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REVIEW

The Discovery of Magnetic Resonance in the Context of 20th Century Science: Biographies and Bibliography. III: First Decades in the Soviet Union Following the Discovery of Magnetic Resonances in Matter

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Abstract—To some extent, fortune favored announcement of the ERP discovery: Zavoisky's paper was published fairly promptly in both Russian and in English in 1945 and thus fortunately slipped through the tiny gap between the two epochs – just in time before the Iron Curtain descended across Europe. Thus, scientists beyond the borders of the USSR became aware of the discovery and were in fact the first to cite and acknowledge Zavoisky's work. In 1944-early 1945, Zavoisky delivered his paper at a series of seminars attended by a number of renowned physicists, chemists, chemical physicists, biophysicists, and geophysicists from the USSR's best scientific institutions. Nevertheless, for nearly a decade EPR had been of interest almost exclusively to physicists who belonged to Zavoisky's school he established in Kazan. Beyond Kazan, A. I. Shalnikov, P. L. Kapitsa, and Ya. K. Syrkin appeared to have been the only scientists in the Soviet Union who immediately recognized promise of the EPR discovery. Moreover, there were the works of Syrkin's student L. A. Blumenfeld and his friend V. V. Voevodsky that paved the way for the EPR method to spread beyond Kazan and physics, into chemistry and biology research all across the USSR. After late 1950s, the number of publications on EPR in Soviet journals grew exponentially. Research groups studying magnetic resonance phenomena were established in many other scientific institutions. In the present paper, those groups and their studies, as well as scientific instrumentation for EPR and NMR spectroscopy in the USSR are briefly discussed.

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DISCOVERY AND ITS ANNOUNCEMENT

Irrespective of the magnitude, from the science point of view a discovery is "born" on the day when the findings are published. Fortune favored announcement of the ERP discovery: the paper was published fairly promptly in both Russian language [1] and in English [2], which at that time started to gain its status of international language of science. Zavoisky's findings fortunately slipped through the tiny gap between the two epochs – "Iron curtain"

Deceased.

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was about to descend across Europe. In just two years, the *Journal of Physics*, *USSR*, a Soviet English-language peer-reviewed journal, where Zavoisky published his first paper (followed later by a number of his other works), would be shut down and Soviet scientists would eventually be completely cut off any opportunity to share their discoveries with their peers on the other side of the Iron Curtain.

In terms of informing the international scientific community of the EPR discovery, Zavoisky's publication in the *Journal of Physics*, *USSR*, was definitely instrumental. Earlier in this book, the role this paper might have (or might have not) played in the Purcell's and in F. Bloch's discovery of the nuclear magnetic resonance was already discussed. Although it came out too late to have a strong direct influence on the work of any of the two, it had become available for the Western scientists by the time both Purcell and Bloch were already conducting their experiments. Ironically, the very issue of the *Physical Review* journal (issue 69, 1946) in which F. Bloch published his NMR research findings contained a reference to the article from the very issue of the *Journal of Physics*, *USS*R, in which E. K. Zavoisky published his EPR research findings. As if this was not a big enough coincidence, they were placed on the same page! This circumstance, spotted by N. E. Zavoiskaya [3], speaks to the fact that the Soviet English-language journal, meaning all the papers published in it, was available to and scanned by scholars in the West.

The press was not the only channel to make the EPR discovery known to the scientific community. By June 1944, Zavoisky finalized his doctoral dissertation presenting his findings and submitted it to the Physical Institute of the USSR Academy of Sciences, Moscow (now the Lebedev Physical Institute or LPI) [4]. On December 30, 1944, he delivered his paper at a seminar at the Institute for Physical Problems (IPP) now bearing the name of P. L. Kapitsa, the famous "kapitsnik"[1] as called among Soviet physicists. Quite a number of renowned Soviet physicists, chemists, chemical physicists, biophysicists, and geophysicists from the USSR's best scientific institutions attended that seminar. Among the participants there were academician A. F. Ioffe, "farther of the Soviet physics" and director of the Physical-Technical Institute (now the Ioffe Institute); academician N. N. Semenov, director of the Institute of Chemical Physics of the USSR Academy of Sciences[2], and a number of his fellow scientists, including Ya. B. Zeldovich, I. L. Zelmanov, and Yu. N. Ryabinin; G. S. Gorelik, a prominent radio physicist, who at the time worked with A. A. Andronov at the Gorky State University[3], the cradle of oscillation theory; G. N. Flerov, one of the founders of the Soviet nuclear program (Laboratory No. 2); E. V. Shpolsky (Moscow State Pedagogical Institute[4]), co-founder and lifelong editor of the *Soviet Physics Uspekhi* journal; K. V. Vladimirskii from the Physical Institute, who, a year later, would author the first ever publication on NMR in the Soviet Union; S. E. Bresler, a physicist, a chemical physicist, and a biophysicist; many of the renowned scientists from the IPP, including L. D. Landau, E. M. Lifshitz, A. B. Migdal, Y. A. Smorodinsky, E. L. Andronikashvili, and, of cause, A. I. Shalnikov, who helped Zavoisky to reproduce his experiment in Moscow, and academician P. L. Kapitsa, the host of the event. The seminar was also attended by the scientists from the Institute of Geological Sciences[5], Laboratory for Geochemical Problems[6], Moscow State University's Research Institute of Physics, and from other schools [5]. That is to say, Zavoisky shared his findings with a multidisciplinary audience representing the country's major scientific institutions. A month later, on January 30, 1945, Evgeny Konstantinovich defended his dissertation at the Physical Institute of the USSR Academy of Sciences with the crème de la crème of the Soviet physics sitting in the Dissertation Committee. Among his doctoral thesis opponents there were S. I. Vavilov (President of the Committee), G. S. Landsberg, S. M. Rytov, V. I. Veksler, V. L. Levshin, E. I. Kondorsky, and, again, A. I. Shalnikov [6]. The list of attendees is obviously far from complete, for both events. In other words, quite a representative part of the Soviet scientific community, hardly confined to physicists only, was given a firsthand account of the EPR experiment.

For some unknown reason, the discovery made by E. K. Zavoisky escaped attention of the Soviet science. Analysis of the Soviet scientific literature shows that it had little to no presence on the pages of the peer-reviewed journals of that time. Apparently, neither was his or his collaborators' work

[1] A wordplay about the surname Kapitsa.

[2] Now N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences.

[3] Now Lobachevsky State University of Nizhny Novgorod.

[4] Now Moscow State Pedagogical University.

[5] Now Geological Institute of Russian Academy of Sciences.

[6] Now Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences.

on EPR, a topic commonly discussed at the scientific gatherings held in the Soviet Union in that period. The biggest and most relevant (in the context of EPR) conferences took place in December 1946 – two years after Zavoisky had first announced his findings at the IPP seminar and a year and a half after his groundbreaking paper had been published. They were: the Meeting on Electric Oscillations and Electric Waves in Gorky[7] (9-12 December, 1946), organized by the All-Union Scientific Council for Radiophysics and Radio Technology (the USSR Academy of Sciences) and by the Gorky State University [7]; the 5th All-Union Conference on Spectroscopy held in Leningrad[8] (10-16 December, 1946) organized by the Commission for Spectroscopy (Academy of Sciences, USSR) [8]; the First All-Union Conference on Physics of Magnetic Phenomena in Sverdlovsk[9] (11-16 December, 1946) organized by the USSR Academy of Sciences (Department of Physical and Mathematical Sciences) and its Ural Branch [9]. The latter was the most relevant in the context of magnetic resonance, its program covering topics like "Nuclear Magnetic Moments in Solids and in Liquids" and "Nuclear Magnetism". According to the report published by the Bulletin of the USSR Academy of Sciences, "apart from Sverdlovsk physicists, the Conference was attended by magnetologists from Moscow, Leningrad, Kharkov, Kazan, Gorky, Chelyabinsk, Molotov[10], and Krasnoyarsk. A total of 9 plenary sessions were held with over 40 papers delivered" (Vonsovsky, 1947). The list of speakers included prominent Soviet physicists like V. K. Arkadyev, Ya. I. Frenkel, Ya. G. Dorfman, E. I. Kondorsky, L. V. Kirensky, and S. V. Vonsovsky. According to N. E. Zavoiskaya, B. M. Kozyrev, Zavoisky's collaborator, was among the attendees as well [3]. Evgeny Konstantinovich was also invited [4], although he was not among the speakers.

De facto the only paper to some extent pertaining to magnetic resonance was delivered by Ya. G. Dorfman ("Nuclear magnetic moments in the condensed phase") [10]. He was the only speaker at the Conference who referred to Zavoisky's experiment (he at least did mention his work!). This reference, though, was in the context of magnetic resonance methods being "equivalent to magnetomechanical methods" and "hardly useful for determining nuclear magnetic moments in the condensed systems". Judging from the Conference materials that were published [9], no other speaker mentioned the discovery of EPR. N. E. Zavoiskaya wrote about this in her book: "Curiously, none of the speakers at the Conference said a word on the promise of Zavoisky's pioneering research. Neither Ya. I. Frenkel, nor V. K. Arkadyev, nor Ya. G. Dorfman considered his discovery to be outstanding, that is to say promising, the first two knowing Zavoisky personally and being acquainted with his work firsthand" [3]. Time brought about a little change. A year later, on September 28, 1947, A. F. Ioffe, farther of the Soviet physics, delivered a commemorative speech "Thirty Years of the Soviet physics" (to celebrate the 30th anniversary of the October Revolution of 1917). Quite a number of lines of investigation and fields of study that had emerged since 1917 received an honorable mention from him. EPR, though, was not among the advancements he considered worth noting [11]. In the same 1947, I. K. Kikoin, when reviewing Zavoisky's paper nominated for the Stalin Prize[11], all but doubted the existence of EPR as a phenomenon: "If this hypothesis proves valid, physicists would obtain a simple and powerful method for determining nuclear magnetic moments..." [3].

Given a plethora of magnetic resonance studies and research burgeoning in the West, both in Europe and in the United States (a fact the Soviet physics could not have been totally ignorant about), such an attitude seems strikingly peculiar. Noteworthily, in 1947 (in January, 1948, at the latest), C. Gorter and G. Wentzel nominated F. Bloch for the Noble Prize in Physics. Magnetic resonance research was growing dramatically. Within several years that passed since F. Bloch and E. M. Purcell had each published his findings, hundreds of papers pertaining to magnetic resonance (EPR, NMR, nuclear quadrupole resonance and ferromagnetic resonance included) were published. New resonance-related phenomena and instrumentation was frequently the talk of major international scientific gatherings. In 1948-1949, a rare meeting of the American Physical Society (APS) failed to discuss related problems. In 1949, for example, as many as 25 papers on the new phenomenon were delivered (for a selected list of papers see Online Resource 1). In 1948, APS held a Symposium on Microwave and Radio-Frequency Spectroscopy with another gathering, a Radio-Frequency Spectroscopy Conference, taking place at Oxford University in the same year, and yet another one held in 1950 in Amsterdam.

[7] Now Nizhny Novgorod.

[8] Now St. Petersburg.

[9] Now Ekaterinburg.

[10] Now Perm.

[11] The highest honor in the Soviet Union bestowed in recognition of a single piece of work in science or culture. The Prize was established in 1939 and existed till 1955. Later it was given the same status as the newly established (in 1966) State Prize of the USSR.

Fig. 1. Ya. K. Syrkin (left), his former student and long-time co-author M. E. Dyatkina (right) and their colleagues in the Kurnakov Institute of General and Inorganic Chemistry, 1960s. Source: personal archive of S. P. Dolin.

