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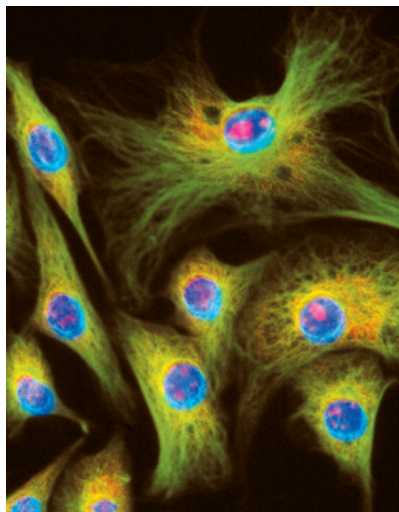
Please feel free to contact us with items (news, notices, technical notes, and comments) or ideas for the *EPR newsletter*.

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The cover picture illustrates aspects of the research carried out in the group of Michael J. Davies, recipient of the 2003 IES Silver Medal for Biology/Medicine, and in particular the work of his group in examining the degradation of biological macromolecules by oxidants. The cell image shows artery endothelial cells stained for macromolecules that make up the cell cytoskeleton (green) as well as nuclear DNA (blue) and RNA (red). Oxidative damage to these macromolecules results in alteration in cell behaviour and function. Cell image copyright of Molecular Probes, Inc.

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Are you interested to become a member of the International EPR (ESR) Society? Please find the registration/information form for new/continuing members of the IES and non-credit-card payment instructions for individual members on this Web site: www.epr-newsletter.ethz.ch/contact.html

Editorial

Dear colleagues,

I would bet that all of you who enjoyed the sound of the first movement of the Sinfonia Concertante for 2 flutes and orchestra by Domenico Cimarosa downloadable from the “Playing Flute” article of the *EPR newsletter* 14/3, immediately realized that one of the flutes is played by Uwe Eichhoff but nobody guessed that the other flute was played by Irina Stachinskaya (Moscow) who was only 13 when this music was performed.

This issue allows us to look back at 2004, the year of the 60th anniversary of the discovery of the electron paramagnetic resonance phenomenon by E. K. Zavoisky. His daughter, Nataliya Evgen'evna Zavoiskaya, tells us in more detail about a lesser known passion of her father which she has already mentioned in her interview published in the *EPR newsletter* 13/1-2, 13–14 (2003), his fascination by the avant-garde art. In addition to this insight into the inner world of the founder of EPR, this article allows us to use the links given as a guide in the virtual museum of Russian avant-garde art in the middle and the second half of the 20th century. Igor Silkin, curator of the Zavoisky Museum, inducts us into the reconstructed

experimental setup of E. K. Zavoisky. Now when we have commercial spectrometers it is thrilling to look at the extremely simple equipment, which gave birth to this great discovery. The photo of the issue and our quiz also refer to E. K. Zavoisky. Even if many readers might know the answer, it would be a pleasure for us to disclose the answer in one of the forthcoming issues.

In this edition, we are delighted to include an impressive account of the life and achievements of Anatole Abragam provided by Maurice Goldman and Ionel Solomon. Our readers might well wonder why such a distinguished scientist has not received the Zavoisky Award. We are pleased to tell them that Anatole Abragam has more than once been recommended by the Zavoisky Award Committee but under the rules the recipient of the Award has to travel to Kazan to receive the prize and unfortunately Anatole Abragam has been unable to do this. We regret that this is so but are pleased to take this opportunity to acknowledge his pre-eminence and extraordinary contributions to magnetic resonance. Delightful articles by Keith McLauchlan and George Feher, which are full of humor, warmth and references to personal relationships, add to the understanding of the personality of this great man. I phoned Anatole Abragam on December 15, 2004 to congratulate him on his 90th birthday. Imagine, he spoke perfect Russian with me and I was immediately charmed by

his humor, friendliness and the courtoisie of a perfect Frenchman. 75th birthday of Tengiz Sanadze and 65th birthday of Dietmar Stehlik give us a nice opportunity to congratulate these outstanding scientists and wish them all the best for the years to come.

Pro and Contra of pulse ELDOR, a powerful tool to characterize molecular reorientation and cross relaxation processes, are comprehensively presented in a concise article by Gunnar Jeschke.

As you might remember, 2005 marks the 100th anniversary of what physicists refer to as Albert Einstein’s “miraculous” year. In 1905, he wrote five papers. To name three of them: his first paper gave a theory on the behavior of light; Einstein’s second paper offered an experimental test for the theory of heat; the third paper “Zur Elektrodynamik bewegter Körper” was the Theory of Special Relativity, which sought a way to connect electromagnetic theory and ordinary motion. The United Nations is encouraging events worldwide to make 2005 the World Year of Physics. Look forward to the forthcoming issue 15/1 of the *EPR newsletter* dealing with this subject in more detail!

I would like to attract your attention to the call for nominations (this *newsletter*, p. 3). We have to think of new Executives of the IES: the future of our Society to a great extent depends on its CEOs. Name your candidates please!

Laila Mosina



Take our quiz!

Send an e-mail message to the editor telling what international society, when and where posthumously awarded E. K. Zavoisky in recognition of his discovery of electron paramagnetic resonance. Deadline June 30, 2005. If we will get more than one correct

answer, a raffle will be held to decide who is the prize winner. The prize is a special envelope issued in 1994 to mark the 50th anniversary of this discovery and stamped in Kazan with a special stamp during the 27th AMPERE Congress, August 21–28, 1994, together with a photo of E. K. Zavoisky.

Call for Nominations Office Bearers for Oct 2005–Sept 2008

Our Constitution Article VIII. Elections, reads:

“Nominations for all positions of Office Bearers shall be made by the Executive that shall have regard to geographical and international distribution of nominees. Nominations may also be made by at least ten paid-up members of the Society, in writing to the Secretary, and received by a date specified with appropriate notice in the official Bulletin or Newsletter of the SOCIETY. Where there are one or more nominations for any position, the Elections Committee shall conduct the election according to the provisions following in clauses 2 and 3.”

There are thus two ways a person may be nominated for Office in the Society. The current Executive is required to make nominations for all positions. Nominations can also be made by ‘at least ten paid-up members of the Society...’ for all elected positions: President, Vice-President Americas, Vice-President Asia/Pacific, Vice-President Europe, Secretary and Treasurer.

Nominations in writing should reach the Secretary,

Dr. Shirley A. Fairhurst,
John Innes Centre,
Norwich Research Park, Colney,
Norwich NR4 7UH, UK

by post,

e-mail: shirley.fairhurst@bbsrc.ac.uk or

fax: +44 (0)1603 450018

before 1st May 2005.

From the President

In November 2004 I participated in the International School on EPR/ESR Spectroscopy and Free Radical Research (ISEPR-04) held in Mumbai, India. The school provided a forum for young scientists engaged in EPR/ESR spectroscopy in biophysical, chemical, biomedical and materials science research to gather together with expert faculty from around the world.

As President of the IES I delivered a message of congratulation to the School organizers and presented the Convener of School,

Dr. K. P. Mishra with a Congratulatory Diploma. The citation read:

The International EPR/ESR Society congratulates Dr. Kaushala Prasad Mishra for his contribution to the teaching and development of EPR spectroscopy and free radical research by bringing together students, young scientists and a wide range of expert lecturers.

Later in November I attended the 4th Asia Pacific EPR/ESR Symposium (APES'04) held in Bangalore, India. The Asia Pacific EPR Society, APES is affiliated to the IES and as IES President I made a welcome address and presented Professor Czeslav Rudowicz, the retiring President of Asia-Pacific EPR/ESR Society, a Congratulatory diploma: The citation read:

Professor Czeslaw Rudowicz of the City University, Hong Kong is honored by the IES for his contribution to the EPR community. In 1997 he founded the Asia-Pacific EPR Society and became its first President. He initiated the Asia-Pacific EPR/ESR Symposium Series (APES) held in Hong Kong 1997, Hangzhou 1999, Kobe 2001 and Bangalore 2004. Throughout his tenure as APES President there has been a productive interaction with the IES. Professor Rudowicz is retiring as APES President at this meeting and the IES wishes him success on his forthcoming move to the Technical University, Szczecin, Poland.

Yuri D. Tsvetkov

Elena Bagryanskaya – the New President of the Russian EPR Society

In March 2004, I was elected President of the Russian EPR Society. I consider this as a great honor and will do my best to support the development of the Russian EPR community and its relationships with the International EPR Society. My own scientific experience in EPR is in the development of methods to record short-lived radicals and radical pairs in photochemical reactions, such as dynamic and stimulated nuclear polarization, time-resolved EPR, and time-resolved CIDNP. Full information on the recent

projects of my research group can be found on the website www.tomo.nsc.ru/structure/departments/pcri.

