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† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

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To the history of EPR discovery†

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The circumstances that contributed to the discovery of the EPR phenomenon by E.K. Zavoisky are analyzed. The emphasis is made on the applying of magnetic field modulation.

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1. Introduction

The study of Eugeny Konstantinovich Zavoisky's scientific heritage is associated with the names of two people: Semen Alexandrovich Altshuler and Igor Ivanovich Silkin. S.A. Altshuler together with Boris Michailovich Kozyrev were the colleagues of E.K. Zavoisky and worked with him before the Great Patriotic War (1941-1945). By the way, beginning from January 1941 they tried to find NMR, and as S.A. Altshuler told us, sometimes they managed to see some signals resembling NMR signals.

Figure 1. "Three whales" of Kazan school of radiospectroscopy: S.A. Altshuler, E.K. Zavoisky and B.M. Kozyrev

In the late seventies, S.A. Altshuler, at that time the head of the Department of Quantum Electronics and Radio Spectroscopy, invited Igor Ivanovich Silkin to search for archival materials, physical devices, radio equipment, books and other items related to the Kazan period of scientific and pedagogical activity of Zavoisky.

†This paper was selected at the International Conference devoted to the 80th anniversary of the discovery of Electron Paramagnetic Resonance "Magnetic Resonance – Current State and Future Perspectives" (EPR-80), September 23-27, 2024, Kazan, Russia. The guest Editor, Prof. M.R. Gafurov, was responsible for the publication, which was reviewed according to the standard MRSej procedure.

Figure 2. Igor Silkin (1939-2021), the creator and the first Director of the Memorial Laboratory-Museum of E.K. Zavoisky

Igor Silkin was a unique person. He did not have any academic degrees, or even a document of higher education. Silkin began his career at the age of 16, in August 1955 he was hired as an electrician at the Kazan Fur Factory. In 1958, he went to the army. In 1962, after his service, he returned to the Fur Factory again, continued to work as an electrician until January 1998. He studied at the Physics Department of Kazan State University for two years. Due to health reasons, I.I. Silkin was forced to leave his studies, but continued to attend the University and the Magnetic Radiospectroscopy Laboratory. As a result of many years of searching, I.I. Silkin managed to gather a unique collection of manuscripts, drafts of articles, letters, experimental tables, graphs, drawings, etc., written by the hand of academician E.K. Zavoisky. The collection gathered by Silkin served as the basis for the opening of the E.K. Zavoisky Laboratory-Museum at Kazan University in November 1997.

2. New, indirect methods of studying interaction of matter with electromagnetic fields

E.K. Zavoisky, long before the rest of the scientific community, realized that radio engineering methods allow indirect methods to study the interaction of matter with electromagnetic fields. The reason is that Zavoisky became interested in amateur radio from a young age. Before Zavoisky, attempts were made to detect interaction of magnetic moments with alternating magnetic fields, including magnetic resonance, using "direct" methods, for example, "observe the mechanical couple acting on a paramagnetic substance in a low-frequency ... magnetic field" [1] or heating of the sample [2]. To be fair it should be said that, according to Cornelis Jacobus Gorter [1], one of his teachers, Paul Ehrenfest, after a visit to one of the industrial radiotechnical labs in early 1930's told Gorter that, "although he understood hardly anything of the wonderful techniques being developed in the radio industry, he felt that such techniques might become of great benefit to pure scientific research". And Gorter himself in 1930's made a lot to incorporate radiotechnics in the scientific research.

One of the discoverers of the NMR phenomenon, Nobel laureate Robert V. Pound, in his article "From radar to nuclear magnetic resonance" [3] concludes that in his scientific group such realization came only as a result of the fact that they spent all the years of World War II at the Massachusetts Institute of Technology developing a Radar. The Zavoisky generator, although

Figure 3. The Zavoisky's generator (without power supply blocks) found at the Astronomical Observatory of Kazan University in the building of a meridian circle

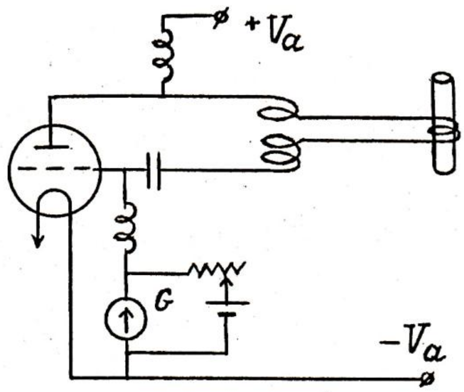

Figure 4. One of the generator circuits Zavoisky used in his studies currently known as marginal oscillator with grid detection of a signal

it operated at very low frequencies, not typical of modern EPR spectrometers, had excellent sensitivity to additional losses in the coil of the oscillatory circuit of the generator arising from EPR absorption. The sensitivity was so high that in order to get rid of the interference created by radio stations, Zavoisky conducted some experiments at the Astronomical Observatory of Kazan University in the building of a meridian circle made of iron sheets. By the way, it was there that I.I. Silkin discovered Zavoisky's original generator.

