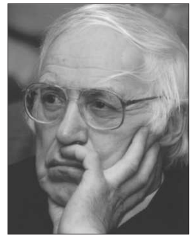
Zavoisky and the Discovery of EPR

K M Salikhov and N E Zavoiskaya

The name of the Soviet physicist Evgenii Konstantinovich Zavoisky (1907–1976) belongs to the history of science due to his discovery of a fundamental physical phenomenon – electron paramagnetic resonance (EPR) and a series of brilliant works in nuclear physics, controlled thermonuclear fusion and physical electronics. In this article, we concentrate only on his discovery of EPR.



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Nataliya Zavoiskaya is the daughter of Evgenii Zavoisky, the discoverer of EPR. She is a historian, and has written two Russian books dedicated to the life and work of her father. The books are: *The History of the EPR-discovery* and *The Contemporaries*.

Keywords

E K Zavoisky,discovery of EPR, Kazan State University.

Brief Scientific Biography

Evgenii Konstantinovich Zavoisky was born on September 28th (15th) 1907, in a Southern Russian town Mogilev–Podol'skii on the Dnestr river, in the family of a surgeon. In 1908, the family moved to Kazan. In 1926, after finishing the nine-year secondary school, he entered the Mathematical branch of Physico-Mathematical faculty of the Kazan State University.

His interest in his future profession was aroused as early as his school years: he became a passionate radio amateur. As a second-year student, he got a patent for an invention. Zavoisky was absorbed in the news of science, dreaming of finding his fruitful subject. In his student years, he conceived an idea of using the radio-frequency electromagnetic radiation for studying matter.

After graduating from the university in 1930, Evgenii Konstantinovich Zavoisky became a post-graduate. His scientific tutor was the well-known scientist V A Ul'yanin (1863–16 March 1931). According to the plan prepared by Ul'yanin, the post-graduate student Zavoisky was sent to the Leningrad Central Laboratory. Here, he developed a new way of generating ultrashort waves and managed to strongly increase the efficiency in comparison with that of devices known at that time. After defending the candidate's thesis in 1933, Zavoisky became an associate professor and Head of the Experimental Physics Chair of the Kazan State University.

At that time, ultrashort wave laboratories were organized in the USSR. One such laboratory was also organized at the Kazan State University. Zavoisky started his studies of the physical and chemical impacts of ultrashort waves on matter. First, he hoped and tried to observe the electric resonance in the radio-frequency range, but these works failed.

Early Attempts at NMR and Interruption by World War II

A stimulus to study magnetic resonance was the acquaintance of Zavoisky with Gorter's experiments on paramagnetic relaxation in solid paramagnetic salts.

A stimulus to study magnetic resonance was the acquaintance of Zavoisky with Gorter's experiments on paramagnetic relaxation in solid paramagnetic salts [1]. Zavoisky carefully studied Gorter's experiments, in which Gorter attempted to observe nuclear magnetic resonance absorption by means of the calorimetric detection method but failed. In the spring of 1941, Zavoisky repeated the Gorter experiments on paramagnetic relaxation and the determination of nuclear magnetic moments using his grid current technique which was much more sensitive than the calorimetric detection method of Gorter. It should be mentioned that Zavoisky began his own experiments not with electron but nuclear resonance as evidenced by his notes in his research notebook. However, as he had at his disposal only an old Dubois magnet with the inhomogeneous field, the reproducibility of experiments was poor.

The development of results of this research was interrupted by the Second World War. Many institutes of the Academy of Sciences of the USSR from Moscow and Leningrad were evacuated to Kazan and the Kazan State University hosted laboratories of these institutes. As a result, many studies on searching for nuclear magnetic resonance at the Kazan State University, including those of Zavoisky, were terminated. Only by the end of 1943, Zavoisky could resume this work, now on electron spins. Zavoisky modulated the constant magnetic field at audio frequency (broadband modulation) and, in some cases, he did not even apply the constant magnetic field.

Discovery of EPR

The official date of the discovery of EPR is conventionally considered as July 12, 1944 – the date when the paper [2] was submitted for publication in *JETP*. However, Zavoisky observed an EPR signal for the first time on January 21, 1944 as indicates the corresponding entry from his research notebook: "The presence of the same maximum (peak) for $MnSO_4$ in a perpendicular field and its distinct sinusoidal shift as H_0 is increased were found. The change in the sign of H_0 results in the change of the direction of the peak shift. The picture is very distinct and easily reproducible." [2–4].