Each attracted researchers from all over the world: the Unites States, the United Kingdom, the Netherlands, Japan, France, Sweden, Switzerland, and Germany [3]. At the Oxford Conference in 1948, C. Gorter acknowledged E. K. Zavoisky's priority of discovery. Paradoxically, Western scientists paid much more attention to Zavoisky's findings and had been referring to his works before his fellow Soviet physicists did. Cummerow and Halliday [12] were the first to refer to Zavoisky and his discovery [2] in their paper. C. Gorter was next with his book [13]. Meanwhile in the USSR, apart from Ya. G. Dorfman who referred to Zavoisky's findings at the Conference in Sverdlovsk (as mentioned earlier), his work was for the first time cited by V. L. Ginzburg in the *Physics Uspekhi* (*Advances in Physical Sciences*) [14] along with the papers by Purcell [15] and Bloch [16].

Basically, for nearly a decade EPR had been of interest to physicists in Kazan almost exclusively. In those years, any EPR-related developments in the USSR were almost exclusively due to the efforts of S. A. Altshuler (1911-1983) and B. M. Kozyrev (1905-1979), Zavoisky's friends and colleagues. Within ten years after 1947 (the year when E. K. Zavoisky left Kazan for Arzamas-16), the two of them published over 70 research papers on various aspects of magnetic resonance (it was the overwhelming majority of all the research published on the subject in the USSR in that period). Those works are discussed in detail by L. K. Aminov [17], Yu. V. Yablokov [18], N. S. Altshuler and A. L. Larionov [19], and in the book "Paramagnetic Resonance" [20].

Other research groups in this new area of scientific inquiry emerged in the USSR later. Of them, the first to be noted is the group led by A. M. Prokhorov, the future Nobel Prize laureate. His group embarked on its EPR-related investigations at the Physical Institute in 1953, the first publications dated 1955 [21, 22]. A. M. Prokhorov obviously pursued his own original ideas, yet his works on EPR were closely related to the research performed by the Kazan group of physicists – his EPR experimental work started only after A. A. Manenkov, a post-graduate student of B. M. Kozyrev, had come to work at the Physical Institute. From then on, Manenkov played a crucial part in the Prokhorov's EPR experimentation. It must be acknowledged though, that the first experiments performed by Manenkov and Prokhorov were strongly influenced by the works published by Bleaney and his group, the first to focus on monocrystalline oxides and transition-element-doped diamagnetic salts.

P. L. Kapitsa and A. I. Shalnikov appear to have been the only physicists in the Soviet Union who immediately recognized promise of the discovery made by E. K. Zavoisky and his colleagues. They both generously provided him with support, financial and administrative. For instance, he was offered to reproduce his experiment at the IPP; its technical capabilities being much stronger than those of the Kazan University. It was the Institute for Physical Problems that nominated Zavoisky for the Stalin Prize. What is more, Kapitsa included EPR research in the IPP's scope of work for the year 1946 [23].

Fig. 2. Left to right: V. V. Voevodsky, L. A. Blumenfeld. Akademgorodok (science city), Novosibirsk, 1961. Source: M. V. Voevodskaya's personal archive.

Today, one can only speculate what could have been the course of EPR research in the Soviet Union, had Kapitsa not fallen from the grace in 1946, removed from all of his positions and basically from science. Thus, frustratingly, this line of EPR spectroscopy development in the USSR was interrupted.

Apart from P. L. Kapitsa and A. I. Shalnikov, in the Soviet scientific community only Ya. K. Syrkin, a chemical physicist, was known to have a strong interest in the EPR phenomena. Yakov Kivovich Syrkin (1894-1974) (Fig. 1), an expert in theoretical chemistry well versed in quantum methods, chemical bonds and molecular interactions, endeavored, in 1948, to launch his own EPR-spectroscopy related research [24] at Karpov Institute of Physical Chemistry, where he was in charge of the Laboratory of Electric Properties of Molecules.

Since 1920, the focus of his attention had been the development of physical methods for chemical research (for example, [25]), including X-ray structural analysis, infrared vibrational spectroscopy, optical and electron methods (Kerr effect, depolarization, anisotropic polarizability). He appears to have been among the first in the USSR to use Raman scattering in his chemical experimentation (for example, [26]). In 1930s, he organized experimental studies of the structure of chemical compounds with the use of the dipole moments method (for example, [27]), the first of its kind in the USSR. Finally, in mid-1940s his focus was on studying the chemistry of radicals, along with editing the Russian translation of "The Chemistry of Free Radicals" by W. A. Waters [28]. Evidently, it was due to his unique scientific background that he could see right away potential of the EPR method for chemical research. Syrkin entrusted the study of the new method to L. A. Blumenfeld, his post-graduate student [24]. Yet, once again, ideological battles in science (the struggle against "the idealism in chemistry[12]") and politics ("The Doctor's Plot[13]") put the efforts of the two chemists on hold for several years.

Blumenfeld, however, managed to resume his scientific investigations, when he got a job at the Central Institute for Advanced Medical Education, Moscow. There, his studies of oxygenation of hemoglobin prompted him to revisit the idea of using EPR methods for his research. Change of magnetic properties of proteins with oxygenation paved the way for EPR spectroscopy to be Blumenfeld's method of choice, after he had exhausted other methods (primarily, that of magnetic balance). In the same period but in a

[12] A campaign rejecting Pauling's theory of resonance as antimaterialistic and anti-Marxist. The campaign was prompted by the publication, in 1947, of the Russian translation of Pauling's *Nature of the Chemical Bond* which was done by Ya. K. Syrkin and M. E. Diatkina. Both eventually had to leave the Karpov Institute of Physical Chemistry and lost almost all of their scientific posts. Only after 1957 Syrkin and Diatkina were able to resume their structural chemistry related research.

[13] An alleged conspiracy of prominent Soviet medical specialists to murder leading government and party officials (1953).

different branch of chemistry (namely, free-radical chemistry), another young chemist and Blumenfeld's friend, V. V. Voevodsky (Fig. 2), found himself in a similar situation. Apparently, close scientific cooperation between the two young and enthusiastic researchers and friends led to the "EPR virus" quickly penetrating chemical kinetics and to the ERP spectroscopy finding its way into chemistry and biology research. Ultimately, two new scientific schools or, broadly speaking, two new fields of the Soviet science were born: radio-frequency spectroscopy in chemistry and radio-frequency spectroscopy in biology.

The first publications by L. A. Blumenfeld and his collaborators [29, 30] pertained to the hypothesis of A. Szent-Györgyi (1941) for semiconductive properties of proteins, severely criticized by Soviet scientists at the time (for example, [31]). In those early papers, bio-tissues, proteins and isolated biochemical substances exposed to ionizing radiation were studied. V. V. Voevodsky and his group, at the Institute of Chemical Physics, started with investigating free radicals produced by ionizing radiation as well [32, 33], along with organometallic compounds [34], and gas-phase chain chemical reactions [35].

From 1957 on, the number of papers on EPR spectroscopy and its numerous applications was growing exponentially. In 1958-1960, V. V. Voevodsky and his colleagues at the Institute for Chemical Physics alone published over 30 research papers on EPR spectroscopy's potential for chemistry research. In the same period, EPR methods began to increasingly "spread out" across other scientific institutions and groups.

NUCLEAR MAGNETIC RESONANCE

NMR investigations, on the other hand, had an earlier start in the USSR. K. V. Vladimirskii [36] led the way in experimental research at the Physical Institute in Moscow, and G. R. Khutsishvili [37] of the Institute of Physics in Tbilisi[14] pioneered in theoretical studies of the phenomenon in the Soviet Union. Noteworthily, G. R. Khutsishvili was an intern of L. D. Landau, while K. V. Vladimirskii was Landau's doctoral student. L. D. Landau himself worked with P. L. Kapitsa at the IPP and was among the first scientists in the USSR to know about the discovery of EPR. Late in the 1940s, at the Moscow State University, groups led by S. D. Gvozdover [38] and E. I. Kondorsky [39] launched their experimental research programs on NMR as well. For the Soviet nuclear program, NMR in matter was first observed in 1951 by G. A. Goncharov at the Thermal Technological Laboratory of the USSR Academy of Sciences[15]. Later on, though, similar research, including studies on NRM in molecular beams, "moved" to Sukhumi Physical Technical Institute[16]. There, in Sukhumi, in July 1952, the first ever meeting on radio spectroscopy in the Soviet Union took place. Papers on NMR were delivered by speakers from the Physical Institute (K. V. Vladimirskii) and from the Sukhumi Physical Technical Institute (N. I. Leontyev) [40]. In Sukhumi, some of the experiments on NMR were conducted by W. Hartmann, a German physicist. In that period, the capabilities of instrumentation available to the Soviet NMR researchers provided for quite modest outcomes, a circumstance discussed in more detail later in this Chapter.

Further development of NMR methods in the USSR was delayed for decades, although rare efforts to advance in this area that took place against all odds, to some extent, set the stage for their future evolution. S. D. Gvozdover and his laboratory at the MSU[17] Department of Physics (N. M. Ievskaya, N. M. Pomerantsev, and later – Yu. S. Kostantinov), for example, persisted with their NMR experimentation, although all they had at their disposal was basically homemade apparatus. In 1951-1959, every year one or two students graduated from the Moscow State University with a specialization in NMR. Up till 1957, NMR experiments could have only been conducted with the use of rather primitive instruments, like electromagnets capable of producing rather inhomogeneous fields or like marginal oscillators similar to those built by Pound and Hopkins. In those years, NMR experiments were undertaken predominantly for demonstration purposes: to validate theoretically predicted resonance line shapes, to determine relaxation times by the logarithmic decrement, to measure or stabilize magnetic field. In 1953-1961, E. I. Kondorsky, at his laboratory at the MSU Department of Physics, endeavored to study conduction-electron magnetization density with the use of the nuclear Overhauser effect, but to no avail, as some of the physical laws involved were yet to be discovered (namely, the mechanisms of nuclear and electron spin relaxation in metals heavier than ^{7}Li, metal in which the Overhauser effect was first observed). Needless to say, those experiments at their core were reminiscent of the works published abroad, mainly in the US.

[14] Now the Andronikashvili Institute of Physics, Georgia.

[15] Now the A. I. Alikhanov Institute of Theoretical and Experimental Physics.

[16] Now the Ilia Vekua Sukhumi Institute of Physics and Technology, Georgia.

[17] Lomonosov Moscow State University.

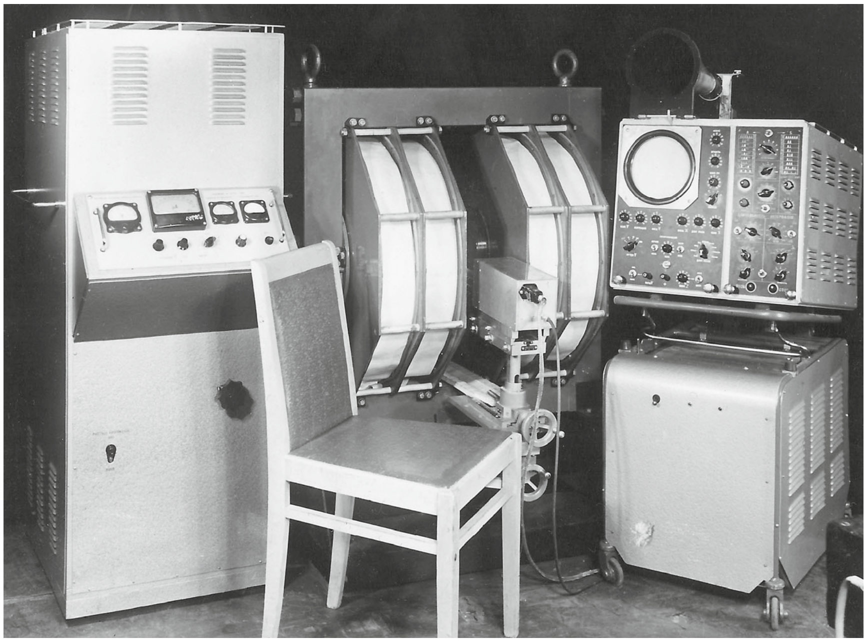

Fig. 3. NMR spectrometer built by L. L. Dekabrun's laboratory. Source: personal archive of E. O. Vetrova.

