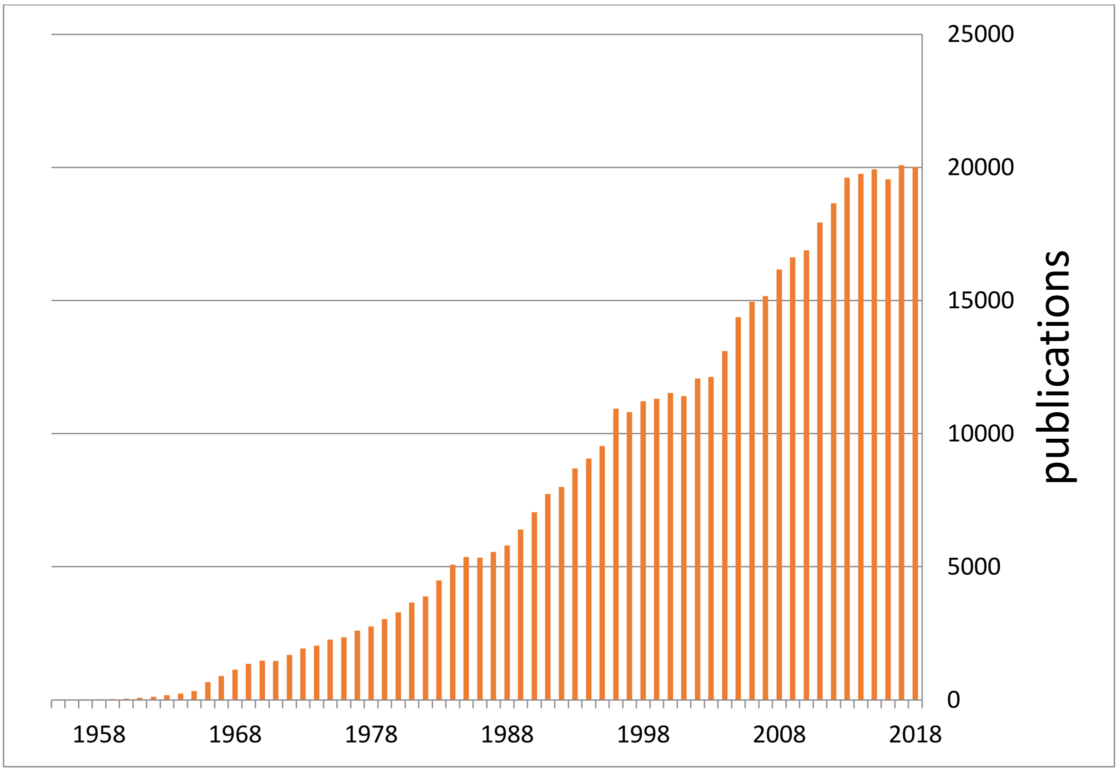


Fig. 3. Trend in the development of NMR and its applications in all areas of research worldwide (Scopus Keyword: “NMR”)

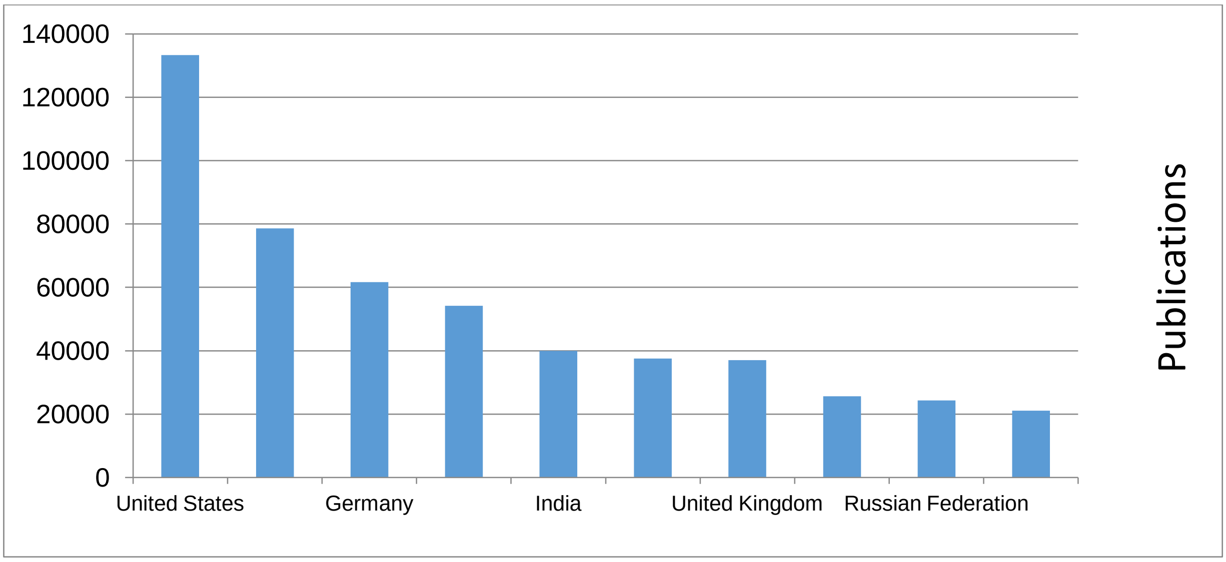


Fig. 4. Contribution of world leaders to magnetic resonance research (Scopus Keywords: “NMR”, “ESR”, “EPR”)

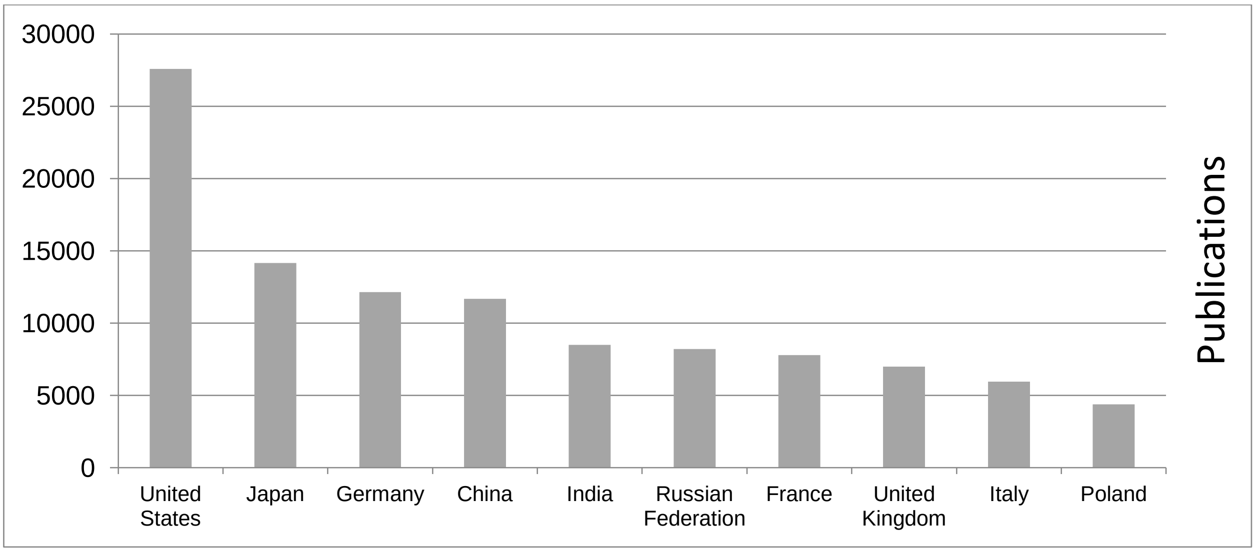


Fig. 5. Contribution of countries - world leaders in EPR research (Scopus Keywords: “ESR”, “EPR”)

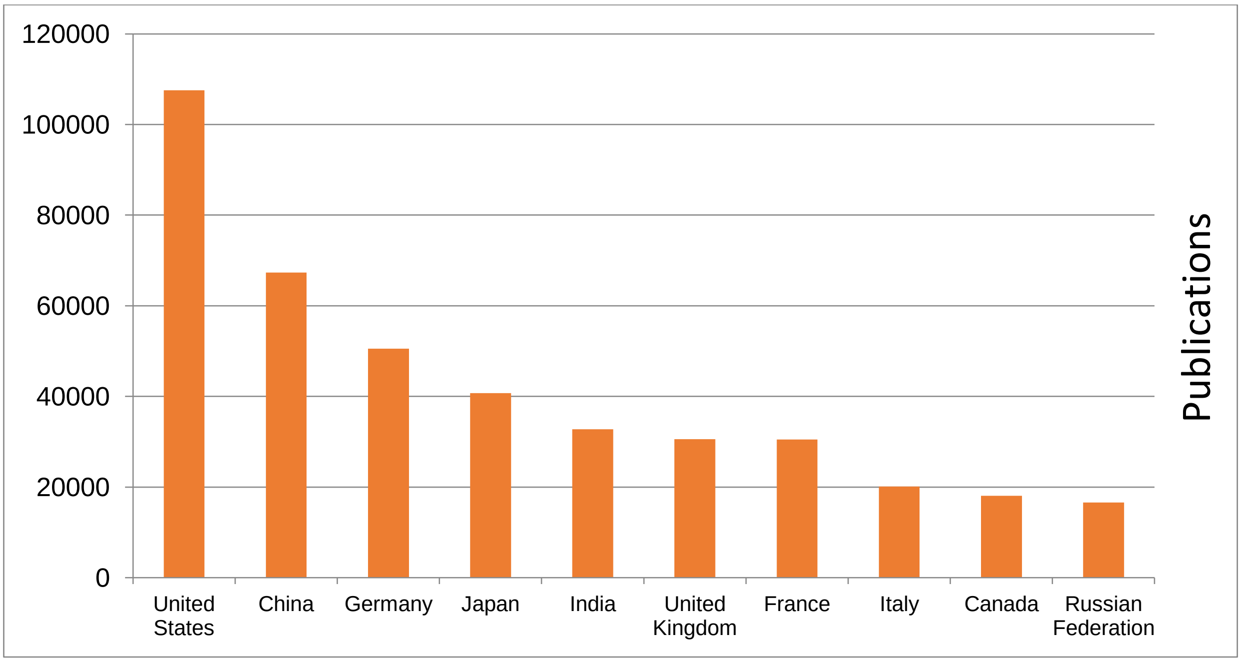


Fig. 6. Contribution of contries - world leaders to NMR research (Scopus Keyword: “NMR”)

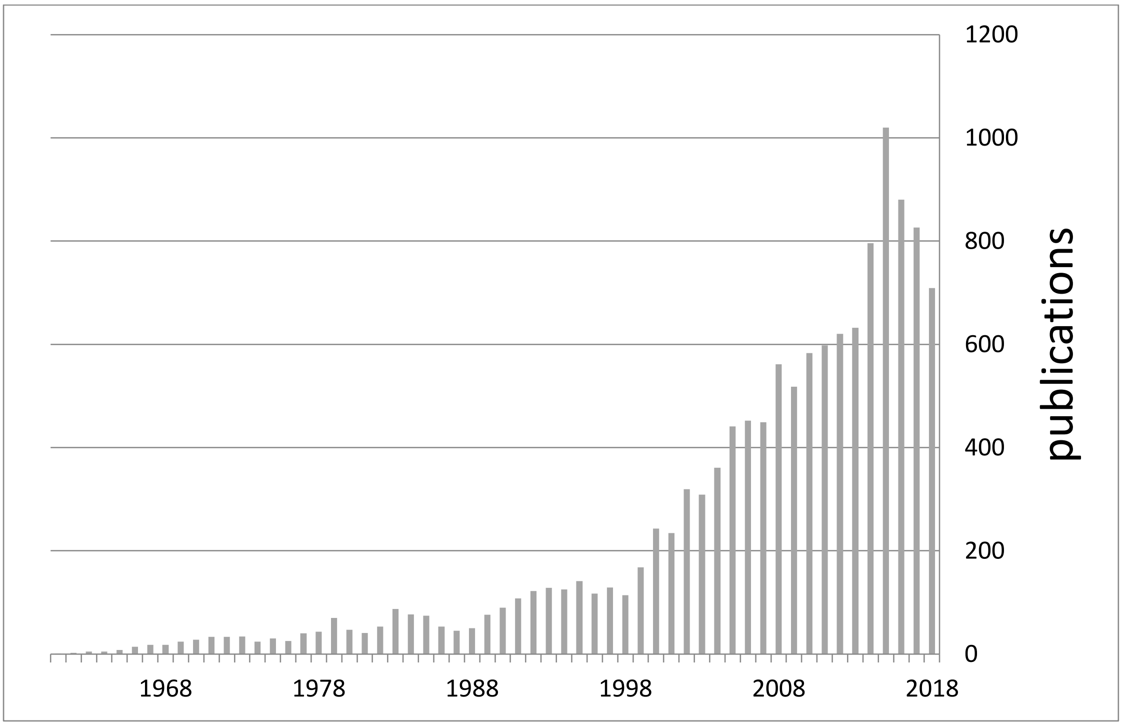


Fig. 7. Trend in the development of EPR studies in chemistry (Scopus Keywords: “chemistry”, “ESR”, “EPR”)

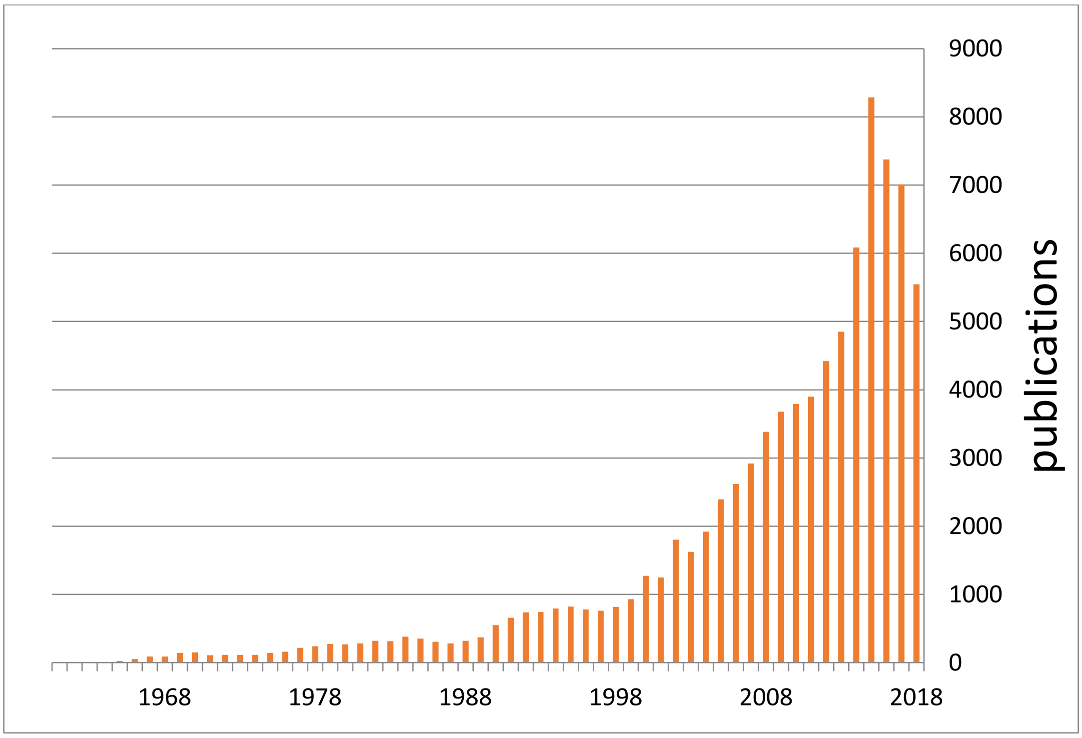


Fig. 8. Trend in the development of NMR research in chemistry (Scopus Keywords: “NMR”, “chemistry”)

