

epr news letter

2017
volume **27** number **1-2**



The Publication of the International
EPR (ESR) Society



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The official publication of the International EPR (ESR) Society is supported by the Society, by corporate and other donors, the Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, Kazan, Russian Federation, and the Swiss Federal Institute of Technology, Zürich, Switzerland.

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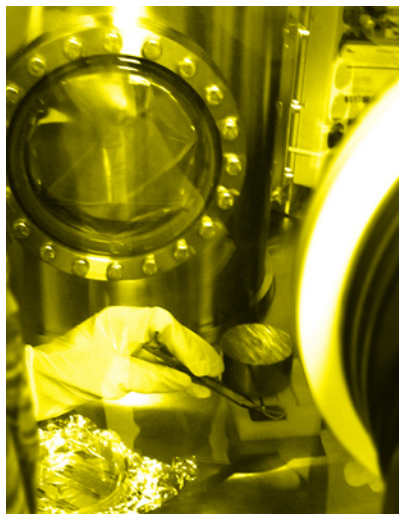
Please feel free to contact us with items (news, notices, technical notes, and comments) or ideas for the *EPR newsletter*.

The *EPR newsletter* is published quarterly by the International EPR (ESR) Society and is available in electronic and printed form to all members of the Society. The deadlines for submission of news for upcoming issues: Spring March, 15; Summer June, 15; Fall September, 15; Winter December, 15.

ISSN 1094-5571



PRINTING: LaPlume and Sons Printing, Inc.
One Farley Street, Lawrence MA 01843 USA
phone: (978) 683-1009, fax: (978) 683-4594



The cover picture illustrates aspects of research carried out by Christoph Boehme, recipient of the IES Silver Medal for Physics/Materials Science 2016. It shows graduate student Marzieh Kavand holding an EPR-resonator compatible thin-film device template in a glovebox facility during one of the last fabrication steps of a polymer semiconductor sample that is prepared for electrically detected magnetic resonance spectroscopy



ETH

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epr news letter

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Editorial

Dear colleagues,

Thanks a lot your patience that gave us time to prepare this double issue of the *EPR newsletter*. Hopefully, your patience is rewarded properly. As promised, you meet with Christoph Boehme, IES Silver Medal 2016 recipient, who tells us his history of (and with) pulsed EDMR and also introduces the University of Utah Spin Electronics Group (pp. 3, 4). You remember it was George Cutsail who shared the 2016 Ulderico Segre Prize with Claudia Tait (yes, you are right, it was Claudia Tait who secured a hat-trick of prestigious magnetic resonance awards in 2016, see 26/3, pp. 4, 5. Who is to repeat her success if ever?! Keep reading the *EPR newsletter* and we will let you know in due time). In this issue George's success story (pp. 5, 6) is accompanied with the success story of Shoko Okazaki, SEST Young Investigator Awardee 2016 and is nicely balanced by interviews with Zavoisky Awardees 2016, Michael Bowman (pp. 8, 9) and Arnold Raitsimring (p. 10).

Marina Brustolon, Dante Gatteschi and Angelo Alberti provided a realistic account of the birth, rise and establishment of EPR spectroscopy in Italy (pp. 13–24). You may be also interested to read John Pilbrow's article on EPR in Australia (18/2-3, pp. 24–30), which started a series of articles on EPR at Argonne National Laboratory (19/3, pp. 16–22), in Slovenia (20/1, pp. 12–14), in Israel (20/2-3, pp. 14–22), in Greece (21/1, pp. 8–12), and in Japan (24/3, pp. 7–9) written by experts in the field.

By now many of us know sad news about the recent passing away of Erwin Hahn. This is a great loss. The letter of Bernhard Blümich, President of the Groupement AMPERE (p. 12), expresses the feelings of the whole international magnetic resonance community. John Pilbrow reflects about what magnetic resonance, in general, and EPR in particular, owe to Erwin Hahn (pp. 25, 26). Charlie Slichter (Erwin and Charlie have been friends for 68 years!) tells about the early days of magnetic resonance in their lives and gives the details of Erwin's biography (pp. 26–29). Erwin was a true friend of the *EPR newsletter* and he generously contributed to our publication. I

enjoyed our e-mail correspondence. It was a delight indeed. Our readers can have a review of Erwin's contributions to the *EPR newsletter* which nicely illustrate the infinity of his fascinating personality and diverse talents (Erwin Hahn playing Rossini 14/3, p. 20; The Russell Varian Prize 2004 to Erwin L. Hahn 15/1, p. 3; Einstein Tidbits 15/1, p. 14; A Brief History of the Physics of Music 16/2-3, pp. 10–12; Felix Bloch Reminiscences 16/4, pp. 15, 16). Our grateful memory will keep Erwin Hahn alive for the years to come.

Laila Mosina

PS I guess you are looking for the success story of Sergey Veber, IES Young Investigator Awardee 2016?! Do not worry, his article reached us and we will publish it in the forthcoming issue along with the material of the ESR Group of the Royal Chemistry Society with regards to its 50th annual international meeting.



IES Business

IES GENERAL MEETING 2017

The General Meeting of the International EPR (ESR) Society will take place during the biennial International Society of Magnetic Resonance (ISMAR) meeting scheduled to

be held on July 23–28, 2017, in Quebec City, Canada. The 2017 Rocky Mountain Conference on EPR spectroscopy will be held jointly with this meeting. Some of IES Awards 2017 will be handed out during the meeting, accompanied by talks from the Awardees. All IES members and Conference Attendees are welcome to participate.

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The Bruker Prize 2017

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Bruker Thesis Prize 2017

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My brief history of (and with) pulsed EDMR



Christoph Boehme:

My first encounter with EPR spectroscopy took place in the course of a student laboratory experiment in 1996 when I was a physics undergraduate at Heidelberg. I had never heard about EPR and the setup associated with this strange experiment looked more than suspicious: A pair of Helmholtz coils, an RF coil in which a small plastic container could be inserted that was entirely filled with a strange powder – DPPH! Beyond this, there were lots and lots of electronics. What was all of this supposed to do? My lab partner and I diligently followed the list of assignments given to us. We recorded our data – the RF coil impedance – while we increased the magnetic field, step by step, through hand-adjusted settings of the Helmholtz-coil current. Surprisingly, when all was said and done, the hand-made plot of our data on mm-scale paper looked remarkably like a resonance peak. Our experiment had been successful, albeit, in all honesty, the usefulness of this stunt remained elusive to me at the time.

Fast forward four years to my return to Germany from a Fulbright exchange at North Carolina State University, where, with the exception of meeting my wife Kristie and getting married, I had spent most of my time training as a semiconductor physicist with a strong focus on silicon materials in the research group of

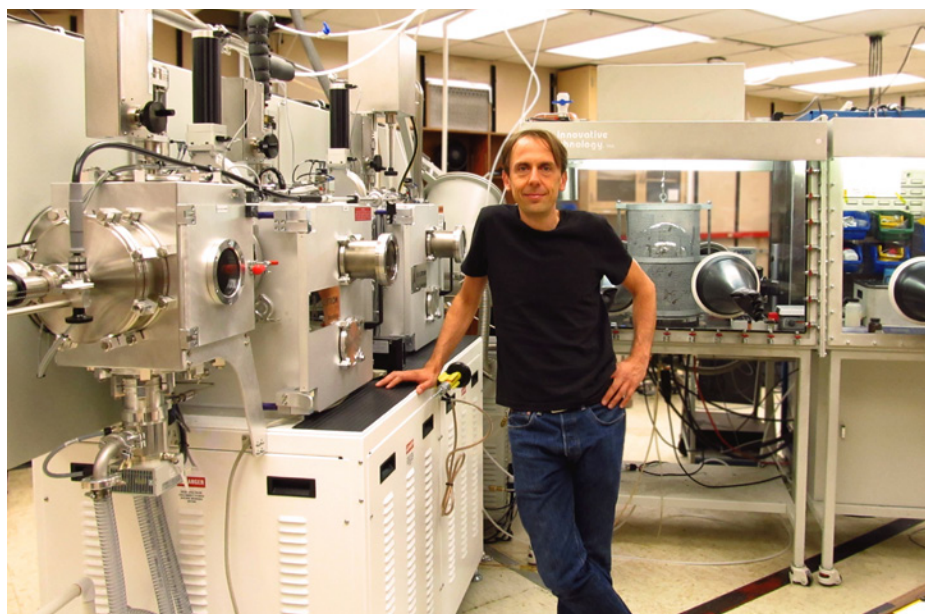
Gerald Lucovsky. Even though I had become a Ph.D. student at University of Marburg, being officially supervised by Walter Fuhs, who was also a silicon researcher, I spent most of my time in Klaus Lips' laboratory at Hahn-Meitner-Institut in Berlin. Klaus was my de-facto Ph.D. supervisor and my job in his lab was to understand the influence of point defects on charge carrier transitions – recombination, trapping, transport, etc. Most localized electron states in silicon are either paramagnetic or they can become paramagnetic under appropriate device conditions such as illumination or bias. Thus, the method of choice for their study is EPR. It finally dawned on me what this student lab experiment in Heidelberg had been all about and I started to dig deeper into the things that an EPR spectroscopist should know – spin Hamiltonians, density matrices, Liouville equations, continuous wave, pulsed (p) EPR and, eventually, EDMR, electrically detected magnetic resonance spectroscopy that is based on the measurement of electric currents in semiconductors which are controlled by spin-dependent electronic transitions.