Stronger effort to advance high resolution NMR methods was undertaken by the Soviet scientists in late 1950s-early1960s and was still drawing on the international experience. At the MSU Department of Physics, this effort was led by Y. S. Konstantinov and N. M. Ievskaya. At the Physical Institute, a relatively high-resolution spectrometer was developed by K. V. Vladimirskii. Later, spectrometers using a permanent magnet were designed in Moscow by L. L. Dekabrun, V. F. Bystrov, and A. U. Stepanyants of the Institute of Chemical Physics (Fig. 3), and in Kazan by Y. Y. Samitov, A. V. Aganov et al. of the Kazan State University. The latter two instruments were ready for mass production but in the end only a couple of experimental models were assembled by the Research & Development group (OKB in Russian) in 1963. All the designs referred to above provided for resolution of the order of magnitude of 10^{-7}, while to observe the proton magnetic resonance (PMR) a resolution of 10^{-8} to 10^{-9} was required. In terms of resolution and sensitivity, the early designs met the needs of high-resolution ^{19}F and ^{31}P NMR research and were put to use accordingly by Konstantinov (the Moscow State University) assisted by the INEOS[18] chemists, and by Y. Y. Samitov (the Kazan State University) and B. A. Arbuzov (the Kazan Institute of Organic Chemistry[19]), respectively. To some extent, those early spectrometers were suitable for PMR studies of organic acids and aldehydes, as well as of aromatic compounds with aliphatic substituents (the difference between proton chemical shifts exceeding 10^{-6}), and were indeed used in their research by V. F. Bystrov and his colleagues from L. L. Dekabrun's laboratory at the Institute of Chemical Physics. In Leningrad[20], F. I. Skripov and his laboratory entered the field with broad-line NMR studies (resolution of 10^{-5}). In the same period, Skripov's laboratory, as well as their colleagues in Sverdlovsk[21], embarked on the developing the Earths's field NMR technique. In Krasnoyarsk, the A. G. Lundin's research laboratory was making its way into NMR spectroscopy with low-resolution NMR studies as well. Meanwhile, according to A. V. Aganov, the first task for the Samitov's graduate students specializing in NMR was to demonstrate the Pake doublet, or splitting of the resonance line shape in crystalline hydrates – a task requiring resolution of 10^{-5}. That is to say, international advances in the field set the benchmark for the Soviet researchers irrespective of the capabilities of the instrumentation available!

After the broad-line NMR, both in Kazan and in Leningrad, studies continued into the high-resolution ^{19}F NMR spectra (the first dissertation on the subject defended by P. M. Borodin at the Leningrad State University[22], in 1955).

[18] The Institute of Organoelement Compounds of the USSR Academy of Sciences.

[19] Now the Arbuzov Institute of Organic and Physical Chemistry of the Russian Academy of Science.

[20] Now St. Petersburg.

[21] Now Ekaterinburg.

[22] Now St. Petersburg State University.

It was only in the late of 1950s that three research groups were established in the USSR equipped to develop modern (as of that time) high-resolution NMR spectroscopy instrumentation for chemical investigations.

FERROMAGNETIC RESONANCE (FMR), ACOUSTIC PARAMAGNETIC RESONANCE (APR), AND ACOUSTIC NUCLEAR MAGNTIC RESONANCE (ACOUSTIC NMR)

In the USSR, ferromagnetic resonance studies were mainly the domain of S. V. Vonsovsky [41] at the Ural State University in Sverdlovsk. Early in 1950s, in the Soviet Union, the ferrites were in wide use and thus were extensively studied and researched, including with the use of resonance methods. At the Ural University, such investigations were carried out by S. V. Vonsovsky, and at the Moscow University – by E. I. Kondorsky. In 1952, an excellent volume of collected works on ferromagnetic, ferrimagnetic and antiferromangetic resonances translated into Russian was published, under the editorship of Vonsovsky. The volume is cited in Chapter IV. Acoustic resonances theoretically predicted by S. A. Altshuler in 1952 were experimentally studied in the early 1960s in Kazan, in Kharkov (APR), and in Leningrad (acoustic NMR). Some of the research is cited later, in the "geographical" review.

Following Kastler's metaphor [42] comparing EPR and the Volga River beginning from a small spring to become a mighty river, one must admit that, in the USSR, ERP and magnetic resonance research in general continued to be a small spring in those years. As was said earlier, the amount of research papers on the applications of EPR (and later NMR) spectroscopy began to grow exponentially in the late 1950s prompting emergence of a number of new research groups, institutes, and centers. Below is an overview of major scientific schools and lines of research pertaining to EPR and NMR spectroscopy, however incomplete it might be. The time period discussed below for the most part ends in 1969 – the 25th anniversary of the EPR discovery. Let us start with Kazan – the birth city of electron paramagnetic resonance, central for EPR spectroscopy advancement in the Soviet Union.

MAJOR CENTERS FOR MAGNETIC RESONANCE SPECTROSCOPY DEVELOPMENT IN THE USSR

Kazan: major lines of MR spectroscopy research in 1950s-1960s. In Kazan, the first studies of magnetic resonance phenomena were launched by the Zavoisky's EPR immediate collaborators in two scientific institutions; S. A. Altshuler and B. M. Kozyrev had close ties with, namely, the Kazan State University and the Physical-Technical Institute of the Kazan Branch of the USSR Academy of Sciences. With time, their scientific schools developed to intertwine with other Soviet research schools and to entrain other Kazan-based institutions, such as the Kazan Aviation Institute (KAI[23]), the Kazan Branch of the Moscow Aviation Institute, the Kazan Branch of the Moscow Power Engineering Institute, the Institute of Organic and Physical Chemistry of the Kazan Branch of the USSR Academy of Sciences, Alexander Butlerov Institute of Chemistry, etc. The scope of research was growing too as new discoveries opened up new avenues for scientific investigation.

In 1952, S. A. Altshuler predicted resonant absorption of sound in paramagnetic media – the acoustic paramagnetic resonance (APR) [43]. From then on, for many years, this phenomenon had been studied in Kazan, both theoretically [44, 45] and experimentally [46, 47]. Likewise, role of spin–phonon interactions with regards to other phenomena (e.g., in antiferromagnets) was demonstrated by the S. A. Altshuler's students [48].

Findings by B. I. Kochelaev and L. K. Aminov, of the Altshuler's school, contributed to the "classic" field as well – namely, to the theory of magnetic relaxation with regards to spin–lattice and spin–spin interactions [49-51]. The new mechanism of paramagnetic relaxation proposed by L. K. Aminov following his studies of the two-step relaxation processes is now known as the Orbach–Aminov processes.

EPR studies of the transition-metal complex ions in isotropic solvents [52] set the stage for investigations of the said complex compounds in anisotropic liquid crystalline solvents [53]. As a result, a whole new field of research was born – magnetic liquid crystals formed by coordination compounds [54-56]. Exchange interactions in the spin clusters were also researched [57-59].

Of particular note are the investigations of EPR in metals and in superconductors. To study metals, magnetic resonance techniques were first used in the 1950s-1960s by the founders of the Kazan EPR school and their immediate students. One of the first works on the subject [60] reported observation of EPR in alkali metals (Li and Na) and dependence of the resonance line shape on the size of metallic particles. Akin to other ERP researchers of his time, N. S. Garifyanov used a homemade spectrometer in his experiments. The line shape asymmetry

[23] Now the Kazan National Research Technical University named after A. N. Tupolev – KAI.

he observed was in qualitative agreement with the Dyson's theoretical description [61]. Later, after the Laboratory of Metal Physics (E. G. Kharakhashyan, laboratory chief) was set up at the Physical-Technical Institute in 1974, the problem of the EPR line shape for conduction electrons was thoroughly studied by I. G. Zamaleev in thin films [62], and by Y. I. Talanov in spherical particles [63].

Apart from the line shape, no less important is the problem of spin relaxation of conduction electrons, its mechanisms and relaxation channels, was investigated at the Laboratory. In particular, the scope of studies covered the impurity-dependent relaxation (due to spin–orbit interaction) [64], relaxation at a metal surface [65], and relaxation in metallic lithium (due to the spin-current mechanism) [66]. It should be noted that the latter research employed the technique of EPR relaxometry and reported a record narrow EPR line observed in the samples of LiF single crystals – 0.04G (!) – at room temperature, with the use of the conduction–electron spin–echo method [67]. Apart stood the studies of electron spin–lattice relaxation in the metallic nanoparticles in which, by means of the electron–spin–echo method, freezing of spin–lattice relaxation of conduction electrons (due to the energy levels indicative of the quantum size effect) was directly observed (in alkali metal particles: silver and magnesium) [68, 69]. In the West, this experiment was reproduced only over a decade later [70].

To observe EPR in superconductors, the problem of magnetism and superconductivity being incompatible must have been solved. Magnetic field needed for the EPR to be observed destroys superconductivity in the type-I superconductors and makes the type-II superconductors transit to the mixed (vortex) state (if $H_{c1} < H < H_{c2}$). That is to say, superconducting materials with λ magnetic field penetration depth and a critical field H_{c2} stronger than the resonance field must have been found. Once they were determined (La_{3-x}GdxIn and $La_{1-x}Er_x$), S. A. Altshuler and his colleagues at the Physical-Technical Institute in Kazan were the first in the world to observe EPR in superconductors [71, 72]. A year later, in the US, a similar paper by R. Orbach [73], who was studying the same phenomenon, was published. (With regard to priority of the discovery, it must be said that in the US it took less time for the findings to be published in comparison with the USSR.)

After high-temperature superconductivity was discovered in 1987, EPR studies of the electronic phase separation [74] and the resulting local magnetic field distribution [75] were conducted, along with the studies of the properties of the high-temperature superconductivity energy spectrum; of vortex lattice; of spin waves in superconductors [76]; etc. To perform some of the experiments, the EPR slide screw tuner (~0.1 mm in size) scheme had to be developed [77].

After, in 1947, B. M. Kozyrev and S. G. Salikhov published their paper on paramagnetic relaxation in pentaphenylcyclopentadiene [78], the first work on EPR spectroscopy in chemistry in the USSR, it was not until the late 1950s that this line of research began to develop. In 1960s, starting with [79], EPR spectroscopy for chemical research was mostly the domain of N. S. Garifyanov, Y. V. Yablokov, and some of their colleagues [80, 81]. In particular, intra- and intermolecular interactions and corresponding relaxation times were investigated in cooperation with A. E. Arbuzov and F. G. Valitova, the latter assisting with the chemical side of the experiments. In 1958, A. V. Ilyasov, a chemical physicist, developed an interest in this new, unexplored avenue of research as well; G. S. Vozdvizhensky, N. V. Gudin and M. S. Shapnik, all of the three electrochemists, joined him shortly. It was due to their efforts that EPR studies of electrode processes were launched [82, 83]. In the late 1960s, A. V. Ilyasov, Y. M. Kargin, and Y. A. Levin embarked on the development of the method of electrochemical generation of free radicals [84] (Fig. 4).