Thus, in 1944, Zavoisky discovered the phenomenon of EPR in the condensed phase. He studied aqueous and non-aqueous solutions of manganese salts using the radio-frequency field and checking the coefficient of paramagnetic absorption as a function of the applied static magnetic field. The curves he obtained showed a maximum of absorption[1] in the region of weak fields (*Figure* 1). Under higher frequencies for the radio-frequency field, this maximum shifted toward the region of higher fields. Zavoisky demonstrated clearly that the ratio ν/H_0 corresponding to the maximum was constant and equal to the value expected for the magnetic dipole transitions between quantum states of electron spins [2–8].

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[1] Here, the EPR signal is observed as a maximum (the peak) in the absorbed radio-frequency power when the applied magnetic field, H_0, is changed so that the Larmor frequency of the electron spins in the magnetic field matches the frequency, ν, of the applied electromagnetic radiation.

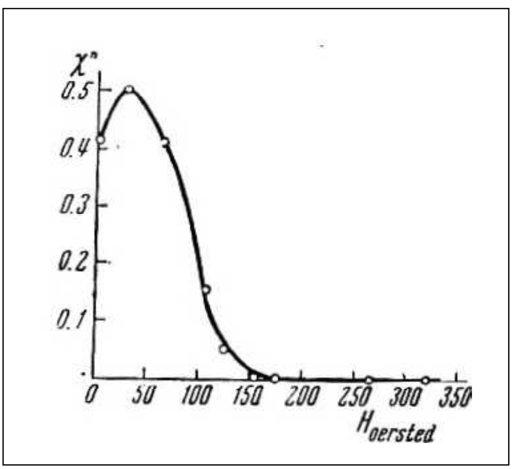

Figure 1. First EPR signal obtained for a solution of manganese chloride tetrahydrate in absolute methyl alcohol at the concentration 0.175 g/cm^3, wave length of 25.0 m and room temperature.

Other Scientific Contributions

In 1945–1946, Zavoisky became a co-founder of the Kazan Physical-Technical Institute of the Academy of Sciences of the USSR. In 1947–1951 in Sarov, Zavoisky developed a method for the registration of extremely short and weak light signals. As a result of this work, multi-cascade electron-optical converters were produced which allowed one to measure signals of duration from 10^{-12}–10^{-14} s. Zavoisky also proposed and constructed the first luminescent camera for studying nuclear processes and also developed a method of nuclear polarization by using the Lamb shift[2] [9].

Then he worked at the Academy of Sciences of the USSR in Moscow. He participated in the plasma physics projects. Zavoisky achieved remarkable success in the field of plasma research. He developed a method of turbulent heating to obtain thermonuclear plasmas[3].

Worldwide Recognition

The main scientific achievement of Zavoisky is his discovery of EPR. This discovery had a very happy destiny. In 1957, Zavoisky was awarded the Lenin Prize for the discovery of EPR. In the period from 1959 to 1976, he was nominated for the Nobel Prize many times.

In 1969, to mark the 25th anniversary of the EPR discovery, the international scientific conference took place in Kazan. From the rostrum of the conference, A Kastler, Nobel Prize laureate and an outstanding French physicist, said the following: "The river Volga starts from a little spring, grows more and more and finally transforms into an enormous stream, as full as the sea. The same happened with paramagnetic resonance. It started with a modest experiment carried out here at the Kazan University, 25 years ago. In the years that have passed, it transformed into an enormous field of investigations and resulted in thousands of experiments and publications".

[2] The Lamb shift, named after Willis Lamb (1913–2008), is a small difference in energy between two energy levels $^2S_{1/2}$ and $^2P_{1/2}$ (in term symbol notation) of the hydrogen atom in quantum electrodynamics (QED). According to the Dirac equation, the $^2S_{1/2}$ and $^2P_{1/2}$ orbitals should have the same energy. However, the interaction between the electron and the vacuum (which is not accounted for by the Dirac equation) causes a tiny energy shift which is different for states $^2S_{1/2}$ and $^2P_{1/2}$. Lamb was awarded the Nobel Prize in 1955 for this work.

[3] Matter in the plasma state, i.e., a state where atoms or molecules are dissociated into positive and negative ions due to the extremely high temperatures occurring in the fusion reactions.