EDMR is an extremely powerful technique when it comes to the study of what makes optoelectronic properties of a material what they are. It is highly sensitive, ultimately capable of detecting single spins, yet, it is also inherently blind to paramagnetic centers which do not affect the conductivity of a material. Given all this and the focus of my Ph.D. studies, I was, of course, in the business of EDMR rather than traditional EPR spectroscopy.

As I learned the intricacies of EDMR, while having at the same time a brand new Bruker Elexsys E580 Spectrometer at my dis-

posal, I soon realized that, while pEPR had been used widely for decades, pEDMR was all but nonexistent. In spite of the scientific and technological revolutions that pulsed magnetic resonance techniques had produced since Erwin Hahn's first spin echo experiments in the early 1950s, EDMR spectroscopy was still almost entirely carried out as an adiabatic field sweep experiment. It appeared that no one had thought about pEDMR. This, of course, was not true as I soon learned when I had a conversation with Michael Mehring at a conference in 2001. At least throughout the 1990s, several research groups had thought about pEDMR and a few studies reporting on transient EDMR current detection under amplitude modulated EPR microwave application existed. Unfortunately though, most EDMR signals occur in material with long dielectric relaxation times, which puts fundamental time resolution limits on the real-time detection of coherent spin-motion effects. In essence, most semiconductors will swallow transient current signatures caused by spin coherence before these can reach the sample contacts.

It was this problem that would eventually lead Klaus Lips and me to the realization that pEDMR experiments had to be carried out in a similar way as some of the early pulsed optically detected magnetic resonance (pODMR) experiments in the late 1970s: Instead of measuring coherently controlled spin-dependent electronic rates transiently, spin-ensemble states can be measured after an applied pulse sequence. This approach is similar to optical pump-probe spectroscopy: At the moment when a resonantly driven coherent



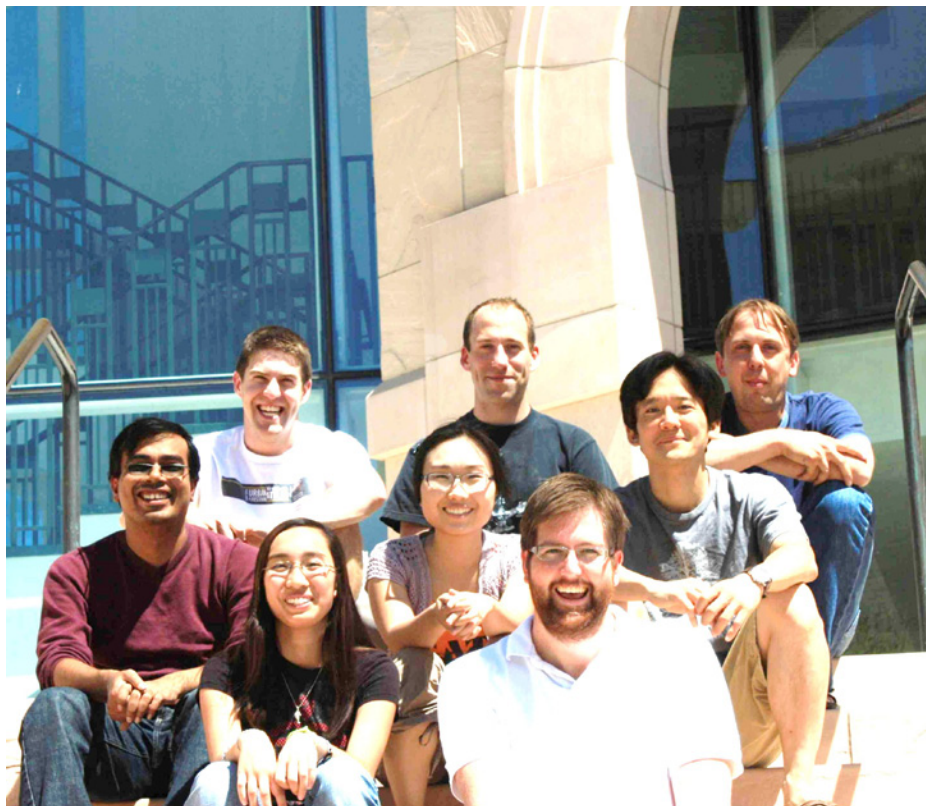


Photo of the University of Utah Spin Electronics Group taken in 2009, showing from left to right: Kapil Ambal, David Waters, Janvida Rou, Seo Young Paik, William Baker, Dane McCamey, Sang-Yun Lee, Christoph Boehme.

spin propagation ends, a time-integration of the transient current change is made on whatever time scale the studied system responds (coherent or not). This integral, revealing a charge, will then represent a projection of the spin ensemble state at the end of the coher-

ently driven spin excitation sequence onto an observable governed by the particular nature of the observed spin-dependent process.

The realization that pEDMR had to be a pump/probe experiment, rather than a transient current measurement, was the starting

point for the development of pEDMR spectroscopy. In contrast to pODMR, pEDMR requires different technological prerequisites (current detectors, sample-holders and -contact systems, resonators, etc.) and compared to pEPR, it also requires the adjustment of pulse sequences and phase cycling schemes. It is these challenges, as well as the application of pEDMR, that my research program has been all about since I moved to Utah in 2006.

More than 15 years after the work on pEDMR began, this technique has been demonstrated to be applicable to the investigation of a broad variety of different spin-dependent electronic processes, including spin-selection rules, bolometric effects, and recently, the inverse spin-Hall effect. These results have revealed insights into the physical behavior of materials used for sensors, lighting, photovoltaics and other electronic applications.

Credit for all these exciting developments must be given where it is due – for the early work of pEDMR, to my Ph.D. supervisor Klaus Lips. For the work since then, also to many people who have visited and worked in my research group in Utah and who have made great contributions on methods and instrumentation development, including Chad Miller, Dane McCamey, David Waters, Douglas Baird, Gajadhar Joshi, Hans Malissa, Hiroki Morishita, Kapildeb Ambal, Kipp van Schooten, Mandefro Terferi, Marzieh Kavand, Sang-Yun Lee, Seo-Young Paik, Shirin Jamali, and Will Baker. Equally, there have, of course, been many colleagues and collaborators, both theorists and experimentalists, whose wonderful work has advanced this field, including Aharon Blank, Alexander Schnegg, Clayton Williams, Felix Hoehne, Gavin Morley, Hans Huebl, Jan Behrends, Johan van Tol, John Lupton, Kohei Itoh, Louis-Claude Brunel, Mark Limes, Martin Brandt, Martin Stutzmann, Mikhail Raikh, Pat Lenahan, Rachel Glenn, Sergei Baranovskii, Valy Vardeny, and Wolfgang Harneit.

I am humbled to have received the 2016 Silver Medal of the International EPR Society. The international EPR community is an incredibly diverse group of outstanding people from a broad range of both scientific as well as geographic backgrounds, producing extraordinarily impressive work.



Photo of the University of Utah Spin Electronics Group taken in 2014, showing from left to right: Christoph Boehme, Hans Malissa, Gajadhar Joshi, Kapil Ambal, Kipp van Schooten, Shirin Jamali, Richards Miller, Marzieh Kavand, Doug Baird, Rachel Baarda, Mandefro Terferi.



2016 Ulderico Segre Prize



George Cutsail:

I am honored to be awarded the 2016 Segre Prize for excellent PhD work in the field of advanced EPR Spectroscopy from the Gruppo Italiano di Risonanza di Spin Elettronico. I thank the Segre family for their generous support of this prize in memory of Prof. Ulderico Segre. For this award, I am grateful to my doctoral advisor, Prof. Brian Hoffman (Northwestern University, Evanston, IL USA) for his guidance and support throughout my graduate education and as a current colleague and mentor. This award also afforded me the privilege to present and share a portion of my PhD with the community during the August 2016 meeting of the European Federation of EPR.

Throughout my graduate career, a broad range of techniques were employed to interrogate an equally extensive range of (bio)inorganic research interests. One overarching theme of my graduate research was the catalytic reduction of N_2 to NH_3 by either the iron-sulfur-molybdenum nitrogenase enzyme or biomimetic chemistry. The reduction of dinitrogen had been proposed to proceed down either distal or alternating hydrogenation pathways, yielding unique N_xH_y intermediates. While several catalytic intermediates of some early transition metals have been isolated and characterized, intermediates resultant of the direct protonation of $Fe-N_2$ species had remained very elusive. In 2013, Prof. Jonas Peters and coworkers reported the first biomimetic iron-based catalysis for dinitrogen reduction [1], expanding the biomimetic models for nitrogenase and further converging the model chemistry with protein active site. Working with the Peters group, I characterized the protonation of the $S = 1/2$ $Fe(I)$ $[(TPB)Fe(N_2)]$ $[Na(12-crown-4)]$ to form a new $S = 1/2$ $Fe(I)$ species. By employing Electron Nuclear Double Resonance Spectroscopy (ENDOR), in particular 1H ENDOR, a structural model of a doubly protonated $[(TPB)FeN-NH_2]^+$ product was built [2]. Based on the hyperfine coupling magnitudes and tensor orientations, the distal nitrogen of the end-on bound N_2 was determined to be doubly protonated forming a hydrazido(2-) complex. The 1H hyperfine tensor orientations reveal that the $Fe-N(NH_2)$ unit is slightly bent at a bond angle of approximately 151° . Additionally, $^{14}/^{15}N$ ENDOR and ^{14}N (X- and Q-band) ESEEM were employed to characterize the N_2 and hydrazido ligands. Of particular interest, the spin density on the trans-axial boron ligand decreases as observed by a reduction of the isotropic ^{11}B hyperfine coupling, also measured by ENDOR spectroscopy.