Since 1950s, NMR spectroscopy had also been used in experiments in chemistry (by Y. Y. Samitov, at first at the Kazan State University, and later – at the Institute of Organic and Physical Chemistry of the Kazan Branch of the USSR Academy of Sciences).

In conclusion, it must be said that in Kazan, in addition to the wide range of original research being carried out, the All-Union Conference on Magnetic Resonance took place on a regular basis (every two years starting with 1955), its themes and speakers' geographical origins becoming ever more diverse with time (Fig. 5).

Moscow: some of the EPR and NMR spectroscopy developments in the 1950s-1970s. Beyond Kazan, among the first who relied on EPR spectroscopy was A. M. Prokhorov's group in Moscow. After its first research was published in 1955 [21], the group proceeded to a broad-scale investigation (or "scanning", in modern language) of paramagnetic crystals [85-87] in search of the materials for quantum electronics [88]. The Physical Institute of the Academy of Sciences continued to be the "headquarters" of EPR studies in Moscow. In 1954 it was joined by the Research Institute of Nuclear Physics[24], Moscow State University, after A. M. Prokhorov had been appointed the head of the Laboratory of Radio Spectroscopy there. The newly established Institute of Radio

[24] Now Skobeltsyn Institute of Nuclear Physics (SINP MSU).

Fig. 4. V. N. Linev (left), I. V. Ovchinnikov (center), J. Hyde, (3rd right), A. V. Ilyasov (2nd right), Y. V. Yablokov (right) at the XXIV Congress Ampere on Magnetic Resonance and Related Phenomena, Poznan, 1988. Source: personal archive of V. N. Linev.

Fig. 5. Left to right: ?, H. C. Pfeiffer, H. Benoît, ?, C. Franconi, A. Lösche, E. K. Zavoisky, B. M. Kozyrev, N. S. Garifyanov at the Conference on Magnetic Resonance in Kazan, 1969. Source: personal archive of Y. I. Talanov, the author M. L. Blatt.

Engineering and Electronics of the Soviet Academy of Sciences[25] became another center for magnetic resonance research after M. E. Zhabotinsky, a colleague of A. M. Prokhorov moved there from the Physical Institute. The Institute of Radio Engineering and Electronics eventually attracted a strong group of experimental and theoretical physicists (M. I. Rodak, A. E. Mefed, V. A. Atsarkin et al.), who performed classic studies of magnetic relaxation and spin–spin interactions, and verified experimentally the B. N. Provotorov's theory of cross relaxation (and the two adjacent energy reservoirs created as a result) [89-91].

Along with physical phenomena, EPR and NMR spectroscopy was gaining momentum as a method for chemical and biological research. The works

[25] Now Kotelnikov Institute of Radio Engineering and Electronics (IRE) of the Russian Academy of Sciences.

Fig. 6. Left to right: G. I. Likhtenshtein, A. L. Buchachenko, E. G. Rozantsev, and N. N. Semenov, 1977. Source: [232], courtesy to G. I. Likhtenshtein.

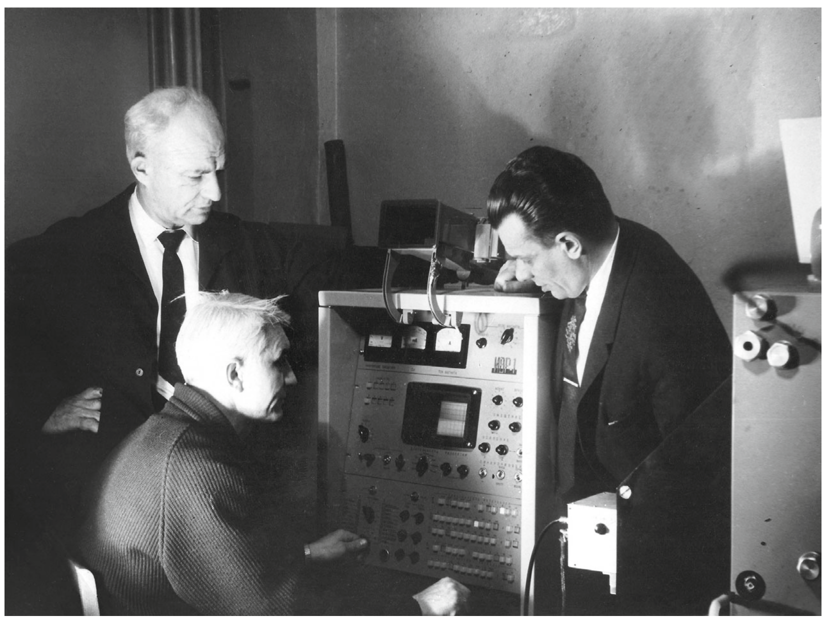

Fig. 7. L. L. Dekabrun (left) and O. D. Vetrov (center). Source: personal archive of E. O. Vetrova.

discussed below are classified as EPR in chemistry or EPR in biology only arbitrary, for obvious reasons.

NMR spectroscopy in chemistry. At the Institute of Physical Chemistry, magnetic resonance studies were launched in the late 1950s by M. B. Neiman's group – A. L. Buchachenko, G. I. Likhtenshtein, and E. G. Rozantsev, his students and colleagues. Out of their research spin chemistry was eventually born (A. L. Buchachenko, Y. N. Molin, K. M. Salikhov), as well as the spin-label method [92-97] (Fig. 6).

Experimental work in chemical kinetics started by V. V. Voevodsky's group at the same Institute in mid-1950s was continued by his students, after he (and a considerable number of his colleagues) left in 1961 for the newly established Institute of Chemical Kinetics and Combustion in Novosibirsk. The range of studies carried out by Voevodsky and later by his students included absorption and heterogeneous catalysis [98-101], free-radical reactions in the solid state [102, 103], EPR studies of the structure of substances, and publishing of the Atlas (chart) of the EPR Spectra [104, 105], among other things. Recognizing limitations of the EPR method in the "common" ultrahigh-frequency range (3 cm, 8 mm), Y. S. Lebedev would eventually create a new field in EPR spectroscopy – high field electron paramagnetic resonance [106, 107] – and supervise the development of the first D-band (2 mm) EPR spectrometer (it went as far as into small series production in the USSR) [108].

In the early period (late 1950s-early 1960s), NMR spectroscopy investigations at the Institute for Chemical Physics were the domain of L. L. Dekabrun's Laboratory [109]. L. L. Dekabrun himself was for the most part concerned with the development of NMR spectroscopic tools [110-112] (Fig. 7). In this he advanced as far as it was possible in such a complex field as high-resolution NMR and in the context of the USSR mass production standards (more on this in Scientific Instrumentation for EPR and NMR Spectroscopy in the USSR later in this Chapter). Roughly in the same period, NMR spectroscopy as a method for chemical research was studied by his fellow colleagues in Moscow and at the Institute's branch in Chernogolovka[26] [113-114].

The findings obtained by the young theoretical chemists of the Theoretical Department and of the Quantum Chemistry Lab at the Institute of Chemical Physics (I. V. Alexandrov, N. N. Korst, E. E. Nikitin, B. N. Provotorov, T. N. Khazanovich, and their students) would later become classic for the theory of paramagnetic relaxation. B. N. Provotorov, for example, suggested a theory of two energy reservoirs created by cross relaxation (similar to the Zeeman and spin–spin reservoirs).

After the Institute of Chemical Physics had grown to set up a branch in Chernogolovka, this science town near Moscow became another center for magnetic resonance research. By the beginning of 1970s, the resident researchers of the branch's labs (I. F. Schegolev, I. S. Krainsky, V. A. Zabrodin, G. V. Lagodzinskaya) and engineering workshops (V. K. Enman and others) had designed and built high-field NMR spectrometers using superconducting solenoids, the only of their kind in the USSR. They were a 180 MHz NMR spectrometer manufactured in 1970 and a 294 MHz NMR spectrometer that went into production in 1974 [115, 116]. A double NMR spectrometer and a solid-state NMR spectrometer were developed by L. N. Erofeev at G. B. Manelis' laboratory. Theoretical research (B. N. Provotorov, E. B. Feldman) "moved" to Chernogolovka in mid-1970s as well.

In 1960s, NMR spectroscopy was adopted as an indispensable research method by many of the chemical institutes in Moscow, such as: Zelinsky Institute of Organic Chemistry, the Institute of Organoelement Compounds and the Institute of Fossil Fuels of the USSR Academy of Sciences, Karpov Research Institute of Physical Chemistry, etc. At the Institute of Organic Chemistry, for example, its Special Design Bureau had a dedicated NMR Department that employed outstanding Soviet instrumentation designers A. N. Lyubimov and A. F. Varenik. The Institute of Organoelement Compounds had a strong group of NMR experts (E. I. Fedin, P. V. Petrovsky, I. P. Amiton et al.) working at its Laboratory of Structural Analysis led by A. I. Kitaigorosky. A. N. Nesmeyanov, Director of the Institute, who was also head of the Department of Organic Chemistry at Lomonosov Moscow State University, established the NMR spectroscopy group, later-laboratory, there as well, originally studying, for the most part, metal-organic compounds [117]. At Lomonosov Moscow State University, NMR spectroscopy in chemistry research had another advocate in A. V. Kiselev, Professor, Department of Physical Chemistry.

After the political controversy over the resonance theory in the USSR had ended, Y. K. Syrkin and M. E. Dyatkina returned to their EPR studies they had to pause for nearly a decade, at Kurnakov Institute of General and Inorganic Chemistry and at Moscow Institute of Fine Chemical Technology. Their research, after 1959, was mostly focused on studying metal-organic compounds [118, 119].

EPR spectroscopy in biology. 'EPR in Biology' in the USSR started with L. A. Blumenfeld [29, 30], whose works published in 1957 prompted a rapid growth of EPR spectroscopy applications in biological research. A. F. Vanin, his student, was the first to detect nitric oxide in biological tissues [120]; in 1998, discoveries concerning the role of nitric oxide as a signaling molecule in cardiovascular system would win the Nobel Prize in Physiology or Medicine. The double electron–electron resonance [121] discovered by Blumenfeld's group, completely independently but simultaneously with J. Hyde [122], was a breakthrough in the field as well. Studies of bioenergy processes was another significant line of research conducted by Blumenfeld and his students E. K. Ruuge, A. N. Tikhonov and others [123, 124] (Fig. 8). Eventually, Blumenfeld's experimental work developed into a strong school of biophysics, the range of problems it covered going well beyond EPR studies in biology [125, 126].

In the beginning of the 1960s, EPR investigations in physiology and medicine were launched at the Institute of Biological Physics[27] of the Soviet Academy of Sciences in Moscow, and later in Pushchino[28]. Its scope of research covered the structure [127]

[26] A science town (naukograd) in the Moscow Region (Oblast).

[27] Now the Institute of Theoretical and Experimental Biophysics and the Institute of Cell Biophysics of the Russian Academy of Sciences.

[28] A science town in the Moscow Region, the Research Center for Biological Studies of the Russia Academy of Sciences.