As the main goal of my activity as President of the Russian EPR Society for the next three years, I consider the development of



the communication among the Russian EPR spectroscopists and the creation of an educational program on EPR for students and young scientists. To this end we established a website of the Russian EPR Society www.tomo.nsc.ru/RussianEPRSociety, where information about Russian EPR groups, meetings, conferences, schools and other subjects related to EPR (e.g., about open positions, exchange of EPR equipment, etc.) are presented.

To support young scientists working in the field of EPR, we plan to continue the tradition of the Magnetic Resonance School founded by the late colleague Ya. S. Lebedev in Moscow, which took place during the last ten years in Kazan. We plan to organize the next School as a satellite of the Asia-Pacific EPR Symposium in 2006 in Novosibirsk. We would like to invite distinguished scientists from all over the world as lecturers.

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Nominations Open for the Zavoisky Award 2005

The Zavoisky Award 2005 will be presented at the Annual Workshop "Modern Development of Magnetic Resonance" to take place in Kazan in September 2005.

This prestigious award is given in recognition of an outstanding contribution to the development of electron paramagnetic resonance. It is presented by the Kazan Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, Kazan State University, the Tatarstan Academy of Sciences, and Springer-Verlag Wien New York. The lecture of the award-winner will be published in the journal "Applied Magnetic Resonance".

Nominations are being sought from the EPR community worldwide. A brief presen-

tation of the applicant covering 1–2 pages is expected. The final decision is made by the Award Selection Committee which comprises G. Feher (La Jolla), D. Gatteschi (Florence), H. M. McConnell (Stanford), K. A.

McLauchlan (Oxford), K. Möbius (Berlin), A. Schweiger (Zurich), and the chairman, K. M. Salikhov (Kazan). The selection of the awardee is made after consultations with the Advisory Award Committee which comprises B. Bleaney (Oxford), C. A. Hutchison Jr. (Chicago), Yu. N. Molin (Novosibirsk), and Yu. D. Tsvetkov (Novosibirsk).

Nominations should be submitted to:

Dr. Laila V. Mosina
Executive Secretary of the Zavoisky Award Committee
Kazan Zavoisky Physical-Technical Institute of the Russian Academy of Sciences
Sibirsky trakt, 10/7
Kazan, 420029
Russian Federation
e-mail: mosina@kfti.knc.ru
fax: 7-8432-725075

The deadline for submission of nominations is April 30, 2005.

The Bruker Prize 2005

Klaus-Peter Dinse
Darmstadt University, Darmstadt, Germany

The IES Young Investigator Award 2005

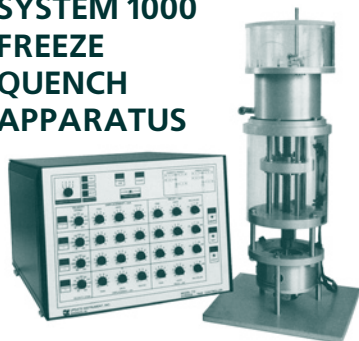
Eric McInnes
The University of Manchester, Manchester, UK

Detailed information on these awards will be given in a future issue of the *EPR newsletter*



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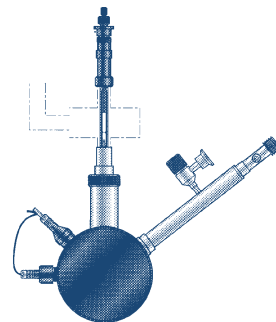
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To judge my father by his cover, he was an exceptionally even-tempered man. His only and overwhelming passion was physics. Having experienced its attraction in his childhood, he served physics faithfully all his life. This was the case when he became interested in the functioning of radios and in radio waves in general while studying at school in Slobodskoi on the banks of the Vyatka river; this was the case as well when he became a student and later an Associate Professor of the Kazan University; and the same was true when he was in Moscow. “What is

including the 20th, has to transfer to the following centuries something of its own, new, and peculiar. He had a sharp feeling for lies and imitations and never approved them.

In the Institute of Atomic Energy (the Kurchatov Institute) where my father worked after a 4-years mission in Arzamas-16, the Scientific Secretary was Yuri V. Adamchuk. As an energetic person, Yuri was extraordinarily active both in science and art. It was the time of Khrushchev’s thaw (“otpepel”). What bright and unforgettable years! Adamchuk was one of the organizers of meetings of poets, writers, actors, and public figures with scientists in the Culture House of the Kurchatov Institute. To name a few, these were the writer Aleksandr I. Solzhenitsyn, the poet Naum Korzhavin, the cellist Mstislav L. Rostropo-

My father bought a small Sidur sculpture called “Ironer”. It was a hunchbacked woman with enormously overworked muscles (“No woman would iron in this way” – sighed my mother). On a miniature head without face there was a small bunch of hair. Nothing in this figure reminded a woman: a real mechanism for ironing.

We also visited the studios of Robert R. Falk⁷, Igor Galanin⁸, Ernst Neizvestny⁹, and Mikhail A. Kulakov¹⁰. I remember a discussion between my father and Boris M. Kozzyrev, his friend and colleague, a great connoisseur of art, about the paintings of Robert Falk, one of the founders of the “Bubnovyi valet”¹¹ (The Jack of Diamonds) group. Kozzyrev liked his paintings, but my father did not like them at all, stating that this painter

E. K. Zavoisky: A Less Known Passion

N. E. Zavoiskaya

happening in the country and in the rest of the world is of minor importance compared to the great desire to wrest from nature even a little grain of her mysteries. What is life for then?!” – my father wrote in his diary about the time when he worked in Kazan attempting to observe EPR.

I would like to tell about his another passion, which, in fact, was not as strong as his passion for physics: it was painting and also sculpture.

My parents had different views as far as painting was concerned: while my mother was delighted with pictures by Ivan Shishkin¹, Mikhail Vrubel², or Ilya Repin³, my father although paying tribute to the artistic heritage of the past, preferred modern art. But of course not the one of socialist realism. My father considered that every century,

vich together with his wife the singer Galina P. Vishnevskaya. Adamchuk organized most interesting visits to the studios of Moscow’s avant-garde painters, in this way supporting them both morally and financially (researchers often bought their paintings). Thanks to Adamchuk my father and I visited the studio of the sculptors and painters Vadim A. Sidur⁴, Nikolay A. Silis⁵ and Vladimir S. Lempert⁶, who shared a cellar in a house near the St. Nicholas Church in Khamovniki in Moscow. My father liked sculptures of Vadim Sidur most of all. In a cosy studio with a large oven to anneal clay figures, sculptures were standing around everywhere. They symbolized life, creative work, and art, and manifested unexpected, nonstandard visions of the world. My attention was mainly attracted by softer, more traditional wooden sculptures of Silis.



“Dry tree”, watercolor.

lacked for the spirit of a discoverer. The discussion ended without any result, every one kept his own opinion. Years ago I reminded Boris Mikhailovich of this discussion and he said: “Nevertheless, Evgenii Konstantinovich was not right”. Interestingly, recently I read the book “My Avant-garde” written by Georgii D. Kostaki¹², a famous collector of

¹ Ivan Shishkin (1832–1898), Russian painter, see, e.g., eprnl.org/14-4/shishkin

² Mikhail Vrubel (1856–1910), Russian painter, see, e.g., eprnl.org/14-4/vrubel

³ Ilya Repin (1844–1930), Russian painter, see, e.g., eprnl.org/14-4/repin

⁴ Vadim A. Sidur (1924–1986), Russian sculptor, painter, see, e.g., eprnl.org/14-4/sidur

⁵ Nikolay Silis (1928), Russian sculptor, see, e.g., eprnl.org/14-4/silis

⁶ Vladimir S. Lempert (1922–2001), Russian sculptor, painter, see, e.g., eprnl.org/14-4/lempert

⁷ Robert R. Falk (1886–1958), Russian painter, graphic artist, theatre artist, see, e.g., eprnl.org/14-4/falk

⁸ Igor Galanin (1937), Russian-American painter, see, e.g., eprnl.org/14-4/galanin

⁹ Ernst Neizvestny (1926), Russian-American sculptor, see, e.g., eprnl.org/14-4/neizvestny

¹⁰ Mikhail A. Kulakov (1933), Russian-Italian painter, see, e.g., eprnl.org/14-4/kulakov

¹¹ “Bubnovyi valet”, the Russian Futurist group of the beginning of the 20th century, see, e.g., eprnl.org/14-4/valet

¹² Georgii D. Kostaki (1913–1990), outstanding collector of Russian avant-garde art, see, e.g., eprnl.org/14-4/kostaki

Милости
 Казанца художника А.А. Анিকেенко очень
 люблю. Это удивительно, но
 именно в Казани, в городе, который
 считается родиной Казанского
 университета, и в котором
 и родился, и вырос, и
 и работал, и учился.
 Казань, родина моего
 родного художника-современника
 и прекрасного человека
 и гражданина, и человека
 и гражданина, и человека
 и гражданина.