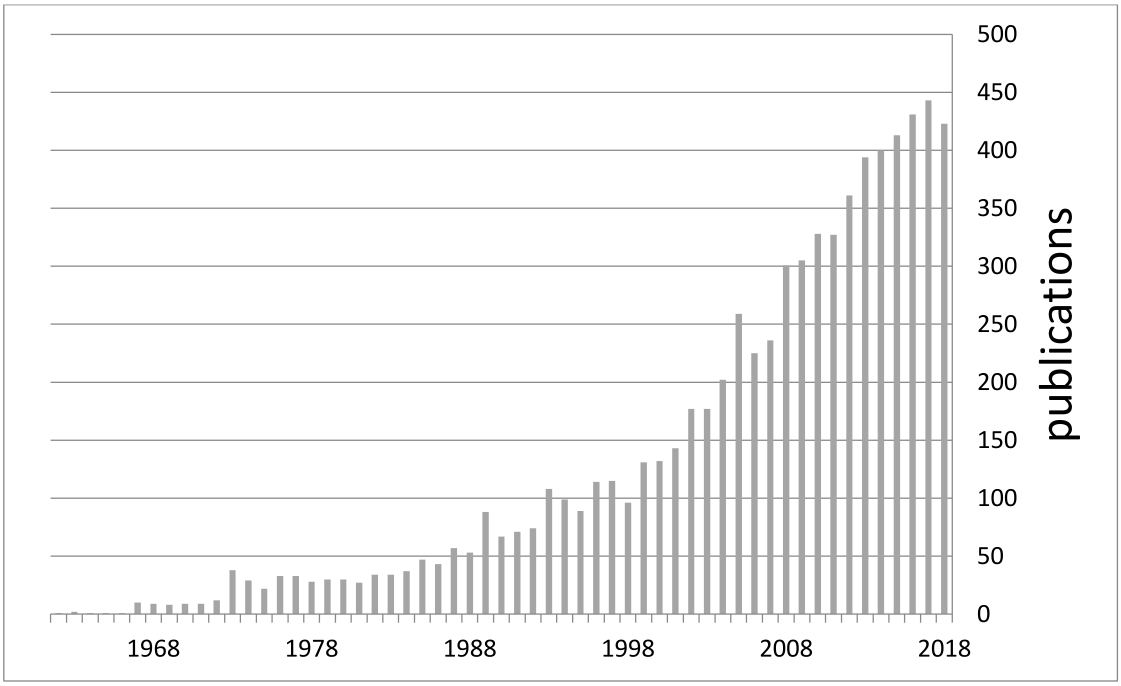


Fig. 9. Trend in the development of EPR studies in biology and medicine (Scopus Keywords: “Biology”, “Medicine”, “ESR”, “EPR”)

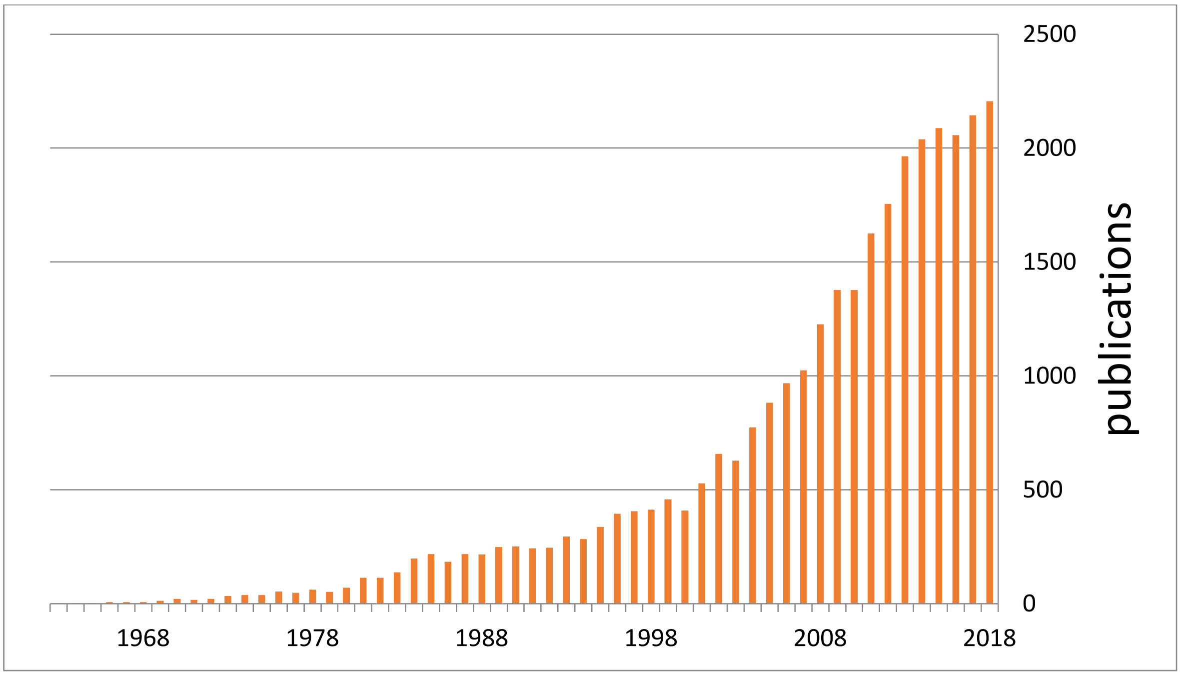


Fig. 10. Trend in the development of NMR research in biology and medicine (Scopus Keywords: "Biology", "Medicine", "NMR")

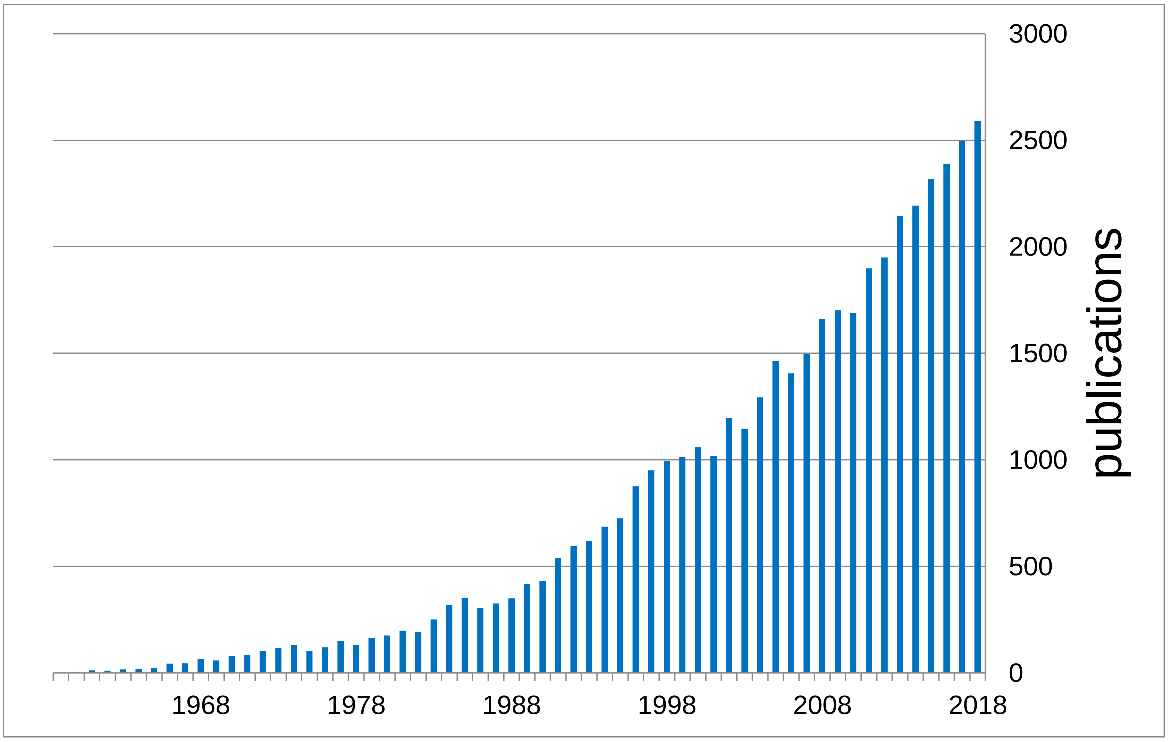


Fig. 11. Trend in the development of magnetic resonance in oil and gas technology (Scopus Keywords: "NMR", "ESR", "EPR", "Oil", "Gas")

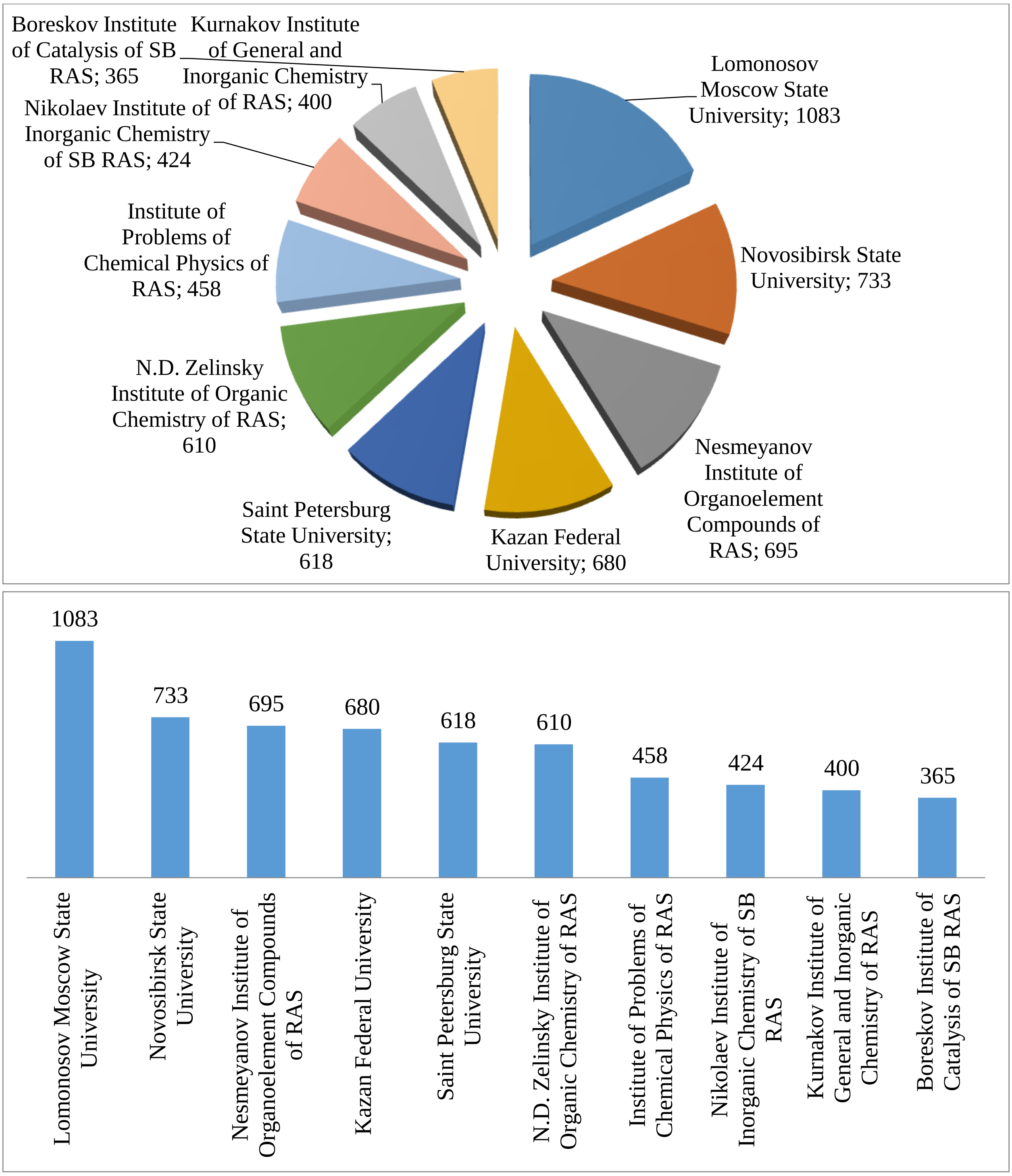


Fig. 12. Publication activity of leading Russian research centers of magnetic resonance in all fields of application. Hereinafter, the publications of the leading centers (groups) of the Russian Federation for the period 2009–2018, indexed in the Scopus database, are taken into account