Fig. 8. A. F. Vanin (left), L. Berliner (center) and A. N. Tikhonov (right) at the IX EPR Workshop on EPR in Biology and Medicine, Krakow, 2013. Source: personal archive of A. F. Vanin.

Fig. 9. M. A. Ostrovsky (right) and his teacher, physiologist V. G. Samsonova (2nd left), early 1960s. Source: personal archive of M. A. Ostrovsky.

and function of myosin [128], respiration and oxidative phosphorylation [129], and other problems. One of the most interesting and fruitful lines of investigations pertained to the photobiophysics of retinal function was studied by M. A. Ostrovsky (the Institute of Higher Nervous Activity and Neurophysiology of the USSR Academy of Sciences) in cooperation with L. P. Kayushin (the Institute of Biological Physics) very early in the 1960s [130, 131]. Basically, they were the first in the world to study photoreception using the EPR method. Following their early findings, M. A. Ostrovsky suggested that the retinal pigment epithelium, previously considered as a neutral density filter in the optic cup passively absorbing scattered light, might in fact be instrumental in visual photoreception [132, 133]. In the end, that and some other research grew into a new field of scientific knowledge – molecular physiology of vision, of which M. A. Ostrovsky is acknowledged one of the founders (Fig. 9).

In the same late 1950s, EPR studies of synthetic polymers [134] were launched to be followed by EPR studies of biological compounds [135, 136] at the Department of Radiobiology of the Institute of Atomic Energy of the USSR[29]. The idea apparently came from V. U. Gavrilov, head of the Department. Primary focus of the studies, at least in the beginning, was on the radicals formed in a substance due to radiation exposure, their composition, stability, and interactions [137].

[29] Now Kurchatov Institute, National Research Center.

Leningrad: selected research. In Leningrad, magnetic resonance spectroscopy studies had a relatively early start – in the beginning of 1950s at the latest. At the Leningrad State University, a magnetic resonance Laboratory was set up by F. I. Skripov. Back then, he began NMR investigations of the Earth's magnetic field [138], an ongoing research up to the present day at now St. Petersburg State University. Interestingly, Skripov was *de facto* the first to apply the Fourier transform technique to NMR spectroscopy [139]. Yet, priority of the discovery was lost due to resistance of the Soviet patent office to patent this method, a frustratingly typical storyline in the history of the Soviet science [140]. Nearly a decade later, in 1966, a similar method would be independently developed by R. Ernst. Another research avenue Skripov had been exploring was high-resolution NMR spectroscopy [141]. In the early 1960s, acoustic NMR studies were launched at the University as well by V. A. Shutilov and his students [142-144].

Late in 1950s, at the Leningrad Physical-Technical Institute[30] EPR spectroscopy was applied to the studies of free atoms trapped in polar and nonpolar media [145, 146] along with experimental work with regards to optical methods of atomic orientation (the "optical pumping" method) [147]. Eventually, each developed into a whole new field of scientific research: EPR studies of conductors and optically detected magnetic resonance (ODMR). In both, the now Ioffe Institute is among the leaders [148, 149].

Magnetic resonance instrumentation design was another magnetic resonance-related area that had a relatively early start in Leningrad. It began in 1960 at the Special Design Department for Analytical Instrumentation (SDD AI) of the USSR Academy of Sciences, with Leningrad Electrotechnical University[31] launching a similar program later (more on this in Scientific Instrumentation for EPR and NMR Spectroscopy in the USSR later in this Chapter).

Minsk: school of EPR spectroscopy. In Minsk, the history of EPR studies began in 1956 after M. A. Elyashevich left the Institute of Chemical Physics (USSR Academy of Sciences) in Moscow for the Belarusian State University. As was said earlier, in the USSR, application of EPR and to some extent NMR, as a method for studies in biology and in chemistry started at the Institute of Chemical Physics. In mid-1950s, potential of the resonance methods in those fields was widely discussed there, and Elyashevich was among the most enthusiastic advocates of the technique [150]. In the next decades, the scientific school he founded contributed a lot to the development of EPR applications in chemistry, geology, medicine, and in other fields. But its major achievement was the development of a new class of compact EPR spectrometers prompting growth of EPR studies in the USSR in general, in particular in the decade before the collapse of the Soviet Union. Several generations of his students stood behind those advancements in instrumentation design with S. S. Shushkevich (in the 1960s-1970s) and V. N. Linev (since mid-1970s) playing the crucial part (Fig. 4) [151]. Their designs are discussed in more detail in the Scientific Instrumentation for EPR and NMR Spectroscopy in the USSR later in this Chapter.

Tallin: works on application of NMR spectroscopy in chemistry by the group of E. T. Lippmaa. In 1962, another outstanding scientist and his group entered the playing field of high-resolution NMR, joining Dekabrun, Bystrov, and Samitov – Estonian chemical physicist Endel Lippmaa of the Tallinn University of Technology [152, 153]. By that time, Lippmaa had already left the University for the newly established Institute of Cybernetics of the Estonian SSR Academy of Sciences to head its Division of Physics; his group and equipment following him to the Institute. He never aimed to provide the Soviet industry with a prototype for serial production of a proton magnetic resonance (PMR) spectrometer. Having mastered the PMR method (proton–proton double resonance included), Lippmaa rather aspired to use spectroscopy in the studies of the ^{13}C isotope, a carbon essential in organic chemistry studies. To that end, special, much more sensitive techniques (proton–carbon double resonance in particular) capable of massive data accumulation, were required. Lippmaa found the solution in equipping his spectrometers (there were at least four of them by that time) with a computer-based add-on system he managed to procure in Finland, and thus made his laboratory one of the world leaders in ^{13}C, ^{15}N and, since 1965, ^{14}N NMR spectroscopy [154, 155].

Kiev and Kharkov: acoustic resonance studies. In 1957, at the Institute of Physics, Academy of Sciences, Ukrainian SSR, Kiev, M. F. Deigen launched his radiospectroscopic studies of nonmetallic crystals that were later scaled up at the Department of Radio Spectroscopy he created at the Institute of Semiconductors, Academy of Sciences, Ukrainian SSR, that spun off the Institute of Physics in 1960. Deigen's focus was to a great extent on the development of the electron nuclear double resonance (ENDOR) method, which he recognized as a remarkably informative and potent. Under his guidance the first ENDOR apparatus in the USSR was built and used to determine energy-band structure and electron density distribution in crystals, among other things. Deigen's systematic research on the influence of external factors (such as tempera-

[30] Now the Ioffe Physical-Technical Institute of the Russian Academy of Sciences.

[31] Now Saint Petersburg Electrotechnical University "LETI".

ture, pressure, electric fields, etc.) on the EPR and ENDOR spectra gave birth to a whole new field of study – radiospectroscopic studies of material properties localized in the vicinity of defect sites [156]. His experimental work contributed to the refined theory explaining ENDOR frequencies, intensities, and line shapes. Likewise, Deigen predicted the electron-nuclear double magneto-acoustic resonance (ultrasound-induced transitions between nuclear sublevels) to be confirmed experimentally two years later [157].

In Kharkov, at the Institute of Radiophysics and Electronics, Academy of Sciences, Ukrainian SSR[32], hypersonic studies were launched early in the 1960s, acoustic paramagnetic resonance studies to follow suit later [158, 159].

Tbilisi. In Georgia, magnetic resonance research started with G. R. Khutsishvili, L. D. Landau's post-graduate student, coming to work to the Institute of Physics, Academy of Sciences, Georgian SSR, in the early 1950s. By mid-1960s, there and at the Tbilisi State University a strong group of theoretical physicists was eventually brought together: G. R. Khutsishvili, L. L. Buishvili, M. D. Zviadadze, and others [160-163]. At the Tbilisi University, T. I. Sanadze's group launched its EPR studies of polymers and crystals [164, 165], investigations of a wide range of phenomena to follow: forbidden transitions and magnetic relaxation, line shapes and saturation effects, the Overhauser effect, EPR, NMR, and FMR. Noteworthily, despite a thousand-mile distance between Tbilisi or Tallinn and Moscow, scientific groups working in the different parts of the Soviet Union collaborated closely, which is clear from the composition of author teams and acknowledgments in some of the papers.

Yerevan. EPR studies in Armenia were directly related to similar research at the Institute of Chemical Physics in Moscow. In 1959, A. B. Nalbandyan – a student of N. N. Semenov and, since 1960, a corresponding member of the Academy of Sciences, Armenian SSR (since 1963, an academician) – established a Laboratory (later Institute) of Chemical Physics, Academy of Sciences, Armenian SSR, in Yerevan. Much of his research stemmed from his earlier work in Moscow [166] pertaining to combustion mechanisms [167-170], in particular to the degenerate branching chain reaction kinetics and mechanism. In addition to ERP and laser magnetic resonance spectroscopy already in use, a new technique – the rapid freezing method to detect radicals – was developed and employed in experimentation at the Laboratory. Strengths and limitations of the three methods, along with the findings obtained with their use, were later summarized in a number of monographs [171, 172].

Molotov[33]: magnetic resonance spectroscopy. In Perm, magnetic resonance related research started with I. G. Shaposhnikov. A person with an extraordinary trajectory of life (Voronezh–Vladivostok–Moscow–Vladivostok–Kazan–Nikolaev–Kazan–Perm[34]), he crossed paths with E. K. Zavoisky at the turning point in EPR history – at the time of the EPR discovery. On his return from the front lines, Shaposhnikov, for a short period of time (1945-1946), worked at the Kazan State University, Department of Experimental and Theoretical Physics headed by Zavoisky. Paramagnetic relaxation was among the subject matters he conducted studies on, according to the Department's report [4]. In 1946, he was appointed head of the Department of Theoretical Physics that "seceded from" the Zavoisky's Department, and in 1948 – left for Molotov State University[35]. Paramagnetic relaxation, however, continued to be a phenomenon of scientific interest for him. After his Kazan-time research [173-175], he returned to the related phenomena in many of his later works [176-179].

Since the late 1950s, other researchers at Molotov State University embarked on the studies of various of magnetic resonance phenomena: EPR, NMR, NQR, and related phenomena in crystals, gases, and biological systems [180-184]. Similarly, development of instrumentation for magnetic resonance studies started at the University in the same period, in particular of instruments for the NQR and quadrupole spin echo observation, NMR sensors, and tools for experiment automation [185-187]. According to the recently published collection of selected works by the scientists of Perm State University [188], a great number of papers came out within the decade (1960-1970). Unfortunately, for the most part, the research was originally published in the local, not readily available, press, such as: "Transactions of ENI[36], Perm State University", "Transactions of Perm State University", "Proceedings of VUZes[37]", "Radio Spectroscopy", collections of conference proceedings, etc. Too many scientists were involved in magnetic resonance studies in Perm to list all of them here. The most frequent names among the authors of theoretical and experimental research include: V. S. Grechishkin, N. E. Ainbinder, G. B. Soifer,

[32] Now Usikov Institute for Radio Physics and Electronics of the National Academy of Sciences of Ukraine.
[33] Now Perm.
[34] Regional centers all across Russia and Ukraine.
[35] Now Perm State University, also Perm State National Research University.
[36] Transliterated abbreviation standing for the Institute of Natural Sciences.
[37] Transliterated abbreviation standing for Higher Educations Establishments.

I. A. Kuntsel, M. L. Zlatogorsky, and L. M. Tsirulnikova. Among the developers, most frequently published V. P. Zelenin, V. A. Kushkov, G. I. Subbotin, S. I. Guschin, V. A. Shishkin, B. G. Derendyaev, Y. I. Rosenberg, G. G. Kudymov, and Y. G. Svetlov.