E. K. Zavoisky's hand-written comments in the guest-book of the Anikeenok exhibition: "I like paintings of the painter A. Anikeenok very much! He uses new expressive means, which provide his paintings with freshness and lyric. Many paintings are strikingly deep, they are full of love to the Russian nature and people. The city on the Volga river may be proud of this new great talent!"

Russian avant-garde, and found that he felt the same way as my father did with respect to the paintings of Falk.

Kozyrev introduced my father to the creative work of the Kazan painter Aleksei A. Anikeenok. Both went to his studio during one of my father's visits in Kazan. Boris Mikhailovich told my father about the fate of this painter, about his fight for the right to have his own visions of the world, and to have his own topics. He also told about the merciless persecution of Anikeenok by the guardians of the Soviet ideology, about an exhibition in the Kazan House of Scientists which did not exist longer than for half an hour: a public man pointed to the famous painting "Shepherds" and asked: "Why are your sheep red?!" and ordered the closure of the exhibition. Thanks to a petition of physicists, which was also supported by my father, a large exhibition of paintings of Anikeenok took place in the Institute for Physical Problems (Moscow) headed by the Academician Petr L. Kapitsa. A nonconformist Academician allowed an exhibition of paintings of a

"Cosmos", pastel, velvet paper.



nonconformist painter in his institute. This was a little deed compared to the greater civil courage of Petr Kapitsa. It was in October-November 1965 when my father and I went to this exhibition. There were crowds of people, the entrance hall and the conference hall were full. The people gathered in front of the paintings and discussed what they saw. My father was deeply impressed by this exhibition. Aleksei Anikeenok understood that some visitors might like to buy some of his paintings. For him it was not an easy decision to sell them. I remember well the astonishment on his face: will he be able to live without his paintings? They were a part of himself. Offerings were numerous: the Academicians Andrei D. Sakharov, Petr L. Kapitsa and others bought Anikeenok's paintings. My father bought the painting "Shepherds". One of the reasons to choose this painting was the fact that the boy on the painting reminded him of his brother Boris shot by the NKVD (People's Commissariat for Internal Affairs) people in December 1937.

like the one at the Kapitsa Institute and meetings full of freedom like those in the Culture House of the Kurchatov Institute I mentioned above again became impossible. At that time the so-called "migrating" exhibitions came up. At our place we had an exhibition with paintings of Anatolii T. Zverev¹³ and Galina I. Satonina¹⁴, a painter and a chess player from Kazan.

In the last years of his life, my father, being heavily ill, started to paint pastels (see, e.g., "Cosmos") and watercolors (see, e.g., "Dry tree"). He never studied painting. However, once in my presence he charcoaled a perfect copy of a drawing from a pre-revolutionary issue of the book "Dead Souls" by Nikolai Gogol. His drawing "Tsunami" makes one think of the numerous victims of the recent horrible tsunami in the Pacific. My father kept a sketchbook and from time to time he painted there. A color-box was always in our house because my daughter being a child of preschool age went to an artistic circle. He did not like to show his paintings. In 1987, when the Museum of History of the Kazan State University celebrated the 80th anniversary of my father, I took his watercolors to the exhibition there.

I hope this brief essay gives some insight into this less known passion of E. K. Zavoisky.



"Tsunami", drawing.

Thus thanks to the efforts of the physicists in Moscow and Kazan the painter persecuted in his hometown experienced an hour of triumph, and found a grateful and sympathetic audience. Later on, exhibitions

¹³ Anatoly T. Zverev (1931–1986), Russian painter, see, e.g., eprnl.org/14-4/zverev

¹⁴ You may see a photo of Galina Satonina with her self-portrait in her hands at eprnl.org/14-4/satonina

90th Birthday of Anatole Abragam

Anatole Abragam has been born in Moscow on December 15, 1914. He left Russia for France at the age of ten. He graduated in Sciences in 1936, and after an interruption due to World War II he resumed studies at Ecole Supérieure d'Electricité, from which he graduated in 1947. He joined the same year the newly founded Commissariat à l'Énergie Atomique (in short CEA, the French Atomic Energy Commission) and he made his entire career at the Centre of Saclay, successively as Physicist, Chief of Section, Chief of Service, Chief of Department and Director of the Physics of CEA. He became Professor of Nuclear Magnetism at the prestigious Collège de France in 1960 and lectured there until his retirement in 1985.

Through his scientific achievements and his lectures and books, Anatole Abragam has become very early, and continued to be in the following and up to now, a leading and prestigious figure in the theory of EPR and NMR, not counting some excursions in other physical domains. It is his career that we have endeavoured to present at the occasion of his 90th birthday, through a brief description of some of his most important scientific contributions.

Initially in the Group of Mathematical Physics, it is during a 2-year visit at the Clarendon Laboratory in Oxford, Great Britain from 1948 to 1950 that he started working on the theory of EPR, essentially in collaboration with Maurice Pryce. He developed with him the theory of the Spin Hamiltonian (1949), which brought about an enormous conceptual simplification in the theoretical description and understanding of localized paramagnetic ions in non-conducting solids. The following year he developed the theory of core polarization, a major theoretical success, which made it possible to explain the anomalous hyperfine structures and was Anatole Abragam's first step towards fame.

Jumping from Oxford (England) to Cambridge (Massachusetts, USA) in 1952, he developed with Robert Pound the complete theory of perturbed angular correlations in a cascade of two radiations emitted in a nuclear radioactive decay, produced in condensed matter by static or variable electric and magnetic



fields. This work was the seed of the formalism of relaxation theory developed a few years later at Saclay.

This development was triggered by the work of Ionel Solomon at Harvard in 1955, who generalized the Overhauser effect to dipolar interactions and discovered cross-relaxation. Abragam's formalism of relaxation was entirely based on the use of operators and of the density matrix. For most cases, it has become and remains up to this day the method of relaxation calculations.

Another major achievement was the invention in 1958, in collaboration with Jean Combrisson and Ionel Solomon, of an earth-field magnetometer of unprecedented sensitivity. It is a MASER oscillating at the proton Larmor frequency in the earth field, based on the Overhauser inversion of the solvent proton polarization by saturating an appropriate hyperfine resonance of dissolved nitroso radicals. This magnetometer is routinely used for geophysical surveys, in particular in connection with oil prospecting, and for the detection of metallic objects underground or under sea, such as sunken ships, submarines, gas pipes, etc.

The validity of the Spin Temperature Concept in the laboratory frame was established

beyond doubts by a series of supremely elegant experiments devised by Anatole Abragam and performed in 1957 with Warren Proctor. Equally important has been the role of Abragam in popularizing the slightly earlier invention, by Alfred Redfield, of Spin Temperature in the rotating frame and in showing how the theories for both cases could be expressed in a common conceptual frame.

Barely a few months after the excitement of the Spin Temperature experiments, another invention of fundamental importance was made by Anatole Abragam, that of Dynamic Nuclear Polarization (DNP), initially under the name of Solid Effect, whereby the polarization of nuclear spins can be made nearly equal to unity, either parallel or antiparallel to the external magnetic field, by off-resonance irradiation of paramagnetic centres at low concentration in non-conducting solids. The main objective of this invention was the production of polarized targets for Nuclear and Particle physics experiments. Initially developed in the Saclay laboratory and in parallel in Berkeley by Carson Jeffries, polarized targets became extremely successful, popular and important tools used at the most important accelerator centres around the world. In recent years, polarized targets proved to be indispensable for new important physics, firstly for the experimental study of Time Reversal and Parity Conservation violation in neutron-nucleus interactions, and secondly for the investigation of the completely unexpected spin structure of the nucleons, that is protons and neutrons, still under study and not elucidated yet. The invention of DNP cannot be dissociated from another one devised in collaboration with Jacques Winter: an experimental scheme for producing polarized proton beams, whose interest complements that of polarized targets in nuclear and particle physics.

One of the most brilliant ideas of Anatole Abragam was to combine the concepts of Spin Temperature and of DNP for inventing the principle of production of Nuclear Magnetic Ordering. The idea was to perform in succession a polarization of the nuclear spins by DNP followed by a nuclear adiabatic demagnetization, either in the laboratory frame or in the rotating frame. Increasing the nuclear polarization amounts to lowering the nuclear entropy. The role of the adiabatic demagnetization it is to turn the Zeeman order into dipolar order at constant entropy. At sufficient low entropy, the nuclear spins undergo a phase transition to an ordered state. The interactions are either the full dipolar interactions, in the laboratory frame, or truncated dipolar interactions, in the rotating frame. In this last case, the interactions depend on the orientation of the single-crystal

sample in the external magnetic field. Furthermore, it is possible to choose at will the spin temperature to be either positive or negative. This method was used in the Saclay laboratory for over two decades and led to the production in a number of different crystals of a whole series of nuclear spin orders: ferromagnetic, antiferromagnetic and rotating transverse helical structures, whose study was made both through NMR and neutron diffraction.

