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HISTORY AND BIOGRAPHY

EPR in the USSR: the thorny path from birth to biological and chemical applications

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Abstract In 1944, electron paramagnetic resonance (EPR) was discovered by Evgenii Konstantinovich Zavoisky in the USSR (Union of the Soviet Socialist Republics). Since then, magnetic resonance methods have contributed invaluably to our knowledge in many areas of Life Sciences and Chemistry, and particularly in the area of photosynthesis research. However, the road of the magnetic resonance methods, as well as its acceptance in Life Sciences and Chemistry, was not smooth and prompt in the (former) USSR. We discuss the role played by many including Jakov K. Syrkin, Nikolai N. Semenov, Vladislav V. Voevodsky, Lev A. Blumenfeld, Peter L. Kapitza, and Alexander I. Shalnikov during the early stages of biological and chemical EPR spectroscopy in the USSR.

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Abbreviations

AICP	Archive of N.N. Semenov Institute of Chemical Physics
ARAS	Archive of the Russian Academy of Sciences
CIAMT	Central Institute for Advanced Medical Training
EPR	Electron paramagnetic resonance
ICP	Institute of Chemical Physics (now N.N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences)
IPP	Institute for Physical Problems (now P.L. Kapitza Institute for Physical Problems of the Russian Academy of Sciences)
KIPC	Karpov Institute of Physical Chemistry
LPI	P.N. Lebedev Physical Institute
MSU	M.V. Lomonosov Moscow State University
NMR	Nuclear magnetic resonance
RAS	The Russian Academy of Sciences
RSAE	Russian State Archive of the Economy
USSR	Union of the Soviet Socialist Republics

Introduction

Magnetic resonance methods have contributed invaluably to photosynthesis research. Sixty-one years ago, the EPR signal of the oxidized primary donor (an ion-radical) of photosystem I, P_{700}^{+}, was published by Commoner et al. (1956); the rest is history. Since then, high-time resolution pulsed EPR and transient EPR spectroscopy have allowed us to learn much more about the primary photochemical reactions of photosynthesis. High-field EPR and its variants (e.g., electron spin echo [ESE], electron spin echo envelope modulation [ESEEM]) have provided detailed structural data, elucidating structure–dynamics–function relations in several photosynthetic complexes. Furthermore, electron nuclear double resonance (ENDOR), double electron–electron resonance (DEER), optically detected magnetic resonance (ODMR), and other double resonance techniques have provided an enormous amount of information on the mechanism of photosynthesis. Results of such studies using a variety of modern magnetic resonance methods have been published in a special issue of *Photosynthesis Research*: "Basics and application of biophysical techniques in photosynthesis and related processes" (see, e.g., papers by Savitsky and Möbius 2009; Van der Est 2009; Kothe and Thurnauer 2009, and; Carbonera 2009).

We note, however, that development of the magnetic resonance methods, as well as their acceptance in Life Sciences and Chemistry, has not been smooth and prompt. It is somewhat of a paradox that in the former USSR (Union of the Soviet Socialist Republics), where, in 1944, Evgenii Konstantinovich Zavoisky (1907–1976) discovered magnetic resonance (EPR, electron paramagnetic resonance), there was a long lag phase, especially in biology and chemistry, before its application became widespread. Possible reasons of this delay may include the ideological campaigns that took place in Soviet science in the late 1940s and early 1950s, as well as the social and political climate in the country. And in the era of global integration, science in the USSR was in many ways isolated and developed independently, going its own way. Jakov K. Syrkin, Nikolai N. Semenov, Vladislav V. Voevodsky, and Lev A. Blumenfeld were among the scientists who played key roles in introducing the magnetic resonance methods into biological and chemical sciences in the USSR. In 2016, the Russian scientific community celebrated the 120th birth anniversary of N.N. Semenov and the 95th anniversary of L.A. Blumenfeld; in 2017, we will celebrate the 110th anniversary of E.K. Zavoisky and 100th anniversary of V.V. Voevodsky. It is timely to recall here the circumstances of the advent of Russian biological and chemical magnetic resonance spectroscopy. The timeline of the main events of this history is presented in Appendix 1.

The beginning of electron paramagnetic resonance

The discovery of magnetic resonance was not incidental for Zavoisky himself or for science in the middle of the twentieth century. Both the phenomena (and the concepts) of "*radio*" and the "*nucleus*" were, in a sense, symbols of physics or even of everyday life in the 1920s and the 1930s. For instance, the famous Soviet writer Ilya Ilf wrote in his 1930 sketchbook: "*Radio was the main dream in science fiction. Its advent was bound to make mankind happy. Now we have the radio but got no happiness*" (see Ilf 2000, p. 311). Accordingly, the *radio*spectroscopy of condensed matter, or of atomic beams, aimed at finding *nuclear* resonance in the magnetic field, was at the intersection of these concepts. We will not dwell on the work that prepared the ground for breakthroughs in this field, such as studying magnetic dispersion (e.g., Arkadiew 1913a, b), paramagnetic relaxation (e.g., Waller 1932; Heitler and Teller 1936; Casimir and Du Pré 1938; Van Vleck 1939), the quantum theory of radiative transitions (Einstein and Ehrenfest 1922), and others, since the early history of the discovery of magnetic resonance has been described in detail, e.g., by Kochelaev and Yablokov (1995, pp. 4–13), Poole and Farach (1998), Bleaney (1998), and Kessenikh (2009). An immediate influence on Zavoisky's studies on magnetic resonance was that of Gorter (1936) and Rabi et al. (1939). Using atomic beams, Rabi et al. (1939) were the first to provide the idea that *magnetic resonance* could be put to practical use. However, Rabi's experiments did not involve interaction of paramagnetic particles with each other and their environment—for the key driver for diverse applications of magnetic resonance, see, e.g., Altshuler and Kozyrev (1971). Just a few years before Rabi, Gorter (1936) was carrying out systematic studies of paramagnetic materials in alternating electromagnetic fields, looking for resonance, but had no success. However, the results of Gorter (1936) and Rabi et al. (1939) inspired Zavoisky leading to the discovery of EPR (Zavoisky 1945a, b; Fig. 1).