This study well represents the ability of the ENDOR and other advanced EPR techniques to structurally characterize catalytic intermediates that are not amenable to crystallography. This study conclusively supports a distal mechanism in early catalytic steps of nitrogen fixation, however an alternating mechanism is favored for the later stages. Therefore we proposed the possibility of the hybrid distal-alternating hydrogenation mechanism of N_2 . Ultimately, this study linked the chemistry of iron-nitrogen multiple bonds to an N_2 fixation cycle.

Prior to the above study, I characterized the electronic and bonding structure of a low-coordinate, $S = 1/2$, $Fe(V)$ nitride complex (Prof. Jeremy Smith, Indiana University, Bloomington, IN, USA) [3], a relevant model for the late stages of nitrogen fixation along a distal pathway. Of particular interest is the unique electronic structure of this trigonal complex. By EPR spectroscopy, a pseudo-Jahn-Teller (PJT) distortion is observed, analyzed formally and complimented by quantum mechanical computations. The doubly degenerate 2E ground state of the trigonally symmetric $Fe(V)$ nitride not only stabilizes the ground e doublet by a PJT distortion, but the distortion from idealized D_{3h} to C_{3v} symmetry now incorporates mixing of the two e orbital doublets. The extent of the 'iron doming' from the ligand plane increases the $e-e$ mixing.

$^{14}/^{15}N$ ENDOR yielded high-precision hyperfine and quadrupole tensors for the nitride. The subsequent nitride hyperfine tensor decomposition reveals that at a first approximation, the nitride center has a filled 2s-orbital and essentially unhybridized 2p-orbitals. What is particularly unique for the $Fe(V)$ nitride is the lack of any resolvable ^{14}N quadrupole splitting of the nitride, contrasting with typically observed nitride quadrupole splittings of ~ 2.2 MHz. The lack of quadrupole splitting

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Awards

for nitride imposes a unique scenario: it is a spherically bound nitride!

In addition to my various studies of catalytic intermediates [2] and other iron-nitrogenous biomimetic complexes [3], I would also like to highlight my extensive collaboration with Prof. Amy Rosenzweig (Northwestern University) to determine the oxidation-state and coordination environment of the copper-dependent trans-membrane particulate methane monooxygenase (pMMO). Utilizing a dicopper active site, pMMO catalyzes the conversion of methane to methanol, a key reaction of fuel and energy research. The exact origin of the type-2 copper(II) EPR signal of pMMO had eluded researchers for many years. Employing a soluble recombinant mimic of the active domain of pMMO along with the native protein, we quantitatively determined the oxidation states of the monocopper and dicopper centers [4]. Through EPR, ENDOR and ESEEM spectroscopy, the coordination of

the dicopper was fully characterized and modeled as a scrambled trapped valent copper(I)-copper(II) center, where the positions of the copper(II) has equivalent probability between a bis-histidine and a histidine/N-terminus amino coordination environment with no aquo (H_xO) ligand. Through the combined biochemical approaches, analytical methodology and advanced EPR techniques, the origin and further characterization of the Cu(II) EPR signal of pMMO is now fully described.

Currently, I am an Alexander von Humboldt Postdoctoral Fellow at the Max Planck Institute for Chemical Energy Conversion (Mülheim an der Ruhr, Germany), working with Prof. Serena DeBeer where I am continuing research in bioinorganic chemistry utilizing many X-ray spectroscopic techniques. In the future, I plan to form a bioinorganic research program utilizing both EPR and X-ray spectroscopy to yield insight into the coordina-

tion environment, electronic structure and reactivity of metalloactive sites.

I am thankful to my advisor, colleagues, and many collaborators for their engaging discussions, sharing of knowledge, and their interest in my work. I contribute much of my success and this award to their support.

I may be contacted at george.cutsail@cec.mpg.de for any inquiries.

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Bench-Top ESR Spectrometer MS5000

High Performance Electron Paramagnetic Resonance Spectrometer

Technical data

Sensitivity: 8×10^9 spins/0.1 mT
Magnetic field range: 5 – 600 mT

Properties

- Cost efficient
- Compact size
- High sensitivity
- Outstanding magnetic field stability
- Wide range of accessories and glassware



Wide field of applications

- Life sciences
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- Biophysical features
- Environmental toxicology
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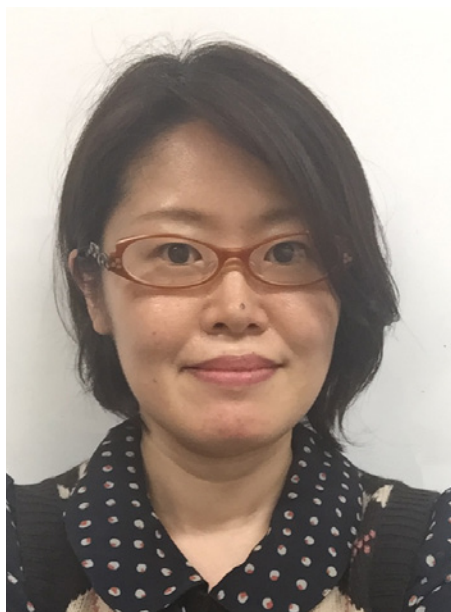
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SEST Young Investigator Award 2016



Shoko Okazaki:

I am honored that the Society of Electron Spin Science and Technology (SEST) selected my study, entitled “Basic study for the application of electron spin resonance to the medical field”, for the SEST Young Investigator Award. I would like to thank the committees of SEST for this award and the International ESR society for the opportunity to present my study here. I would also like to thank Prof. Keizo Takeshita at Sojo University and the other collaborators for their kind support.

The oxidative stresses caused by reactive oxygen species (ROS), such as superoxide anion radical and hydroxyl radical, are regarded as important factors in many diseases. Our group was interested in how to measure the oxidative stress in live animals by the *in vivo* ESR technique. The *in vivo* ESR technique is useful for the measurement of the oxidative stress in live animals due to the good response of the ESR signal of cyclic nitroxyl radicals to various redox-related species, such as ROS and antioxidants [1]. In this technique, the oxidative stress is evaluated by the ROS-dependent decay of the signal of the nitroxyl probes right after they are injected. However, the ESR signal of nitroxyl probes decays rapidly even in healthy mice, because they are enzymatically and non-enzymatically reduced to the corresponding hydroxylamines

in the body. This biological reduction of the probes shortens the half-lives of the nitroxyl probes in the body, and it is hard to measure the ROS-dependent decay of the probe signal. We formulated two approaches to resolve this problem. One was the development of the reductase-resistant nitroxyl probes [1], and the other was the measurement of redox status by *in vivo* ESR using an acyl-protected hydroxylamine probe [2].

We designed two new nitroxyl probes, 4-hydroxy and 4-oxopiperidine-*N*-oxyls having 4'-hydroxyspirocyclohexyl groups at the 2- and 6-positions of the piperidine ring (hydroxy-DICPO and oxo-DICPO, respectively) to suppress enzymatic reduction of the nitroxyl group. Existing nitroxyl probes, such as 4-hydroxy- and 4-oxo-2, 2, 6, 6-tetramethylpiperidine-*N*-oxyl (hydroxy-TEMPO and oxo-TEMPO, respectively), are reduced by the reductases in liver and ascorbic acid. We therefore examined the resistance of DICPO-derivatives to such reduction. The decay of the ESR signal of these probes in mouse liver homogenates was significantly suppressed in comparison with those of TEMPO-derivatives, while there was no difference in reactivity with ascorbic acid between the DICPO- and TEMPO-derivatives. The $E_{1/2}$ values of anion/nitroxyl radical couples of the DICPO- and TEMPO-derivatives were estimated to be around -0.1 V vs. Ag/AgCl, regardless of type of probe. These findings indicate resistance of the DICPO-derivatives to enzymatic reduction. This may result from decreased accessibility of nitroxyl moiety of DICPO-derivatives to the active sites of reductases. In the reactivity with ROS, both hydroxy- and oxo-DICPO lost their EPR signals by the reaction with hydroxyl radicals, although only the signal of hydroxy-DICPO decreased by the reaction with superoxide anion radical in the presence of cysteine. This feature is similar to that observed for hydroxy- and oxo-TEMPO. These results suggest that the introduction of bulky groups like the spirocyclohexyl groups next to the nitroxyl group is effective for inhibiting the enzymatic reduction without changing the characteristics of the reaction with oxygen radicals.

Next, we attempted to use 1-acetoxy-3-carbamoyl-2,2,5,5-tetramethylpyrrolidine (ACP) as a precursor of the nitroxyl probe for the measurement of oxidative stress in sepsis model mice, as another approach to resolving this problem. ACP is quickly hydrolyzed to yield hydroxylamine and is distributed throughout the body within 10 min after the intravenous injection of ACP to a mouse. Hydroxylamines

are oxidized by oxidants, such as superoxide anion radical and peroxynitrite, to their corresponding nitroxyl radicals, while nitroxyl radicals are reduced to the hydroxylamine by biological reduction systems. This means that redox reaction of the probes reflects the *in vivo* redox balance. Therefore, after an injection of ACP in a mouse, the oxidative stress may cause an increase of the ESR signal. The *in vivo* ESR signal increased up to 7–8 min after the ACP injection and then started to decrease. Decay of the *in vivo* signal for sepsis model mice was significantly slower than that for healthy mice, whereas there was no significant difference in the decay rate of the total amount of redox probes (hydroxylamine + nitroxyl radical) in the blood and liver between these groups. ESR imaging revealed that the appearance and decay of the ESR signal occurred in the chest and upper abdomen of healthy mice, but the decay was very slow in sepsis model mice. These results indicate that sepsis model mice are under oxidative stress, and this stress is induced mainly in the lungs and liver. Suppression of the decay in sepsis model mice was cancelled by the administration of either a combination of pegylated superoxide dismutase and catalase, or an inhibitor of nitric oxide synthase. In sepsis model mice, the concentration of plasma TNF- α , an indicator of macrophage activity, was markedly higher than that in healthy mice. The administration of gadolinium chloride, an inhibitor of macrophages, also cancelled suppression of the decay in sepsis model mice. These reagents had no effect on the amount of total probes. Our results indicate that ROS, such as superoxide and peroxynitrite, related to macrophages are mainly involved in the oxidative stress.