As an offspring of Abragam's pondering about the possibility of using neutron diffraction for studying nuclear magnetic ordering, he invented the so-called nuclear pseudo magnetism. When a neutron travels through a polarized material, the average spin-dependent interaction between the neutron and the nuclear spins has the same form as a Zeeman interaction for the neutron. The corresponding pseudo-magnetic field is proportional to the nuclear concentration, their polarization and their "pseudo-magnetic moment". The latter has nothing to do with magnetism: it describes the spin-dependent neutron-nucleus interaction originating from strong interactions. Although the analogy with a Zeeman interaction had been found slightly earlier by two soviet physicists, it was Abragam's merit to push the concept to its limits and to devise experimental schemes to investigate it. This was done essentially in the Saclay laboratory. After a verification of the reality of pseudo-magnetic precession and resonance, a systematic campaign of measurements yielded the pseudo-magnetic moments of more than 25 nuclear isotopes, providing the practitioners of neutron scattering with information of fundamental importance.

Last but not least, Anatole Abragam has revolutionized the practice of μ SR (Muon Spin Rotation) with the idea of level crossing, an idea which arose during his last course at the Collège de France before his retiring. Physicists then used pulsed beams to implant polarized muons into matter, and followed the

time evolution of their polarization, oscillation or damping, through the angular anisotropy of the μ emission. Abragam's idea was to sweep a magnetic field parallel to the initial muon polarization. At those fields where a level crossing takes place in the system of the muon coupled to other spins, flip-flop processes result in a decrease of the muon polarization, which is monitored. There is a double advantage in this procedure. Firstly, one can use a continuous beam rather than a pulsed one, thereby increasing by an enormous factor the counting rate, and as a consequence the sensitivity of the method. Secondly, one can detect not only the resonance frequency of the muon itself, but also the level structure of the spins coupled to the muon, which was a decisive progress that turned μ SR into a completely mature spectroscopic method. Both μ SR and level crossing had a long history at the time of this discovery, but nobody had had the idea of combining them together.

Anatole Abragam's prestige is not only due to his scientific achievements, but also to his remarkable pedagogical qualities and his prominent role in diffusing an elaborate and theoretically rigorous "wisdom" in Magnetic Resonance. This was done for the benefit of the members of his laboratory through his constant interest in their work, his advice and example. The French community took advantage of his remarkably brilliant and penetrating lectures, at Saclay and later at the Collège de France. The rest of the world was deeply influenced by his classic books. The first of them, *The Principles of Nuclear Magnetism*, published in 1961 by Oxford University Press, was welcome as a major event in scientific literature and became known as "The Bible". Forty-three years later, and after all the important developments that were done in NMR since, it is still considered as the fundamental basic treatise in the field. Among his principal other books, two are purely scientific:

1970: *Electron Paramagnetic Resonance of Transition Ions*, with B. Bleaney (Oxford University Press),

1982: *Nuclear Magnetism: Order and Disorder* with M. Goldman (Oxford University Press), one is a collection of essays about science and scientists:

1983: *Réflexions d'un Physicien* (in French) (Hermann), and three consist of the respective French,

English and Russian versions of his memoirs:

1987: *De la physique avant toute chose* (Odile Jacob),

1989: *Time Reversal* (Oxford Press),

1991: *Physicist, where have you been?* (in Russian) (Nauka).

Anatole Abragam was recognized and honoured in many ways through Prizes and Medals in France and abroad, and through becoming Doctor Honoris Causa of various universities and institutes. He has been President of the French Physical Society and Vice-President of the International Union of Pure and Applied Physics (IUPAP). He has been Invited Professor in the universities of Oxford, Harvard, Amsterdam, Yale, Washington, Leiden, etc. He is Member of the Académie des Sciences in France and Foreign Member of the American Academy of Arts and Sciences, of the National Academy of Sciences (USA) and of the Royal Society of London.

Maurice Goldman

Ionel Solomon

Anatole Abragam: Some Personal Reminiscences

In this issue celebrating the science of Anatole Abragam it is all too easy to forget him as the person he is, blessed with outstanding erudition and a wonderfully mischievous sense of humour. He is the only person I know to be able to tell jokes in three languages, English, French and Russian.

I first heard him at an early meeting in London where he addressed the Royal Society on the subject of the Knight shift in solid-state NMR. He wrote the name on the black board as Night to the great amusement of the English audience. The Chairman corrected him and pointed out the existence of the K in the name. Anatole said "you mean that I should pronounce in Knight, with emphasis on the K?" No said the Chairman, the K is silent. Some half an hour later Anatole turned to the Day shift and without hesitation wrote Kday on the board. He had, of course, thought out this elaborate joke beforehand.

I attended my first scientific meeting, a Gordon conference in New Hampshire, with my then head of department John Pople, sitting through every lecture of the first day. But at coffee on the second John told me that I was taking things too seriously and that the most important aspect of a Meeting was to meet

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new people. He actually forbade me to go to any further lecture before lunch. I knew no one else and sat lonely in a chair on the lawn before a very nice man came and sat beside me and introduced himself. This was my first meeting with Anatole and was typical of this already very distinguished man, ready and willing to talk to a beginner.

We became friendly in the years that followed and I attended many conferences with him. At one he confessed to being an avid reader of the detective stories of Dorothy L. Sayers and of her detective character, Lord Peter Wimsey, as English a person as one could imagine. He turned to me and said: "I hope you do not mind me saying so, but you always remind me of Sir Peter. You have a very English air about you and you go through life never quite understanding what is happening around you!" I thought I could get my revenge years later when my wife and I entered a clothing shop in Oxford only to find Anatole standing in the middle of the floor without his trousers on. With great delight I went up to him and introduced Joan. He did not waiver. He shook her by the hand and said: "How nice to meet you, Mrs. McLauchlan. As Dr. Johnson once said, you have never really known a man unless you have seen him with no trousers on!"

This is Anatole all over. He is immensely well read and civilised, and indeed as one of the few members of the Academie Francaise has for many years lectured on subjects widely removed from science. He is the most entertaining man I have ever met besides having the most penetrating mind. It is a measure of the man that I am sure that on his 90th birthday his sense of fun and sheer pleasure of life remain as important to him as the science he has accomplished. But all of us are grateful for the clarity and vision of his scientific writing and the "Principles of Nuclear Magnetism", and his second book with Brebis Bleaney on

EPR, will long remain classic expositions of the subjects to which us lesser mortals will return time and time again to be corrected and enlightened.

K. A. McLauchlan

Anatole Abragam on his 90th Birthday: Reminiscences

The impressive scientific contributions of Anatole Abragam are well known and described in detail in the article by Maurice Goldman and Ionel Solomon. I would like to add my own personal warm feelings towards Anatole and describe a few episodes that show his delightful sense of humor and whimsical nature.

In 1958 a conference on Double Resonance was held in Paris. Anatole who gave an invited paper could not squeeze all the material that he wanted to cover into the allotted time. He tried to solve this problem by instructing one of his assistants to ask during the question period about the extra lines on one of his slides. This way he could cover the additional material that he wanted to get across. After the talk the assistant duly followed instructions and asked the question. Alas, the assistant must have fallen asleep during the talk, because Anatole had run out of time and never showed the slide. Many people might have tried to obfuscate such a debacle and shove it under the rug, but not Anatole. He came right out with the true story to the great amusement of the audience.

In 1962 at the international conference on Electron Paramagnetic Resonance in Jerusalem, Anatole was asked at the banquet, without prior warning, to give an after-dinner speech. Anatole was apparently neither pre-

pared nor in the mood to comply with this sudden request. After a moment of hesitation he got up and told, instead, the following story: At the time of Nero a gladiator whispered something into the ear of an attacking lion upon which the lion meekly retreated to the corner of the arena. Nero ordered a fiercer lion to be brought in but the same scene repeated itself. After a few more lions with a repetition of the scene, Nero became curious and promised the gladiator to spare his life if he divulged what he whispered to the lion. The gladiator complied and said what he had whispered: "You can eat me, but then you will have to give an after-dinner speech." Anatole sat down to an appreciative applause from the audience. Thank you, Anatole, for this story; I have used it successfully on a similar occasion.

In spite of his wit and seemingly easy-going manner, Anatole has a certain European formality about him – by California standards that is. When he was introduced to the members of our group in the usual informal way as Roger, Jim, Ian, Mike etc., he seemed at first puzzled but quickly regained his composure and remarked with a smile: "It is nice to meet all of you; I hope I will get to know you better and find out your family names."