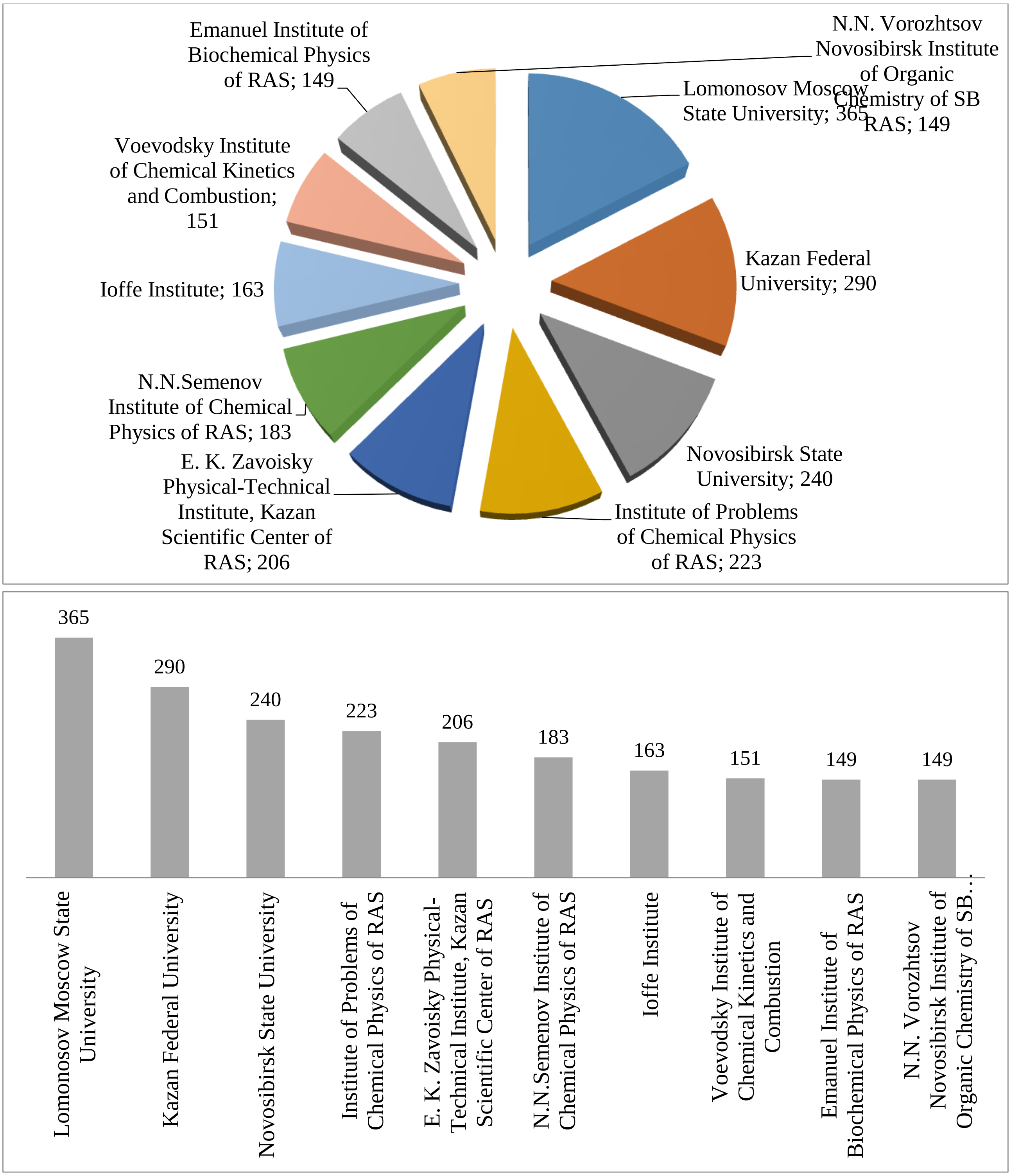
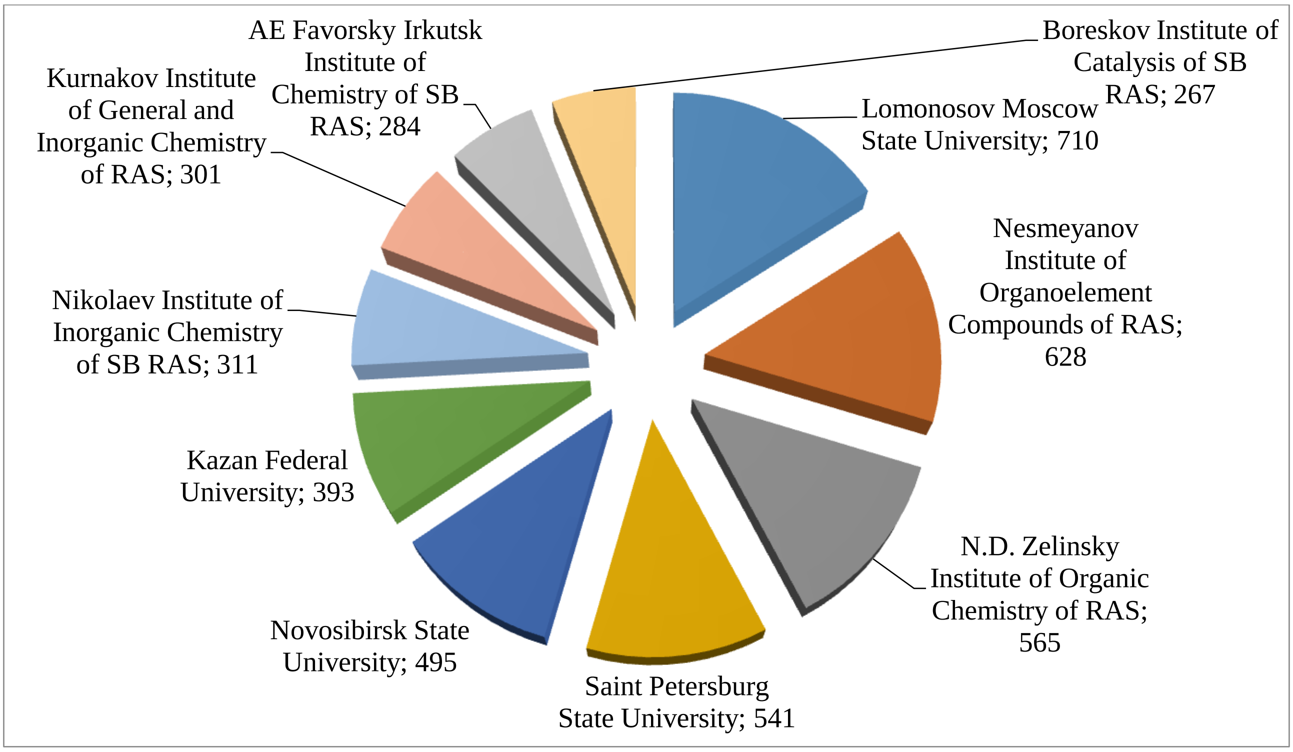


Fig. 13. Publication activity in all areas of EPR application from 2009 to 2018. In total 2622 articles were published (RAS 1464)



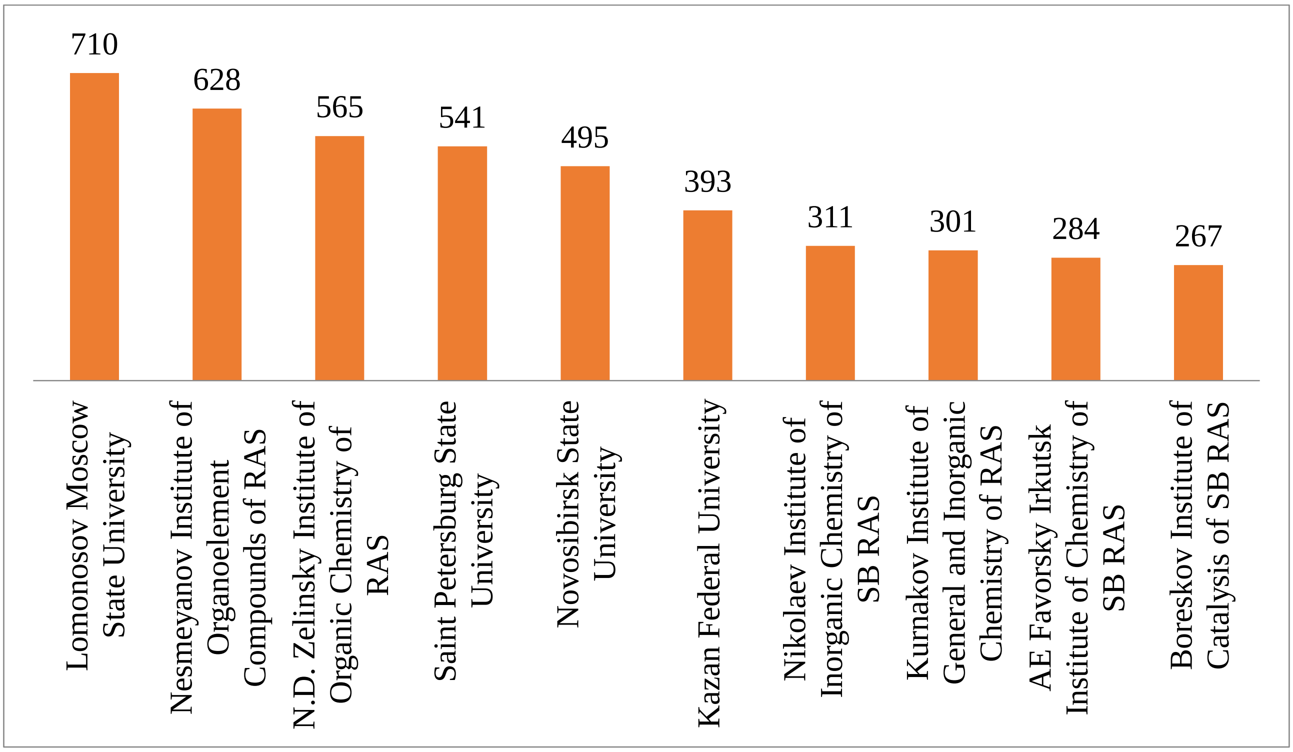


Fig. 14. Publication activity in all areas of NMR application from 2009 to 2018. In total 7126 articles were published (RAS 3457)

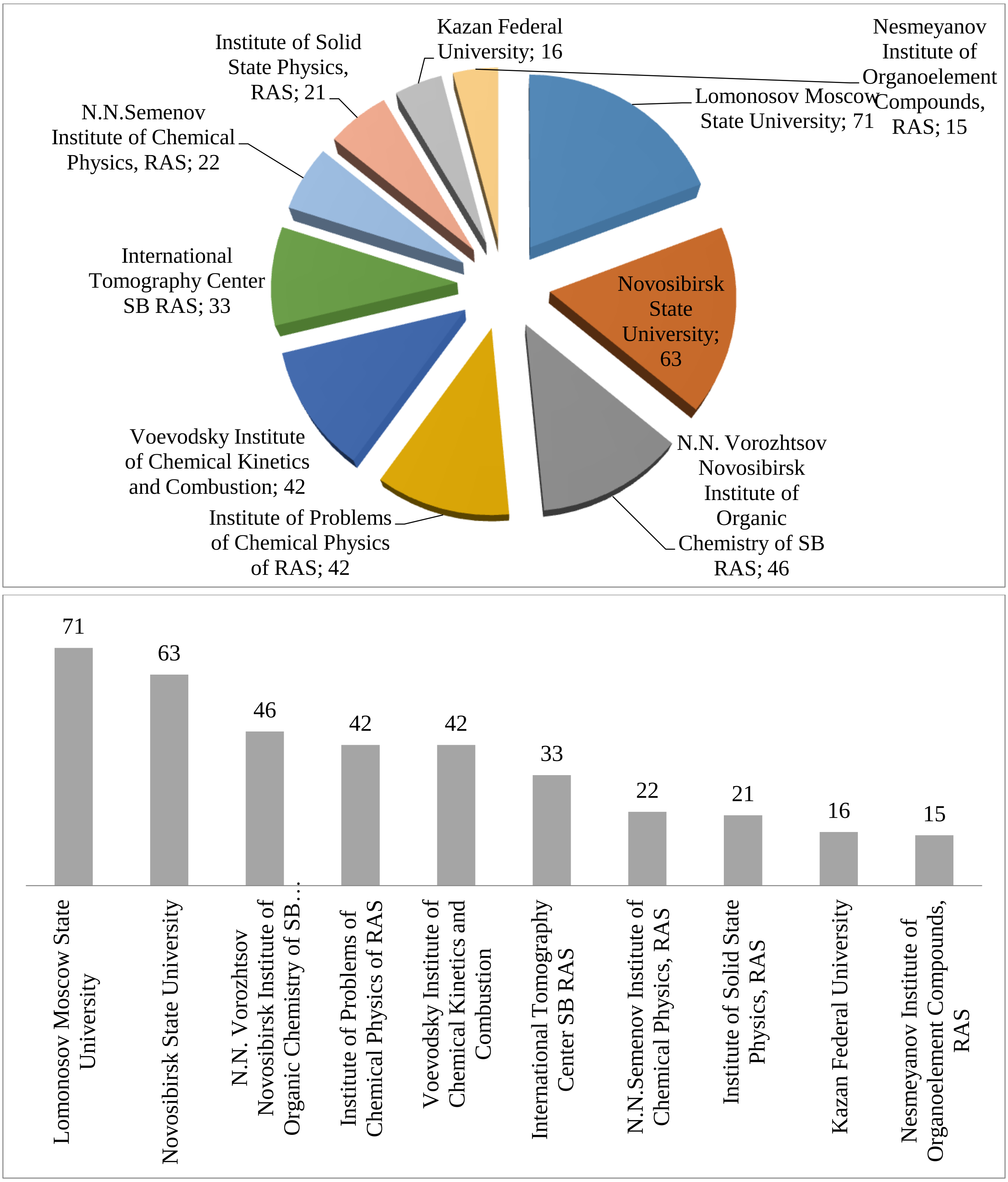
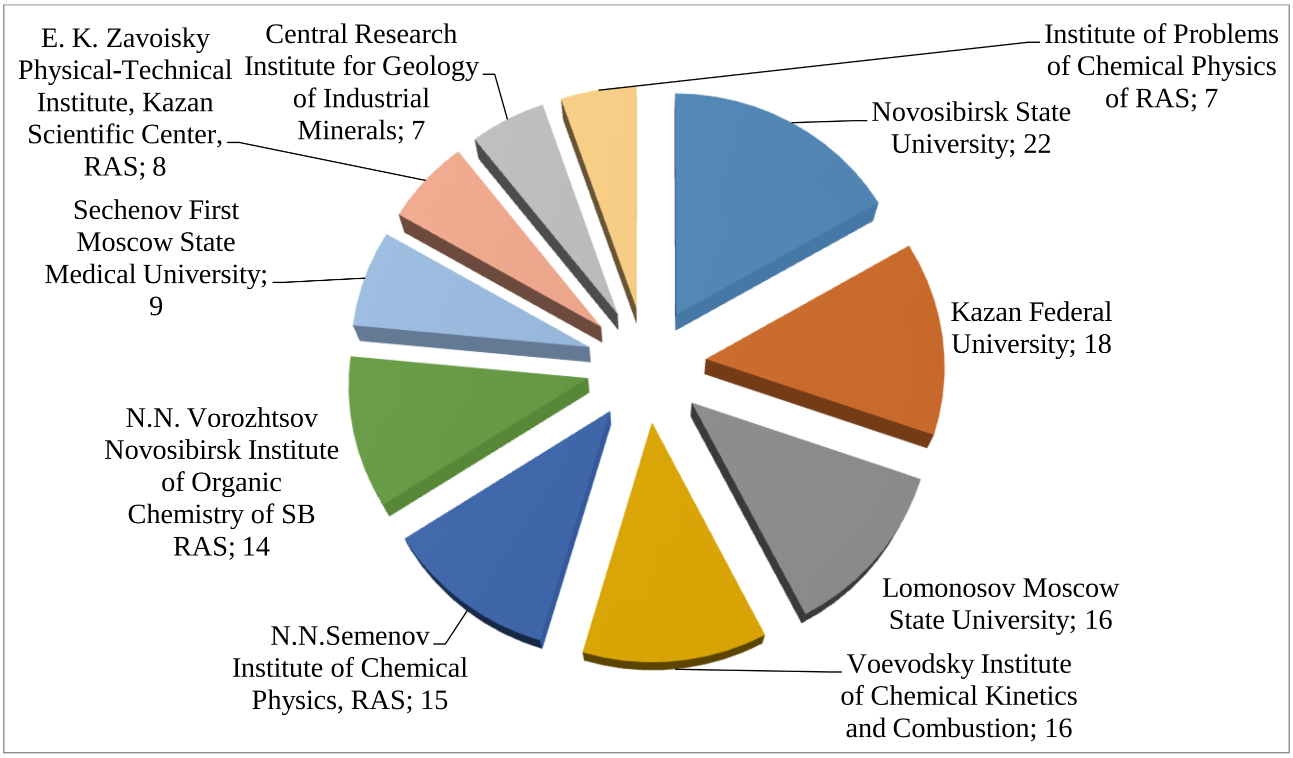


Fig. 15. Publication activity in EPR studies in chemistry from 2009 to 2018. In total 352 articles were published (RAS 146)