We also analyzed the pharmacokinetics of nitroxyl probes [3]. The urinary excretion for the hydrophilic probes was one of the important factors in signal decay. This makes it difficult to apply the *in vivo* ESR technique to diseases with a decreased renal function. I will address this problem in future to further improve the *in vivo* ESR technique.

1. Okazaki, S.; Mannan, MD A.; Sawai, K.; Masumizu, T.; Miura, Y.; Takeshita, K. *Free Radic. Res.* 2007, **41**, 1069–1077.
2. Okazaki, S.; Tachibana, Y.; Koga-Ogawa, Y.; Takeshita, K. *Free Radic. Biol. Med.* 2014, **68**, 72–79.
3. Takeshita, K.; Okazaki, S.; Hirose, Y. *Free Radic. Biol. Med.* 2016, **97**, 263–273.

Interview with Professor Michael Bowman on the Occasion of His Zavoisky Award 2016



EPR newsletter: *Dear Professor Bowman, on behalf of the readers of the EPR newsletter we congratulate you on your Zavoisky Award 2016. We are most appreciative that you agreed to answer the questions of this interview. Why did you start towards your career in science?*

Thank you, it really is an honor receiving the Zavoisky Award because many of the other recipients of the award wrote the books and papers that I learned magnetic resonance from and that I still refer to today.

I have always been fascinated by science and attracted to it. My father was a clinical chemist and my mother was a bacteriologist and I was fascinated as a youngster with the hospital labs they worked in, the instruments they used, the chemicals and glassware. I got to look through microscopes and see things that were otherwise invisible. As I grew older, I understood that they used their scientific training to discover what diseases each patient had and how to treat them. One attraction of science for me is working with something new and unknown, pushing back the limits, at least of my own knowledge.

In high school and college I found that the intersection of chemistry, physics, and biophysics to be extremely interesting to me. The concepts and principles from each of those areas could be applied in the other areas to gain insights into how and why nature behaves the way it

does. The rest of my career has been guided by these early interests.

Who introduced you into magnetic resonance?

I did my first EPR work as an undergraduate with John Zimbrick who had just joined the faculty at the University of Kansas. We used solvated electrons in frozen glassy solvents to cryogenically reduce the bases, nucleotides and sugars of DNA. The initial products we saw were generally radical anions. But optical excitation or thermal annealing from 77 K to 120–150 K readily produced new sets of products by additional chemical reactions even at those low temperatures.

For graduate school, I went to work with Larry Kevan at Wayne State University. Because I already had some experience in EPR, Larry started me building a simple saturation-recovery EPR spectrometer to measure T_1 of some of the free radicals his group were studying at low temperatures: trapped electrons, hydrogen atoms, and other free radicals in irradiated frozen glassy solvents. I started with components: klystron, power supply, Pound stabilizer, waveguide, Varian cavity, crystal detector, oscilloscope, boxcar integrator and a magnet. After two months I measured a very nice saturation-recovery curve from radicals in irradiated plastic at room temperature. We realized that I had to use much less observing power for radicals at cryogenic temperature and I embarked on rebuilding the spectrometer and didn't see another saturation-recovery signal for two years. I went through several iterations before coming up with a single-klystron, superheterodyne bridge with 60 MHz intermediate frequency and coherent IF demodulation that worked from 6 K to room temperature.

While completing that spectrometer, I also did other work, primarily on trapped electrons, which were a major focus of the Kevan lab. These included ENDOR measurements with Barney Bales and Bob Schwartz; spin echo and ESEEM measurements with Ian Brown, P. A. Narayana, Yuri Tsvetkov, and Valery Yudanov. But Larry had a very large group and applied a lot of other techniques to the study of the structure and properties of trapped electrons, including: quantum chemical calculations; optical spectroscopy; transport properties; ELDOR; and kinetics. Group meetings were often intense and resembled the fable of the

blind men and the elephant. Each of us had our own measurements that we had great confidence in. But the results often seemed unrelated to what others in the group found using different techniques. We all had to go to great depths to understand exactly what each of the different experimental methods were actually telling us about the trapped electron. One of the important lessons I learned then was that the more you know about the fundamentals of the techniques you use, such as EPR, the more you can learn about the system you are studying. It is not just that you can interpret the data better, it is also that you will take all the needed data.

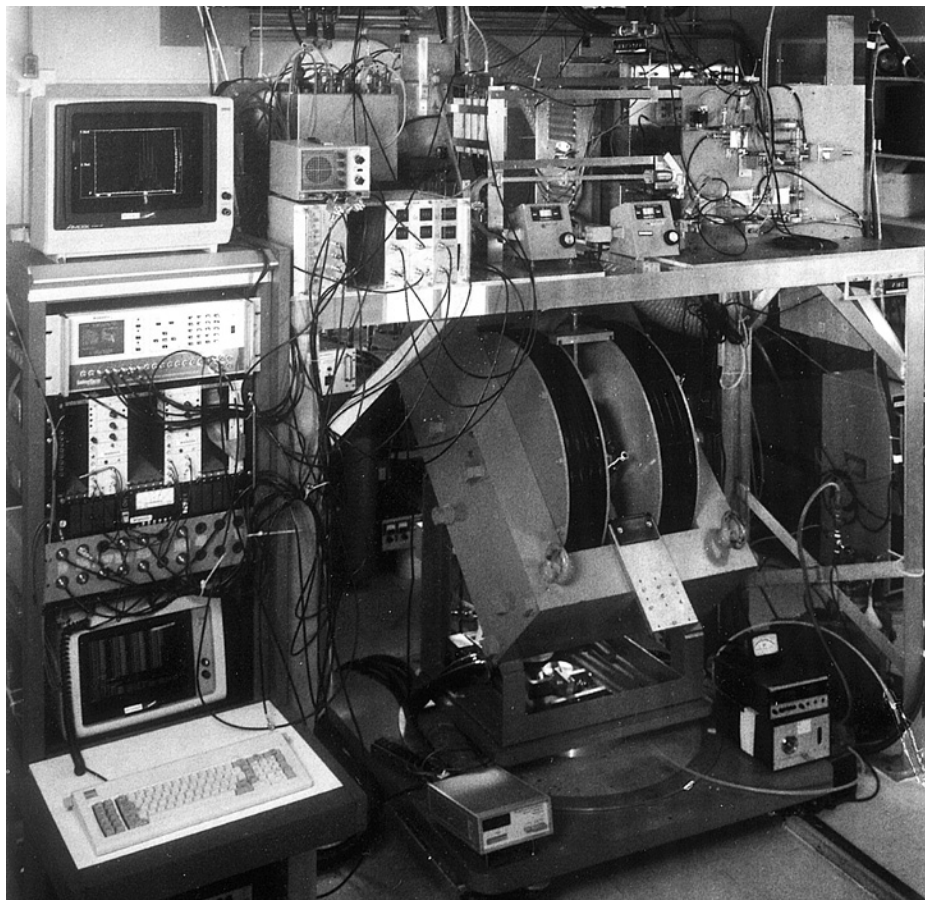
I learned a lot about EPR during that time because we were always trying to apply the latest developments in EPR. Techniques and theory for ENDOR, ELDOR, relaxation in liquids, and saturation transfer were being developed by Hyde, Freed, Möbius and Larry Dalton. Electron spin echoes, phase relaxation, and ESEEM were being developed and applied to chemical systems by Tsvetkov, Salikhov, Mims and Brown. What I learned as a graduate student about this broad range of EPR approaches was very useful when I went to Jim Norris' lab as a postdoc and was plunged into new and equally exciting EPR problems involving electron transfer, spin chemistry, and chemical exchange.

What is the driving motivation for you in your research?

I get the most satisfaction from figuring out how to make a new measurement of a property that has no established method. The feeling reminds me of looking through a microscope as a youngster at something for the first time. Usually, new measurement are made possible by recognizing that there is a connection or relation between two facts or two properties. It is as if two of the blind men in the fable were able to integrate what they each know about the elephant.

What is your message to the younger generation of magnetic resonance researchers?

Magnetic resonance methods are used in many different areas of science and technology research. Some people view the magnetic resonance measurement as pushing a button to get a spectrum that goes into a figure and a few numbers that are put into a table. The



A completely computer controlled FT-EPR spectrometer that Prof. Bowman helped design and build in the early 1980s at Argonne National Lab. It was used for spin echo and FT-EPR studies of stable radicals, excited states, and free radical reactions in solids and liquids.

measurement contains much more information than that, some of it may be very important and useful and relevant, but often it is not recognized. It takes someone who understands magnetic resonance to know what information is available. But someone who understands the research must select the really valuable information. So as a researcher, you become more valuable as you understand more about the fundamentals of the tools and methods, like magnetic resonance, that you use; and the

more you understand the research problem and what information is critical for it.