The sensitivity of the generator was so high that if Zavoisky had an electromagnet with a highly uniform magnetic field, he could have discovered the NMR phenomenon [4]. Zavoisky used various circuits of high-frequency generators. The Figure 4 shows one of them. Zavoisky noticed that the constant component of the tube grid current depends on the losses in the generator circuit. Currently, such a scheme is known as marginal oscillator with grid signal detection.

3. From electromagnet to solenoid

E.K. Zavoisky realized that at a frequency of the order of 10 MHz, the EPR phenomenon should be observed in a magnetic field of several Oersteds. As was mentioned above, before the

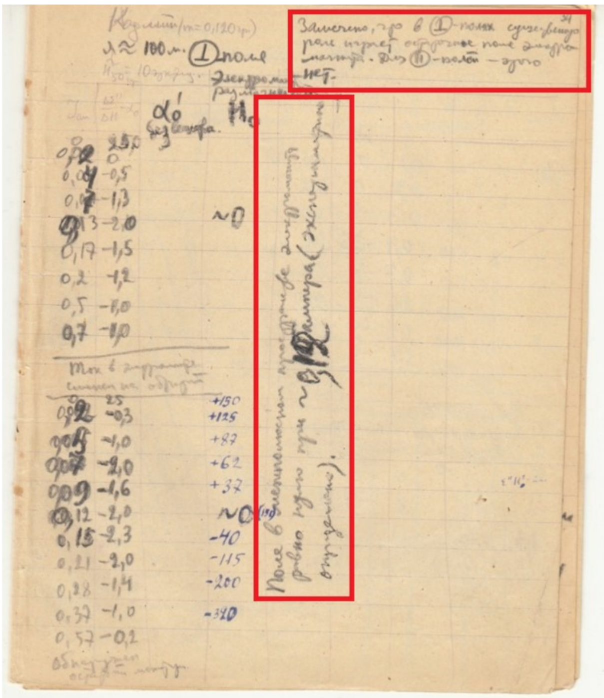

Figure 5. Note in the logbook, January 13, 1944: "It is noticed that in the ⊥ fields the substantial role is played by the residual field of the electromagnet. This effect is absent for || fields. The residual magnetism is detected ... The electromagnet current is set to the opposite. Experimentally found that the field in the interpolar space is zero at the current 0.12 A"

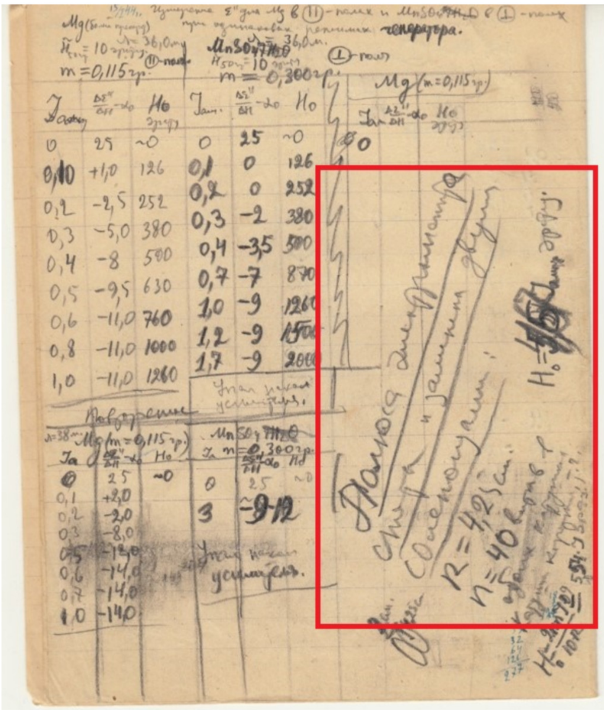

Figure 6. Note in the logbook, January 15, 1944: The electromagnet poles are ... replaced by two solenoids: $R = 4.25\,\mathrm{cm}$, $n = 40$ turns

Great Patriotic War (1941-1945) Zavoisky looked for NMR and used the electromagnet which could give a high magnetic field. He had noticed that at zero current in the magnet windings the magnetic field in the magnet gap was not zero (residual magnetization). To get rid of the residual magnetization of the electromagnet used, Zavoisky switched from an electromagnet to two coreless solenoids, which, as is known, does not have a residual field (Figures 5 and 6).

Later, two solenoids were replaced by one with a bigger diameter (Figure 7).