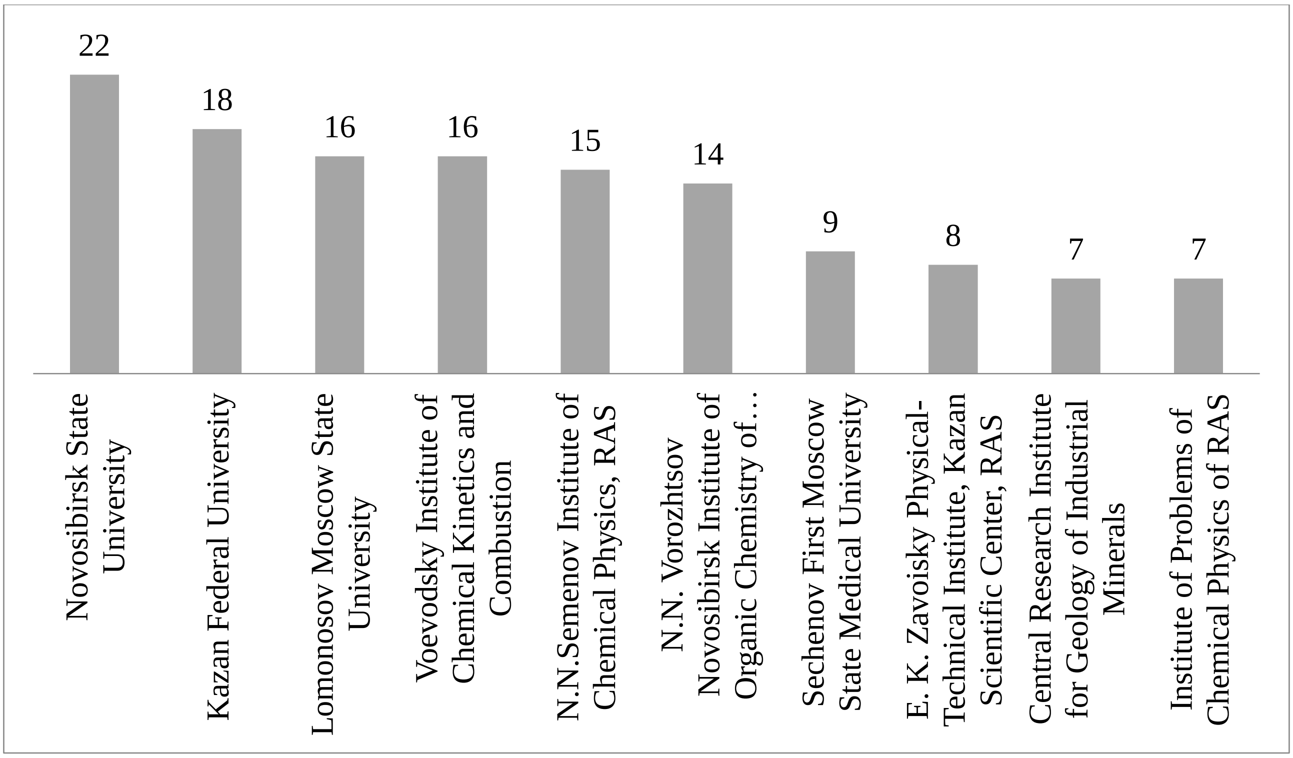


Fig. 16. Publication activity of EPR studies in biology and medicine from 2009 to 2018. In total 165 articles were published (RAS 56)

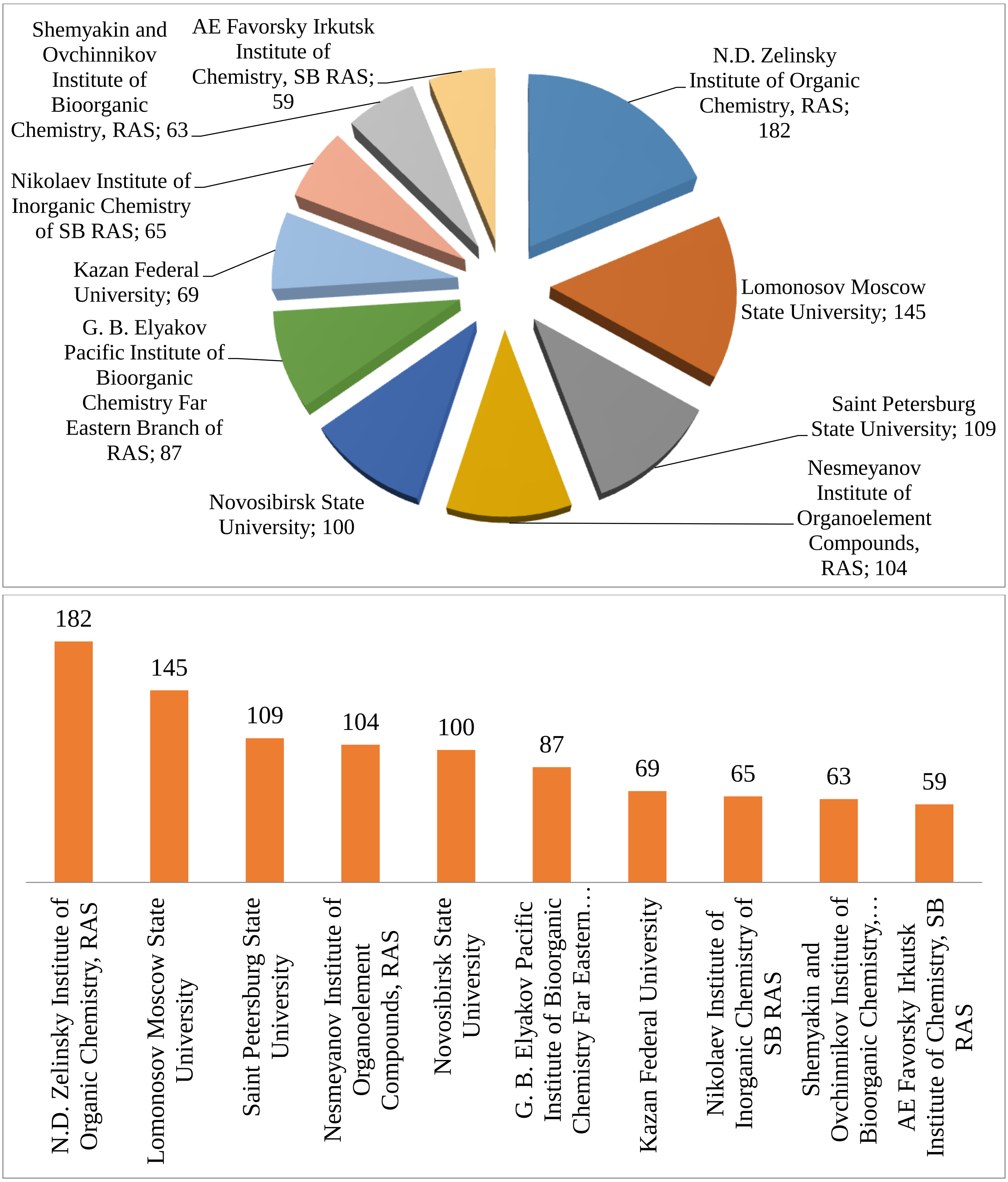


Fig. 17. Publication activity on the use of NMR in chemistry from 2009 to 2018. In total 1266 articles were published (RAS 645)

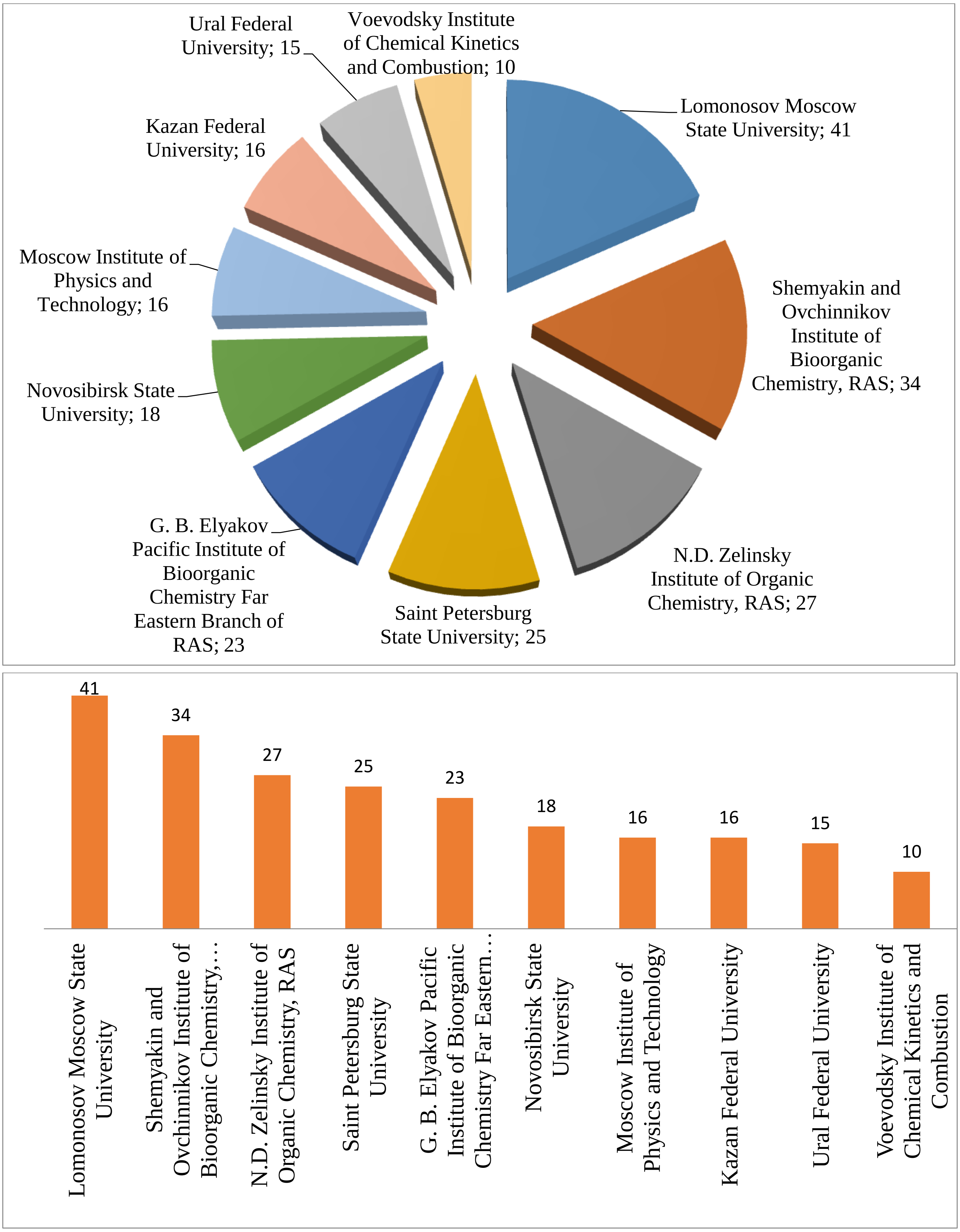


Fig. 18. Publication activity on the use of NMR in biology and medicine from 2009 to 2018. In total 351 articles were published (RAS 157).

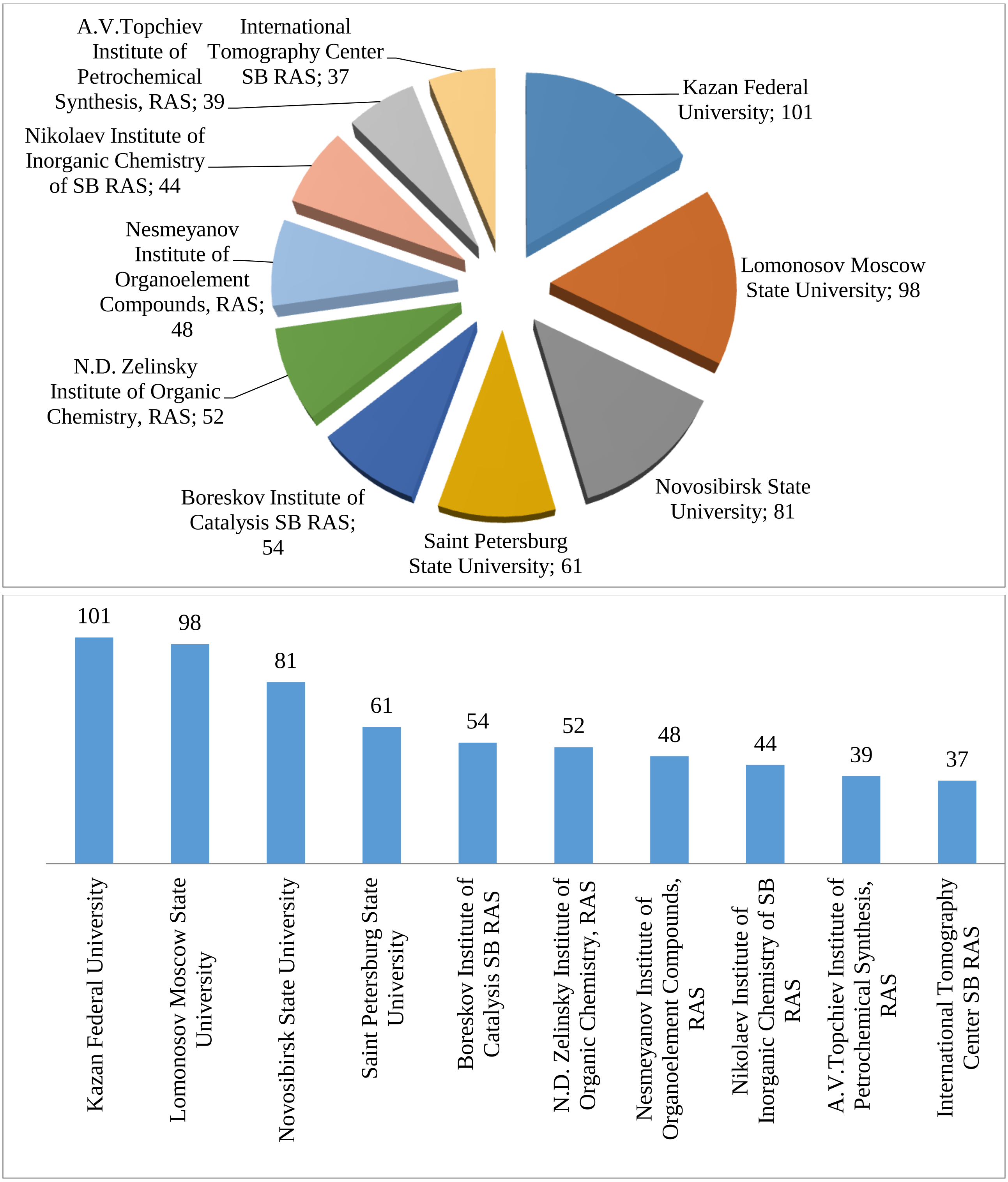


Fig. 19. Publication activity on the use of magnetic resonance in oil and gas technology from 2009 to 2018. In total 895 articles were published (RAS 326)

In the field of magnetic resonance in the international ranking (in the Scopus database) 600 largest scientific centers all around the world are taken into account. These graphs reflect their contribution. The leading research centers of Russia are also represented in this rating. Kazan University is represented in it in almost all fields of application of magnetic resonance. For all fields of application of magnetic resonance, KFU is one of the 150 leading centers of the world in all areas of application of EPR, in the field of NMR it is in the first hundred, and in several highly specialized areas it is among 10 world leaders: NMR in the field of superfluidity and non-linear NMR, PFG NMR, in particular, in oil and gas technologies, in the field of time-resolved light-induced EPR spectroscopy.