Sverdlovsk[38]. In Sverdlovsk, a school of physics of magnetic phenomena emerged already in 1940s, driven mostly by S. V. Vonsovsky and his research (as early as in 1948 his monumental work [189] was published). It was no coincidence that the First All-Union Conference on the Physics of Magnetic Phenomena held in 1946, E. K. Zavoisky and B. M. Kozyrev invited, took place in Sverdlovsk. In mid-1950s, EPR, NMR, and FMR studies began there too, carried out mostly at the Ural Polytechnic Institute[39]. The renowned Urals school of magnetic resonance was eventually established by G. V. Skrotsky [190-193], at the very least it was strongly influenced by his work.

Apart from its scientific contribution, the Ural school, or its leader G. B. Skrotsky to be precise, created a valuable phenomenon of a different kind – the All-Union Workshops on Magnetic Resonance held every other year starting with 1968 all across the Soviet Union. The Workshops attracted young (and not so young) scientists from all over the USSR to share knowledge and build working and friendly relationships within the Soviet magnetic resonance community.

Novosibirsk: school of EPR-spectroscopy (V. V. Voevodsky school). In Novosibirsk, EPR and NMR spectroscopy development is associated with V. V. Voevodsky and his group, who was transferred from the Institute of Chemical Physics, Moscow, to the newly established Institute of Chemical Kinetics and Combustion, USSR Academy of Sciences, Siberian Branch. Although officially Voevodsky and his team started working there in 1959, the Institute's building was still under construction at the time and thus in actual fact they moved to Novosibirsk only two years later, in 1961. That year was the starting point in the history of magnetic resonance research in Novosibirsk and a new stage in the development of Voevodsky's school of radio spectroscopy in chemistry. They never lost touch with their Moscow colleagues, though, in particular with those at the Institute of Chemical Physics, and many of the works were carried out in close cooperation.

In the decade discussed here (1961-1970), Voevodsky and his colleagues continued EPR radiolysis research they started back in Moscow in 1957 with the launch of EPR spectroscopic studies using the Institute's electron beam accelerator. In Novosibirsk, the scope of EPR research grew to include radical recombination reactions and intramolecular energy transfer [194-197], as well as combustion reactions involving radical generation detectable by EPR spectroscopy [35, 198] (Fig. 10). Problems pertaining to photochemistry [199], polymer chemistry [200], and catalysis [201] had all been within the realm of scientific inquiry of the new school of radiospectroscopy. In the biology related research Voevodsky's group was assisted by the Institute of Cytology and Genetics, the USSR Academy of Sciences, Siberian Branch [202].

Fig. 10. Yu. N. Molin (left) and Yu. D. Tsvetkov (right), Novosibirsk, 1962. Source: the Electronic Photo Archive of the Siberian Branch of the Russian Academy of Sciences, http://www.soran1957.ru/?id=krai_100616111436_2725_0. Courtesy of I. Yu. Pavlovskaya.

Another important avenue explored in Novosibirsk pertained to the relaxation and spin echo methods [203-207] including theoretical explanation and interpretation of the spin echo experimental results. Theoreticians at the Institute of Chemical Kinetics and Combustion, K. M. Salikhov in particular, contributed a lot to the advancement of the theory of exchange interactions, the theory of spin waves, and other theoretical problems [208-211]. Finally, in the same period, spin chemistry, a new field of study that would burgeon in the next decade, was already emerging in the works of the scientists in Novosibirsk [212] (Fig. 11).

NMR spectroscopic studies in chemistry were advancing in Novosibirsk along with the EPR research, including those regarding biophysical problems [213], such as studying structures of glycosides from Ginseng, denaturation of tRNAs [214, 215].

[38] Now Ekaterinburg.

[39] Now part of the Ural Federal University named after the First President of Russia B. N. Yeltsin.

Fig. 11. K. M. Salikhov (left), R. Z. Sagdeev (2nd left), Yu. N. Molin (right), Novosibirsk, 1989. Source: personal archive of Yu. N. Molin.

A standalone comparative research was launched to study correlation between the findings obtained in both methods [216]. In the same years, spin labelling (iminoxyl radicals) was being researched [217, 218]. Continuing their cooperation with the Institute of Chemical Physics, Voevodsky's group was part of the "exotic" positronium studies carried out by V. I. Goldansky.

It must be said that another center for NMR studies emerged in Novosibirsk later in the same period – the Institute of Organic Chemistry, USSR Academy of Science, Siberian Branch[40], EPR research eventually added to its scientific agenda as well.

Krasnoyarsk: NMR spectroscopy. Krasnoyarsk's school of NMR spectroscopy was founded by A. G. Lundin – one the few who passed Landau's Theoretical Minimum[41], alumnus of Moscow Power Engineering Institute and of the Institute of Physical Problems, the legendary "kapitsnik", where he had been working for three years. In 1950, amid the battle against cosmopolitism[42] gaining momentum in the USSR, he was posted to Krasnoyarsk to the radio engineering plant. There he spent the next 13 years. Lundin, however, never surrendered to his "excommunication" from the scientific work and, in 1951 decided to conduct research, off work, at the Siberian Forestry Engineering Institute[43], Department of Physic, headed by P. S. Sarapkin, in cooperation with G. M. Mikhailov. The NMR method, he developed a strong interest for back at the "kapitsnik", was his field of choice for the studies he embarked on in Krasnoyarsk. Supported by L. V. Kirensky, a friend of P. S. Sarapkin, Lundin was well equipped to make quick progress in his experiments. By the year 1957, A. G. Lundin and his colleagues had built an NMR spectrometer using a rotating magnet (placed on an anti-aircraft gun mount) to investigate effects of crystal orientation [219]. In 1963, after 13 years at the radio engineering plant, A. G. Lundin was offered a position at the Institute of Physics, USSR Academy of Sciences, Siberian Branch, by L. V. Kirensky. Since that year the Institute of Physics had been the heart of NMR research in Krasnoyarsk.

Lundin's school focused predominantly on NMR investigations of crystals: crystalline hydrates, organic acids crystals, minerals, etc. [220, 221]. Worth particular mention are the studies of ferroelectric phase transitions and of the nature of ferroelectricity [222-224]. On the theoretical side, effects of internal molecular motions in NMR spectra [225, 226] were investigated, as well as an approach was developed to the line-shape inverse problem in the NMR spectra, that is to determination of the crystal cell parameters by means of orientation-dependent spectra [227].

Although as early as in 1964 the Institute of Physics somehow got hold of a brand-name Japan

[40] Now the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Russian Academy of Sciences, Siberian Branch.

[41] Landau developed a comprehensive exam called the "Theoretical Minimum" which students were expected to pass before admission to his seminar. The exam covered all aspects of theoretical physics. Between 1934 and 1961 only 43 candidates passed.

[42] An euphemism for the anti-Semitic campaign in the USSR waged in 1948-1953.

[43] Now part of Reshetnev Siberian State University of Science and Technology.

NMR spectrometer JNM-3H-60, experimental instrumentation was, for the most part, assembled at the Institute itself, including by the Lundin's team. For example, for the studies of solids, they built a wide-line NMR spectrometer using a superconducting magnet (NMR-213M[44]), one of the most impressive strides made by Lundin and his colleagues in spectroscopic instrumentation. It would later go into a small-series production (more on this in Scientific Instrumentation for EPR and NMR Spectroscopy in the USSR later in this Chapter). Apart from this major piece of equipment, Lundin's team designed and built a great many of simpler tools, such as high-temperature sensors for NMR spectroscopy, instruments for recording spectra at high hydrostatic pressures, automation tools for processing NMR spectra, and experiment automation systems. New methods, including pulsed NMR [228], were advancing as well. In the domain of EPR instrumentation, a Q-band (8 mm) EPR spectrometer capable of applying uniaxial pressure to the sample was developed, along with the set of EPR magnetometers (EPRAN-1200) for geophysical measurements (E. P. Zeer, G. F. Lybzikov, V. V. Menshikov, S. A. Trofimov, V. V. Lisin et al.), although it was in the later years – in the second half of the 1970s.

SCIENTIFIC INSTRUMENTATION FOR EPR AND NMR SPECTROSCOPY IN THE USSR

Rapid development of radiospectroscopic studies in chemistry and biology, as was said earlier, began with the groups led by V. V. Voevodsky and L. A. Blumenfeld launching their research at the Institute of Chemical Studies, USSR Academy of Sciences, in mid-1950s. Voevodsky's group meanwhile contributed to yet another breakthrough in the field of EPR instrumentation design, owing mostly to the efforts of his younger colleagues, namely N. N. Bubnov, Y. N. Molin, A. G. Semenov, Y. D. Tsvetkov (Fig. 10), and V. M. Chibrikin [229]. As a result of extended enough collective efforts, A. G. Semenov developed an original spectrometer that came to be known as EPR-2[45] spectrometer. Its design allowed to study free-radical reactions with high precision (resulting from the use of a transmission-type resonator, a double-modulation technique, and a tunable frequency oscillator [230]). To a certain extent, EPR-2 spectrometer filled the void of the Soviet original instrumentation for the years to come. Using EPR-2 as a prototype, Leningrad Special Design Bureau for Analytical Instrumentation, USSR Academy of Sciences, designed a model optimized for mass production. It had been on the market for the next 15 years (up to 1976) as a RE1301[46] spectrometer produced by the Smolensk Plant of Automation Equipment [231]. Studies using ERP spectroscopy grew in number as new scientific institutions were established on the wave of the so called "Big Chemistry"[47] program, namely, in the Institute of Chemical Kinetics and Combustion in Novosibirsk and the Branch of the Institute of Chemical Physics in Chernogolovka. The Institute of Chemical Physics itself continued to widely use the EPR method in its research. Quality of the instrumentation manufactured in the USSR, no doubt, had room for improvement. G. I. Likhtenshtein [232], for example, reminisced how academician A. L. Buchachenko had to fine-tune his manufactured RE1301 himself. The important thing though was that there *were* EPR instruments produced in the USSR. As there was original literature on the EPR methods published in the Soviet Union, especially so in the early 1960s (more on this in Chapter IV, part II).

In the context of EPR instrumentation development in general, though, one must say that in the later years progress was rather modest. Considering the scientific-technological revolution in the world, scientific instrumentation engineering in the USSR was, alas, behind the knowledge-intensive industries in the West. New instruments, however, continued to be developed. The Special Design Bureau for Analytical Instrumentation, for example, in the 1960s-1970s designed a series of EPR spectrometers of the RE[48]-family, both the traditional 3-cm instruments (X-band), and 8-mm models (Q-band). The RE family of spectrometers was the most common in the USSR: several hundred of them were manufactured over two decades (early 1960s-mid-1980s). Along with the RE spectrometers, more advanced instruments were designed and produced in small series. Of them the most commonly known was the EPR-3 (Siberia)[49] spectrometer developed by A. G. Semenov at the Institute of Chemical Kinetics and Combustion, USSR Academy of Sciences, Siberian Branch, in Novosibirsk. It was manufactured by the Pilot Plant, USSR Academy of Sciences, Siberian Branch, as a small series of 45 instruments.

[44] In Cyrillic, ЯМР-213М.

[45] In Cyrillic, ЭПР-2.

[46] In Cyrillic, РЭ1301.

[47] A large-scale program announced by the USSR government to develop chemical industry in the country for the years 1959-1980.

[48] In Cyrillic, РЭ.

[49] In Cyrillic, ЭПР-3 "Сибирь".