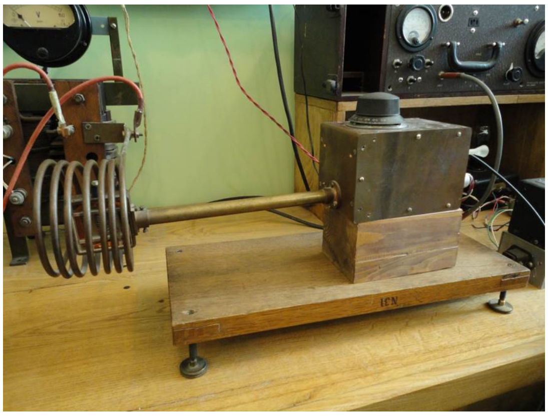

Figure 7. Two solenoids were replaced by one of bigger diameter fed from the welding transformer

4. Field modulation

The use of low-frequency (50 Hz) magnetic field modulation made it possible to easily observe the EPR phenomenon on the screen of the oscilloscope he had, the horizontal sweep of which was synchronized with the modulation voltage (Figure 8).

In addition, it became possible to replace the DC amplifier in the signal registration path, which has known disadvantages, with an AC amplifier, as which Zavoisky used the amplifier of the American profilometer used at the Kazan Aircraft Plant (Figure 9). An analysis of the scientific literature allows us to conclude that E.K. Zavoisky was the first to apply relatively shallow low-frequency modulation of the magnetic field and signal amplification at the modulation frequency using an AC amplifier tuned to the modulation frequency. In his doctoral dissertation [5] Zavoisky notes that the amplitude of the alternating signal at the output of the amplifier in this case is proportional to the derivative of the EPR absorption. The discoverers of the NMR phenomenon in a solid body in their pioneering work [6] used a direct method for detecting the NMR signal, but even then they noted that it was possible to increase the sensitivity of the method hundreds of times by changing the detection method. The article does not provide details, but in their next work [7], the authors apply a method identical to the Zavoisky's method: a magnetic field is modulated from the power network and the amplitude of the variable component of the signal at the output of an AC amplifier is measured, but the fact that the derivative of absorption is measured is not mentioned. It seems that for the first time the measurement of the derivative modulus was mentioned in an article at the end of 1946 [8] (the width of the NMR line is measured between the inflection points, which is typical when recording the derivative of an absorption line: at the inflection points the derivative modulus is maximum). Finally, at the beginning of 1947, the use of phase detection was reported, i.e. the derivative of the absorption signal was observed (though point by point, without recording on a recorder), and not its module [9]. Finally, in the famous article by N. Bloembergen, R.V. Pound, E.M. Purcell [10], the complete scheme of a spectrometer with synchronous detection of an NMR signal and a bridge spin detector (albeit without recording the signal on a recorder, point-by-point measurements on a microammeter) is given.