Anatole is a marvelous teller of stories and jokes. On his visit to La Jolla and other occasions we spent hours, late into the night, telling each other jokes. After awhile we knew most of each other's jokes and decided to try the proverbial time-saving system of assigning numbers to each joke. But when I told him "7", which represented a particularly good joke, Anatole did not laugh. When I expressed my disappointment at his lack of response Anatole replied with a straight face: "You didn't tell it well."

Anatole, all our best wishes on your 90th birthday; keep up your humor for many years to come and don't forget "7".

George Feher

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75th Birthday of Tengiz Sanadze

On January 30, 2005, colleagues and friends celebrated the 75th birthday of Professor Tengiz Sanadze at the University of Tbilisi, Georgia.

He studied Physics at the University of Tbilisi and finished his PhD in 1958. Then he went to Moscow to work in the group of A. M. Prokhorov. Later he returned to Georgia and became Head of the Radiophysics Department at the University of Tbilisi. He finished his habilitation in 1971. An official opponent of his dissertation was E. K. Zavoisky.

In 1967 Tengiz Sanadze together with his coworkers at the University of Tbilisi discovered a new phenomenon in EPR called discrete saturation. They observed the creation of a series of “holes” in the EPR spectra after application of a strong microwave pulse. Later they showed that this phenomenon is due to forbidden transitions involving spin flips of both electrons and the surrounding nuclei.

On the basis of this observation the Tbilisi group created a new direction in EPR – the

discrete saturation (DS) spectroscopy and the radio-frequency discrete saturation (RFDS) spectroscopy. These methods found wide applications in EPR, especially for the study of the local geometry of paramagnetic impurity ions in crystals.

Tengiz Sanadze received many prizes and honors for his outstanding scientific work, among which are the 1st Prize of the Tbilisi State University (1968) and B. Melikishvili Prize (1970). He is Academician of the Georgian Academy of Sciences. In recognition of his pioneering contributions in EPR, Tengiz Sanadze was chosen as Fellow of the International EPR (ESR) Society.

Tengiz Sanadze has a rare skill as an experimentalist. He can set up radioelectronic devices and put in operation the most complex, unusual installations, to do a joiner’s work at home or to convert a 14-carat gold to a pure one to make a wedding ring for his wife. All those who have the privilege to communicate with Tengiz Sanadze, know his open mind, kindness, and good sense of humor. He is full of enthusiasm and energy and is always



ready to share his valuable experience with the young generation of physicists working in the field of magnetic resonance at the University of Tbilisi. We wish Tengiz Sanadze many more years of his research activity and all the best to him and his family.

Boris Kochelava
Alexander Shengelaya

TAKEN BY STEFAN WEBER, CAPUTH, MAY 14, 2004



Would it have been to Dietmar Stehlik all by himself, the 65th birthday of this distinguished EPR scientist would have gone uncelebrated by the magnetic resonance community. It was probably his southern-German modesty that prevented Dietmar from accepting an appropriate and highly desired official celebration of this important personal event. He firmly declined any offers of friends to organize a “birthday party” for him at one of the magnetic resonance conferences or a dedicated symposium.

finally took place as an after-dinner session at the Sfb-Symposium held in the village of Albert Einstein’s summer residence, Caputh near Berlin, in May 2004. The speakers in the session were three well-known members of the magnetic resonance community: Andreas Kamlowski, a former PhD student of Dietmar, now at Bruker BioSpin, Michael Mehring, President of ISMAR, and Hans-Wolfgang Spiess, Director at the Max-Planck-Institut in Mainz, AMPERE President and former colleague of Dietmar in the

65th Birthday of Dietmar Stehlik

“Completely unauthorized” birthday celebrations took place in Caputh

Nevertheless, within the collaborative research center Sfb498 “Protein-cofactor interactions in biological processes” – a research network led by Dietmar – an event has been secretly planned and

Hausser group at the Max-Planck-Institut in Heidelberg. In their talks, shedding light on Dietmar’s scientific life – recently honored by the Zavoisky award (for details see *EPR newsletter* 14/3, pp. 6–7, 2004) – at different times and from different perspectives, they had the pleasure to incorporate a letter from Ken Sauer and Erwin Hahn and their wives to Dietmar on the occasion of his birthday. As evidenced by the photograph, Dietmar seems to have enjoyed listening to the words of his friends: “...As we all feel the effects of a steadily increasing applied field, we can begin to resolve wisdom that was previously hidden, but it is important at the same time to keep our spins fundamentally resonating and more-or-less under control...”. We hope Dietmar had with this, according to his closing remarks “completely unauthorized”, event as much pleasure as had the audience.

The Discovery of Electron Paramagnetic Resonance by E. K. Zavoisky*



Igor I. Silkin

Curator of the Zavoisky Museum of the Kazan State University

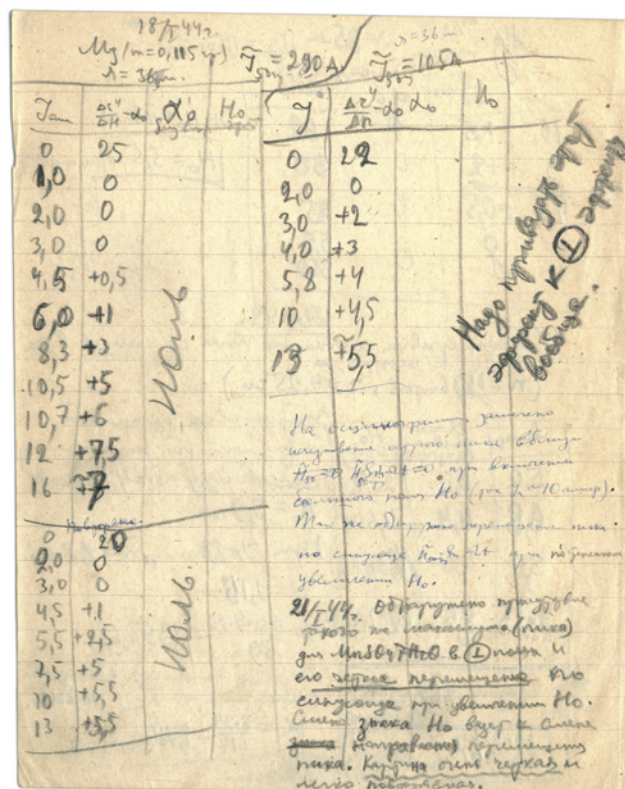
2004 marked the 60th anniversary of the discovery of electron paramagnetic resonance (EPR) by E. K. Zavoisky. Historically, everything started with Gorter's experiments on paramagnetic relaxation in solid paramagnetic salts. However, Gorter [1] failed to observe nuclear magnetic

resonance absorption by means of the calorimetric detection method. In Spring 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. According to the reminiscences of S. A. Al'tshuler and B. M. Kozyrev, both colleagues of E. K. Zavoisky [2] (a the photo of all three is shown in the *EPR newsletter* 13/1-2, p. 14, 2003), the results were promising, but WWII started and this research was interrupted. Only in the end of 1943 Zavoisky resumed this work. Now Zavoisky modulated the constant magnetic field at audio frequency (broadband modulation) and in some cases he did even not apply the constant magnetic field. For more details on the scientific research of E. K. Zavoisky see refs. 2 and 3.

E. K. Zavoisky observed an EPR signal for the first time on January 21, 1944. Let me cite the respective entry from his research notebook: "The

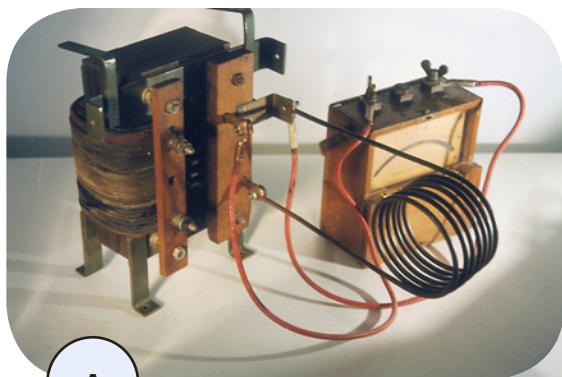
presence of the same maximum (peak) for $MnSO_4$ in a perpendicular field and its distinct sinusoidal shift as H_0 is increased were found. The change in the sign of H_0 results in the change of the direction of the peak shift. The picture is very distinct and easily reproducible." I demonstrate here the celluloid films on which E. K. Zavoisky copied the EPR signals from the screen of the oscilloscope. The concentrated paramagnetic salts of manganese, chromium and copper were studied.