The more engaged you are and the more you understand about the research and methods being used, then the more you are able to contribute and the more valuable your efforts are. It is possible to focus on a specific facet of magnetic resonance and study it in depth so that you become a real expert about the measurements and methods you use in a research project.

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Interview with Professor Arnold Raitsimring on the Occasion of His Zavoisky Award 2016



EPR newsletter: *Dear Professor Raitsimring, on behalf of the readers of the EPR newsletter we congratulate you on your Zavoisky Award 2016. We are most appreciative that you agreed to answer the questions of this interview. Why did you start towards your career in science?*

Perhaps, because I had quite naïve ideas about science. My top 'rule of thumb' is to work with people (or at least give it a good try) who have a much higher level of intelligence than myself. Such an interaction can be exhausting, humbling, and even annoying but at the same time, it is very stimulating and exciting and more often than not it results in

nontrivial and very efficient solutions to complicated problems, saving a lot of precious time and resources. In my rather long scientific career, I was fortunate enough to work closely with at least a dozen of such highly intelligent colleagues and three of my exceedingly bright former students: V. Tregub, V. Kurshev and L. Rapatskii, all leaving an indelible impression on my scientific life.

Who introduced you into magnetic resonance?

Yu. D. Tsvetkov was my first mentor in EPR. It was a "right place, right time" situation back in 1965. As a student of Novosibirsk State University, I was sent on loan by now academician V. V. Boldyrev to now, academician Yu. D. Tsvetkov to explore the application of EPR for investigating the radiation damage of some nitrates. In the same lab, A. Semenov, V. Khmelinsky and M. Shirov had just finished the construction of a pulsed EPR spectrometer that was not yet being applied to any chemical or physical research, so I was tasked with putting it to use. It just happens that I never stopped.

There are a lot of first-rate scientists that are and have been involved in EPR... just look at the Zavoisky awardee list. Some of them I have been acquainted with personally, and I've collaborated with some of the others. Of course, I have learned from and was influenced by many of them. As I deliberate this question, however, I realize that the greatest influence came from Bill Mims, who had a universal approach in solving scientific problems, and whom I've tried to emulate in my research *modus operandi* during the last 25 years.

What part of your research is most dear to your heart and why?

I think it was solving the problem of how dipolar interactions in magnetically diluted solids work in pulsed, and in part, CW EPR. The results of this research set a foundation for a variety of modern pulsed dipolar spectroscopies (PDSs) and for understanding fundamental problems of EPR such as spin and spectral diffusion.

I can say that I certainly had some interesting life experiences outside of EPR. I did some exciting research in photoelectron injection and in fundamental radiation chemistry. It was fun to work with academician Yu. Molin and Dr. O. Anisimov on problems of positronium formation in condensed matter. It was very gratifying to be one of the first researchers in the USSR to use a newly made synchrotron radiation source that had been installed in one of colliders at the Institute of Nuclear Physics. I also hope that I helped to save a few lives applying my research on slow electron thermalization to the surface modification of medical catheters.

What is the driving motivation for you in your research?

Pure curiosity. It was just interesting to understand how things work.

What is your message to the younger generation of the magnetic resonance researchers?

You know, any advice or message to the younger generation is just waste of time. They are much smarter than we are now and we were in the past.

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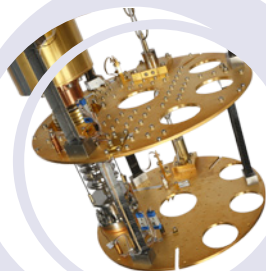
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EPR in Italy

**Marina Brustolon,
Dante Gatteschi,
Angelo Alberti**

When we were asked to write a history of EPR in Italy, we felt it was a simple job. We were wrong, and it turned out it was not so easy. First, because we found out that the number of EPR groups that had intensively operated in the last half century in Italy spanning a wide range of applications was larger than expected, and secondly considering that the three authors are no longer as efficient as they used to be.

Anyway, we have managed to produce something that we hope can be useful: indeed, we believe that although not exhaustive the following provides a realistic account of the birth, rise and establishment of EPR spectroscopy in Italy.

We asked the senior scientists of the main EPR groups and laboratories in Italy to write a history on the use and development of paramagnetic resonance spectroscopy in their Universities and research centers. Our editing of their texts produced the following cards.

We have also collected as much information as possible from the web and the literature on the significant contributions given by other groups, where the use of EPR has been relevant. We acknowledge that it would have been impossible to include absolutely everyone who had ever undertaken EPR research in Italy and we apologize for any omission. A list of many of these groups is given at the end.

We start with detailed accounts of the history of EPR in Italy at a number of academic and research institutions.

EPR in Ancona (Pierluigi Stipa and Lucedio Greci)

EPR at the Università Politecnica delle Marche in Ancona started in 1970 when P. Bruni moved from Bologna (Martino Colonna's organic chemistry group) to the newborn Engineering Faculty in Ancona. In 1986 the group was joined by L. Greci and his youngest student P. Stipa, also from Colonna's group. This team made considerable use of EPR

spectroscopy (a Varian E4 spectrometer with digital acquisition) for the characterization of new radical species and the detection of transient radicals in electron transfer and in photochemical reactions.

Neutral radicals, namely nitroxides, had a central role in the research activity of the group. Thus many different nitroxides, e.g. indolinonic, quinolinic, benzothiazolic, fenanthridinic etc., were synthesized. These found several applications, e.g. as antioxidants in biological systems and polymers. Single crystals of pure indolinonic nitroxides or mixed with isomorphs were also obtained for ENDOR characterization (collaboration with the group in Padova) and for a study with polarized neutron diffraction (in collaboration with the Physics Dept in Ancona). Several collaborations with other research groups were consolidated or established, the most relevant being those with the University and National Research Council groups in Bologna, the Universities of Pavia and Padova, the Université de Provence in Marseille (France), Lund University (Sweden) and Duisburg University (Germany). From 1991, following Stipa's postdoctoral experience in Marseille (in Tordo's group), the interest of the group shifted towards EPR Spin Trapping techniques and the synthesis of heterocyclic nitrones leading to collaborations with Ciba Geigy and ENICHEM on the use of additives for polymers such as HALS (Hindered Amines Light Stabilizers) and alkoxyamines. In 2000, the group acquired a Bruker EMX spectrometer and a photochemical apparatus. Further collaborations with the research group in Marseille and with Elf-ATOCHEM (now ARKEMA) led to some international patents in the field of Nitroxide Mediated Polymerization methods. Presently, the study of nitrones from the amidinoquinoxaline series as spin trapping agents and as possible

antioxidant, in collaboration with the Faculty of Pharmacy of the Buenos Aires University (Argentina) is in progress.

This research activity has produced to date more than 200 papers in international journals.

EPR in Bologna (Gian Franco Pedulli, Angelo Alberti and Marco Lucarini)

The history of EPR in Bologna began towards the end of the 1950's following the far-sighted scientific views of the Professor of Organic Chemistry, Angelo Mangini. In the mid 1960's G. F. Pedulli participated in the NATO School on EPR spectroscopy held at the University of Coimbra (Portugal), and later on, the Institute of Organic Chemistry of Bologna purchased a Varian V-4502 EPR spectrometer. The first paper on the EPR spectra of Isatogen radicals was published by Pedulli (in collaboration with A. Mangini, G. Maccagnani and L. Lunazzi) in 1966 in *Tetrahedron Letters*. He then spent a one-and-a-half-year period with G. Luckhurst and his group in Southampton (UK). This extremely fruitful period led to the publication of many papers dealing with the EPR spectra of biradicals and triplet states as well as some monoradicals. After his return to Italy, Pedulli continued to work on these systems for some time.

In 1973 A. Alberti, joined the Bologna group from the CNR-ICoCEA institute in Ozzano Emilia, a small town on the outskirts of Bologna, using a JEOL JES-ME1X spectrometer. From November 1976 to October 1977 Alberti continued his EPR training with Andrew Hudson at the University of Sussex in Brighton (UK) working on radicals from organometallic derivatives. This was the birth of a long term collaboration that lasted until Hudson's retirement in 2000.



In 1977 the ICoCEA lab was totally destroyed by a fire and had to be rebuilt. For two years Alberti was hosted by Pedulli at the University of Bologna, and his return to ICoCEA coincided with the purchase of a new Bruker ER200D spectrometer. During that time, Alberti was joined at CNR by M. Guerra, who took care of the theoretical side of the EPR research. In 1993, following the transfer of ICoCEA to Bologna and its merging with the FRAE Institute to create ISOF, the ER200D was repeatedly upgraded with the implementation of photolytic, electrochemical and time resolved facilities.

In 1976 Pedulli moved to a Chair in Organic Chemistry at the University of Cagliari. When after ten years he was called back to Bologna to the Faculty of Pharmacy, his EPR facilities moved with him, supplemented by the acquisition of a Bruker ESP300 spectrometer. In its new environment, the group increased in size as new researchers were recruited. M. Lucarini was the first, to be followed over the years by L. Valgimigli, R. Amorati and P. Franchi. Eventually, just before Pedulli's retirement in 2010, the ESP300 was replaced by a Bruker Elexsys E500. More recently, Lucarini, who had been appointed Professor of Physical Methods in Organic Chemistry, be-

came the head of the University-based unit of the Bologna group.