Fig. 1 From left to right: C.J. Gorter, E.K. Zavoisky, C.D. Jeffries, A. Abragam, and B.M. Kozyrev; Kazan, 1969. Source: Archives of the Russian Academy of Science (ARAS 1969)

Being a passionate radio amateur, "Zavoisky almost from his student days nurtured the idea of using radio-frequency electromagnetic fields for studying the structure and properties of matter" (Altshuler and Kozyrev 1971). By the end of the 1930s, he had developed a number of highly sensitive radiotechnical methods allowing precise measurements in radiospectroscopy (Zavoisky 1936, 1944). His first studies

Fig. 2 From left to right: S.A. Altshuler, E.K. Zavoisky, and B.M. Kozyrev; Kazan, 1968. Source: Personal archive of N.E. Zavoiskaya; photo by M.L. Blatt

Fig. 3 The device made by E.K. Zavoisky, which made it possible, for the first time, to detect EPR signals. Reconstructed by I.I. Silkin in the Memorial Laboratory of Zavoisky at Kazan Federal University. Photo by I.I. Silkin, the curator of the Memorial Laboratory

were focused on searching for resonance absorption of the electric components of radiofrequency fields by different liquids and gases (Zavoisky et al. 1934; Zavoisky 1935). However, after the work of Rabi et al. (1939), he switched completely to magnetic resonance (Altshuler and Kozyrev 1971; Salikhov and Zavoiskaya 2015). By June 1941, Zavoisky (with his friends and collaborators Semen A. Altshuler and Boris M. Kozyrev) detected the first, though unstable and unassured, nuclear magnetic resonance signals of protons in water (Altshuler and Kozyrev 1971; Kochelaev and Yablokov 1995, pp. 64–66; Salikhov 1998; Fig. 2).

Since the war between Germany and the USSR had started on June 22, 1941, and there was a lack of understanding of the above-mentioned work by others, Zavoisky (and his group) were prevented from completing the experiments and obtaining decisive nuclear magnetic resonance (NMR) spectra. Thirty years later, Zavoisky recalled bitterly the dramatic events of those days (Zavoisky 1993). The Commission of the Academy of Sciences of the USSR, appointed to identify research topics worthy of continuation, had glanced at his device and within half a minute issued a verdict: "*Everything is homemade and has no scientific value*", and then a warrant was issued to remove the unique device from the room. The war prevented Kozyrev from continuing his research collaboration with Zavoisky, while Altshuler was drafted in to the army (Altshuler and Larionov 2014). Zavoisky had to switch to military related work in V.K. Arkadiev's laboratory. However, after 2 years, Zavoisky was able to resume magnetic resonance research on his own. He succeeded in detecting reliable resonance spectra by the end of January 1944 on a device he assembled de novo (Silkin 2007, p. 130). Soon thereafter, Zavoisky (Silkin 2007, p. 132) confirmed that these spectra reflected the magnetic moments of atoms in crystalline hydrates of the paramagnetic salts $MnSO_4 \times nH_2O$ and $CuSO_4 \times nH_2O$. Thus, EPR was discovered at the beginning of 1944 (January 21) in Kazan, the capital of the Republic of Tatarstan, Russia (Fig. 3).

Coming out of the electron paramagnetic resonance

Metaphorically speaking, it was the birth of the EPR, and its *coming out* had happened shortly afterwards (see above), both in the scientific press as well as through personal communications: in May and July 1944, Zavoisky submitted his manuscript "*Paramagnetic relaxation in liquid solutions with perpendicular field*" to the "Journal of Experimental and Theoretical Physics" (Zavoisky 1945a) and its English version to the "Journal of Physics, USSR" (Zavoisky 1945b), respectively, followed by publication during May and June of 1945, with likely delivery outside USSR by November 1945. This fact was discovered by one of the authors (Zavoiskaya 2007, 2016) based on citation of articles by two American physicists: Post (1946) and Schiff (1946), the former from the Naval research laboratory in Washington, DC, and the latter from the University of Pennsylvania. This sounds like an anecdote, but reference to one of the articles from the journal containing that of Zavoisky (1945b) is given on the same page, just ten lines above the title of the short communication of Bloch et al. (1946a), reporting on the NMR discovery! At the same time, Zavoisky used these results in his doctoral thesis and brought it, in June 1944, to the P.N. Lebedev Physical Institute (LPI) in Moscow (Silkin 2007, p. 139). This then becomes the beginning of the acquaintance of the Soviet scientific audience with the outstanding discovery of EPR by Zavoisky. Half a year later, on December 30, 1944, he gave a talk at a seminar held in the P.L. Kapitza's Institute for Physical Problems (IPP), the famous "*kapichnik*" (nickname for these seminars; derived from the surname "Kapitza", used by soviet physicists). A month later, on January 30, 1945, Zavoisky defended his doctoral thesis at the Academic Council of the Physical Institute, just mentioned. Many famous Soviet physicists, chemists, physical chemists, biophysicists, and geophysicists attended these two events (see Appendix 2); those attending were from the top USSR institutions (see the list in Appendix 3). Thus, a representative circle of the Soviet scientific community—not just "pure" physicists—had the opportunity to learn firsthand about the discovery of EPR. However, for unknown reasons, this discovery fell out of the scope of the attention and interests of Soviet scientists. In our literature search, we did not find any citation of Zavoisky's work in the Soviet scientific journals at that time; further, there seems to have been no discussion on this topic at conferences for quite some time.