What about research in our country as a whole? In 2018, about 23 000 articles were published in the world in all fields of application of magnetic resonance, about a third of these use EPR. The number of similar domestic publications of scientific, educational, and industrial organizations is about 400–450 and is up to 2.3% of the total number of publications in the world (one third of them is using EPR). This indicator correlates with Russia's overall contribution in research and the global economy. About 2/3 part is the contribution of the universities, which received enormous financial support under the Development Program during 2010–2015, due to which re-equipment of the magnetic resonance laboratories of universities was carried out, where the magnetic resonance actually originated: Kazan, Moscow, St. Petersburg, which ensured high dynamics of their development. Novosibirsk State University is close to these centers and is deeply integrated with the institutes of the Siberian Branch of RAS. These four universities are invariably in the top-10 as a whole and fill the first five positions in several areas of application. The remaining positions, as a rule, are occupied by the Institutes of the Russian Academy of Sciences (Moscow) and the Siberian Branch of RAS, which regularly updated the park of spectrometers. The formal rating (according to the number of publications indexed in the Scopus database without taking into account the normalization for the number of scientists employed in these studies) of Russian research centers using magnetic resonance methods was announced at two previous conferences held in Kazan in 2015 and 2016 (VI All-Russian Conference “New Advances in NMR in Structural

Research” with the participation of foreign scientists with elements of a school for young researchers, Kazan, KFU, April 6–9, 2015; International symposium “Magnetic resonance: from basic research to practical applications” with elements of a school for young researchers, (Kazan, KFU, April 21–23, 2016), at the Russian conference YALCHIK 2017, International School “Actual problems of magnetic resonance and its application” (Kazan, 2018)).

Despite the conventionality of compiling such a rating of publication activity, since the data are given without taking into account the impact factors of journals and the cross-joint publications of scientists from Russian centers are not highlighted, they generally reflect the real state of affairs in research, development and applications in the field of magnetic resonance of leading magnetic resonance centers in Russia.

Unfortunately, the total contribution of Russian centers of magnetic resonance in the field of tomography is about an order of magnitude lower. We only note that in Russia the leading positions in the development of MRI methods are held by the Center for Magnetic Resonance and Spectroscopy of Moscow State University and the International Tomographic Center of the Siberian Branch of RAS, the increase in the activity of clinical applications is noted in medical universities in Moscow, and Kazan Federal University is among the Russian top ten leaders.

In place of Conclusion

The discovery of electron paramagnetic resonance was met with skepticism and distrust. However, soon after the publication of the first papers in the field of magnetic resonance (EPR and NMR), the prospects for the development of magnetic resonance and its applications became apparent. But the active use of magnetic resonance methods began only with the advent of the first industrial spectrometers in the mid–1950s. Since the mid-1990s, when multifunctional, high-performance spectrometers appeared, provided with programs for spectra processing, a triumphal march across the planet of magnetic resonance began. Its crown is magnetic resonance imaging, for the creation of which P. Lauterbur and P. Mansfield were awarded the 2003 Nobel Prize in Medicine (MRI is a separate and large topic that is not addressed in this article). The Nobel Prizes were also awarded for a number of other outstanding works performed using magnetic resonance: **in physics**: **1966** – A. Kastler (Double optical magnetic resonance), **1989** – N.F. Ramsey (for the invention of the separated oscillatory field method, which had important applications in the construction of atomic clocks.), **1991** – P. DeGennes (Liquid crystals and NMR in antiferromagnets), **1996** – D. Lee, *et al.* (Discovery of superfluid helium-3 by NMR), **1997** – Van Vleck *et al.* (For contribution to the study of the magnetic and electrical properties of materials), **2003** – A. Leggett (pioneering work on superconductivity and superfluidity, including NMR of superfluid helium-3), **in chemistry** – **1998** – J. Pople (For his contribution to the computational methods of quantum chemistry, including spin-Hamiltonian parameters).

It is no coincidence that the Nobel Prize winner Academician V.L. Ginzburg ranked the EPR discovery as one of the “outstanding achievements of 20th-century physics”.

The authors are grateful for the materials, comments and corrections to our colleagues: R.R. Amirov, I.S. Antipin, M.R. Gafurov, A.V. Dooglav, A.V. Zakharov, A.A. Kalachev, F.Kh. Karataeva, V.V. Klochkov, I.A. Larionov, B.Z. Malkin, Yu.N. Proshin, V.D. Skirda, L.R. Tagirov, M.S. Tagirov D.A. Tayurskii, N.M. Khasanova.

The authors are grateful to N.F. Galiullina for the preparation of the materials for publication, associate professor K.S. Usachev for preparing the data for Fig. 1–19.

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Annex 1

Theses for the doctoral degree, performed at the Kazan State (Federal) University by employees, doctoral students and applicants from the Faculty of Physics (Institute of Physics) in the field of radio spectroscopy and its applications

1. **Zavoysky E.K.** “Paramagnetic absorption in perpendicular and parallel fields for salts, solutions and metals”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1945)**.
2. **Altshuler S.A.** “The theory of some phenomena of paramagnetic resonance”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1954)**.
3. **Valiev K.A.** “Theoretical issues in the study of liquid matter by spectrometric methods (magnetic resonance and molecular scattering and absorption of light)”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1963)**.
4. **Vinokurov V.M.** “Magnetic properties of minerals”. Doctoral dissertation (Doct. of Geological and Mineralogical Sciences) **(1964)**.
5. **Zaripov Maks. Mukham.** “Investigations of the spectra of electron paramagnetic resonance in crystals”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1966)**.
6. **Kochelaev B.I.** “Theory of dynamic effects in paramagnetic crystals”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1967)**.
7. **Samitov Yu.Yu.** “Nuclear magnetic resonance spectra and stereoisomerism of molecules”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1967)**.
8. **Popel A.A.** “The use of nuclear magnetic relaxation in inorganic analysis”. Doctoral dissertation (Doctor of Chemical Sciences) **(1968)**.
9. **Maklakov A.I.** “The study of molecular mobility and some other properties of polymer systems by nuclear magnetic resonance”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1970)**.

10. **Bashkirov Sh.Sh.** "Application of nuclear gamma resonance to the study of paramagnetic crystals". Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1970)**.
11. **Pen'kov I.N.** "Investigation of the features of the chemism and structure of minerals by the method of nuclear quadrupole resonance". Doctoral dissertation (Doct. of Geological and Mineralogical Sciences) **(1971)**.
12. **Aminov L.K.** "On the theory of spin-lattice relaxation in paramagnetic ionic crystals". Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1973)**.
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16. **Dautov R.A.** "Relaxation and transfer of magnetization of nuclear spin systems in solids". Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1978)**.
17. **Kharakhashyan E.G.** "Experimental studies of the phenomenon of electron spin resonance in metals". Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1980)**.
18. **Teplov M.A.** "Nuclear magnetic resonance in Van Vleck paramagnets". Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1981)**.
19. **Zaripov Makhm. Mub.** "Theoretical issues of relaxation processes in liquids". Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1981)**.
20. **Safin I.A.** "Nuclear quadrupole resonance of the nuclei of the elements of the fifth group". Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1981)**.

21. **Yulmetyev R.M.** “The study of particle correlations in liquids by the abridged description method”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1981)**.
22. **Malkin B.Z.** “The crystal field and electron-phonon interaction in ionic rare-earth paramagnets”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1984)**.
23. **Osokin D.Ya.** “Pulse spectroscopy of nuclear quadrupole resonance”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1984)**.
24. **Vishnevskaya G.P.** “Intramolecular and intermolecular relaxation and electron resonance of paramagnetic ions in solutions and polymers”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1985)**.
25. **Khasanov A.Kh.** “An experimental study of strongly nonequilibrium spin systems in paramagnetic ionic crystals”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1985)**.
26. **Aganov A.V.** “NMR spectroscopy and molecular dynamics of organic derivatives of elements of groups V and VI”. Doctoral dissertation (Doct. of Chem.Sci., Phys.Chem.) **(1986)**.
27. **Eremin M.V.** “Charge transfer processes and the interaction of spin and orbital moments in ionic crystals”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1987)**.
28. **Aminova R.M.** “Non-empirical models in the study of magnetic properties, spectral parameters of NMR and their relationship with the electronic and spatial structure of molecules of organic compounds”. Doctoral dissertation (Doct. of Chem.Sci.,Org. and Phys.Chem) **(1990)**.
29. **Klochkov V.V.** “Dynamic NMR of medium sized carbo- and heterocycles”. Doctoral dissertation (Doct. of Chem.Sci., Doct. of Chem.Sci.,Org. and Phys.Chem.) **(1991)**.
30. **Skirda V.D.** “Self-diffusion in polymer systems”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1992)**.
31. **Tagirov M.S.** “Nuclear magnetic relaxation due to fluctuations in hyperfine fields”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1992)**.

32. **Kosov A.A.** “Kinetic phenomena in superconductors with local electronic and vibrational states”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1993)**.
33. **Nigmatullin R.R.** “The physics of fractional calculus and its implementation on fractal structures”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1993)**.
34. **Sadykov E.K.** “Questions of the theory of NGR spectroscopy and radio frequency methods in the study of modulation phenomena in magnetic systems”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1993)**.
35. **Tsarevsky S.L.** “Theory of spin-wave and electron-nuclear resonances in superconductors”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1994)**.
36. **Dvoyashkin N.K.** “An experimental study of fluid self-diffusion in porous media by the PMFG NMR method”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1995)**.
37. **Proshin Yu.N.** “Theory of magnetic breakdown with spin flip”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1995)**.
38. **Fatkullin N.F.** “On the theory of spin-lattice relaxation and diffusion decay of a stimulated spin echo signal in polymer systems and inhomogeneous media”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1995)**.
39. **Tagirov L.R.** “Theory of electron paramagnetic resonance in superconductors”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1996)**.
40. **Khusainov M.G.** “Superconducting and magnetic properties of layered structures”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1997)**.
41. **Zyablikova T.A.** “Nuclear magnetic resonance spectra and the structure of molecules with a phosphorus-carbon bond”. Doctoral dissertation (Doct.of Chem.Sci.) **(1999)**.
42. **Latypov Sh.K.** “Design of chiral derivatizing reagents for determining the absolute configuration of organic compounds by NMR”. Doctoral dissertation (Doct. of Chem.Sci.,Org. and Phys.Chem.) **(1999)**.

43. **Usachev A.E.** “EPR study of phase transitions and the Jahn-Teller effect in perovskite-like compounds”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(1999)**.
44. **Karataeva F.Kh.** “Stereodynamics and tautometry of organic derivatives of four-coordinated phosphorus”. Doctoral dissertation (Doct.of Chem.Sci., Phys. and Element-org. Chem.) **(2000)**.
45. **Nizamutdinov N.M.** “EPR and patterns of distribution of paramagnetic point defects in crystals”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2000)**.
46. **Talanov Yu.I.** “The study of the vortex state of oxide superconductors by microwave absorption”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2000)**.
47. **Tayurskii D.A.** “Magnetic coupling of liquid ^{3}He and dielectric Van Vleck paramagnets”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2001)**.
48. **Krutikov V.F**. “Radiospectroscopy of minerals and rocks of non-metallic mineral deposits”. Doctoral dissertation (Geological and Mineralogical Sciences) **(2002)**.
49. **Tarasov V.F.** “Submillimeter EPR spectroscopy of impurity paramagnetic centers in dielectric crystals”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2002)**.
50. **Filippov A.V.** “Self-diffusion in multiphase systems with restriction”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2003)**.
51. **Bashirov F.I.** “Spectroscopy of inhibited movements of molecules in crystals”. (Doct.of Phys.-Math.Sci.) **(2006)**.
52. **Krushelnitsky A.G.** “Molecular dynamics of proteins and polypeptides. Study by relaxation and exchange NMR spectroscopy”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2006)**.
53. **Mironov G.I.** “The theory of two-dimensional and nanoscale systems with strong correlations in the Hubbard model”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2008)**.

54. **Ivanshin V.A.** “The study of strongly correlated electronic systems by electron paramagnetic resonance”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2009)**.
55. **Silkin N.I.** “Optical and EPR spectroscopy of materials for quantum electronics and nonlinear optics based on fluoride crystals, families of dihydrogen phosphate and potassium sulfate”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2009)**.
56. **Grevtsev V.A.** “Mineralogical and technological assessment of the quality of non-metallic minerals by radiospectroscopy methods”. Doctoral dissertation (Geological and Mineralogical Sciences) **(2011)**.
57. **Eremina R.M.** “The study of low-dimensional magnetic structures by the EPR method”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2011)**.
58. **Ilyasov K.A.** “Development of magnetic resonance imaging methods in the study of self-diffusion and temperature fields in living systems”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2011)**.
59. **Bulatov F.M.** “Crystal chemistry of industrial minerals in solving problems of applied mineralogy by Mössbauer spectroscopy”. Doctoral dissertation (Geological and Mineralogical Sciences) **(2012)**.
60. **Andronenko S.I.** “The magnetic state of impurity ions and defects in magnetic semiconductors and their dielectric analogs”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2013)**.
61. **Mamin R.F.** “Phase transitions and the formation of inhomogeneous states in ferroelectric and magnetic semiconductors”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2013)**.
62. **Anikeenok O.A.** “The method of secondary quantization with a non-orthogonal basis and its application to the theory of local fields on the nuclei of diamagnetic ions in crystals with unfilled 3d and 4f shells”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2015)**.
63. **Eremin I.M.** “Spin excitations and electron correlations in non-ordinary high-temperature superconductors”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2016)**.

64. **Mukhametshin I.R.** “Investigation of sodium cobaltates Na^xCoO^2 by NMR, NQR and muon spectroscopy”. Doctoral dissertation (Doct.of Phys.-Math.Sci.) **(2019)**.

Annex 2

The dissertations for the degree of candidate of science (Ph.D.), performed at the Kazan State (Federal) University by graduatestudents, employees and applicants of the Faculty of Physics (Institute of Physics) in the field of radio spectroscopy and its applications

1. **Kozyrev B.M.** “Paramagnetic relaxation in the crystals of some salts”. 1945. Research Supervisor (Res.Sup.) – E.K. Zavoisky.
2. **Romanov I.M.** “Paramagnetic dispersion in perpendicular fields at frequencies of 10^8 Hz”. 1950.
3. **Glebashev G.Ya.** “Application of the moments method to the studied of the shape of resonant paramagnetic absorption curves”. 1954. Res.Sup. – S.A. Altshuler.
4. **Neprimerov N.N.** “Paramagnetic resonance and rotation of the plane of polarization in the microwave range”. 1954. Res.Sup. – S.A. Altshuler.
5. **Sitnikov K.P.** “Paramagnetic absorption in some salts of elements of transition groups”. 1954.
6. **Zaripov Maks. Mukham.** “On the theory of the fine and hyperfine structure of paramagnetic resonance spectra”. 1955. Res.Sup. – S.A. Altshuler.
7. **Shekun L.Ya.** “Spin-lattice interaction in salts of rare earths”. 1956. Res.Sup. – S.A. Altshuler.
8. **Avvakumov V.I.** “Theory of spin-lattice relaxation in paramagnetic salts of elements of the iron group with an even number of electrons”. 1957. Res.Sup. – S.A. Altshuler.
9. **Dautov R.A.** “The influence of a high-frequency magnetic field on the electrical resistance of ferromagnets”. 1957.
10. **Bashkirov Sh.Sh.** “On the theory of paramagnetic spin-lattice relaxation”. 1958. Res.Sup. – S.A. Altshuler.