Fig. 12. Specialized compact EPR spectrometer constructed by V. N. Linev's team at BSU early in the 1980s. Source: personal archive of V. N. Linev.

At the same Institute, Y. D. Tsvetkov designed a pulsed EPR spectrometer, although it failed to go into production. Y. S. Lebedev's laboratory at the Institute of Chemical Physics, Moscow, was another player in the field of EPR instrumentation development. In cooperation with the Donetsk Institute for Physics and Engineering, Academy of Sciences, Ukrainian SSR, Lebedev's team designed the first high-field (2-mm) spectrometer in the USSR. Also involved in the development of special purpose EPR spectrometers was Ulyanov Leningrad Electrotechnical Institute (LETI). Small series of the LETI's spectrometers were produced by the Leningrad Association of Electronic Instrumentation "Svetlana", USSR's famous electronic instrumentation manufacturer.

In the latest years of the discussed period arguably the most important, in terms of small series EPR instrumentation production, was the development of compact EPR spectrometers at the Belarusian State University. The project was launched in mid-1970s by S. S. Shushkevich, a student of A. M. Elyashevich, who would eventually be thrown into the international spotlight but in a totally different context[50]. V. N. Linev was the central person in terms of development as such. Eventually, he would be the one to keep production of the benchtop EPR spectrometers afloat amid the economical turmoil in the USSR and, later, in independent Belarus. Back in 1970s, within several years, he and his group developed extraordinarily compact instruments weighing 28 to 50 kg. Later, by introducing a permanent magnet instead of a cumbersome electromagnet, spectrometer weight was decreased down to 8 kg. To compare, a regular EPR spectrometer, including the spectrometers of RE-family, weighed over a ton at the time in the USSR. Compact size, lower power consumption, stronger noise immunity and other parameters made Belarusian compact EPR spectrometers instrumentation of choice in mineral exploration, manufacturing, hospitals, etc. (Fig. 12) [151]. The Belarusian family of benchtop EPR spectrometers is the only one that survived the USSR and is still on the market, under the brand name LINEV, former Adani.

In the development of NMR instrumentation, meanwhile, the situation was much more complicated. Early in 1960s, literature on NMR (mostly by non-USSR authors) only began to be published. Although after 1955 restrictions on international contacts for the Soviet scientists were eased, an international exchange program was still an impossible dream at the time. There was a huge void of NMR instruments in the country. Attempts that were made to set up manufacturing of NMR instrumentation all but failed. While the Academy's Special Design Bureau succeeded in designing a basic EPR spectrometer suited for production, it was still an impossible undertaking for the USSR non-military industry to generate a stratospheric by its standards stability of magnetic field and frequency, and magnetic field homogeneity (10^{-8}). The first designs developed by the Special Design Bureau offered the ratio of 10^{-5}, which was enough for conducting some studies of broadened lines in solids. The resulting prototype though was cumbersome, expensive, and, basically, useless for chemistry labs.

[50] In 1991-1994, S. S. Shushkevich was Chairman of the Supreme Soviet of Belarus, the first head of state after Belarus seceded from the Soviet Union. He was one of the three leaders who in December, 1991, signed the Belovezha Accords that ended the USSR and established the CIS as a successor entity.

As early as in the beginning of 1960s, there were other endeavors to develop NMR spectrometers and put them into small-series production, apart from the "model range" designed by the Academy's Special Design Bureau. By 1961, L. L. Dekabrun's lab at the Institute of Chemical Physics had designed an NMR spectrometer operating at 27 MHz proton frequency [110]. Two years later, in 1963, it was used as a prototype by the Design Bureau, Academy of Sciences, Estonian SSR (headed by Enno Laud), to produce several prototype samples of the SNMR-63[51] spectrometer using a 0.5 T permanent magnet, for NMR studies of ^{1}H and ^{19}F. Karpov Institute of Physical Chemistry in Moscow was among the reputable scientific institutions that had been using the SNMR-63 spectrometer for many years in its experimental work. Simultaneously, a 27 MHz proton NMR spectrometer was developed by Y. Y. Samitov of the Kazan State University. Named KGU-1[52], the Kazan spectrometer was used by some institutions of the USSR chemistry industry.

It was a godsend to the Soviet NMR spectroscopy that M. B. Neiman, a pioneer of EPR in chemistry, found two accomplished experts in building magnets and electronic instruments in the depths of a Design Bureau of the USSR Ministry of Ferrous Metallurgy, one of the Soviet Union's "sharashkas"[53]. They were Alexander Nikolayevich Lubimov and Anatoly Fedoseevich Varenik, both political prisoners. Out of their cooperation came the development of an almost up to date NMR spectrometer (CLA 5535[54], later RS-60[55]), although it still was some 5 years behind its Western analogues. The endeavor was described by E. I. Fedin (Fig. 13) in his memoirs [233] and by I. Y. Slonim [234] in his interview, among others. Success of Lubimov and Varenik was based on the principle of stabilization of gyromagnetic ratio with the help of an auxiliary NMR signal. This was accompanied with the impeccable mechanical and thermal processing (in the reducing atmosphere) of the magnet pole tips. With their CLA 5535 model Lubimov and Varenik dispelled the myth about the Western instrumentation designers forging magnet poles from the monocrystalline iron, a desperate idea once suggested by the participants of N. M. Ievskaya's NMR seminar at the Moscow State University. E. I. Fedin, who worked directly with A. N. Nesmeyanov (Fig. 13), President of the USSR Academy of Sciences in 1951-1961, initiated a campaign in support of Lubimov and his group and against the conventional approach to NMR instruments design adopted by the Special Design Bureau of the USSR Academy of Science. This essentially a tragicomic story stemming from an article in the *Literaturnaia Gazeta* (Literature Newspaper) in 1963 [235], was told in the Fedin's memoirs and in the recent article [236]. Following the outrage expressed by the leadership of the Special Design Bureau, Erlen Ilyich Fedin had to act as a mediator between the different members of the budding NMR instrumentation industry. To some extent, he succeeded in his mission. By 1966, both the Special Design Bureau of Analytical Instrumentation in Leningrad (headed by Y. K. Kleiman) and the Special Design Bureau of the Institute of Organic Chemistry, USSR Academy of Sciences, in Moscow had designed more or less adequate prototypes of the 60 MHz proton NMR spectrometers. (It was the latter institution that the Lubimov's group was eventually transferred to with the help of Fedin.) The prototype designed in Leningrad was put into production at the Smolensk Plant of Automation Equipment, while Lubimov's design was manufactured at the Instrumentation Engineering Plant in Sumy, Ukrainian SSR, as the RS-60[56] model. Unfortunately, as experience showed, none of the two were fully equipped to manufacture such an intricate instrument. Both manufacturers barely scraped through with a total of two dozen instruments produced, and only a few of them were used in real chemistry research after being fine-tuned.

By 1974, E. P. Zeer from the Lundin's lab at the Institute of Physics in Krasnoyarsk had developed a wide-line solid-state NMR spectrometer using a superconducting solenoid (designed by A. G. Lundin, E. P. Zeer, G. F. Lybzikov, V. V. Menshikov, Y. A. Zagorodny, and V. A. Babaev, with E. P. Zeer as a head of the development group). In 1974, the spectrometer was for the first time exhibited at VDNH[57], USSR's biggest trade show. In 1975, after major improvements, it was put on display in Leipzig, East Germany, where the International Autumn NMR Workshop was being held [228]. In 1976, it was once again

[51] In Cyrillic, СЯМР-63.

[52] In Cyrillic, КГУ-1, an abbreviation standing for Kazan State University.

[53] Secret research and development facilities operating through the work of prisoners within the Soviet Gulag labor camp system and beyond under the supervision of NKVD, the Soviet secret service, from 1930 to the 1950s.

[54] In Cyrillic, ЦЛА 5535.

[55] In Cyrillic, РС-60.

[56] In Cyrillic, РС-60.

[57] A transliterated Cyrillic abbreviation standing for the Exhibition of Achievements of National Economy. A permanent trade show and amusement park in Moscow, USSR (now in Russia), designed to demonstrate the best accomplishments of Soviet industries.

Fig. 13. Left to right: E. I. Fedin, A. N. Nesmeyanov, and P. V. Petrovsky. The Institute of Organoelement Compounds, Moscow, early 1970s. Source: personal archive of I. P. Amiton.

displayed at VDNH and this time was awarded golden, silver, and three bronze medals. A. G. Lundin was friends with E. I. Fedin, head of the Commission for Radio-Frequency Spectroscopy, USSR Academy of Sciences. Fedin's former colleague at the Institute of Organoelement Compounds, L. A. Fyodorov, was at the time deputy for science at the Department of Science Instrumentation, USSR Academy of Sciences. Not least because of those friendships and enthusiasm on the part of Lundin and Fedin the Department approved manufacturing of a small-series of NMR spectrometers designed in Krasnoyarsk, at the Experimental Factory of Scientific Engineering in Chernogolovka. Within several years, 10 spectrometers were produced under the brand-name NMR-213M[58].

Finally, in the late 1970s-early 1980s, the Academy's Special Design Bureau made an effort to set up mass-production of a high-field NMR spectrometer. According to the Bureau itself, it "had been entertaining the idea of developing a radio-frequency spectrometer with a superconducting magnet since the early seventies, but for various reasons could not move ahead before 1979" [231]. In 1979, encouraged by the enthusiasm of E. I. Fedin, head of the Academy's Commission for Radio-Frequency Spectroscopy, the Bureau proceeded with the development of such instrument. The high-resolution laboratory NMR spectrometer designed by I. F. Schegolev, I. S. Krainsky, V. A. Zabrodin, G. V. Lagodzinskaya, V. K. Enman et al. at the Institute of Chemical Physics, Chernogolovka Branch was used as a starting point (Fig. 14). By 1982, the Bureau had "finished building its RI2304[59] model – a pulsed-Fourier-transform ^{1}H NMR spectrometer with a superconducting magnet, operating at 200 MHz, the first in the USSR" [231]. Alas, the instrument missed its chance to be put into production. In 1982, the Smolensk Scientific Development and Production Center "Analitpribor". suspended its magnetic resonance instruments production, while MicroInstrumentation Plant in Lviv, Ukrainian SSR, was not to start manufacturing MR instrumentation until several years later. Moreover, production of the RI2304 model required stronger technical capabilities than those of the EPR or NMR spectrometers manufactured before, which was out of reach for any of the two plants.

Meanwhile, Soviet chemists had been growing to understand that foreign instrumentation had to be employed. The first were the chemists of the Academy's Institute of Macromolecular Compounds in Leningrad who, in 1960, acquired a Japan 40 MHz PMR spectrometer. In 1961, two 25 MHz NMR spectrometers manufactured by Trüb, Täuber & Co, Switzerland, were acquired – one by the Karpov Institute of Physical Chemistry, the leading scientific institution of the USSR chemical industry, and the other by the Institute of Organoelement Compounds headed by the president of the USSR Academy of Sciences A. N. Nesmeyanov. Structural studies of organic and organoelement compounds with the use of the imported instruments produced some results, providing basis

[58] In Cyrillic, ЯМР-213М.

[59] In Cyrillic, РИ2304.