In December 1946, i.e., nearly 2 years after the thesis seminar, and one-and-a-half years after the first publication on EPR by Zavoisky, the USSR Academy of Sciences held three conferences covering issues close to EPR. These meetings brought together many highly qualified physicists capable of appreciating the fundamental and applied significance of the new phenomenon: the First All-Union Conference on the *Physics of Magnetic Phenomena*, held in Sverdlovsk (now Yekaterinburg); the *Conference on Electric Oscillations and Waves*, held in Gorky (now Nizhny Novgorod); and the *Conference on Spectroscopy* in Leningrad (now St. Petersburg). Although Zavoisky was invited as a delegate to the Conference on the Physics of Magnetic Phenomena, he was not given any opportunity to give a talk. The conference proceedings, including the discussion of the talks, were published (Bulletin 1947). The only reference to the discovery of EPR was in the phrase that magnetic resonance methods "are equivalent to magnetomechanical methods", and "are hardly suitable to determine magnetic moments of atoms in condensed matter", as was stated by Dorfmann (1947; also spelled as Dorfman). Several decades earlier, Dorfmann (1923) had discussed the possibility of quantum transitions between the Zeeman sub-levels, an idea based on a prediction of Einstein and Ehrenfest (1922). In his jubilee report in honor of the 30th anniversary of the Soviets (dedicated to the main discoveries of Soviet physicists since 1917), A.F. Ioffe (the "father" of Soviet physics) did not mention the discovery of EPR (Ioffe 1947). However, Ginzburg (1947), who received a Nobel Prize in 2003, did mention the work of Zavoisky along with that of Purcell et al. (1946) and Bloch et al. (1946b). It seems that even before the Soviet colleagues, European and American scientists did cite the EPR discovery by Zavoisky (see: Cummerow and Halliday 1946; Gorter 1947). This seems unusual against the background of very high interest in magnetic resonance in Europe and USA. Hundreds of articles on magnetic resonance (including EPR, NMR, ferromagnetic resonance) were published in a few years after Purcell's and Bloch's reports. The new phenomena and techniques in the field became the subject of discussion at many conferences. Thus, the American Physical Society held a symposium on radio- and microwave spectroscopy in Washington, DC in 1948, and in 1949 almost no meeting of the Society was without a talk on magnetic resonance (see the 1949 Bulletin of the American Physical Society). There were conferences on radiospectroscopy in Oxford (UK) in 1948 and 1950; these conferences brought together scientists from the USA, Japan, and many European countries (UK, the Netherlands, France, Sweden, Switzerland, Germany; Zavoiskaya 2007, pp. 98–101).

Fig. 4 Left to right (sitting): A.I. Shalnikov, and L.D. Landau; left to right (standing): A.I. Alikhanov, and P. Savich; Moscow, IPP, 1946. Source: Personal archive of N.A. Tikhomirova (Shalnikova)

It seems that, in the USSR, the only physicists (besides Zavoisky, Alltshuler, Kozyrev and some of their closest colleagues in Kazan) who appreciated the significance and promise of EPR discovery at that time were P.L. Kapitza and A.I. Shalnikov (Figs. 4, 5; see below). The future Soviet Academy of Sciences member Alexander Iosifovich Shalnikov (1905–1986), who specialized in low-temperature physics and founded the famous Soviet journal "*Instruments and Experimental Techniques*", was a virtuoso experimentalist with a wonderful personality (Andreev et al. 1987). From recollections of his students and colleagues, we note that he "had really the passion to help everyone … The help came immediately, as a generous stream … Like Zavoisky, Shalnikov was a master in engineering of physical equipment (and he did it) with his own hands" (Abrikosova 2016); he helped Zavoisky to get the necessary details for the improved version of a microwave low-temperature EPR spectrometer (note that EPR was discovered by Zavoisky, using a radio

Fig. 5 Left to right: L.A. Artsimovich, M.A. Lavrentyev, N.N. Semenov, and P.L. Kapitza, 1956. Source: Memorial Museum of P.L. Kapitza in IPP. Photo provided by T.I. Balakhovskaya

wave spectrometer) and to perform low-temperature experiments (Zavoisky 1945c). We note that the Head of IPP and future Nobel laureate "for basic inventions and discoveries in the area of low-temperature physics" (Hudson 1978) Peter Leonidovich Kapitza (1894–1984; also spelled Pyotr Kapitsa) was a very decent person and had an exceptional scientific intuition. What is remarkable and highly significant is that Shalnikov drew Kapitza's attention to Zavoisky and his discovery of EPR. Kapitza invited Zavoisky to his seminar (on December 30, 1944; see above) and to reproduce his EPR results obtained at the Institute of Physical Problems (IPP)—helping him overcome the distrust of Moscow physicists to his discovery. Again and again, in 1945 and 1946, Kapitza provided Zavoisky with opportunities to investigate EPR in IPP, inviting and helping him to obtain a long leave of absence (which was not at all easy during and after the War in the USSR; Silkin 2007, pp. 162–163, 173). Note also that, in addition to a lack of modern scientific equipment in Kazan University, Zavoisky had a huge teaching load, and scientific work was considered by the University administration as a secondary one. In 1947, Kapitza promoted the nomination of Zavoisky for the State Stalin Prize, the highest USSR award of that time (RSAE 1947; quotation from Zavoiskaya 2007, pp. 79–80).

Unfortunately, Kapitza was removed from the Directorship of IPP in August 1946 and, especially after 1949, he became isolated from scientific community (Kapitza and Rubinin 2005; Boag et al. 1990, pp. 66–67). The Rector of Kazan University was not inclined to permit Zavoisky to take long academic trips, and the opportunity for him to work in Kazan also remained very limited (thus, microwave sources and high field magnets were virtually inaccessible to Zavoisky and his collaborators; Silkin 2007, pp. 171–174). The above situation, as well as poor accommodations, dangerous to the health of his family, forced him to leave Kazan in 1947; he accepted the invitation of I.V. Kurchatov, the Head of the Soviet Atomic Project, to join his team. "Journal of Physics, USSR", which disseminated the results of Soviet scientists among their colleagues abroad, was closed in 1947. (We remind our readers that Zavoisky had published his first reports on EPR in this journal!) Furthermore, in 1947 not only all English translations of Soviet journals were terminated, but new harsh rules for scientific publication were established, which, surprisingly, included an embargo on publication of significantly novel results (Resolution… 1947; quotation from Esakov 2000).