11. **Kopvillem U.H.** “On the effect of internal interactions on the shape of paramagnetic absorption lines”. 1958. Res.Sup. – S.A. Altshuler.
12. **Valiev K.A.** “Nuclear magnetic resonance of the of paramagnetic atoms nuclei”. 1958. Res.Sup. – S.A. Altshuler.
13. **Kessel A.R.** “Questions of the theory of acoustic resonance”. 1960. Res.Sup. – S.A. Altshuler.
14. **Kochelaev B.I.** “Some issues of spin-lattice interaction in ionic crystals”. 1960. Res.Sup. – S.A. Altshuler.
15. **Aminov L.K.** “Some issues of spin-phonon interaction”. 1962. Res.Sup. – S.A. Altshuler.
16. **Timerov R.Kh.** “On the influence of the movement and exchange interactions on the lineshape of electronic and nuclear paramagnetic resonance”. 1962. Res.Sup. – S.A. Altshuler.
17. **Volokhova T.I.** “The study of paramagnetic relaxation in single crystals of salts of elements of the iron group in parallel fields at room temperature”. 1962. Res.Sup. – S.A. Altshuler.
18. **Koloskova N.G.** “On the theory of line shapes of paramagnetic resonance in ionic crystals”. 1963. Res.Sup. – S.A. Altshuler.
19. **Leushin A.M.** “Some questions of the theory of electron paramagnetic resonance in the S–state ions in crystals”. 1963. Res.Sup. – S.A. Altshuler.
20. **Morocha A.K.** “The theory of symmetry in paramagnetic resonance problems”. 1963. Res.Sup. – S.A. Altshuler.
21. **Ovchinnikov I.V.** “Some questions of the theory of magnetic phenomena in covalent compounds”. 1963. Res.Sup. – S.A. Altshuler.
22. **Polskii Yu.E.** “Electron paramagnetic resonance of Gd^{3+} ions in CaF_2”. 1963. Res.Sup. – S.A. Altshuler.
23. **Agishev A.Sh.** “Investigation of the thermal motion of molecules in liquids by nuclear magnetic resonance.” 1964. Res. Sup. – K.A. Valiev.
24. **Golenishchev–Kutuzov V.A.** “Relaxation paramagnetic absorption of sound in crystals”. 1964. Res.Sup. – U.H. Copvillem.

25. **Grazhdannikov E.G.** “Chemical factors in magnetic relaxation of fluorine nuclei and protons in solutions of paramagnetic ions”. 1964. Res.Sup. – A.A. Popel.
26. **Kucheryavenko N.S.** “Investigation of nuclear magnetic resonance in solutions of some paramagnetic electrolytes”. 1964. Res. Sup. – K.A. Valiev.
27. **Mazitov R.K.** “An experimental study of the relaxation of protons, deuterons and some other nuclei in pure liquids and electrolyte solutions”. 1964. Res. Sup. – K.A. Valiev.
28. **Sergeev N.M.** “^{19}F NMR spectroscopy of vinyl fluorides”. 1964.
29. **Stepanov V.G.** “An experimental study of electron paramagnetic resonance in of iron groups ions in the S-state”. 1964. Res.Sup. – M.M. Zaripov.
30. **Zaripov Mahm. Mubar.** “Some questions of the theory of spin-lattice relaxation in liquid solutions” 1964. Res. Sup. – K.A. Valiev.
31. **Chernitsyn A.I.** “The development of pulsed Spin Echo NMR equipment and its application in physic-chemical research”. 1965. Res.Sup. – S.A. Altshuler.
32. **Emelyanov M.I.** “The study of the self-diffusion of water molecules in aqueous solutions of electrolytes and molecules of one of the components in binary liquid systems by the spin echo method”. 1965. Res. Sup. – K.A. Valiev.
33. **Livanova L.D.** “Synthesis and study by EPR and optical spectroscopy of the symmetry of point defects in a row of fluorite and molybdate”. 1965. Res.Sup. – M.M. Zaripov.
34. **Malkin B.Z.** “A theoretical study of the influence of electron-vibrational interaction on the optical spectra of paramagnetic crystals”. 1965. Res.Sup. – S.A. Altshuler.
35. **Mekhtiyev G.F.** “On the theory of cross relaxation in various phenomena of paramagnetic resonance”. 1965. Res.Sup. – S.A. Altshuler.

36. **Saprykova Z.A.** "The use of nuclear magnetic relaxation method for the quantitative determination of metal ions in solution". 1965. Res.Sup. – A.A. Popel.
37. **Akhmedov A.G.** "Relaxation and spin diffusion of F^{19} nuclei in non-conducting crystals". 1966. Res. Sup. – R.A. Dautov.
38. **Chirkin G.K.** "The study of electron paramagnetic resonance of iron group ions in NH_4Cl". 1966. Res.Sup. – M.M. Zaripov.
39. **Ivanov E.I.** "The problem of random rotational walks and some other questions of the theory of rotational Brownian motion". 1965. Res. Sup. – K.A. Valiev.
40. **Mineeva R.M.** "On the theory of magnetic resonance of the nuclei of paramagnetic atoms". 1966. Res.Sup. – S.A. Altshuler.
41. **Valishev R.M.** "An experimental study of exchange interactions and paramagnetic relaxation in nickel fluorosilicate". 1966. Res.Sup. – S.A. Altshuler.
42. **Yastrebov V.N.** "The study of magnetic resonance at singlet electronic levels of V^{3+} in corundum". 1966. Res.Sup. – S.A. Altshuler.
43. **Yulmetyev R.M.** "Theoretical questions of the dynamics of the thermal motion of particles in a liquid". 1966. Res.Sup. – K.A. Valiev.
44. **Zykova T.V.** "Study of the structure of organophosphorus compounds by high resolution NMR spectroscopy". 1966. Res.Sup. – A.I. Razumov, Yu.Yu. Samitov.
45. **Chenborisova L.Ya.** "The use of magnetic resonance for the study of plastic polymer systems". 1967. Res.Sup. – A.I. Maklakov.
46. **Kurkin I.N.** "Study of the EPR spectra, line widths and spin-lattice relaxation of rare earth group ions in crystals with scheelite ($CaWO_4$) structure". 1967. Res.Sup. – L.Ya. Shekun.
47. **Murtazin Sh.F.** "Some issues of the nuclear spin-lattice interaction in crystals". 1967. Res.Sup. – S.A. Altshuler.
48. **Terpilovsky D.N.** "Some questions of the theory of nonradiative relaxation in aqueous solutions of rare earth salts". 1967. Res.Sup. – S.A. Altshuler.

49. **Bildanov M.**M. “The study of intermolecular interactions in solutions of paramagnetic ions and free radicals by high resolution NMR spectroscopy”.1968. Res. Sup. – K.A. Valiev.
50. **Ibraimov D.I.** “The study of intermolecular interactions in solutions of paramagnetic ions and free radicals by high resolution NMR spectroscopy”. 1968. Res.Sup. – Yu.Yu. Samitov.
51. **Pimenov G.G.** “Nuclear magnetic resonance in rigid-chain polymers”. 1968. Res.Sup. – A.I. Maklakov.
52. **Aganov A.V.** “The study of the inversion of cyclic molecules by high resolution NMR spectroscopy”. 1969. Res.Sup. – Yu.Yu. Samitov.
53. **Aliev M.N.** “The theory of some effects in paramagnetic crystals at low temperatures”. 1969. Res.Sup. – B.I. Kochelaev.
54. **Altshuler T.S.** “Electron paramagnetic resonance of rare earth ions in solutions”. 1969. Res. Sup. – B.M. Kozyrev, N.S. Garifyanov.
55. **Aminova R.M.** “Some issues of nuclear magnetic shielding in molecules”. 1969. Res.Sup. – B.A. Arbuzov, Yu.Yu. Samitov.
56. **Antipin A.A.** “An experimental study of the EPR spectra and spin-lattice relaxation of trivalent rare-earth ions in single crystals of the fluorite structure series”. 1969. Res.Sup. – L.Ya. Shekun.
57. **Grigoryev V.**P. “The study of molecular mobility in silicon-hydrocarbon polymers by NMR”.1969. Res.Sup. – A.I. Maklakov.
58. **Katyshev A.N.** “EPR study of rare-earth impurity ions in CeO_2 single crystals”. 1969. Res.Sup. – L.Ya. Shekun.
59. **Kropotov V.S.** “Experimental EPR study of elements of the iron group in crystals of a homologous fluorite series”. 1969. Res.Sup. – M.M. Zaripov.
60. **Sadykov E.K.** “Quadrupole superfine interaction of paramagnetic ions in a crystal and questions of the theory of nuclear gamma resonance”. 1969. Res.Sup. – Sh.Sh. Bashkirov.
61. **Selyutin G.Ya.** “On the theory of shift and intensity of the Mössbauer spectrum”. 1969. Res.Sup. – Sh.Sh. Bashkirov.

62. **Teplov M.A.** “NMR and spin-lattice relaxation in crystals containing rare–earth ions with a singlet electronic level”. 1969. Res.Sup. – S.A. Altshuler.
63. **Zaitov M.**M. “The study of spin-phonon interaction in paramagnetic crystals by uniaxial pressure”.1969. Res.Sup. – M.M. Zaripov.
64. **Korepanov V.D.** “The study of the magnetic resonance of F^{19} nuclei in a CaF_2: Gd^{3+} crystal by the pulsed method in the temperature range (0.3 – 300) K”. 1970. Res.Sup. – S.A. Altshuler.
65. **Lantsov V.M.** “The study of molecular mobility in plasticized polyvinyl chloride by pulsed nuclear magnetic resonance”. 1970. Res.Sup. – A.I. Maklakov.
66. **Mokeev A.A.** “Toward a statistical theory of the shape of the paramagnetic resonance line in magnetically diluted crystals”. 1970. Res.Sup. – S.A. Altshuler.
67. **Skrebnev V.A.** “Cross relaxation and some issues of spin-phonon interaction in magnetically diluted crystals”. 1970. Res.Sup. – S.A. Altshuler.
68. **Zaripov M.R.** “The effect of intramolecular movements on the magnetic relaxation of nuclei in some organic polymers”. 1970. Res.Sup. – A.I. Ryvkind.
69. **Zgadzai E.A.** “The study of the structure and structural features of organic compounds of various classes by the method of magnetic susceptibility”. 1970. Res.Sup. – A.I. Maklakov.
70. **Gavrilov V.V.** “The study of exchange-coupled pairs of copper atoms by EPR”. 1971. Res.Sup. – Yu.V. Yablokov.
71. **Gilmanov A.N.** “Proton magnetic relaxation in transition metal hydrides”. 1971 Res.Sup. – M.A. Ilgamov, Sh.M. Sakhabutdinov.
72. **Goldhammer K.A.** “The study of polymers with conjugated bonds and complexes based on them by nuclear magnetic resonance”. 1971. Res.Sup. – A.I. Maklakov.
73. **Khasanov A.Kh.** “The study of the phonon bpttleneck effect by Mandelstam–Brillouin light scattering method”. 1971. Res.Sup. – S.A. Altshuler.

74. **Kurenev V.V.** “The study of relaxation mechanisms and crystallization kinetics in some polymers by nuclear magnetic resonance”. 1971. Res.Sup. – A.I. Maklakov.
75. **Manapov R.A.** “Study of the temperature dependence of the quadrupole splitting of the Mössbauer spectrum of crystalline iron compounds”. 1971. Res.Sup. – Sh.Sh. Bashkirov.
76. **Salnikov Yu.I.** “Investigation of the complexation reactions of iron (III), copper (II) and nickel (II) ions with certain hydroxyacids by the method of nuclear magnetic relaxation”. 1971. Res.Sup. – A.A. Popel.
77. **Tsarevsky S.L.** “Theory of electron-nuclear resonance in conductors”. 1971. Res.Sup. – B.I. Kochelaev.
78. **Zakharov A.V.** “The study of ligand exchange reactions in amine complexes of copper (II) and nickel (II) by nuclear magnetic relaxation”. 1971. Res.Sup. – A.A. Popel.
79. **Aminov N.M.** “The dynamics of the crystal lattice of a paramagnet”. 1972. Res.Sup. – B.I. Kochelaev.
80. **Bashirov F.I.** “Nuclear magnetic relaxation and reorientation of molecules in crystals”. 1972. Res.Sup. – R.A. Dautov.
81. **Chistyakov V.A.** “Mossbauer studies of magnetically ordered systems”. 1972. Res.Sup. – Sh.Sh. Bashkirov.
82. **Falin M.L.** “The study of iron group ions in a homologous series of fluorite-type crystals by the method of double electron-nuclear resonance”. 1972. Res.Sup. – M.M. Zaripov, Yu.E. Polskii.
83. **Aukhadeev F.L.** “Nuclear magnetic relaxation in some diluted and concentrated paramagnets”. 1973. Res.Sup. – S.A. Altshuler.
84. **Belov Yu.V.** “Some issues of double hetero- and homonuclear magnetic resonance”. 1973. Res.Sup. – Yu.Yu. Samitov.
85. **Fedorov V.I.** “Some questions of stabilization of resonant conditions in experiments”. 1973. Res.Sup. – Yu.Yu. Samitov.
86. **Romanenko L.N.** “Investigation of exchange interactions in binuclear copper carboxylates”. 1973. Res.Sup. – Yu.V. Yablokov.

87. **Galeeva S.I.** “Magnetic relaxation method for the analysis and determination of rare earth elements”. 1974. Res.Sup. – A.A. Popel.
88. **Gaponenko V.A.** “Paramagnetic resonance of exchange-coupled triads of some ions of the iron group”. 1974. Res.Sup. – Yu.V. Yablokov.
89. **Garifullina R.L.** “The study of exchange-coupled pairs of manganese and iron ions by EPR”. 1974. Res.Sup. – M.M. Zaripov, V.G. Stepanov.
90. **Greznev Yu.S.** “The study of the mechanisms of substitution and charge compensation of some elements of the iron group in crystals with the structure of potassium sulfate”. 1974. Res.Sup. – M.M. Zaripov.
91. **Klimachev A.F.** “Some issues related to the calculation of spin-lattice relaxation times”. 1974. Res.Sup. – L.K. Aminov.
92. **Mitrofanov Yu.F.** “The study of hyperfine interactions and dynamic processes in single crystals of fluorite structure by the method of double electron-nuclear resonance”. 1974. Res.Sup. – Yu.E. Polskii, B.Z. Malkin.
93. **Nigmatullin R.R.** “Issues of the kinetics of paramagnets at low temperatures”. 1974. Res.Sup. – B.I. Kochelaev.
94. **Popov Yu.L.** “An experimental study of the dynamics of nuclear spin systems in solids by pulsed NMR”. 1974. Res.Sup. – R.A. Dautov.
95. **Sadreev A.F.** “Investigation of the equations of state of the Ising model obtained by the diagram expansion of Green's functions”. 1974. Res.Sup. – Sh.Sh. Bashkirov.
96. **Sinyavsky V.I.** “Mössbauer studies of the processes of formation of the magnetic structure of manganese-zinc ferrites of non-stoichiometric composition”. 1974. Res.Sup. – Sh.Sh. Bashkirov.
97. **Tazeeva N.K.** “Investigation of the spatial structure and pseudorotation of molecules of arsenic-containing compounds by NMR spectroscopy”. 1974. Res.Sup. – Yu.Yu. Samitov.