I have reconstructed the experimental setup used by E. K. Zavoisky to observe the first EPR signal. This setup was quite simple and consisted of a welding transformer, a solenoid, an ammeter, an autodyne generator, an Abbot profile meter, and an oscilloscope. In the solenoid with 6 turns having a diameter of 12 cm, an alternating low-frequency field (50 Hz) was created. This coil was supplied from the secondary winding of the welding transformer with the primary winding switched to the ac network via a rheostat enabling one to adjust the current value. The magnetic field created by the solenoid was measured via the value of the alternating current. To this end, a Hartmann-Brown ammeter up to 200 A was switched successively to the solenoid. The proportionality coefficient between the magnetic field and the



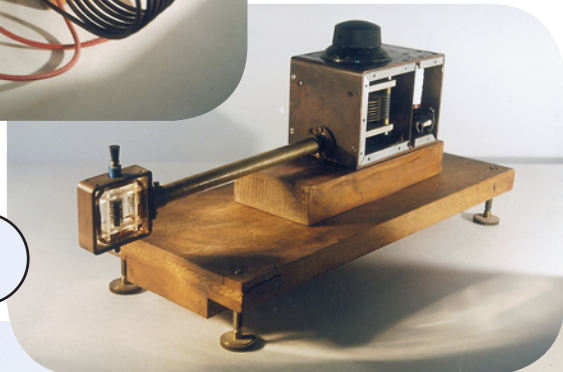
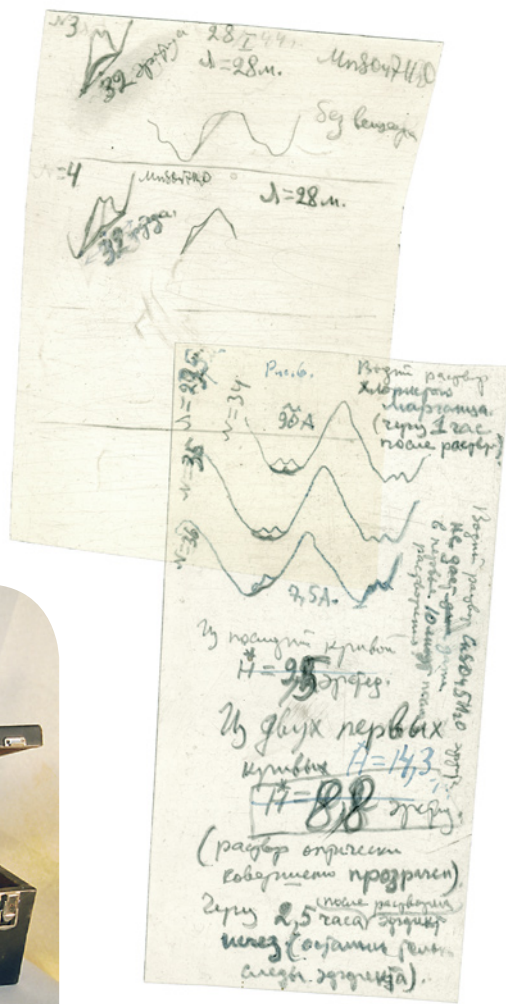
Page from the E. K. Zavoisky's research notebook of January 21, 1944.

* Presented at the 14th Annual Conference "Modern Development of Magnetic Resonance", Kazan, Russian Federation, August 15–20, 2004.

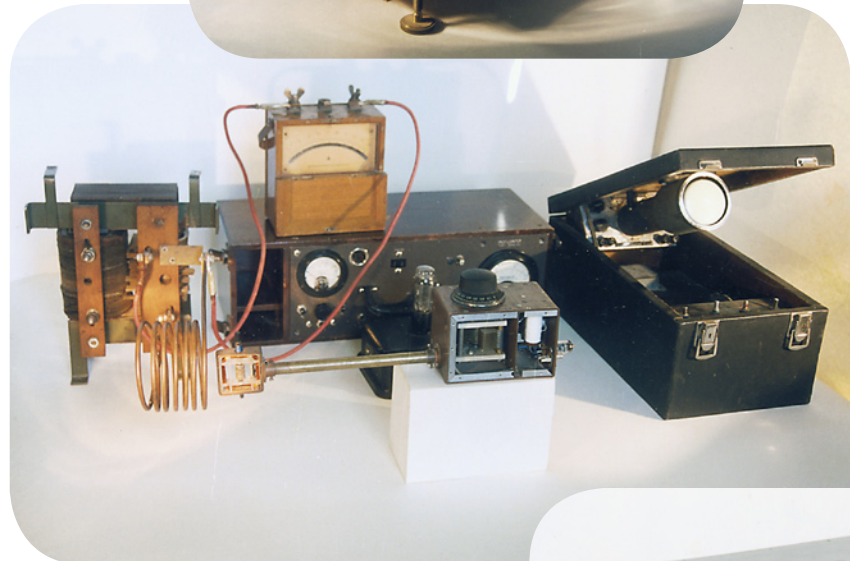


A

Celluloid films showing the EPR signal of $MnSO_4$ at a frequency of about 10 MHz measured by E. K. Zavoisky on January 28, 1944.



B



current was determined experimentally. A radio-frequency coil of the high-frequency generator (10 MHz) assembled with a CO-182 pentode was placed in the magnetic field of the solenoid. The paramagnetic sample sealed off in a hermetic celluloid ampoule was put into the coil. The magnetic field of the solenoid (50 Hz) was oriented perpendicular to the high-frequency magnetic field of the generator coil. One could detect the EPR signal as the watt loading of the generator changed at the time when the alternating magnetic field of the solenoid reaches the resonance value, by registering the change of the grid current of the generator lamp. The low-frequency amplifier from the Abbot profile meter was used. The signal from the amplifier outlet was registered either with a Weston heating apparatus or on the screen of the oscilloscope.



C



D

E. K. Zavoisky's experimental setup:
A) welding transformer with solenoid and ammeter;
B) autodyne generator;
C) profile meter;
D) oscilloscope.

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Pulsed Electron Electron Double Resonance

Distance Distributions

Gunnar Jeschke

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Introduction

Pulsed electron electron double resonance (ELDOR) [1] was originally introduced to characterize molecular reorientation and cross relaxation processes [2] and for more than 20 years was only sporadically used. Its current popularity is based on a pulse sequence for determining the ‘spatial distribution of paramagnetic centres in solids’ as introduced by the Novosibirsk laboratory [3]. Three years later the same group demonstrated, now in a paper published in English [4], that the technique could also be used for spin counting. Yet it took nine more years before the first paper from outside the Novosibirsk lab appeared [5]. This paper introduced orientation selection, with the not-yet-fulfilled promise of obtaining angular information on the arrangement of the centres, and the first acronym DEER (double electron electron resonance). For a short time this acronym appeared to become universal when it was adopted in a paper from the Novosibirsk group that discussed spin systems of dimensionality lower than three [6]. Our lab thus used it when naming a sequence with an additional refocusing pulse that provides dead-time free data with a single-mode cavity [7]. In fact, by that time a schism had already emerged as the first review on the technique named it PELDOR rather than DEER [8]. Unfortunately, nowadays both acronyms are in use. In the following, I use ‘pulse ELDOR’ as a general term for both the three-pulse and four-pulse techniques, while I continue to use the term ‘four-pulse DEER’ when I

refer specifically to the experiment with the refocusing pulse.

Advantages and Disadvantages

The measurement of small couplings between slowly relaxing electron spins is a prerequisite of obtaining distance distributions. In this application pulse ELDOR competes with single-frequency techniques such as the ‘2+1’ experiment [9], double-quantum EPR [10], and the solid-echo based SIFTER experiment [11]. In the limit of excitation bandwidths much larger than the width of the EPR spectrum, single-frequency techniques are more sensitive than pulse ELDOR ones. However, even under such conditions, the sensitivity disadvantage of pulse ELDOR is not as large as one might think, as all single-frequency experiments have more complicated coherence transfer pathways and thus lose part of the magnetization due to branching. In practice, the limit of ideal excitation is rarely achieved with current technology for nitroxide spin labels. Depending on spectrometer and probe head, sensitivity of pulse ELDOR techniques is then similar to the one of single-frequency techniques or even better. With a 1 kW TWT amplifier and a Bruker dielectric or split-ring resonator, pulse ELDOR sensitivity is comparable to sensitivity of the ‘2+1’ and SIFTER experiments and, in our hands, significantly better than sensitivity of double quantum techniques. Pulse ELDOR is sufficiently sensitive for measurements on membrane proteins, even if distances are broadly distributed [12, 13].

In the limit of ideal excitation, single-frequency techniques avoid unwanted orientation selection that may occur in pulse ELDOR. Even if this limit is not achieved, the effect is less prominent with single-frequency techniques. Analysis of pulse

ELDOR data in the presence of unwanted orientation selection is discussed in the section on computing distance distributions. In contrast to single-frequency techniques, pulse ELDOR requires additional hardware, namely a second microwave source with adjustable frequency. A flexible setup is now commercially offered by Bruker with new spectrometers or as an upgrade.