EPR research carried out in Bologna has been, and still is, a "continuous-wave" story. Up to the late 1980's it was carried out jointly at the university and at CNR. The group focused on structural and dynamic studies of organic mono- and poly-radicals, of radical ion pairs with alkali cations both in the absence and in the presence of complexing agents, of electrochemical processes and of photoinitiated radical reactions. Since the early 1990's, the increasing size of the university group led to a separation of the research activities of the two sites that became scientifically independent, though retaining extensive collaborations. Thus the EPR research at the university concentrated upon the determination of the parameters responsible for antioxidant activity of natural and synthetic antioxidants and the use of EPR imaging for the determination of the distribution of radicals in 3D polymeric samples. BDE values were determined by EPR spectroscopy through measurements of the equilibrium constants for the reaction between 2,4,6-tri-tert-butyl phenol, whose O-H bond strength is known from colorimetric studies, and a given phenol, and are commonly accepted as the more reliable

among those reported in the literature. This research involves very active collaborations with the group of K. U. Ingold at the NRC in Canada. Another topic extensively pursued by the Bologna group involved the determination of nitroxide radical distributions within polypropylene polymers containing amine stabilizers. The EPR-Imaging technique represents a powerful tool for investigating the way by which the concentration of nitroxide radicals inside the polymers changes both in time and in space. More recently Lucarini's group has shifted its interests to the preparation of paramagnetic supramolecular architectures such as host-guest complexes, protected nanoparticles and mechanically interlocked molecules that make possible the use of EPR spectroscopy for their investigation.

At the CNR site, where Alberti and Guerra had been joined by M. Benaglia and D. Mac-ciantelli, EPR research continued to be focused on radical addition to unsaturated substrates leading the group into the field of spin trapping. This included conventional traps such as nitroso derivatives and nitrones (collaboration with Greci's group in Ancona) and innovative traps such as thiobenzoylsilanes and dithioesters. The last derivatives prompted a shift towards RAFT (Reversible Addition



7th International Symposium on Free Radicals, 1965, Padova, Italy

In the first row at the center Giovanni Giacometti (no tie), on his left Giovanni Semerano, director of the Padua Institute and chairman of the Symposium, on his right Sir George Porter; behind this latter, B.B. Voevodskii from Novosibirsk. On the left, at the end of the third row (over the lady with white hair) Carlo Corvaja. In the foreground, with a white jacket, D.H. Whiffen (National Physics Laboratory). In the penultimate row, near to the tall gentleman with a black jacket, P. B. Ayscough (Leeds). On the third row, second, third and fourth from the right, J. H. Van der Waals (Leiden), Yuri Tsvetkov (Novosibirsk), Dietrich Haarer (Stuttgart). The fifth and sixth from the left on the last row C. Chachaty (Saclay) and A. Rassat (Grenoble); near to him: on the right Frank Adrian (Maryland), and the lady behind him Rose Marx (Orsay).

Fragmentation Transfer) polymerization: new useful transfer agents were obtained while EPR-kinetic studies allowed the determination of the rate constants critical for RAFT processes (in collaboration with Rizzardo's group at the CSIRO, Melbourne, Australia). On a less fundamental side, EPR research at CNR was also applied to the formulation of EPR protocols for the identification of food-stuffs treated with ionizing radiations (in collaboration with Onori's group at ISS, Rome and with Chiaravalle's group at IZS, Foggia).

Due to changes in the strategic objectives of CNR following Alberti's retirement in 2010, the EPR research at ISOF was brought to an end, the instrument was decommissioned and its component units were donated to different Italian research institutes where they have been used to revive local instrumentation that had been out of order. At the present time, Lucarini's is the only group to carry out research on free radicals and radical based processes via the use of EPR spectroscopy in the Bologna region. Since its establishment, the Bologna group has produced over 400 paper published in high-ranking international journals.

From the mid 1980's L. Grossi may also be considered as connected to the Bologna EPR units without being an institutional member but a very frequent guest, initially at the University and afterwards at the CNR site. After starting his EPR activity in the early 1970's in Milano, with the radical chemist F. Minisci, he soon moved to Zurich where he worked with H. Fischer on photolytically generated transient radical species. After some time he then moved to Ottawa (CND) where he joined the K. U. Ingold group at the local NRC and worked on the EPR studies of the kinetics of radical reactions, a subject that he kept working on after moving to York (UK) where he collaborated with B. Gilbert. Back to Bologna, he continued his international activity collaborating with E. Gimenez Arnau of Strasbourg University in the study of radical-based diseases of human tissues while also studying a wide variety of organic free

radicals in collaboration with A. Alberti. In 1993 he was among the founders of the Italian Nitric Oxide Society (iNOS), that he actually chairs, aimed to discover the role of NO *in vivo*.

The members of both the university and CNR units of the Bologna EPR group were among the founders of GIRSE, the Italian EPR group, and they contributed to the establishing of EFEPR, the European Federation of EPR groups.

EPR in Florence

(Dante Gatteschi, Maurizio Romanelli and Francesco Di Benedetto)

Florence has had an important role in Italian EPR with two different objectives – the physico-chemical one with Burlamacchi, Tiezzi, Martini, Ottaviani (EPR of free radicals) and that of the group of Gatteschi which focused on the spectra of coordination compounds.

The research activity related to EPR techniques started and developed both at the Institute of Physical Chemistry, and at the Institute of General and Inorganic Chemistry. It was also here that the CNR Laboratory for

the study of Stereochemistry and Energetics of Coordination Compounds had its birth.

The history of EPR in Florence arose out of a dramatic event, the large flood that hit Florence in November 1966, badly damaging the Physical Chemistry Institute. However the donation of a Varian V4502 X-band spectrometer by the U.S.A. ushered in the start of EPR spectroscopy in Florence. At that time the Institute was headed by Prof. E. Ferroni whose main scientific interest was the study of surface phenomena, strictly related to conservation and restoration of artistic items. Two of his assistants, L. Burlamacchi and E. Tiezzi, profited from the gift; their work pointed to the possible application of the EPR technique to the study of dynamics at liquid-solid surfaces, leading to many important scientific papers. Indeed, the group was enhanced by the acquisition of another brilliant researcher, G. Martini. Though he graduated in Organic Chemistry, a strong interest in EPR stimulated him so strongly that his first contribution to the work of the group appeared already in 1970 in JCP. They used stable inorganic radicals and paramagnetic transition metal ions as spin probes. Their first published article appeared in 1968 in the *Journal of Molecular*



GIRSE meeting, 1998, Rimini, Italy

1st row, from left to right: 1, Luca Pardi, FI - 2, Dante Gatteschi, FI - 3, Maurizio Romanelli, FI - 4, Francesca Ottaviani, PU - 5, Angelo Alberti, BO - 6, Marina Brustolon, PD - 7, Livietta Pedulli, BO - 8, Gian Franco Pedulli, BO - 9, Giovanni Bizzaro, Bruker - 10, Loris Grossi, BO.

2nd row, from left to right: 1, Marco Lucarini, BO - 2, Andrea Barbieri, FE - 3, Massimo Martinelli, PI - 4, Gualtieri Giancaterino, AQ - 5, Mario Branca, SS - 6, Carlo Corvaja, PD - 7, Giancarlo Agostini, PD.

3rd row, from left to right: 1, Martina Mazzoni, PD - 2, Riccardo Amorati, BO - 3, Enzo Laurenti, TO - 4, Elio Giamello, TO - 5, Marco Bonora, PD - 6, Alessandro Ponti, MI - 7, Antonio Faucitano, PV - 8, Giovanna Oliva, MI - 9, Dante Macciantelli, BO.

4th row, from left to right: 1, Armando Buttafava, PV - 2, Marco Ruzzi, PD - 3, Paola Franchi, BO - 4, Pamela Pedrielli, BO - 5, Cesare Oliva, MI - 6, Pierluigi Stipa, AN. People standing, from left to right: 1, Elena Sartori, PD - 2, Massimo Benaglia, BO - 3, Eileen Campana, BO - 4, Mario Chiesa, TO - 5, Rosa Pia Ferrari, TO - 6, Luca Valgimigli, BO - 7, Fosca Conti, PD - 8, Alfonso Zoleo, PD - 9, Calogero Pinzino, PI - 10, Lorenzo Franco, PD - 11, Andrew Hudson, Brighton - 12, Peter Hoefer, Bruker - 13, Marina Bennati, Göttingen - 14, Geoffrey Luckhurst, Southampton - 15, Maurizio Guerra, BO - 16, Ulderico Segre, PD - 17, Antonio Toffoletti, PD - 18, Claudio Zannoni, BO - 19, Antonio Barbon, PD.

(AN = Ancona; AQ = L'Aquila; BO = Bologna; FE = Ferrara; FI = Firenze; MI = Milano; PD = Padova; PI = Pisa; PV = Pavia; SS = Sassari; TO = Torino)

Structure, and reported on a joint study on the linewidth and association of Mn^{2+} in aqueous solution. Very soon the members of the group became more specialized in their research activity: Burlamacchi focused on the dynamics of adsorbed solutions of nitroxides and paramagnetic ions (mainly Mn^{2+} and Cu^{2+}), while Tiezzi choose applications of EPR on bio-organic samples (continuing his studies done at Washington University in 1966–1967).

In 1970 Tiezzi was appointed to a Chair of Physical Chemistry at the University of Siena (see the Siena section), Burlamacchi got a Chair in Cagliari and Martini became the group leader. M. Romanelli, M. F. Ottaviani and S. Ristori subsequently joined. Romanelli continued the studies on adsorbed solutions on porous solids, with further interesting work on relaxation mechanisms and interactions of solutions of paramagnetic probes absorbed on porous materials as zeolites and silica. Ottaviani focused on micellar systems, following a period at Columbia University in Prof. N. Turro's group where she participated and carried out studies on dendrimers and their interactions in several systems containing paramagnetic species. In 1998 she moved to Urbino, having won an Associate Professorship in the local University. Ristori's research was instead centred on perfluorinated surfactants and polymer aggregation.