Although Zavoisky had left Kazan, his friends Semen Alexandrovich Altshuler (1911–1983), a Ph.D. student of the future Nobel laureate I.E. Tamm, and Boris Mikhailovich Kozyrev (1905–1979) remained there and later established an internationally recognized School of Magnetic Spectroscopy, preserving the lineage of the discovery by Zavoisky for Soviet science! During the decade following the departure of Zavoisky in 1947, more than 70 papers on many aspects of magnetic resonance were published; this amounted to a large percentage of all publications on this subject in the USSR during that period! Moreover, the first work on chemical EPR spectroscopy was performed in Kazan (see, e.g., Kozyrev and Salikhov 1947; Garifianov and Kozyrev 1956), but the research team of Zavoisky's immediate coworkers and their disciples remained unique in this field in the USSR for a very long time. Research on magnetic resonance performed in Kazan was described in detail in "Paramagnetic Resonance" (1975) and by Aminov (1998), Yablokov (1998), and Altshuler and Larionov (2014).

To give a more complete picture of studies on magnetic resonance during the first decade after Zavoisky's discovery, we mention other Soviet research groups working in the field. It was only in 1953 that EPR studies were started in LPI by Alexander M. Prokhorov and his collaborators (including Alexander A. Manenkov and Mark E. Zhabotinsky), resulting in a series of publications starting with those by Manenkov and Prokhorov (1955) and Zhabotinskii (1955). Speaking in a broader context and considering research on several magnetic resonance phenomena, including NMR and ferromagnetic resonance, we name the following scientists: Konstantin V. Vladimirskii at LPI (1947), Samson D. Gvozdover (see: Gvozdover and Magazanik 1950), and Evgenii I. Kondorskii (see: Kondorskii and Smolkov 1953) at MSU, Sergei V. Vonsovskii at Ural State University (see: Turov and Vonsovskii 1953), and Givi R. Khutsishvili (1950) at the Institute of Physics in Tbilisi. Recalling Kastler's figurative comparison of EPR with the river Volga, which begins with a small source and then grows into an enormous stream (see Kastler 1971), one needs to admit that EPR, and even magnetic resonance in general, still remained (in the USSR in those early years) a weak rivulet!

Fig. 6 M.E. Diatkina (sitting second from the left) and Ja.K. Syrkin (sitting 4th from the left) among their colleagues at the Institute of General and Inorganic Chemistry, 1968. Source: Archive of RAS (ARAS 1968, p. 2)

Nevertheless, we believe that the help of Kapitza and Shalnikov in providing Zavoisky conditions to work on EPR (during 1944–1947) and in acquainting the physical community with a new phenomenon was crucial for the destiny of EPR in the USSR. About 30 years later, Zavoisky wrote to Kapitza: "Thanks to you and Alexander Iosifovich Shalnikov, EPR got its good fortune!" (ARAS 1974).

The road to chemistry and biology

Fortunately, there was another outstanding Russian scientist in addition to Kapitza and Shalnikov who appreciated the capabilities of EPR, especially in chemistry. It was Jakov Kivovich Syrkin (1894–1974; see Fig. 6), who was a physical-chemist and expert in theoretical chemistry especially on quantum methods in chemistry, chemical bonds, and molecular interaction; he was a lecturer at Moscow State University (MSU) and the Moscow Institute of Fine Chemical Technology, and Head of the Laboratory of Molecular Structure at the Karpov Institute of Physical Chemistry (KIPC). By that time, he had extensively used Raman spectroscopy in his research (Wolkenstein and Syrkin 1937), studied molecular dipole moments (Wassiliew et al. 1935), and worked on radicals in chemistry (Syrkin and Diatkina 1947). Furthermore, he had edited the Russian edition of a book by Waters (1946) and enthusiastically advocated the use of physical methods in chemistry (Syrkin 1939). We speculate that all this scientific experience may have been responsible for his understanding of the merits of EPR in chemistry.

In 1948, Syrkin decided to organize EPR-based research at the Karpov Institute of Physical Chemistry (KIPC); he assigned his doctoral student Lev A. Blumenfeld the task of "reviewing the newborn microwave spectroscopy and magnetic resonance methods and to present a review at a seminar at our institute" (Blumenfeld 1992). For this review, Blumenfeld thoroughly studied the doctoral thesis of Zavoisky as well as "the first Soviet and international research dealing mainly with the EPR spectra of solid paramagnetic cuprous and manganous salts", all available in the State Library of the USSR (Blumenfeld 1992). Blumenfeld was an admirable person, a World War II veteran, a poet, an excellent scientist, and a wonderful teacher. Some decades later, his lectures, given to several generations of students, provided thorough knowledge on a wide range of problems of present-day biophysics, including biological applications of EPR, and, indeed established a scientific school. One of us (V.P.) had the good fortune of being one of his students who listened to him with bated breath (his lectures were astonishingly deep and extremely insightful). But at that moment, in the late 1940s, ideological campaigns had been launched in Soviet science and in society; thus, there was no way Blumenfeld and Syrkin could implement their excellent plan of research and teaching. One by one, many areas of science were devastated; the most notorious in this regard involved the August 1948 Session of the Soviet Academy of Agricultural Sciences, which condemned Genetics as an "*activity alien and deleterious to the Soviet people*." But similar campaigns, although not always as well known, were held in many other areas of science. In Chemistry, Linus Pauling's resonance theory (a way of describing a real chemical structure with delocalized electrons as a superposition or "resonance" of several contributing structures) was declared idealistic. Blumenfeld, who tried to advocate for it at the institute seminar, was fired from KIPC. Several years later,

Fig. 7 Left to right: A.E. Kalmanson and L.A. Blumenfeld; 1955–1956. Source: Personal archive of S.E. Shnoll; photo by S.E. Shnoll

Syrkin himself became the main victim of this campaign, being condemned as one of the primary (together with M.E. Diatkina and M.W. Wolkenstein—also spelled as M.V. Volkenshtein) advocates of the resonance theory; he was eventually driven away from MSU and KIPC (Graham 1964; Sonin 1991; Hargittai 2015). Much later, beginning in 1959, Syrkin was able to embark on EPR research in organic chemistry; further research was done in collaboration with his and B.M. Kozyrev's scientific schools (Morozova and Dyatkina 1962, 1968). One of the authors (N.Z.) also remembers how Kozyrev, during his visits to the Zavoisky family in Moscow, left them shouting: "To Syrkin and Dyatkina!". But it was an entirely different epoch.