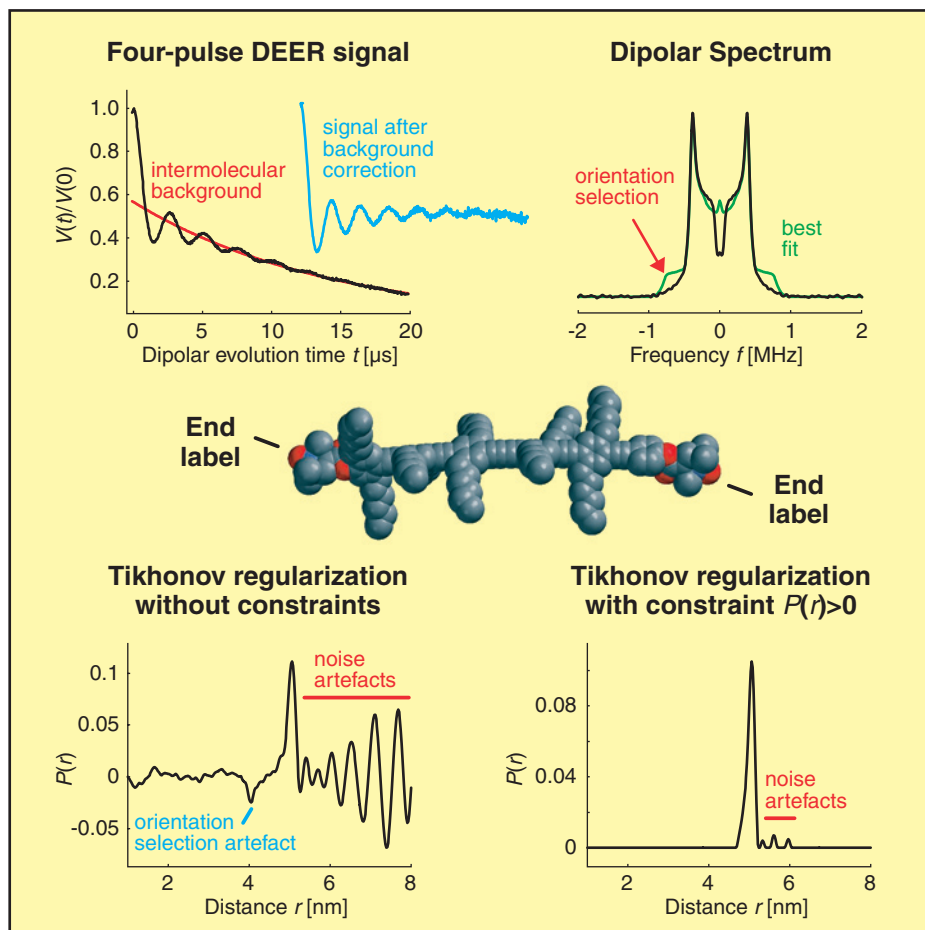
To be daring, I would state that most other advantages are on the side of pulse ELDOR techniques. Pulse ELDOR can be applied even if one of the paramagnetic centres has a spectrum much broader than the excitation bandwidth [14] and in favourable cases, even if this applies to all centres [15]. The relative(!) ease of setting up a pulse ELDOR experiment is an asset in teaching, routine application and when optimizing parameters for a weak sample. However, the main and, in our eyes, decisive advantages of pulse ELDOR is the availability of analytical expressions for the signal due to multi-spin systems rather than only spin pairs. Combined with the high fidelity of the data, i.e., their conformity with these analytical expressions, this allows for separation of contributions due to spins in the same molecule from those due to spins in other molecules. High fidelity is also essential for computation of distance *distributions* from primary time-domain data as this is an ill-posed mathematical problem. Small deviations of the input data from the analytical expressions can thus cause large distortions of the distance distribution.

Obtaining High-Fidelity Data

There are several types of problems that you may want to solve with a pulse ELDOR measurement. The most simple problem is getting a single number for the distance in an isolated spin pair with well-defined geometry. Most published experiments and ways of data analysis will give a reasonable value. The more difficult problems are to obtain information on the width or shape of the distance distribution, or the number of coupled spins. Of course, weak samples may also present additional difficulties. In all difficult cases, choice of experiment and hardware as well as proper setup decide on success or failure.

Improving Sensitivity

Pulse ELDOR sensitivity has two aspects, total amplitude of the echo and modulation depth. In the absence of phase noise, signal-to-noise ratio in the wanted signal is proportional to the product of amplitude



Q-band frequencies may lead to an increase in signal-to-noise ratio at given concentration. At even higher frequencies, concentration sensitivity deteriorates. If sample amount is limited, sensitivity is likely to be best at the minimum frequency where you can still fill the whole active region of the resonator.

Sensitivity and reproducibility are crucially affected by proper adjustment of the flip angle for the pump pulse. Our procedure is to apply an inversion recovery sequence with coinciding pump and observer frequencies at the maximum of the nitroxide spectrum. The inversion pulse is at the pump frequency and its power is adjusted for maximum inversion. Then the pump frequency and magnetic field remain unchanged while the observer frequency is increased by 65–70 MHz to position it at the low-field maximum. With this procedure and maximum overcoupling of the resonator, modulation depths are reproducible.

Dipolar Evolution Time

The most important parameter of a pulse ELDOR distance measurement is the maximum dipolar evolution time. If it is too short, it is difficult to separate the intermolecular background from the intramolecular contribution of interest. If it is too long, signal-to-noise ratio deteriorates strongly. For routine measurements of distances up to 5 nm, a dipolar evolution time of 2.5 μ s is recommended as the minimum, so that the second maximum of the dipolar oscillation is within the observation time. This is sufficient for a *rough* estimate of the width of the distribution, while assessing the *shape* requires observation of the dipolar oscillation until it has fully decayed. Particularly long times are thus required for narrow distributions (see Figure).

Dead Time Free Measurement

A short delay between pump and observer pulses leads to signal distortions when using a single-mode resonator. In the original three-pulse experiment [3, 4] the signal is then unreliable close to dipolar evolution time zero. This dead time precludes the measurement of short distances (<2.5 nm) if these are broadly distributed. Even more significantly, the amplitude of the echo at time zero cannot be measured. For determination of distance distributions this introduces an additional fit parameter, which is very unfortunate for an ill-posed problem. For that reason we routinely use four-pulse DEER, although the

and depth. With phase noise, increasing the total amplitude does not help. Similarly, the ratio of the electron-electron modulation to (unwanted) nuclear modulation depends on modulation depth, but not on total amplitude. Hence, if a compromise must be made, larger modulation depth is to be preferred to larger total amplitude.

Optimizing total amplitude is largely a matter of optimizing concentration and temperature. Pulse ELDOR measurements can be performed at concentrations of 50–200 μ M of spins. Using concentrations larger than 200 μ M is often counterproductive, as this leads to appreciable echo decay by instantaneous diffusion on the time scale of a few microseconds corresponding to the typical length of a pulse ELDOR sequence. With respect to temperature, a compromise has to be found between lengthening T_2 and keeping T_1 short enough for fast repetition. This compromise is dominated by the T_2 requirement, as the pulse sequence is usually longer than T_2 . Experiments should thus be performed at the maximum temperature where T_2 is still at its low-temperature maximum limited by proton spin diffusion. At X band, this temperature appears to be around 50 K

in most matrices. By deuteration of the matrix, T_2 can be lengthened, which increases sensitivity tremendously [13]. Working with variable instead of fixed interpulse delays in the observer sequence may also help [13].

Modulation depth is best for the largest excitation bandwidth where the two excitation bands are still separate. At X band, this parameter can be optimized by using a 3 mm X-band split-ring resonator from Bruker, which provides larger microwave fields at same incident power than a 4 mm resonator. As a further advantage, 50–60 μ l of sample are sufficient with the 3 mm resonator, while 150 μ l are required with a 4 mm one. The optimum parameters of the pump pulse are a flip angle of π at a length of 12 ns and irradiation at the global maximum of the nitroxide spectrum. The excitation band of such a pump pulse does not significantly overlap with the one of detection pulses of 32 ns length irradiated at the local maximum near the low-field edge. Any further shortening of pulses leads to overlap of excitation bands or requires less advantageous positioning in the spectrum.

Increasing EPR frequency typically leads to a decrease in modulation depth, but up to

additional refocusing pulse causes some loss of magnetization and may increase the amplitude of nuclear modulations.

Quadrature Detection and Phase Cycling

If detection phase is properly set the integrated echo signal has only a real part. Experience shows, however, that phase is not completely stable over the many hours that may be required to achieve good signal-to-noise for weak samples. Generally, data quality is better if the signal is acquired in quadrature and phase correction is performed afterwards.

In principle, pulse ELDOR does not require phase cycling. However, without phase cycling instrumental receiver offset is retained in the signal. Zero level is then unknown, which introduces an additional fit parameter. Offsets also preclude proper phase correction of a quadrature signal. Therefore, I strongly recommend $[(+x) - (-x)]$ cycling of the $\pi/2$ pulse in the observer sequence, which eliminates receiver offsets.