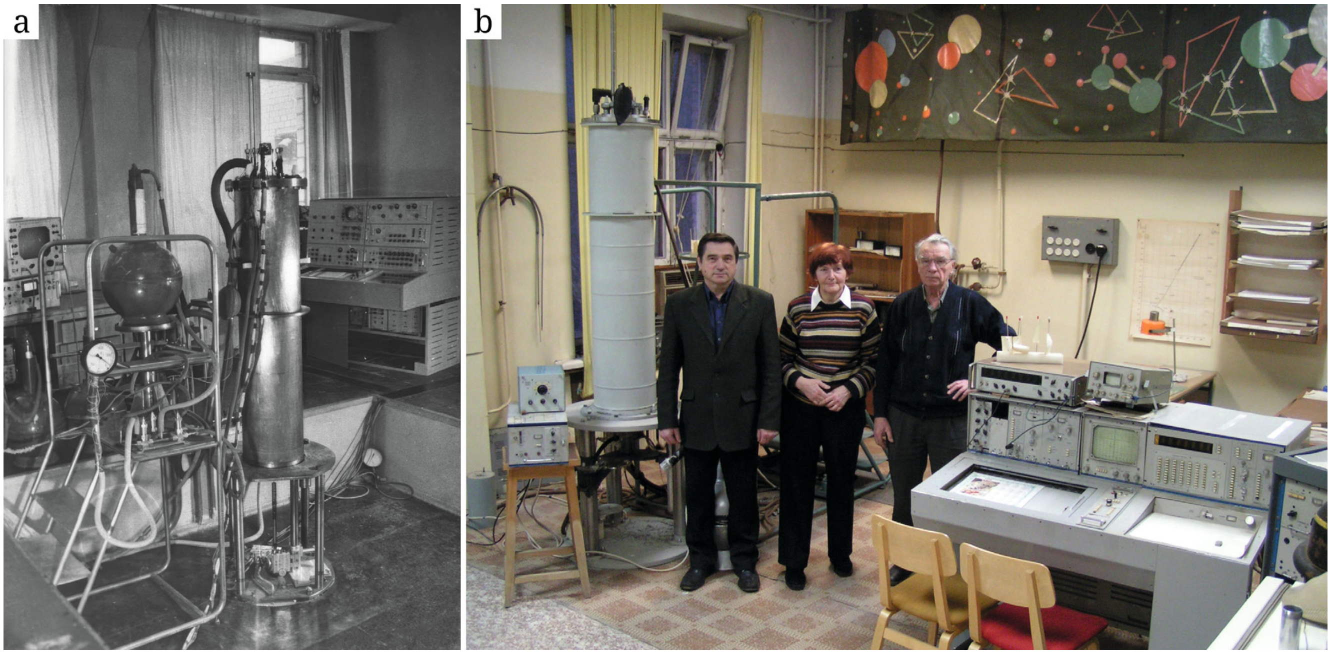

Fig. 14. The first prototype of the ChG-180 MHz NMR spectrometer developed in Chernogolovka in 1971 (a) and its authors – V. P. Bubnov, G. V. Lagodzinskaya, and V. A. Zabrodin, after the instrument was made ready to be transferred to the museum, 2006 (b). The intended transfer, however, fell apart in the end. Source: personal archive of G. V. Lagodzinskaya.

for a meaningful discussion with the Western peers for whom NMR spectroscopy was already an integral part of their research work. Practical experience with the Trüb–Täuber spectrometers using a permanent magnet made it clear that, given technical capability of the USSR instrumentation industry at the time, endeavors to build a decent permanent-magnet PMR spectrometer would have been a lost cause. Magnetic induction below 2 T was sufficient to provide neither the necessary sensitivity nor the resolution required for proton resonance in organic compounds (due to specific characteristics of proton spectra, indirect spin–spin interactions – at low PMR frequencies – often being of the same order of magnitude as chemical shifts). In fluorine NMR, though, magnetic fields of such a strength were at least in some instances operative. Foreign instrumentation thus made its way into the budgets of USSR leading chemistry researchers. In the West, Japan JEOL spectrometers could not compete with the ones manufactured by the US Varian Associates with its instruments based on the Bloch–Hansen patented technology and laboratories employing the best of the US NMR experts. Despite the US embargo on strategic materials, equipment, and arms exports to the USSR[60], JEOL spectrometers were shipped to the Soviet Union to be used by scientific institutions of the Academy of Sciences, such as Lomonosov Moscow State University (Y. A. Ustynuk and N. M. Sergeev, Faculty of Chemistry), some of the Institutes of the defense industry, and some of the medical research facilities. The funds allocated to Techsnabexport, a Soviet technology export and import bureau, for purchasing spectroscopy instrumentation most likely came from the oil export revenues. The first Japan 100 MHz PMR spectrometers were purchased for the Faculty of Chemistry of Lomonosov Moscow State University and for the Institute of Molecular Biology, the USSR Academy of Science.

Since late 1960, it had been in the air that a new era in the magnetic resonance development was about to begin. The USSR was no exception – magnetic resonance research in the country reached a turning point. In terms of theoretical studies, Soviet scientists were on equal grounds as their Western colleagues, and in some respects ahead of them (B. N. Provotorov of the Institute of Chemical Physics, with his theory of cross relaxation, and his students M. A. Kozhushner and O. I. Olkhov; M. I. Rodak of the Radio Engineering and Electronics Institute, USSR Academy of Sciences; theoreticians of the Tbilisi State University). In experimental instrumentation development, however, the Soviet Union was frustratingly behind the West. Although, the EPR saturation studies on dynamic nuclear polarization in crystals and polymers did bear fruit. *De facto*, the USSR physicists discovered the multi-particle method of dynamic nuclear

[60] US Export Control Act of 1949. Under pressure from the US, the embargo was joined by 17 other countries, US allies, including Japan.

polarization (DNP) (V. A. Atsarkin, A. E. Mefed, et al. of the Radio Engineering and Electronics Institute; V. I. Luschikov, Y. V. Taran et al. of the Joint Institute for Nuclear Research, who completed an apprenticeship at the A. A. Manenkov's lab at the Physical Technical Institute). Following their international counterparts and drawing on the experimental findings by Manenkov's laboratory, Soviet physicists at the Joint Institute for Nuclear Research developed a polarized proton target to investigate the effect of proton spin on neutron beams. Yet, breakthroughs were few and far between, the real problem – manufacturing of NMR instrumentation for chemistry research – remaining unresolved.

The new era in magnetic resonance development came, firstly, with the emergence of pulse excitation and Fourier transform techniques. New methods required every instrument to have a computer attached to it to program the algorithm and collect the measurements.

Secondly, it was the time of type II superconductors with high enough critical magnetic fields to obtain magnetic fields of 4 T or higher (at PMR frequencies of 200 MHz and higher). Thirdly, vacuum tubes were becoming history, superconductors gradually taking their place in electronic instrumentation. Soviet instrumentation industry switched over to superconducting components eventually, although it took time. There were fruitful, yet cautious, endeavors to build original superconducting solenoids (dubbed "supercons" by Soviet instrumentation designers). The process of integrating computers and the Fourier transform method into MR instrumentation was, however, stalling. Mainframe computer systems developed in the USSR were quite good until the ES[61] series, a Soviet analogue of IBM's System/360, that was basically strongly 'advised' to be used since the early 1970s. Regardless, the mainframes were too big, both in size and in power consumption, to be used in NMR spectrometers. Personal computers, on the other hand, would have been up to the task, but for some reason they were all but prohibited in the Soviet Union.

While the world's scientific community was preparing for the breakthrough in the magnetic resonance instrumentation industry, the USSR found itself not ready for this. Nonetheless, the explosive development, of which the Soviet Union was hardly a part of, proved to be of some use for its NMR instrumentation conundrum, although indirectly.

In 1967, Endel Lippmaa became firmly established as one the leading designers of NMR instrumentation in the USSR and beyond. On May 13, 1967, the USSR Academy of Sciences, Division of General and Industrial Chemistry, held a meeting on NMR spectroscopy at its Institute of Organic Chemistry. Among the speakers there were E. I. Fedin, Y. Y. Samitov, V. F. Bystrov, and E. Lippmaa, papers by the latter two standing out. The discussion led to a definitive resolution – there was a growing need for foreign instruments to be purchased. By this time, foreign companies such as Varian Associates and emerging Bruker-Physik AG, coincidentally, had grown ready to bypass the US embargo on electronic instrumentation exports to the USSR that proved detrimental to business (previously, only Finland and Japan had taken the risk of ignoring the embargo).

In the summer of 1967, Varian Associates showcased its instruments in Moscow. Right from the trade show the long-awaited 60 MHz and 100 MHz PMR spectrometers equipped with add-ons for other nuclei (fluorine, phosphorus), NMR stabilizer, and a magnetic field inhomogeneity correction (shim) system were shipped to the Academy's institutions. Only they missed (!) computer add-ons and the Fourier transform. Basically, Varian get rid of the outdated instrumentation. Bruker-Physik AG chose to pursue a different strategy. Right from the beginning, Bruker offered Fourier transform spectrometers to its customers in the USSR, operating at 90MHz instead of 100 MHz but suitable for ^{13}C NMR spectroscopy. This, however, would be a later development that would take place in a year or two after the Varian's trade show. When it did, Varian Associates had to defy the US embargo with regard to Fourier transform spectrometers as well, including the ^{13}C NMR instruments.

In the period of 1967-1969, the Soviet magnetic resonance community finally consolidated. In September 1967, the All-Union Symposium on Nuclear Magnetic Resonance was held in Tallinn, Estonian SSR. At the time, Lippmaa's laboratory was the only one in the Soviet Union equipped to collect ^{13}C spectral data that, according to Lippmaa himself, "was impossible to be collected even by means of the fine instruments purchased by the institutes in Moscow and Novosibirsk."

In 1968, in Sevastopol, Ukrainian SSR, the First All-Union Workshop on Magnetic Resonance – a project of G. V. Skrotsky, leader of the Urals school – was held under the aegis of Ukrainian experts. On a side note, the Workshop was warmly welcomed by the Black Sea Fleet Command. In the years to come a total of 11 Workshops would be held all across Russia – from Chernogolovka (1975) near Moscow to Kungur (1991) in the Urals. The most memorable were the "floating" Workshops that used a motor ship as a venue and traveled from Krasnoyarsk to Dudindka (Siberia) in 1975 and from Perm to Volgograd (east

[61] In Cyrillic, EC.

of European Russia) in 1979. The Workshops covered nearly all of magnetic resonance phenomena.

It would only be fitting to conclude this monograph with the events of the year 1969, central to both the USSR and the world in the context of magnetic resonance.

In that year, the *Journal of Magnetic Resonance* and the *Organic Magnetic Resonance* (later, *Magnetic Resonance in Chemistry*) – world's leading journals in the field of magnetic resonance – were established. In the editorial board of the latter the USSR was represented by E. Lippmaa who, on a side note, in the same year earned his doctoral degree in physics and mathematics at the Institute of Chemical Physics, USSR Academy of Sciences.

Finally, in 1969, the International Conference was held in Kazan to mark the 25-year anniversary of E. K. Zavoisky's discovery of EPR. Despite all the faults and pitfalls, magnetic resonance and related phenomena research continued to develop in the USSR, although, leading positions in the world were hardly the case. There were rare exceptions though. Physicists of the Novosibirsk school (Y. N. Molin, K. M. Salikhov, R. Z. Sagdeev, et al.) made breakthrough developments in the studies of chemically induced nuclear spin polarization in radical combination reactions, while their colleagues at the University of Kazan (S. A. Altshuler, M. A. Teplov et al.) delivered groundbreaking results in exploring Van Vleck paramagnetism.

Supplementary information

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Ethics approval and consent to participate

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Conflict of interest

The authors of this work declare that they have no conflicts of interest.

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