The International Society of Magnetic Resonance posthumously conferred on Zavoisky the International Society of Magnetic Resonance Award for the year 1977 in recognition of his discovery of the electron paramagnetic phenomenon in Kazan, USSR, in 1944. The Award was signed by Alfred Kastler, Chairman, Prize Committee and Daniel Fiat, Chairman, International Society of Magnetic Resonance.

At the Sixth International Symposium on Magnetic Resonance, Banff, Alberta, Canada, May 1977, Professor Karl Hausser gave the Award address. He said: "We are here in memory of a great scientist and his important discovery, Professor E K Zavoisky and electron paramagnetic resonance… The full impact of Zavoisky's discovery together with the independent discovery of nuclear magnetic resonance by Purcell and Bloch becomes clear at this meeting, to which, 30 years later, so many scientists – physicists, chemists, and biologists – have come together from many countries in order to discuss the different aspects of magnetic resonance".

How was it that the discovery of EPR was a major scientific event? Electrons have spin magnetic moments which undergo certain motions in magnetic fields, i.e., electrons have a spin degree of freedom. There are two aspects related to the spin degrees of freedom of electrons. On the one hand, the electron spin state and its motion in a magnetic field in many cases are important in itself. For example, it is well known that the state of electron spins is crucial for the formation of covalent chemical bonds, the occurrence of magnetic properties of substances, luminescence, etc. EPR is important for it provides a means to control systems by influencing the motion 'along' the spin degrees of freedom. This has led to new fields of science and technology: spin physics, spin chemistry and spin technology. On the other hand, spin dynamics sensitively reacts to the state and motion of molecules along non-spin degrees of freedom. These facts make EPR a unique tool for scientific research. By means of EPR, one can study electron structure of paramagnetic particles, molecules, local defects, structure of proteins, molecular and spin

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dynamics of particles, kinetics of chemical reactions, electron transfer, spin transfer, energy transfer, etc.

Powerful Tool for Physics, Chemistry, Biology and Medicine

To date the discovery of EPR remains an outstanding scientific event. EPR is widely applied to research covering various fields of science, from molecular properties, spin and chemical dynamics in the nanosecond time scale, to dating archeological objects, electronic structure of paramagnetic particles, phase transitions, measurement of electron density distribution in quantum dots, dosimetry, quality control of tea, beer and wine, etc. [10, 11]. With the development of pulse EPR methods, high-frequency and high-field EPR, new opportunities for the EPR method continue to abound.

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Suggested Reading

[1] C J Gorter, *Physica*, Vol.3, p.995, 1936.
[2] E K Zavoisky, Paramagnetic Relaxation of Liquid Solutions for Perpendicular Fields. Zhur. Eksperiment. *i Theoret. Fiz*., Vol.15, pp.344–350, 1945, Received July 12, 1944.
[3] Al'ltshuler, B M Kozyrev in *Paramagnitnyi Rezonans* 1944–1969, All-Union Jubilee Conference, Kazan, June 24–29, 1969 (Rivkind A.I., ed.) pp.25–31, Nauka, Moscow, 1971.
[4] I I Silkin, *EPR Newsletter*, Vol.14, No.4, pp.12–13, 2005.
[5] E K Zavoisky. Paramagnetic Relaxation of Liquid Solutions for Perpendicular Fields, *J. Phys.*, Vol.9, pp.211–216, 1945. Received July 12, 1944.
[6] E K Zavoisky. Paramagnetic Absorption in Some Salts in Perpendicular Magnetic Fields, *Zhur. Eksperiment. i Theoret. Fiz*., Vol.16, pp.603–606, 1946. Received July 28, 1945.
[7] E K Zavoisky. Paramagnetic Absorption in Some Salts in Perpendicular Magnetic Fields, *Journal of Physics*, Vol.10, pp.170–173, 1946. Received July 28, 1945.
[8] E K Zavoisky, Spin Magnetic Resonance in the Decimetre-Wave Region, *J. Phys*., Vol.10, pp.197–198, 1946. Received February 12, 1946.
[9] N Yu Smirnov, *EPR Newsletter*, Vol.17, No.4, p.7, 2008.
[10] K M Salikhov, Ed., *The Treasures of EUREKA*, Electron Paramagnetic Resonance, From Fundamental Research to Pioneering and Zavoisky Award, New Zealand, 2009.
[11] K M Salikhov, in *Foundations of Modern EPR*, Eds. G R Eaton, S S Eaton and K M Salikhov, pp.45–50, World Scientific, Singapore, 1998.