In the early 1980's Romanelli served as visiting scientist in the EPR lab headed by Prof. L. Kevan at the University of Houston in order to become acquainted with pulsed EPR techniques (ESE). Thus the group's research activity was enhanced by the acquisition of this technique. Romanelli produced several papers dealing with ESE theory and applications. He won an Associate Professor position at the University of Basilicata in 1987 and in 1992 returned to the the University of Florence. Since 1998 his interest has been focused on solid state ESE.

An original research field was introduced in 1998 by F. Di Benedetto who applied continuous wave ESR spectroscopy (but also high field EPR and ESE) to minerals and other geomaterials, with the aim to determine valence state and speciation of metal ions, to identify the presence of inorganic radicals, and to define the magnetic properties of these phases. In this field, EPR greatly contributed to unravelling details relevant to human health and environmental issues (as e.g. the study of the arsenic incorporation in calcite and the definition of the fingerprints of bioprecipitation of calcite).

The coordination chemistry research was started by D. Gatteschi who moved into the new field independently. In the 70's there had been the first wave of interest in high symmetry compounds but the attention of researchers was increasingly being driven to consideration of low symmetry coordination compounds. Gatteschi, who had started to investigate the electronic structure of transition metal complexes, mainly using UV-Vis spectroscopy, independently of the activity of the big groups working in transition metal compounds, decided to enter the field of EPR, recognizing its potential that had not been much cultivated in the 70's, but was of emerging importance for coordination chemistry. The focus was directed towards the low symmetry features of coordination compounds, the first results being on the detection of the Jahn-Teller distortions in compounds which seemingly were exceptions to the JT theorem. Measuring the EPR spectra provided evidence that the high symmetry of the copper ethylene diamine was only due to dynamic distortion averaging. The work on the Jahn-Teller effect was carried out in collaboration with Bertini and Scozzafava. They moved shortly after into studies of paramagnetic compounds using NMR. It must be stressed that the emerging research activities, both in EPR and NMR developing in Florence, provided the opportunity for complementary investigations. This collaboration was reflected in the development of the first magnetic resonance interest group of the Italian Chemical Society that was dedicated to both NMR and EPR. There were many discussions as to whether EPR should be a section of a joint NMR-EPR section, or whether EPR should be better represented by an independent EPR group, and eventually the latter format prevailed.

The important successful results of the EPR investigation of low symmetry coordination compounds prompted the Florence team to investigate a number of coordination compounds with increasing complications. In addition to Gatteschi, the people

involved in this research were A. Bencini, C. Benelli, C. Zanchini, L. Banci, R. Sessoli, and A. Caneschi. Unfortunately, Viezzoli, who brought innovative contributions to EPR of biological systems prematurely passed away. Bencini, was involved in all aspects of the research, from recording spectra to working out the interpretation at the spin Hamiltonian level to eventually working out theoretical models. This complemented Gatteschi's contributions and their collaboration was extremely fruitful. Sadly, also Bencini passed away much too early.

The new generation of Florentine EPR spectroscopists includes L. Sorace, who is developing the large clusters field, with important contributions from A. Cornia, a Florentine spectroscopist working in Modena, and M. Fittipaldi who is investigating the EMR spectra of magnetic nanoparticles of variable size, exploiting the existence of variable size ferritins which are obtained through collaborations with biologists.

At the beginning, interest in the EPR spectra was focussed on the characterization of the electronic energy levels of various transition metal ions in low symmetry environments. The trend continued in the sense that the interest moved to higher nuclearity systems, including dinuclear species, to understand the factors affecting the isotropic and anisotropic exchange. Particular attention was dedicated to the so called Single Molecule Magnets, SMM, that were discovered in Florence using several different experimental techniques, of which the high field EPR, available in Grenoble, was the most important. Within the framework of the strong interaction between Florence and Grenoble, the collaboration with A. L. Barra was particularly important. She spent two years in Florence becoming acquainted with all the details of the EPR of transition metal compounds, and the colored Florentine language.

The first EPR in the Institute of General and Inorganic Chemistry was an X-band spectrometer. Unfortunately, most systems



the group was interested in were fast-relaxing. The development of instrumentation however continued with the implementation of a Q-band facility that later was expanded with a W-band spectrometer working down to 4.2 K.

The Florence group was very active also at the level of divulging the underlying science, producing books on different aspects of EPR in dinuclear, oligonuclear, two dimensional and three dimensional systems.

Last but not least, it should be mentioned that the Florence EPR group obtained prestigious international recognition, such as the Bruker and the Zavoisky awards (both to Gatteschi).

EPR in ISS, Rome

(Paola Fattibene, Donatella Pietraforte, Emanuela Bortolin and Cinzia De Angelis)

EPR at ISS was started at the end of the 1960's by professors M. Ageno and P. Indovina, who were later joined by A. Rosati, S. Onori, A. Bartolotta, F. Bordi, M. Pantaloni and E. Petetti. The EPR facilities from the first Varian E4 grew to four spectrometers (Varian E4, E102, Bruker ESP300 and EMX104). In the late 1980's Indovina moved to Naples while Bartolotta moved to Palermo which led to a collaboration with Brai, Marrale and D'Oca that has continued since then until now. In the early days, EPR research ranged from studies of metalloproteins in blood to the effects of ionizing radiation in solid state materials (P. Indovina, M. T. Santini, A. Rosi, F. Ianzini, S. Onori). At the beginning of the 1990's the EPR laboratory was split between the Physics and Cell Biology Departments, with the availability of four CW-EPR Bruker spectrometers (Bruker Elexsys, EMX, e-scan, ECS104). The general goal of the Physics research branch is the detection of damage induced by ionizing radiation in materials, implemented in three lines of research. Firstly, the development and patenting of alanine dosimeters (Indovina, Bartolotta, Onori, Petetti, Rosati, De

Angelis and Fattibene). Secondly, the study of radiation damage caused by ionizing radiations in polymers, pharmaceuticals, and food (Onori, Pantaloni and Fattibene) that led to the development of methods and protocols for the identification of foodstuffs treated with ionizing radiations (collaborations with Alberti in Bologna and with Chiaravalle and Mangiacotti in Foggia). Thirdly, the research into materials suitable as markers for ionizing radiation exposure (Onori, Fattibene, De Coste and Della Monaca).

The biomedical research addressed the oxidative damage induced by reactive oxygen/nitrogen species in several biological systems, such as cell cultures and human blood (M. Minetti, V. Quaresima, M. Soriani, T. Forte and D. Pietraforte), and an in-depth study of the intracellular pathways of oxidant formation, the oxidant-dependent radicals formed in biomolecules, and the role of the antioxidant systems in counteracting the oxidative damage.

The current group consists of E. Bortolin, C. De Angelis, S. Della Monaca, P. Fattibene, D. Pietraforte and M. C. Quattrini. It is foreseen that from 2017 all EPR spectrometers will be assembled in a core facility, which will also include the NMR spectrometers and the NMRI facilities.

EPR at the MDM Laboratory and at the University of Milano Bicocca (Marco Fanciulli)

In 1998 Marco Fanciulli, at that time at the Institute of Physics and Astronomy of the University of Aarhus, Denmark, was hired by the national (Italian) Institute for condensed matter physics (INFN) to set up a new public-private laboratory, the Materials and Devices for Microelectronics (MDM) Laboratory, in close collaboration with STMicroelectronics in Agrate Brianza. Thanks to Prof. Jørgen Byberg, at the Institute of Chemistry of the University of Aarhus, he had the opportunity to bring to Italy a Varian E15 and later on a

Bruker ESP300 with ENDOR. In 2004 Fanciulli acquired a Bruker Elexsys 580. Later on a Bruker ESP300, donated by Prof. S. Cannistraro and, again from Denmark, another Bruker ESP300 with X- and Q-bands were added to the MDM facilities. Based on these systems Marco Fanciulli continued his work on the characterization of defects in semiconductors and oxides, started the investigation of defects at the Semiconductor/Oxide (mainly high-k dielectrics for ultra-scaled CMOS) interface with electrically detected magnetic resonance (EDMR), and the characterization of the relaxation and coherence times of donors in silicon for quantum information processing. The activity continued unaltered during the MDM Laboratory merging from INFN into CNR in recent years. In 2007, while maintaining the associate position at MDM, Marco Fanciulli joined, as Full Professor of Condensed Matter Physics in the Department of Materials Science at the University of Milano Bicocca. He established a new EPR lab, with 2 Varian and 2 Bruker spectrometers and additional complementary characterization techniques and materials processing facilities, the materials and spectroscopies for nanoelectronics and spintronics lab (MSNS).

Currently the research focuses on the investigation of: defects in Si, Ge, Silicon Nanowires, SiGe heterostructures and 2D materials; T_1 and T_2 of donors in Si, Ge, and Silicon nanowires, defects at the Si/oxide and Ge/oxide interfaces and conduction electron in Ge with EDMR, development of innovative methods for the investigation of defects in semiconductor nanostructures and of schemes for spin-based quantum information processing.

The group consists of M. Fanciulli (UniMiB and MDM), M. Belli (MDM) and S. Paleri (UniMiB). Several students and researchers have contributed to the research effort, here the most relevant are mentioned: Silvia Baldovino (now at STMicroelectronics), Sergey Nokrin (now at the University of Toronto), and Dmitry Azamat (now at the Academy of Science in Prague).