98. **Vaisfeld M.P.** “On the theory of spin-lattice relaxation of paramagnetic ion nuclei in solids”. 1974. Res.Sup. – S.A. Altshuler.
99. **Valeev I.I.** “Nuclear magnetic resonance and relaxation in rare earth ethyl sulfates”. 1974. Res.Sup. – S.A. Altshuler.
100. **Glebov A.N.** “Study of complexation reactions of titanium (III), vanadium (III) and vanadium (IV) with some hydroxy acids by nuclear magnetic relaxation”. 1975. Res.Sup. – A.A. Popel.
101. **Safiullin R.K.** “Some questions of the theory of constants of spin-spin interaction involving the nucleus of the ^{31}P isotope”. 1975. Res.Sup. – R.M. Aminova, Yu.Yu. Samitov.
102. **Silkin N.I.** “Paramagnetism of atoms and ions in a $^{2}S^{1/2}$ state in low-symmetric crystals”. 1975. Res.Sup. – V.G. Stepanov.
103. **Tukhvatullin R.S.** “The study of impurity $3d^n$-ions by EPR in a series of low-symmetric artificial crystal hydrates with a variable number of oxygen ligands”. 1975. Res.Sup. – V.M. Vinokurov.
104. **Voronkova V.K.** “Paramagnetic resonance of Cu (II) and Co (II) ions in a tetrahedral environment”. 1975. Res.Sup. – Yu.V. Yablokov, M.M. Zaripov.
105. **Deminov R.G.** “Some questions of the theory of nonlinear optical effects in paramagnets and molecular crystals”. 1976. Res.Sup. – B.I. Kochelaev.
106. **Ivoilov N.G.** “Gamma-resonance studies of magnetic conversion in ferri- and antiferromagnetic crystals”. 1976. Res.Sup. – Sh.Sh. Bashkirov.
107. **Liberman A.B.** “Mössbauer studies of the magnetic structure and exchange interactions in complex ferromagnetic compounds with the structure of spinel and magnetoplumbite”. 1976. Res.Sup. – Sh.Sh. Bashkirov.
108. **Nizamutdinov N.M.** “Schemes for removing orientational equivalence and EPR spectra of paramagnetic centers in crystals”. 1976. Res.Sup. – V.M. Vinokurov.

109. **Volkov V.Ya.** "The study of translational movements of liquid molecules in porous media by pulsed NMR". 1976. Res.Sup. – N.N. Neprimerov, R.A. Dautov.
110. **Bikchentaev I.G.** "EPR of copper, vanadyl, and chromium complexes in liquid crystals". 1977. Res.Sup. – I.V. Ovchinnikov.
111. **Konov I.S.** "The study of Van Fleck dielectric paramagnets by magnetic resonance". 1977. Res.Sup. – S.A. Altshuler and M.A. Teplov.
112. **Musina (Nafikova) A.A.** "Study of the constants of magnetic screening and spin-spin interaction in the ^{31}P nuclear spin system". 1977. Res.Sup. – Yu.Yu. Samitov.
113. **Sabirov R.Kh.** "Issues of relaxation due to two-particle interactions in spin systems". 1977. Res.Sup. – B.I. Kochelaev.
114. **Schepkin V.D.** "Pulse double nuclear nuclear resonance in crystals". 1977. Res.Sup. – V.M. Vinokurov, R.A. Dautov.
115. **Evgenieva I.I.** "Research of ligand exchange reactions in mixed copper (II) complexes by nuclear magnetic relaxation methods". 1978. Res.Sup. – A.A. Popel, A.V. Zakharov.
116. **Kornienko A.A.** "The effects of metal-ligand exchange in the theory of the crystalline field in dielectrics". 1978. Res.Sup. – A.M. Leushin.
117. **Kotelnikov Yu.E.** "Some questions of the theory of the collective properties of excitons in molecular crystals". 1978. Res.Sup. – B.I. Kochelaev.
118. **Mosina L.V.** "EPR of the triplet excitons in coordination polymers constructed from binuclear molecules". 1978. Res.Sup. – Yu.V. Yablokov.
119. **Odintsov B.M.** "The study of some complex compounds of transition metals by EPR and dynamic polarization of nuclei". 1978. Res.Sup. – B.M. Kozyrev.
120. **Solovyov B.V.** "Investigations by electron paramagnetic resonance methods of the magnetic properties of copper ions in some crystals of chelate complexes with covalent bonds". 1978. Res.Sup. – L.K. Aminov.

121. **Tsvetkov E.A.** “A study of the structure and properties of the activator centers of rare-earth ions in calcium fluorophosphate crystals”. 1978. Res.Sup. – S.A. Altshuler, I.N. Kurkin.
122. **Usmanov R.Sh.** “The study of the electric field effect in dielectric impurity crystals”. 1978. Res.Sup. – S.A. Altshuler.
123. **Abdulsabirov R.Yu.** “The study of the structure of paramagnetic complexes of chromium and vanadium in crystals by EPR”. 1979. Res.Sup. – V.G. Stepanov.
124. **Bulka G.R.** “Investigation of the crystal structure and volumetric distribution of impurity ions in crystalline hydrates by NMR and EPR methods”. 1979. Res.Sup. – V.M. Vinokurov.
125. **Fediy A.A.** “Investigation of the orientation and temperature dependences of spin-lattice relaxation of trivalent rare-earth ions in single crystals of double fluorides”. 1979. Res.Sup. – S.A. Altshuler, A.A. Antipin.
126. **Ivanova T.A.** “EPR study of glasses containing transition group ions in the centimeter and decimeter wavelength ranges”. 1979. Res.Sup. – M.M. Zaripov, R.S. Abdrakhmanov.
127. **Khaliullin G.G.** “On the theory of exchange interactions and crystalline fields in metals”. 1979. Res.Sup. – A.M. Leushin.
128. **Konstantinov V.N.** “On the theory of the shape of the EPR line in magnetically diluted solid systems”. 1979. Res.Sup. – I.V. Ovchinnikov.
129. **Krutikov V.F.** “EPR of ions in the $^2S_{1/2}$ state in crystals of fluorite and perovskite fluoride”. 1979. Res.Sup. – V.G. Stepanov.
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288. **Yurichuk A.A.** “Coherent dynamics of Mössbauer spectroscopic transitions in magnetic materials”. 2006. Res.Sup. – Sh.Sh. Bashkirov.
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291. **Mutina A.R.** “Internal magnetic field gradients in porous media: an experimental study”. 2007. Res.Sup. – V.D. Skirda.
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294. **Klochkov A.V.** “Residual dipole-dipole interaction in NMR studies of the spatial structure of oligopeptides”. 2008. Res.Sup. – V.D. Skirda, A.V. Aganov.
295. **Savostina L.I.** “Study of the mechanism of bimolecular reactions involving phosphorus-containing compounds by the density functional method”. 2008. Res.Sup. – R.M. Aminova.
296. **Useinov A.N.** “The effects of giant magnetoresistance in ferromagnetic nanocontacts.” 2008. Res.Sup. – L.R. Tagirov.
297. **Vanyunin M.V.** “A theoretical study of the EPR spectra and spin dynamics in $LiYF_4$ crystals activated by rare-earth ions”. 2008. Res.Sup. – B.Z. Malkin.
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306. **Shkalikov N.V.** “The study of heavy oils and their components by NMR”. 2010. Res.Sup. – V.D. Skirda.
307. **Badrutdinov A.O.** “Quantum transport in vertical double quantum dots based on gallium arsenide at ultralow temperatures”. 2011. Res.Sup. – D.A. Tayurskii.
308. **Baybekov E.I.** “Resonance effects in the dynamics and relaxation of paramagnetic centers in crystals”. 2011. Res.Sup. – B.Z. Malkin.
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313. **Achkeev A.A.** “A study of the nature of ferromagnetism in titanium dioxide (TiO_2) implanted with iron transition group ions”. 2013. Res.Sup. – L.R. Tagirov, R.I. Khaibullin.
314. **Alakshin E.M.** “The synthesis of nanosized crystalline powders of PrF_3 and the study of their magnetic properties”. 2013. Res.Sup. – M.S. Tagirov.
315. **Efimov S.V.** “The spatial structure of biologically active peptides in solutions and in combination with a model membrane according to two–dimensional methods of NMR spectroscopy”. 2013. Res.Sup. – V.V. Klochkov.
316. **Galiullina L.F.** “Study of the structure of the components of the atherosclerotic plaque by magnetic resonance methods”. 2013. Res.Sup. – A.V. Aganov, N.I. Silkin.
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318. **Gizatullin B.I**. “Peculiarities of molecular mobility and phase transitions of liquids adsorbed in surface of Vycor porous glasses”. 2013. Res.Sup. – G.G. Pimenov.
319. **Lysogorsky Yu.V.** “Hydrodynamics of quantum liquids in nanoporous media”. 2013. Res.Sup. – D.A. Tayurskii.
320. **Munavirov B.V**. “Influence of lipid composition and presence of polymers on lateral diffusion and state of lipids in model biomembranes”. 2013. Res.Sup. – A.V. Filippov.
321. **Orlova A.Yu.** “NQR study of antimony-containing chalcogenides Ag_5SbS_4 and $CuPbSbS_3$”. 2013. Res.Sup. – A.V. Dooglav.
322. **Usachev K.S.** “The spatial structure of amyloidogenic A_β peptides and their complexes with model membranes in solutions by NMR spectroscopy”. 2013. Res.Sup. – V.V. Klochkov.

323. **Blokhin D.S.** “The spatial structure of oligopeptides in solution and in combination with a model of the surface of a biological membrane according to NMR spectroscopy methods”. 2014. Res.Sup. – V.V. Klochkov.
324. **Kutin Yu.S.** “The nature and structure of a number of impurity centers in according to the data of high-frequency EPR / ENDOR spectroscopy”. 2014. Res.Sup. – S.B. Orlinsky.
325. **Romanova I.V.** “An experimental and theoretical study of the magnetic properties of single crystals of lithium-rare earth tetrafluorides $LiLaF_4$ (Ln = Tb, Ho, Dy, Tm)”. 2014. Res.Sup. – B.Z. Malkin.
326. **Biktagirov T.B.** “EPR/ENDOR – spectroscopy of biocompatible materials based on nanosize hydroxyapatite”. 2015. Res.Sup. – G.V. Mamin.
327. **Irisova I.A.** “The study of mechanically activated alloying of fluoride powders with the structure of fluorite with rare-earth ions”. 2015. Res.Sup. – D.A. Tayurskii, R.V. Yusupov.
328. **Volodin M.A.** “The study of the dynamics of complex hydrocarbon systems using high-frequency EPR”. 2015. Res.Sup. – S.B. Orlinsky.
329. **Fayzullin M.A.** “The study of anisotropic exchange interactions in single crystals of Cs_2CuCl_4 and $(2,3\text{-dmpyH})_2CuBr_4$ by EPR”. 2016. Res.Sup. – M.V. Eremin.
330. **Rakhmatullin I.Z.** “The spatial structure and intramolecular mobility of some biologically active substances (pyridoxine derivatives, statins) according to NMR spectroscopy methods”. 2016. Res.Sup. – V.V. Klochkov.
331. **Beisengulov N.R.** “Quasi-one-dimensional electron system on the surface of liquid helium in mesoscopic devices”. 2017. Res.Sup. – YES. D.A. Tayurskii.
332. **Malakhov M.A.** “On the theory of pairing of current carriers in cuprates”. 2017. Res.Sup. – M.V. Eremin.
333. **Petrova A.V.** “Ab initio studies of pressure-induced structural phase transitions in rare earth double fluorides”. 2017. Res.Sup. – D.A. Tayurskii.

334. **Syunyaev D.A.** “The temperature dependence of the London penetration depth in cuprate HTSCs”. 2017. Res.Sup. – M.V. Eremin.
335. **Yavkin B.V.** “The study of nitrogen and surface paramagnetic centers in diamonds by EPR and double resonances”. 2017. Res.Sup. – S.B. Orlinskii.
336. **Batulin R.G.** “Optical spectroscopy of barium atoms and ions in superfluid 4He”. 2019. Res.Sup. – D.A. Tayurskii.
337. **Gilmutdinov I.F.** “Synthesis and study of the transport properties of crystals of sodium cobaltates Na_xCoO_2”. 2019. Res.Sup. – I.R. Mukhamedshin.
338. **Ivanov D.S.** “Structural and dynamic properties of oil and the factors determining its rheological characteristics”. 2019. Res.Sup. – V.V. Skirda.
339. **Kiyamov A.G.** “Experimental and theoretical studies of iron chalcogenides with reduced dimension”. 2019. Res.Sup. – D.A. Tayurskii.
340. **Kolosova O.A.** “Study of the spatial structure of antimicrobial protegrins peptides (PG-2 – PG-5) in solution with micelles by high resolution NMR spectroscopy”. 2019. Res.Sup. – V.V. Klochlov, K.S. Usachev.
341. **Konopleva L.V.** “Optimization of axonal tractography methods according to diffusion-weighted magnetic resonance imaging ”. 2019. Res.Sup. – K.A. Il’yasov.
342. **Mamedov D.V.** “Magnetic properties of thin films of multiferroics”. 2019. Res.Sup. – R.M. Eremina.
343. **Melnikova D.L.** “Translational mobility and features of the supramolecular organization of proteins with an internal disordered structure using α- and κ-caseins as an example”. 2019. Res.Sup. – V.D. Skirda.
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A selection of dissertations made using the methods of radiospectroscopy in the period 1945–2006 was made according to data from the archive of Professor N.N. Neprimerov, which in an expanded version (for all methods and fields of application) were given in a collective monograph [8]. The data for the subsequent period were compiled from materials kindly provided by Prof. M.V. Eremin – Secretary of the Dissertation Council and other sources.

Annex 3

Heritage

The Kazan School of Radio Spectroscopy, together with the Kazan Chemical School has a special place in the social and scientific life of Kazan and the Republic of Tatarstan, in which both the Russian and international scientific community take an active part. This is reflected in the complex of measures associated with the discovery of magnetic resonance.

In the early 1990s, the Museum of E.K. Zavoysky on the initiative of M.A. Teplov, A.V. Aganov, M.S. Tagirov and N.I. Silkin was opened. The creator and custodian of the museum is I.I. Silkin. The museum is part of the KFU museum system.

Established Prizes named after E.K. Zavoisky:

– International prize named after E.K. Zavoisky was established in 1991 on the initiative of Professor K.M. Salikhov after consultations with the international EPR community. Currently, this award has received support from the Kazan Physical-Technical Institute, Kazan (Volga Region) Federal University, Government of the Republic of Tatarstan and Springer Publishing House, Vienna – New York. The prize was recognized by the AMPERE Society, the International ESR Society and the Presidium of the Russian Academy of Sciences. It has received a high international rating as a significant award for scientific achievements in the field of magnetic resonance.