Fortunately, the management of the Central Institute for Advanced Medical Training (CIAMT) offered Blumenfeld a job; thus, he then began his studies on hemoglobin oxygenation (see Kalmanson 1993). Since this reaction changes the magnetic properties of the protein, Blumenfeld decided to resort to EPR after a long period of studies with other methods (mainly the magnetic balance technique). In March 1952, and under rather romantic circumstances, he pictorially described this idea to his younger colleague Alexander Emmanuilovich Kalmanson (1926–1990), and thereafter they started to enthusiastically construct an EPR spectrometer (Kalmanson 1993). However, as the above-mentioned campaign was still going on, half a year later Blumenfeld was dismissed again "*in the frame of struggle with rootless cosmopolitans*" (an euphemism for Soviet "*die Endlösung der Judenfrage*"). Only in 1953, after the death of Joseph Stalin, did the stifling of science cease, setting into motion a slow recovery towards normal life. Blumenfeld survived and was able to return to the CIAMT where he and Kalmanson continued the construction of the first EPR spectrometer for biology (Fig. 7).

The long-awaited burst came up!

Blumenfeld turned to one of the most important issues that stood on the agenda of the physics of biological systems: the problem of electron transfer in proteins. Early in 1941, Albert Szent-Gyorgyi (1893—1986) proposed a hypothesis whereby a protein might be considered as a sort of semiconductor and suggested, as one possibility, the necessity of electron transfer via proteins in photosynthesis, following on the discovery of the photosynthetic unit (i.e., hundreds of chlorophyll molecules working together to serve as a "photoenzyme") by Emerson and Arnold (1932). This hypothesis evoked a robust discussion in the Soviet Union, including severe criticism, e.g., by Terenin and Krasnovsky (1949). Blumenfeld proposed that cofactors or substrates of enzymes could inject electrons into the protein conductivity band, and that EPR could serve as a reliable method for experimental proof of the proposed hypothesis (Blumenfeld 1957). The other possibility to deliver electrons to the conductivity band was thought to be by the use of ionizing radiation; hence, irradiated tissues, proteins, or even isolated biochemicals became the subject of Blumenfeld's research (Blumenfeld and Kalmanson 1957a, b).

Although Blumenfeld was reinstated at the Central Institute for Advanced Medical Training, he became increasingly closely associated with N.N. Semenov's Institute of Chemical Physics, officially in 1959, but his personal contacts, even earlier, were more important for the development of EPR research in ICP. It is possible that Blumenfeld's scientific contacts with N.N. Semenov's scientific school in ICP may have played an essential role in the subsequent history of biological and chemical EPR research in the USSR, acting as a catalyst. In any case, the pioneering work of Blumenfeld and Kalmanson was one of the few known (outside of Kazan school itself!) elements in the Intra-Russian chain (not via publications on the issue in Europe and USA) linking the discovery of EPR by Zavoisky with its applications.

It is difficult to reconstruct with confidence the detailed history of this "prenatal" period of biological and chemical EPR spectroscopy in the former USSR. Perhaps the only line of its evolution documented to some extent is the one concerned with the scientific contacts and research activity of N.N. Semenov, V.V. Voevodsky, and L.A. Blumenfeld and their colleagues, presumably related to ICP. Blumenfeld (1992) recollected that he had become acquainted with Nikolai Nikolaevich Semenov (1896–1986) in 1946 and with Vladislav Vladislavovich Voevodsky (also spelled as Voevodskii; 1917–1967) in 1947. In all these years (i.e., since the very beginning of his work at the Karpov Institute of Physical Chemistry) he "had communicated consistently with Nikolai Nikolaevich, who had become interested in biological problems at that time … Approximately at the same time, we began to discuss the capabilities of EPR with

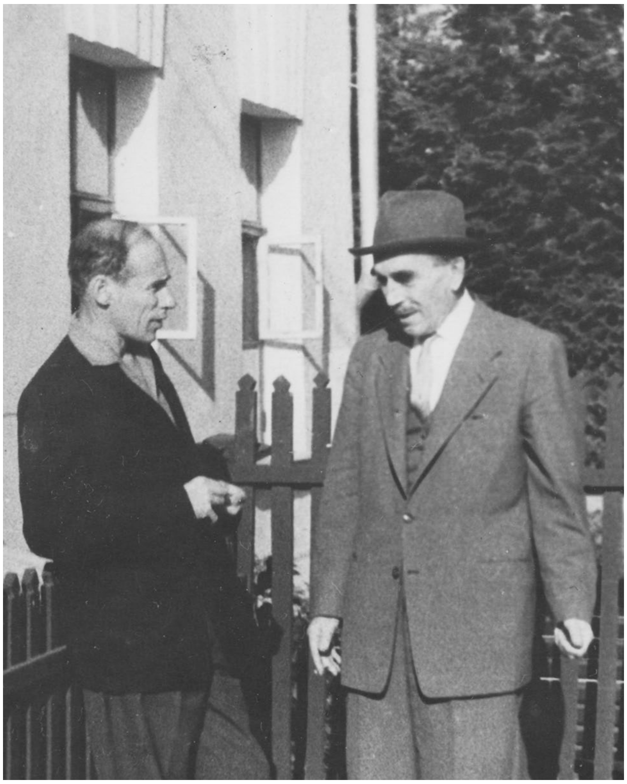

Fig. 8 Left to right: V.V. Voevodsky and N.N. Semenov; Moscow, ICP, late 1950s. Source: Personal archive of M.V. Voevodskaya