Nuclear Modulations

Proton modulations are not as prominent in pulse ELDOR as they are in single-frequency techniques, but they do occur. Their amplitude strongly depends on matrix, with matrices that form hydrogen bonds to nitroxides being more problematic than hydrocarbon solvents. Strong suppression of the modulations can be achieved by adding the signals of 8 four-pulse DEER experiment with values of the first interpulse delay that differ by increments of 8 ns. A pulse sequence and variable set for Bruker Elexsys spectrometers that incorporates this scheme together with phase cycling and includes the experiments required for setup is freely available at www.mpip-mainz.mpg.de/~jeschke/distance.html.

Data Analysis

Even if pulse ELDOR experiments are performed under the best possible conditions, primary data still deviate from theoretical expressions due to noise, residual nuclear modulations, and unwanted orientation selection. Stable mathematical algorithms are thus required to obtain reliable distance distributions. Our software package for Matlab, also freely available at www.mpip-mainz.mpg.de/~jeschke/distance.html offers Approximate Pake transformation [16], fitting by Hermite interpolation between sampling points [17], and Tikhonov regularization based on the program FTIKREG [18]. The latter two approaches constrain the distance distribution to positive values $P(r) > 0$. As is seen in the Figure, this constraint improves suppression of noise-related artefacts tremendously. Artefacts due to orientation selection are eliminated if they correspond to missing contributions of spin-spin vectors that are parallel to the magnetic field (suppressed shoulders of the Pake pattern as in the Figure). Enhancement of such orientations leads to positive artefacts at 0.79 times the actual distance, which are not suppressed.

Outlook

Pulse ELDOR on nitroxides at X-band frequencies is mature as a technique, while potential applications are far from exhausted. In contrast, few systematic work has been performed at other frequencies, with the notable exception of S band [19]. The small available amount of many otherwise suitable biological samples limits application, so that developments at higher frequencies would be useful. Another issue, where as yet only first steps [14, 15] have been taken, involves transition metal ions. Both issues are connected by the largely unsolved question of

defining general measurement protocols and data analysis techniques for situations with strong orientation selection. In general, there seems to be space for many more research groups to become involved in this field.

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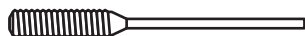
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The idea of such seminars was based on the understanding that presently ESR spectroscopy is in a “transition state” with respect to the exploration of new areas of applications of currently available modern ESR techniques and of potential novel developments of advanced ESR instrumentation. Such explorations require intensive discussions among experts in the field and scientists from various disciplines who are interested in potential applications. We selected our two cities as seminar sites since they are typical ESR places where such discussions are taking place and international cooperation projects are being realized and strongly encouraged also for future projects.

The topics covered during the 3-days seminar were:

- Construction and novel applications of high-field ESR spectrometers.
- Structure-dynamics-function relationships in proteins.
- Ion-pair structure and spin polarization in photoinduced electron-transfer systems.
- Electronic and molecular dynamics of excited high-spin state molecules.
- Development of ESR for studying new nanoscopic magnetic materials.

There were 60 participants of the seminar, 45 from Japan, 12 from Germany and 3 from third countries (Israel, Russia, USA). We were pleased that 13 graduate students were among the participants. All participants actively took part in the seminar either by scientific presentations or by serving as chairpersons. Interestingly, 50% of the participants from Germany were young post-doctoral or faculty scientists, the other 50% were professors. Hence, the German professors were nicely contrasted with the many young scientists from Japan. We strongly recommended that oral presentations should be

given by as many young people as possible. As a result, the seminar was not dominated by distinguished professors, but young people from both countries clearly played their parts in the discussions of both the oral and poster sessions. In the poster session, one of the graduate students, Mr. T. Miura from the University of Tsukuba, received the best-poster prize, comprising a document signed by the participants and a bottle of special rice wine, at the conference banquet. For the banquet, we went by bus to a Japanese style hotel, the Ichino-bo Ryokan, at a hot spring place, the Sakunami Onsen, and spent a very pleasant night with excellent Japanese food, wines and outdoor baths in a stimulating atmosphere.

We are convinced that by this 2nd Sendai-Berlin joint seminar sustaining scientific and

personal contacts between Japanese and German scientists have been promoted – mostly to the benefit of the many young scientists who probably will be responsible for the future of ESR in our two countries. They have been encouraged to play their parts in the international science competition by participating in international meetings and by joining research laboratories abroad.

In the final discussion there was a consensus of opinion that the traditional format of the joint Sendai-Berlin ESR seminars should be continued, but should be extended next time to a triangular Sendai-Berlin-Novosibirsk Joint Seminar. Dr. Sergei Dzuba from Novosibirsk, Russia, kindly offered to organize it in Novosibirsk in autumn 2006.

Seigo Yamauchi and Klaus Möbius
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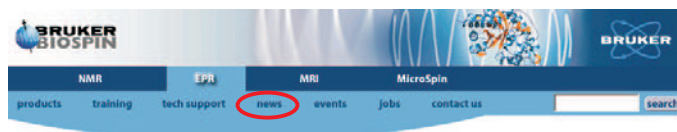
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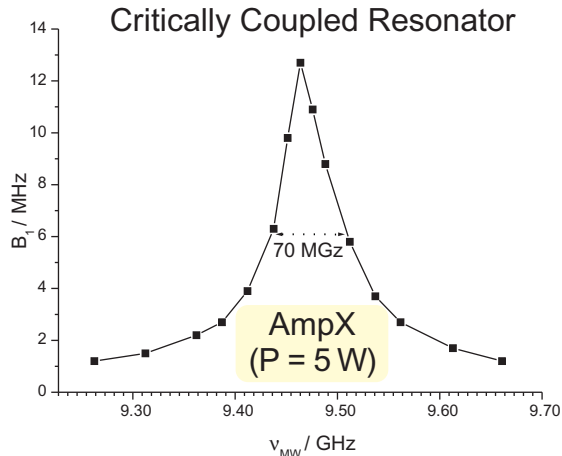
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EPR POWER OPTIONS

The X-Band 2 mm Split-Ring Probe

Meeting the requirements of both low and high power experiments

Critically Coupled Resonator



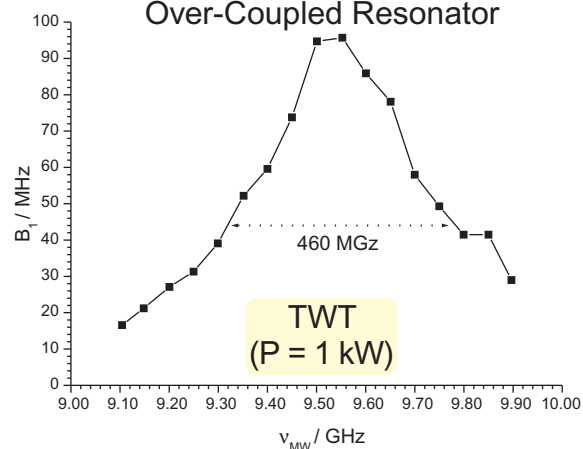
Experimentally Versatile

- Saturation Recovery EPR/ELDOR
- Distance Determination

Increase Pulse Sensitivity

- Short dead-time when critically coupled
- Maintains high sensitivity when over-coupled

Over-Coupled Resonator



The W-Band High Power Upgrade

Providing the power necessary for DEER measurements at W-band

Solid-State **Power** Amplification

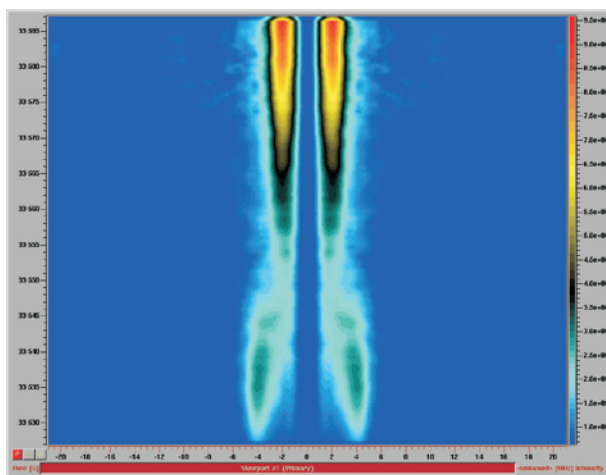
- Short pulses with large excitation bandwidths

Low Noise **Signal** Amplification

- Improved W-Band sensitivity for CW and Pulse detection

Full Software Control

- Safe and flexible performance



2D DEER (Field vs DEER)

Exploiting the sensitivity and orientation selection available at W-band offers extended opportunities in DEER measurements.

Selectively probing the ELDOR powder pattern further adds to the structural studies by providing the relative orientation of one spin proe to another.