The prize is awarded annually for an outstanding contribution to the use or development of electron paramagnetic resonance in any field of science. The laureate is elected by an international committee. The laureate's lecture on his work is published in the journal “Applied Magnetic Resonance”. The award ceremony is held in Kazan, where the laureate and his (her) spouse are honored guests of the Government of the Republic of Tatarstan.

– Kazan Prize named after E.K. Zavoysky for young scientists “For work in the field of physics and its applications” since 1998. Initiators – Mayor of Kazan K.Sh. Iskhakov and Dean of the Faculty of Physics of KSU A.V. Aganov. Founders: Kazan State (Federal) University, KPhTI, KazSC RAS, Administration of Kazan. Deputy Chairman of the Organizing Committee (and expert council) for the award of the prize A.V. Aganov, Scientific Secretary M.S. Tagirov.

Regular conferences are held:

– Annual International Conference “Modern Development of Magnetic Resonance”. Co-Chairs of the Organizing Committee A.A. Kalachev and K.M. Salikhov;

– From 1997 to the present, annual regional, then Russian, and then International Youth Schools “Actual Problems of Magnetic Resonance and its Application” are held. School Rector M.S. Tagirov, Vice-rector V.A. Zhikharev;

– All-Russian conferences “New Achievements in Structural Research” with the participation of foreign scientists, (April 1990, 1995, 2000, 2005, 2011, 2015). Kazan, Kazan State (Federal) University;

– Since 1994, the All-Russian Conference “Structure and Dynamics of Molecular Systems” has been held annually and organized by the Kazan State University, the Mari State Technical University, the Institute of Physical Chemistry of the Russian Academy of Sciences (Moscow), as well as the Institute of Molecular and Crystal Physics, Ufa Scientific Center of the Russian Academy of Sciences (Ufa) and “Magnetic resonance Ltd.” (Kazan).

Large international meetings were held on the anniversary dates associated with the discovery of magnetic resonance:

1969: Anniversary All-Union Conference dedicated to the 25th anniversary of the EPR discovery. Honorary chairman of the organizing committee E.K. Zavoisky. June, Kazan. KSU – KPhTI.

1984: All-Union Conference on Magnetic Resonance in Condensed Matter, dedicated to the 40th anniversary of the EPR discovery. June, Kazan.

KSU – KPhTI. Chairman of the organizing committee M.M. Zaripov, Deputy Chairman M.A. Teplov.

1994: XXVIIth Congress AMPERE “Magnetic Resonance and Related Phenomena”, August, Kazan. Chairman of the organizing committee K.M. Salikhov. KPhTI – KSU.

2007: A set of events dedicated to the year of E.K. Zavoisky:

– International conference “Modern Developments in Magnetic Resonance Imaging and Spectroscopy in Medicine” and ESMRMB lectures on MR “MR physics for basic scientists“, July 02–05, 2007, Kazan, Russia Chairman of the Organizing Committee A.V. Ilyasov;

– International Symposium “Quantum Fluids and Solids” QFS-2007, Kazan, August 01–06, 2007, KSU – P.L. Kapitsa Institute (RAS, Moscow). Chairman of the organizing committee M.S. Tagirov, Chairman of the Program Committee D.A. Tayurskii;

– 3rd international symposium “EASTMAG – 2007. Magnetism on a Nanoscale ”, August 23–26, 2007. Chairman of the organizing committee L.R. Tagirov;

– Forum “Zavoysky Week” dedicated to the 100th anniversary of his birth. September 24–29, Kazan, KSU – KPhTI. Chairman of the forum M.Kh. Salakhov, deputy Chairman A.V. Aganov. Within the framework of this forum, a set of events was held: International Conference, XI International Youth Scientific School “Actual problems of magnetic resonance and its application” (School Rector M.S. Tagirov, Vice-rector V.A. Zhikharev), master classes on contemporary magnetic resonance methods (Bruker company), International Exhibition of Equipment. Award Ceremonies of prizes named after E.K. Zavoysky.

2011: International scientific conference “Resonances in Condensed Matter” (ALT100, to the 100th anniversary of S.A. Altshuler). June 21–25, Kazan. KSU – KPhTI. Chairman of the organizing committee B.I. Kochelaev, chairman of the local committee M.S. Tagirov, Scientific Secretary A.V. Dooglav.

2019: International Conference “Magnetic resonance: current state and future perspectives (EPR–75)”. From September 23 to September 27, Kazan, KFU – KPhTI. Co-Chairs of the Organizing Committee D.A. Tayurskii and A.A. Kalachev, Deputy Chairman M.S. Tagirov, chairmen of the program committee S.I. Nikitin and K.M. Salikhov, chairman of the local committee E.M. Alakshin, Scientific Secretary A.V. Dooglav. XXI International Youth Scientific School “Actual problems of magnetic resonance and its application”. School Rector M.S. Tagirov.

Opening of the “E.K. Zavoysky Week”. On the podium from left to right: V. Lubitz (Poland), Corr.member RAS K.M. Salikhov, Vice–President of AST A.L. Abdullin, Deputy Prime Minister of the Republic of Tatarstan R.F. Muratov, rector of KSU M.Kh. Salakhov, Mayor of Kazan I.R. Metshin, Acad. RAS K.A. Valiev, Dean of the Physics Department of KSU Prof. A.V. Aganov, Prof. G.Kh. Grisienger (Germany), Prof. KSU M.S. Tagirov

In addition to regular meetings, a number of scientific meetings have been held in the last decade. Some of them are presented below.

2001: International Workshop “Modern Development of Magnetic Resonance Imaging and Spectroscopy. Basic Physics and Applications in Medicine and Biology ”, June 11–13, Kazan. Co-chairs of the organizing committee A.V. Aganov, J. Hennig (University of Freiburg. Germany).

2014: The International conference “Magnetic resonance: fundametal research and pioneering applications (MR–70)”, June 23–27, Kazan, KSU – KPhTI. Conference Co–Chairs A.V. Aganov and K.M. Salikhov, chairman of the organizing committee and chairman of the local committee M.S. Tagirov.

2015: MRI–25, 4th International Scientific Conference “Modern Development in Magnetic Resonance Imaging and Spectroscopy in Medicine” (2015). Chairman of the organizing committee A.V. Ilyasov (AST), Chairman of the Program Committee J. Hennig (Germany). June 16–18. Kazan. AST, KFU, RKH – 2.

2015: XXXVII Meeting on Low Temperature Physics (NT–37). From June 29 to July 3, Kazan, KFU – P.L. Kapitsa Institute of Physical Problems (RAS, Moscow), AST. Deputy Chairman M.S. Tagirov and D.A. Tayurskii. Chairman of the local committee A.V. Klochkov, Scientific Secretary A.V. Dooglav.

2016: International symposium “Magnetic Resonance: from Fundamental Research to Practical Application”. April 21–23, KSU. Chairman of the organizing committee A.V. Aganov, chairman of the local committee V.V. Klochkov, Scientific Secretary L.F. Galiullina.

The electronic journal ”Magnetic Resonance in Solids. Electronic Journal” (MRSej) is published. Organized in 1996 on the base of KSU after the initiative of B.I. Kochelaev and Yu.N. Proshin. The founder is Kazan State University, with the support of the International Society of Magnetic Resonance (ISMAR). The journal was registered by the Press Committee of the Russian Federation (Protocol No. 015140 dated August 2, 1996). The first article appeared in 1997, and the first chief editors of the journal were Jean Gener (University of Brussels, Belgium), Boris Kochelaev (KSU), Raymond Orbach (University of California, Riverside, USA).

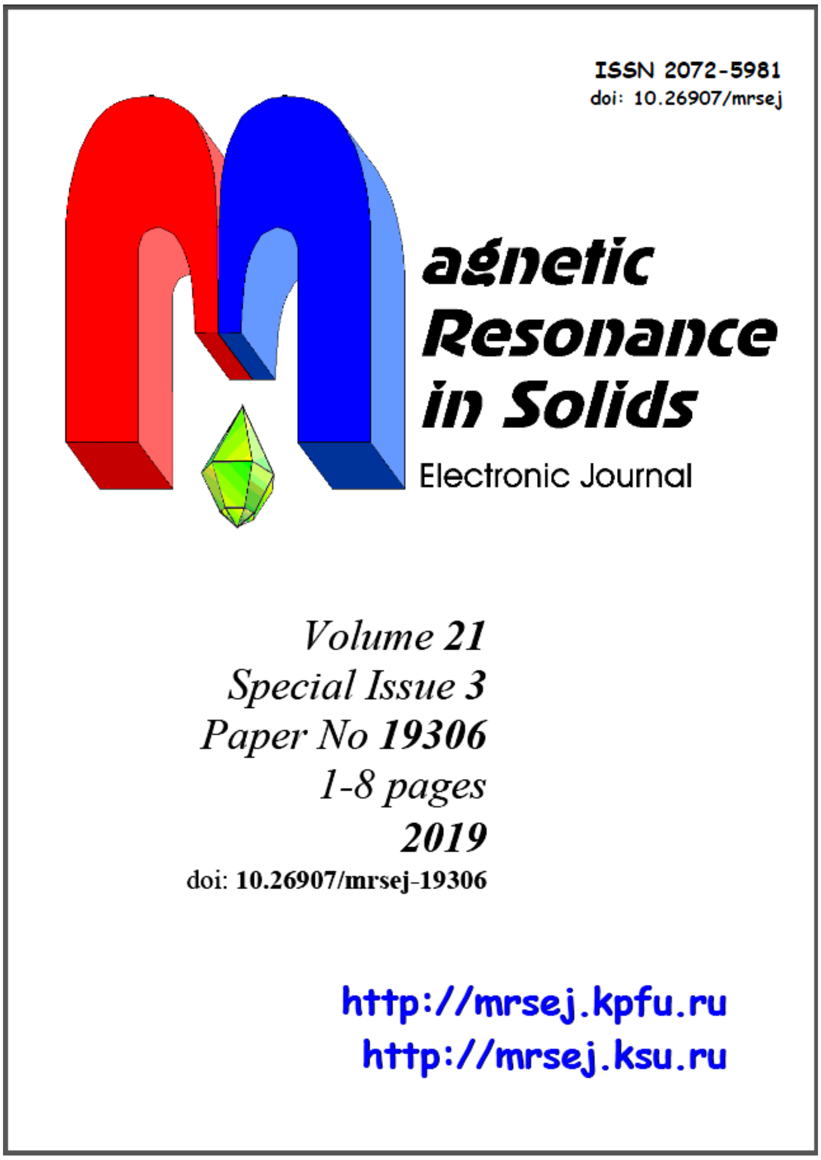
Initial editorial board: Detlef Brinkmann (Zurich University, Switzerland), Andrey Borovik–Romanov (Institute of Physical Problems of the Russian Academy of Sciences, Moscow), Yuri Bunkov (CNRS, Grenoble, France), John Drumheller (Montana State University, Bozeman, USA), Mikhail Eremin (KSU), Yoshio Kitaoka (University of Osaka, Japan), Boris Malkin (KSU), Mikhail Teplov (KSU), Haruhiko Suzuki (Kanazawa University, Japan). At present, Murat Tagirov (KFU), Dmitry Tayursky (KFU) and Valentin Zhikharev (KCTI) are members of the editorial board.

Executive editor is Yurii Nikolaevich Proshin (KSU).

The journal website is located on the KFU servers (http://mrsej.kpfu.ru/). From the annotation of the journal on its website: “MRSej is a peer–reviewed electronic journal publishing articles that meet the highest standards of scientific quality in the field of fundamental research of magnetic resonance in solids and related phenomena. MRSej is free for both authors and readers. Articles in the journal are published in English only. All information exchanges take place via the Internet. MRSej – an open access journal (an open access journal is licensed under a Creative Commons Attribution–ShareAlike 4.0 International License), i.e. all content is freely available and free for users.” In 2006, the journal fell into eLibrary – the Russian scientific index (RSCI – RusIndexSC), in 2012 the journal was included in the Scopus database, and in 2017 – in the Web of Science (Core Collection). The journal is assigned the international code ISSN 2072–5981. Since 2019, each article is assigned a digital object identifier index (doi), journal DOI: 10.26907/mrsej.

In electronic databases, the journal is listed as “Magnetic Resonance in Solids,” and for October 2019, journal articles are indexed and referenced by Web of Science (indexed since 2015), Scopus (indexed since 2012), Google Scholar, Crossref, DOAJ, ROAD, SiteFactor, SCImago Journal & Country Rank, Trove (National Library of Australia), Easy Find (Technion, Israel Institute of Technology) and others.

Since 2006, on the eLIBRARY (RusIndexSC) and CyberLeninka sites, in addition to abstracts and indexing of the journal, the full contents of the journal, including article files, are duplicated.



ISSN 2072-5981
doi: 10.26907/mrsej

agnetic
Resonance
in Solids
Electronic Journal

Volume ***21***
Special Issue ***3***
Paper No ***19306***
1-8 pages
2019
doi: **10.26907/mrsej-19306**

http://mrsej.kpfu.ru
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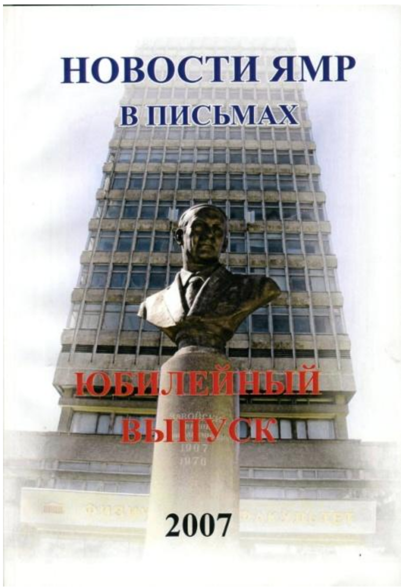
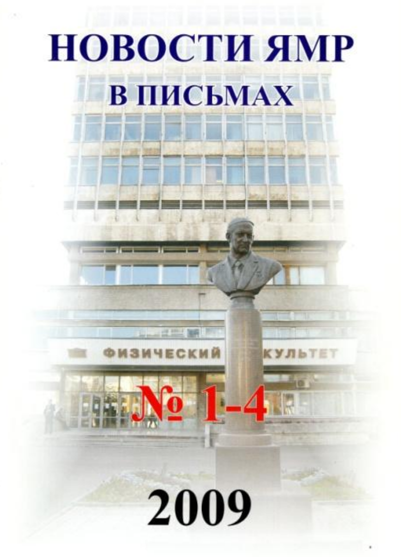
Since 1990, the printed organ of the Association of NMR Spectroscopists of the USSR (now the Russian Federation and the UIS) has been publishing – the Bulletin "NMR News in Letters" (editor-in-chief A.V. Aganov). In the early years of perestroika, this made it possible to publish articles that could be used to defend dissertations. The publication ceased to exist in 2009, as the need for express publications has disappeared.





Since 1996, the reports of the All–Russian Conference “Structure and Dynamics of Molecular Systems” were published as conference proceedings (Ch. Ed. V.D. Skirda). Currently, the publication of materials has been discontinued, as the need for them also disappeared.

Scientific edition

Aganov Albert Vartanovich
Larionov Alexander Leonidovich

ON THE 75-TH ANNIVERSARY OF MAGNETIC RESONANCE DISCOVERY

Pages in history. The development of radiospectroscopy at Kazan University

Подписано в печать