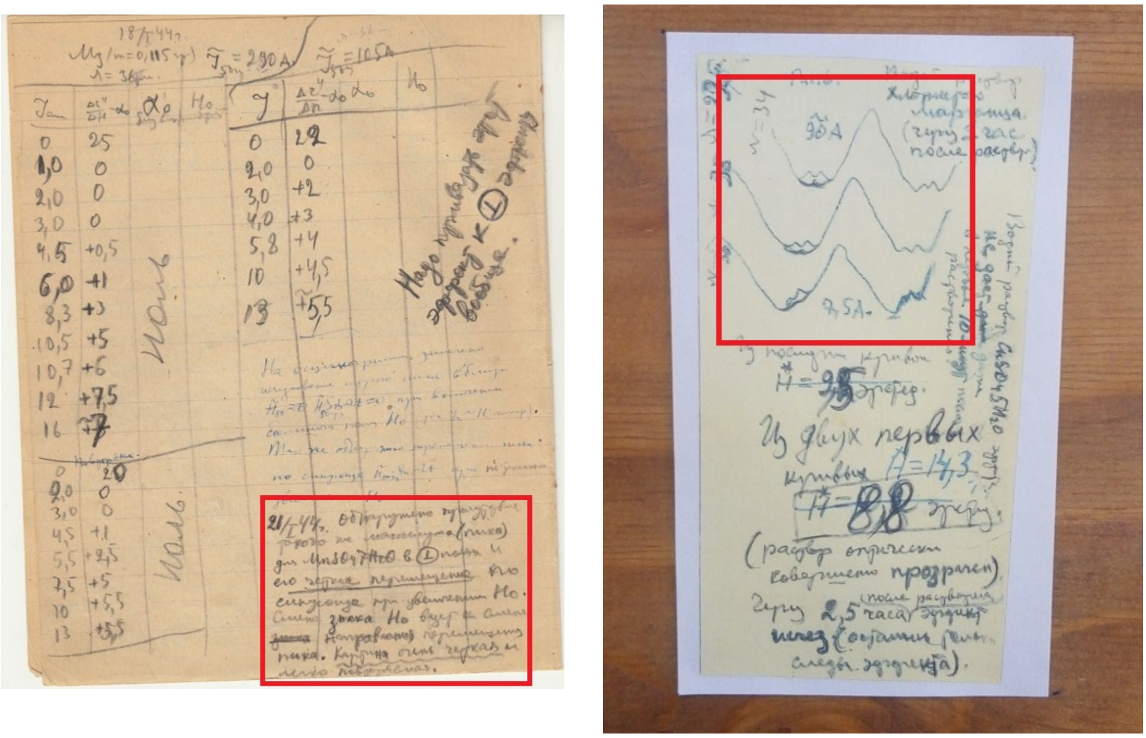

Figure 8. Note in the logbook, 21.01.44: The presence of the same maximum (peak) for $MnSO_4{\cdot}7H_2O$ in ⊥ fields and its clear movement along a sinusoid (electrical pickup) with increasing H_0 were discovered. A change in the sign of H_0 leads to a change in the direction of movement of the peak. The picture is very clear and easily reproducible

Figure 9. The American profilometer used by Zavoisky as the AC amplifier

The use of shallow modulation of the magnetic field in NMR spectrometers (i.e., transfer of the signal to the modulation frequency with subsequent synchronous detection of the signal, i.e., narrowing the receiver bandwidth to a very small value, usually to about 1 Hz and less, which allows you to get rid of noise that is not included in gain band, and thus greatly increase the signal-to-noise ratio) is quite logical, since the NMR absorption signal is very weak. The EPR signal is large, so that at not very low concentrations of paramagnetic centers in the sample, the signal is clearly visible without any special tricks. However, it is clear that the use of a similar method (field modulation) in EPR spectrometers can greatly increase the sensitivity of the spectrometer. Therefore, it is not surprising that the method began to be used in EPR spectrometers. What's especially nice is that EPR spectrometers can use much higher-frequency magnetic field modulation. The permissible modulation frequency is determined by the characteristic width of the EPR or NMR line. The rule for choosing a modulation frequency is: the frequency should not exceed the width of the magnetic resonance line that you want to record without distortion. In solid state NMR the characteristic linewidth is 1 kHz, so the modulation frequency must be less than 1 kHz. In EPR, the minimum linewidth is 1 MHz (for example, the linewidth of the DPPH radical is about 1 Oersted, i.e., about 3 MHz), so it is quite possible to modulate the field with a frequency of up to 1 MHz. However, the choice of modulation frequency in EPR spectrometers is based on another criterion: the modulation frequency is chosen such that at this frequency the spectrometer makes the least noise. The main noise in EPR spectrometers comes from the microwave crystal detector, and typical microwave detectors are least noisy at a frequency of about 100 kHz. For this reason, 100 kHz has become somewhat of a standard magnetic field modulation frequency in EPR spectrometers.

5. EPR linewidth

And finally, Zavoisky was very lucky that the width of the EPR line in the concentrated paramagnets he studied was not the typical several hundred Oersteds due to dipole-dipole interactions, but due to exchange narrowing was much lower. This, by the way, was noted by C.J. Gorter in his speech at the ceremony of his awarding the Fritz London Prize in 1966 [1]. In addition, Zavoisky studied EPR in solutions of paramagnetic salts, in which the EPR line width is quite narrow.

6. After the discovery

As is known, Zavoisky was not able to study the EPR phenomenon he discovered for long: in 1947 he was offered to move to Moscow, and then to Arzamas-16 (now Sarov) and join the work on creating the Soviet atomic bomb. But, as is known, old love never rusts: after retiring, Zavoisky built a home EPR spectrometer. Its interesting that he used metal cans of tea, coffee, caviar, etc. as instrument bodies (Figure 10).

Figure 10. The Zavoisky home-made EPR setup

7. Summary

Zavoisky has discovered EPR due to the next circumstances:

1. Zavoisky, long before the rest of the scientific community, realized that radio engineering methods allow indirect methods to study the interaction of matter with electromagnetic fields.

2. Zavoisky realized that at a frequency of the order of 10 MHz, the ESR phenomenon should be observed in a magnetic field of several Oersteds. To get rid of the residual magnetization of the electromagnet used, Zavoisky switched from an electromagnet to a solenoid, which, as is known, does not have a residual field.

3. The use of low-frequency (50 Hz) magnetic field modulation made it possible to easily observe the EPR phenomenon on the screen of the oscilloscope he had, the horizontal sweep of which was synchronized with the modulation voltage.

4. And finally, Zavoisky was very lucky that the width of the EPR line in the concentrated paramagnets he studied was not the typical several hundred Oersteds, but due to exchange narrowing it was much lower.

The history of Zavoisky's EPR setup restoration is published in [11].

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