Fig. 9 Left to right: V.V. Voevodsky and L.A. Blumenfeld writing their book (Blumenfeld et al. 1962); Novosibirski Academgorodok, 1961. Source: Personal archive of M.V. Voevodskaya

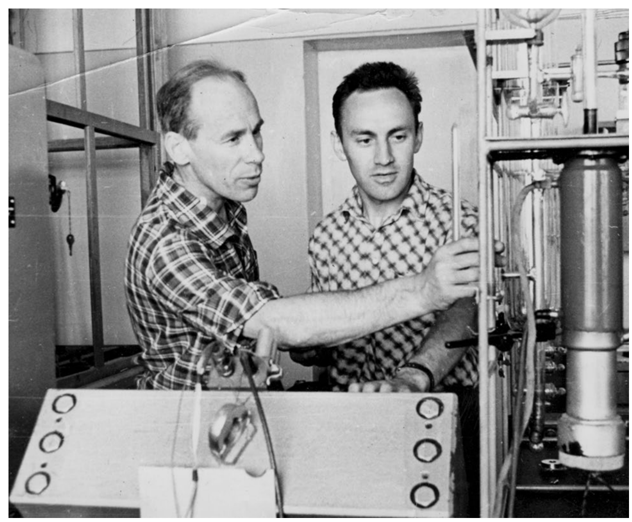

Fig. 10 Left to right: V.V. Voevodsky and Yu.N. Molin discussing their EPR results; Novosibirski Academgorodok, early 1960s. Source: Personal archive of Yu.N Molin

my friend V.V. Voevodsky". Further, Blumenfeld (1992) recalled: "All the time until Voevodsky died… we discussed, in detail, all the EPR research in biology, handled by my colleagues and me, as well as EPR research in the field of chemistry carried out by Voevodsky and his colleagues" (Blumenfeld 1992; Figs. 8, 9, 10).

In 1947, Voevodsky, in his study of oxidation of hydrogen, had attempted to employ classical methods of measuring magnetic permittivity to detect radical intermediates (ARAS 1948, pp. 5–8). Perhaps this attempt, although unsuccessful, may have turned him to using EPR in his research. Using EPR, he studied the reactions of radiolysis and recombination of radicals in solid organic materials (Molin et al. 1958; Cherniak et al. 1958), the gas phase radical reactions (Panfilov et al. 1960), and the chemical bonds and electronic structure of metallo-organic compounds (Tsvetkov et al. 1957). Furthermore, during 1958–1960, Voevodsky and his coworkers published more than 30 papers based on EPR measurements. We can speculate that the early work on EPR of Voevodsky, Blumenfeld, and their coworkers inspired some of the early meetings of the Academic Council of ICP in 1954 and especially since 1955, which were dedicated to EPR applications in chemistry and to the progress of this research in ICP (ARAS 1954, pp. 132–138, 1955, pp. 32–47). Some of the well-known physicists presented their reports. Nikolai Dmitrievich Sokolov (1912–2001), the physical-chemist who established the NMR laboratory in the Moscow State University some years later, reviewed the history and current application of this method and compared it with other spectroscopic techniques (ARAS 1954, pp. 133–134, 137). Mikhail Alexandrovich Eliashevich (1908–1996), a specialist in atomic and molecular spectroscopy (optical, infrared, and Raman), reported on the classification of radiospectroscopy methods, physical principles of magnetic resonance, and results of its application to condensed matter (ARAS 1955, pp. 35, 45–46). It appears that an extended version of this report had

Fig. 11 Barry Commoner sending a message to L.A. Blumenfeld (the poster with a message was photographed by E.K. Ruuge, and the photo was delivered to Blumenfeld); April 1972, Washington University, St. Louis, MO. USA. The text on the poster was: "Dear Lev, Please forgive me for not writing to you. In all this time I think of you, your family and friends often, and with the warmest friendship. As always, Barry (1972)". Source: Personal archive of E.K. Ruuge

been published shortly before in the Soviet Physics-Uspekhi (Advances in Physical Sciences); see Eliashevich (1954). A detailed analysis of the equipment needed to perform EPR and NMR research, including the equipment for microwave generation and detection, magnets, power supplies, as well as of the theoretically and practically achievable sensitivity of magnetic resonance instrumentation, was described by Boris Konstantinovich Shembel (1900–1987), a renowned expert in radio-physical techniques (ARAS 1954, pp. 132–134, 1955, pp. 35, 38, 47). At that time, Blumenfeld delivered a talk on the capabilities of EPR (ARAS 1955, pp. 37–38). As N.N. Semenov mentioned, "this method is in progress in USA, and we keep it down", while "we need our own specialists" (ARAS 1954, p. 135). The first of these sessions was held on June 11, 1954 (ARAS 1954, p. 132–138), and this date may be, in our view, regarded in some sense as the official start of large-scale research in *Biological and Chemical EPR Spectroscopy* in Russia.

In view of the above, a committee headed by V.V. Voevodsky was appointed to extend the efforts to develop magnetic resonance (both EPR and NMR) at the Institute of Chemical Physics (April 15, 1955). The members of this committee were: N.D. Sokolov, M.A. Eliashevich, B.K. Shembel, as well as Nikolai Mikhailovich Chirkov (1908–1972), a specialist in chemical catalysis, and Dmitry Georgievich Knorre (born in 1926), future organizer and first director of the Novosibirsk Bioorganic Chemistry Institute (ARAS 1955, p. 39). A year later, in 1956, Voevodsky employed a talented engineer Anatoly Grigorievich Semenov (1924–1990) who later developed a number of excellent EPR and NMR spectrometers (AICP 1956, pp. 102–103). At the same time, two students of the Moscow Institute of Physics and Technology came to Voevodsky's laboratory: Yuri Nikolaevich Molin (born in 1934) and Yuri Dmitrievich Tsvetkov (born in 1933), who delved into EPR. During 1957–1958, the very first articles of Blumenfeld and Kalmanson and of Voevodsky's research group on biological and chemical EPR were published (see Blumenfeld 1957; Blumenfeld and Kalmanson 1957a, b; Tsvetkov et al. 1957; Voevodsky et al. 1958). Nikolai Nikolaevich Bubnov (1932–2004), a PhD student of Voevodsky, detected the EPR signal of P_{700}^{+} in leaves and began EPR studies of photosynthesis in the late 1950s (Bubnov et al. 1960). See Govindjee and Renger (1993) for Bessel Kok's discoveries that included P700, and Kok and Beinert (1962) on EPR of P_{700}^{+}. By current standards, this research was still quite far from the real biological or chemical EPR, since it used frozen or lyophilized tissues, dried protein specimens irradiated with gamma rays, and organic crystals (i.e., in solid rather than in liquid phase). However, they were the first in the USSR that dealt with biology and chemistry! To be precise, the very first work on EPR was published in USA, where the environment was much more favorable for the development of science, without the obstacles to work and without "life threat", as it was in the USSR before the mid 1950s. It was indeed the work of Barry Commoner (1917–2012), a famous scientist and a remarkable public figure (Commoner et al. 1954) that pioneered this field of study. We are delighted to note that, despite the scientific competition, he and Blumenfeld became friends (Fig. 11).

Simultaneously in the late 1950s, many others in ICP began to do magnetic resonance research; this included Moisey Borisovich Neiman (1898–1967) with his disciples Anatoly Leonidovich Buchachenko (born in 1935), Gertz Ilyich Likhtenshtein (born in 1934), and Eduard Grigorievich Rozantsev (also spelled as Rozantzev; born in 1931). This research paved the way toward new areas of science, such as spin chemistry (which was developed together with Yu.N. Molin and K.M. Salikhov), and spin label studies, which indeed contributed substantially to future biological and especially photosynthesis research (see Neiman et al. 1962; Likhtenshtein 1968, 2016; Buchachenko et al. 1970; Buchachenko 1976).

In 1957, the Siberian branch of the Russian Academy of Sciences was established under the leadership of Mikhail Alekseevich Lavrentyev (1900–1980). Voevodsky moved to Novosibirsk with Yu.N. Molin and Yu.D. Tsvetkov, who later established with Kev Minullinovich Salikhov (born in 1936) their own scientific school of chemical magnetic spectroscopy (Salikhov 2016), and with A.G. Semenov, who thereafter led the technical development and production of a number of specialized EPR and NMR spectrometers for various scientific and applied tasks that served well for many years in numerous Soviet laboratories. Yakov Sergeevich Lebedev (1935–1996), a disciple of Voevodsky, stayed in Moscow and started "a dedicated research program on high-field/high-frequency EPR in physical chemistry" (Savitsky and Möbius 2009). Vladimir Borisovich Kazansky (born in 1931), a scientist from the Voevodsky's scientific school, developed radiospectroscopic methods for studying the mechanism of heterogeneous catalysis (e.g., Kolosov et al. 1977).

The school of Blumenfeld has produced many remarkable scientists: Viktor Adolfovich Bendersky (born in 1938), who discovered, in collaboration with Blumenfeld, double electron–electron resonance (Benderskii et al. 1968)—simultaneously but independently of J. Hyde (Hyde et al. 1968); Anatoly Fedorovich Vanin (born in 1938), who was among the discoverers and investigators of nitric oxide metabolism (e.g., Nalbandyan et al. 1964; Vanin 2014); Enno Kustavich Ruuge (born in 1935), Alexander Nikolaevich Tikhonov (born in 1948), and Ivan Igorevich Proskuryakov (born in 1950), who contributed much to photosynthesis research, and especially to the regulation of photosynthesis (e.g., Izawa et al. 1973; Tikhonov et al. 1981; Tikhonov 2015) and of short-lived paramagnetic states in photosynthetic energy conversion (Hoff and Proskuryakov 1985). At the same time, many new centers involved in biological EPR arose in the late 1950s–early 1960s at other Institutes in Moscow and other Soviet cities. We have already mentioned Syrkin's EPR studies, presumably directed at metalloorganics, which started in 1959 (Kazakova and Syrkin 1959) at the Moscow Institute of Fine Chemical Technology (now Moscow Technological University) and at the Institute of General and Inorganic Chemistry. The radiobiological department of Kurchatov's Institute of Atomic Energy (today the Institute of Molecular Genetics) was established as a result of the efforts of I.E. Tamm and I.V. Kurchatov to preserve and develop the non-Lysenko biology (IMG RAS 2013). However, at the same time, this department, apparently inspired by collaboration with Voevodsky (Tsvetkov et al. 1958), started EPR studies on polymers, and later bioplymers (Kiselev et al. 1960). In the 1960s, the Institute of Biological Physics in Puschino started medical and physiological EPR studies (Razumova et al. 1962; Ostrovskii and Kaiushin 1963). Research efforts in the centers that emerged earlier, e.g., in Kazan (Paramagnetic resonance 1960) or in Tbilisi State University (now Ivane Javakhishvili Tbilisi State University; Sanadze 1957) also expanded and flourished. Soon thereafter, chemical EPR studies were started

Fig. 12 A 2017 photograph of the authors at the entrance to the Russian state archive, in Moscow. Left: Nataliya Evgenievna Zavoiskaya; right Vasily Vitalievich Ptushenko. Source: personal collection of V.V. Ptushenko

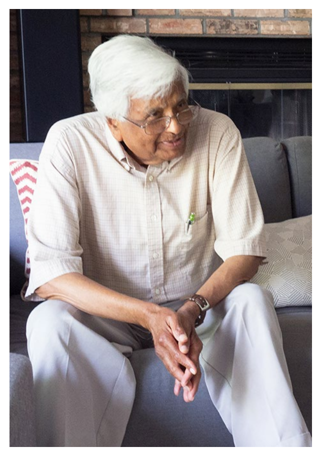

Fig. 13 A 2017 photograph of the editor Govindjee in recognition of his special editorial help (see footnote 1). Photo by Dilip Chhajed of the University of Illinois at Urbana-Champaign

at several places including the Ural Polytechnic Institute in Sverdlovsk (now Ural State Technical University; Chirkov and Matevosian 1957) and the Institute of Fossil Fuels (now A.V. Topchiev Institute of Petrochemical Synthesis) in Moscow (Losev and Bylyna 1959).

The lag-phase finished. The long-awaited burst of interest and activity in the field indeed happened. And, fortunately, the era of magnetic resonance had (and has) come to the USSR (and now, Russia).

We end this historical minireview with a 2017 photograph of the authors (V.V.Ptushenko and N.E. Zavoiskaya; see **Fig. 12**) as well of its editor Govindjee (see **Fig. 13**).[1]

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[1] Both the authors are simply delighted with the care with which Govindjee has corrected their text, and with tremendous diligence – he worked almost twenty-four-hour a day, and always found time to answer letters, even during his trips. It was very interesting for the authors to work with him on this article, though it was difficult to always meet the bar he set for them. **Happy 85th birthday to Govindjee on October 24, 2017!**

Appendix 1: Timeline of the key discoveries and work on magnetic resonance

In this list we mention the key events or publications involving the Soviet scientists. The world-wide events are mentioned only as milestones. As the magnetic resonance studies remained relatively limited and undiversified until the mid-1950s, we highlight here events in the development of both EPR and NMR.

1936—C.J. Gorter reported the "Negative result of an attempt to detect nuclear magnetic spins".

1939—I.I. Rabi reported observing magnetic resonance in molecular beams.

1941 (June)—E.K. Zavoisky with S.A. Altshuler and B.M. Kozyrev observed proton magnetic resonance; however, the NMR signals were not reproducible.

1941 (June)—The war between Germany and the USSR started and terminated the work of E.K. Zavoisky with coworkers.

1944 (January)—E.K. Zavoisky discovered EPR.

1944 (December)–**1945** (January)—First oral reports of Zavoisky on the EPR discovery.

1945 (June; July)—First articles of Zavoisky on the EPR discovery published in English.

1946 (January)—E.M. Purcell et al. and F. Bloch et al. reported about the discovery of NMR.

1946 (September)—R.L. Cummerow and D. Halliday reported about their observation of EPR; here, Zavoisky's work was cited for the first time.

1947—First publication on chemical magnetic resonance in the USSR (Kozyrev and Salikhov 1947).

1948—Unsuccesful attempt by Y.K. Syrkin to organize EPR-based research in chemistry at the Karpov Institute of Physical Chemistry.

1949—Russian edition of Gorter's book (Paramagnetic Relaxation) was published.

1950—Beginning of NMR research in S.D. Gvozdover's group at MSU (which resulted in active research on chemical NMR beginning later in the 1960s).

1953—Beginning of EPR research (presumably of inorganic crystals) at the P.N. Lebedev Physical Institute by A.M. Prokhorov, A.A. Manenkov, and M.E. Zhabotinskii (later at the Institute of Radio Engineering and Electronics).

1954—Beginning of magnetic resonance (both EPR and NMR) research at the Institute of Chemical Physics.

1957—First publication on biological magnetic resonance in the USSR (Blumenfeld 1957).

1957—First publication on chemical magnetic resonance in the USSR beyond the Kazan scientific school (Tsvetkov et al. 1957).

Appendix 2: A partial (alphabetical) list of those attending the seminar talk on December 30, 1944, and the doctoral defense of Evgenii K. Zavoisky on January 30, 1945 (ARAS 1944, 1945; Zavoiskaya 2007, pp. 35–65)

E.L. Andronikashvili, S.E. Bresler, G.N. Flyorov, G.S. Gorelik, A.F. Ioffe, P.L. Kapitza, E.I. Kondorsky, M.I. Kornfeld, G.M. Kovalenko, L.D. Landau, G.S. Landsberg, V.L. Levshin, E.M. Lifshitz, A.B. Migdal, K.I. Narbutt, S.M. Rytov, N.N. Semenov, A.I. Shalnikov, E.V. Shpolsky, Ya.A. Smorodinsky, S.I. Vavilov, V.I. Veksler, and Ya.B. Zeldovich.

Appendix 3: A partial list of soviet institutes from which those attending the seminar talk on December 30, 1944, and E.K. Zavoisky's thesis defense on January 30, 1945, came (ARAS 1944, 1945; Zavoiskaya 2007, pp. 35–65)

- N.N. Semenov's Institute of Chemical Physics.
- A.F. Ioffe's Physical-Technical Institute in Leningrad (now the Ioffe Institute of the Russian Academy of Sciences).
- O.Yu. Schmidt's Institute of Theoretical Geophysics (a year later it merged with the Seismological Institute to form the Geophysical Institute, which afterwards became the Schmidt Institute of Physics of the Earth, Obukhov Institute of Atmospheric Physics, and Fedorov Institute of Applied Geophysics).
- Institute of Geological Sciences (now Geological Institute of the Russian Academy of Sciences).
- Laboratory of Geochemical Problems (2 years later reorganized to Vernadsky Institute of Geochemistry and Analytical Chemistry).
- State University of Gorky (now Lobachevsky State University of Nizhni Novgorod).
- "Laboratory №2" (now I.V. Kurchatov Institute of Atomic Energy).
- Moscow State V.I. Lenin Pedagogical Institute (now Moscow State Pedagogical University).
- Institute of Physics of Lomonosov Moscow State University (was liquidated in 1954).
- Institute for Physical Problems (now P.L. Kapitza Institute for Physical Problems of the Russian Academy of Sciences).
- P.N. Lebedev Physical Institute.

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ARAS (1945) Stenographic record of the 30.01.1945 session of the Academic Council of P.N. Lebedev Physical Institute. F. 532, Op. 1, d. 106

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ARAS (1955) The transactions of sessions of the Academic Council of the Institute of Chemical Physics, 1955. F. 342, Op.1, d. 156

ARAS (1968) Photographs of Ja.K. Syrkin with the members of the Academic Council of the Institute of General and Inorganic Chemistry. F. 1886, Op.1, d. 27

ARAS (1969) Photographs of E.K. Zavoisky. F. 1943

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