EPR in Milan
(Cesare Oliva)

The EPR group in the Chemical Physics Institute (now Chemistry Department) of the University of Milan was born in 1973 in the school of the brilliant physical and theoretical chemist, Massimo Simonetta. The first EPR spectrometer was a Varian V-4502 equipped with a 9-inch magnet. The EPR research group was led by A. Gamba, and included G. Morosi, C. Oliva and V. Malatesta. Within the framework of a research program on aromatic nitroderivatives, the EPR parameters of the radical anions of nitropyridines and nitropyridine N-oxides were compared with the results obtained by quantum-mechanical calculations on their electronic properties. With the contribution of P. Cremaschi (CNR), the EPR investigations were later extended to other nitro-derivatives radical anions, and to their ion pairs with alkali metal cations. The localization of the cations and their intramolecular dynamics, with anions bearing more than one association site (as e.g. in dinitropyridine) could be investigated thanks to the collaboration with M. Barzaghi (CNR) who provided a computer program automatically fitting the ESR spectra in presence of the line-width alternation effect. An unexpected result of these studies was that in some ion pairs, the jumping of the cation between two positions, shown by the linewidth alternation, was not intramolecular but intermolecular, occurring via the formation of an intermediate symmetric triple ion in which two cations were interacting with the two nitrogroups of the same radical anion. This kind of investigation was then extended (1980–1988) to many other radical anions and ion-pair systems, also in collaboration with other researchers, as A. Saba and M. Branca (Sassari) and S. Miertus (Bratislava). In particular, interesting results were obtained on the hindered internal rotation occurring in 3,5-dinitrobenzamide radical anion and related compounds (1980), in nitrobenzophenone and dinitrobenzophenone

radical anions, ion pair and triple ions (1983), in nitroacetophenone radical anions (1983).

A collaboration with Prof. N. M. Atherton (University of Sheffield, UK) was focused on the EPR and ENDOR investigations of radical species in single crystals, e.g. the SO_3 -centre in γ -irradiated sulphamic acid (1987) and Vanadyl doped into magnesium acetate (1989).

In a collaboration with the Department of Medical Chemistry and Biochemistry of the University of Milan (B. Cestaro et al.) from 1983 to 1987, spin-labeled probes were used to investigate the effects of sulfatide on the fluidity and surface dynamics of bilayered and micellar model membranes. The order parameter evaluated from the EPR spectra was correlated with thermodynamic parameters through a numerical procedure based on statistical thermodynamics implemented by Oliva. This method led to a quantitative evaluation of the configurational free energy contributing to the stability of disordered systems. Later on the method was (1999) applied to Triblock Copolymer in water solution.

In 1987 the group acquired a Bruker ESP300 EPR spectrometer, upgraded to Elexsys ten years later.

A new collaboration was begun in 1989, with the Mendelev University of Moscow and, in particular, with A. V. Vishniakov, I. Mukovozov, A. V. Ezerets, and A. Kryukov on the international project “Investigations on new catalysts to reduce or eliminate polluting gaseous releases”. The research team also included L. Forni and I. Rossetti of the University of Milan and L. Bonoldi of Polimeri Europa, Novara, Italy. The catalytic activity of some oxidic catalysts such as spinels or perovskites was correlated with their EPR spectral parameters. Some studies focused on the double spin-exchange and on the formation of polarons propagating along chains. M. Scavini, M. Allietta, M. Coduri also participated in this research.

In the period 1990–1999, in collaboration with E. Selli and I. Bellobono, the research was focused on the radical formation and decay in many processes of photopolymerization and

on obtaining the relevant kinetic parameters. EPR and ENDOR investigations of powdered samples such as alkali-exchanged X- and Y-zeolites (1990–1991) and copper-exchanged mordenites and beta zeolites (1997), were carried out in the course of studying heterogeneous catalysis.

In the meanwhile, the composition of the EPR group had changed. G. Termignone, A. D'Ambrosio and S. Cappelli had joined the group, and A. Ponti and R. Morelli acted as external CNR collaborators. C. Oliva was the new group leader.

Since 2004, a further research theme involves CeO_2 doped by Gd^{3+} (and other 3+ ions) to induce large ionic conductivity through O diffusion via a vacancy mechanism, the aim being to obtain solid electrolytes to employ in electrochemical cells. Sometimes even surface polariton propagation was noticed in these systems (2015).

In the framework of a project on photo-degradation of air pollutants and on other photochemical reactions, EPR investigations on N-doped as well as on Nb-N doubly doped TiO_2 were started in 2009, in collaboration with S. Ardizzzone, G. Cappelletti, D. Meroni, F. Spadavecchia and other colleagues.

At the end of 2015 C. Oliva retired and the group is now comprised of S. Cappelli and M. Scavini.

EPR in Padova
(Marina Brustolon and Carlo Corvaja)

EPR at Padova University started in 1959 in the Institute of Physical Chemistry (since 2003, Department of Chemical Sciences, DISC) with a Varian V 4500 EPR spectrometer. G. Giacometti, a young and bright theoretical chemist was in charge of the EPR research. From 1970 to 2000 he directed the CNR Centre for Studies for Radicals and Excited Molecular States. In the early '60s two young students of Giacometti, C. Corvaja and P. L. Nordio († 1998) recorded the first EPR spectra of the



anions of carbonyl and nitro derivatives, the first focussing on experiment and the second on theory. The EPR results were used to test the existing theories on molecular orbitals. Since then, the tight link between experiment and theory has characterized EPR research in Padova. Nordio with Giacometti and M. V. Pavan coauthored a famous paper in 1963 on the theory of proton hyperfine coupling in π systems. Corvaja visited the H. Fischer lab in Darmstadt, and in the period 1964–1970, Giacometti and Corvaja investigated with him short-lived free radicals. In 1968 Corvaja spent one year in Nijmegen, Holland, studying radical ions and ion pairs in solution in the laboratory of E. De Boer. Back in Padova, he began an intense EPR research program on ion pairs, together with two young graduate students, L. Pasimeni († 2001) and M. Brustolon. In 1974 the latter spent one year with N. M. Atherton in Sheffield (UK) training in ENDOR spectroscopy. Afterwards, a home made ENDOR apparatus was developed in Padova by Corvaja and Brustolon, in collaboration with A. Colligiani from University of Pisa. The ENDOR research addressed radicals in irradiated molecular crystals, determining their hyperfine, quadrupolar and g -tensors. In 1979 A. L. Maniero joined the ENDOR group as a postdoc, becoming a staff member from 1981. During the same period ('75–'80) Corvaja, in collaboration with Pasimeni, began research on triplet states in solid matrices, triplet excitons in single crystals of ion radicals and of charge-transfer (CT) complexes. In 1976 Pasimeni spent one year in the Physical Chemistry Laboratory at Oxford University, working with P. W. Atkins on CIDEP. The research field on photoexcited triplet states studied by EPR and related techniques in Padova has been very successful. In 1983 Pasimeni and Corvaja assembled an Optically Detected Magnetic Resonance (ODMR) spectrometer to study the delayed fluorescence of triplet excitons in charge transfer molecular crystals.

From 1984 Brustolon and Maniero, in collaboration with U. Segre († 2008), from the

Nordio group, worked mainly on dynamics and spin relaxation of radicals produced inside channels in inclusion compounds. Radicals with rotating methyl groups showed a strong temperature variation in ENDOR intensity that was correlated with the rate of rotation, and used to measure the energy barrier hindering the motion.

In 1987 Brustolon and Pasimeni became full professors.

In 1991 the group acquired a Bruker ESP380 Pulse EPR spectrometer. Brustolon, Segre, Maniero and the graduate student A. Zoleo pursued the EchoEPR study of electron relaxation in molecular crystals, leading to methods for radiation dosimetry. At the same time, Corvaja and Pasimeni implemented a home-made EPR detection system (TR-EPR), time-resolved with a resolution of 100 ns, synchronized with a pulse laser photoexciting the sample. For the interaction between photoexcited triplets ($S = 1$) and free radicals ($S = 1/2$) an excited quartet ($S = 3/2$) state was observed for the first time. On this theme Corvaja and Pasimeni produced a number of papers all through the '90s, with intermittent collaborations with Giacometti, Agostini, Maniero, the graduate student L. Franco and the assistant professor A. Toffoletti. Franco became assistant professor in 1999. Toffoletti collaborated also from '95 until now with the group of C. Toniolo in a series of EPR characterizations of peptides containing TOAC, a spin-labelled disubstituted glycine.

In the '90s Giacometti's interest was moving to photosynthesis, a field where EPR methods had proved very valuable. D. Carbonera, a graduate student working in his group spent one year in 1991 in the laboratory of the late A. J. Hoff, University of Leiden, and in 1992 at the Physikalishes Institut, Stuttgart, with A. Angerhofer. Back in Padova, in collaboration with Agostini, she built a zero field ODMR apparatus to study the electronic triplet states in photosynthesis. This led the team of Giacometti, Carbonera and Agostini, to produce numerous papers during the '90s,

some also in collaboration with Corvaja and Pasimeni. In 2000, Carbonera became Associate Professor in Biochemistry. M. Di Valentin, a graduate student, joined the group at the end of the '90s. She joined the group as assistant professor extending the interest to artificial photosynthesis in collaboration with Devens Gust and Tom and Ana Moore (Arizona State University, USA).

In 1996-99 Maniero worked on HF-EPR with L. C. Brunel at the National High Magnetic Field Laboratory in Tallahassee, Florida, with a CNR-NATO fellowship and then as visiting professor. There she participated in developing the ENDOR instrumentation at 220/330 GHz. This collaboration introduced HF-EPR among the techniques used in Padova in several subsequent studies.

At the end of the '90s fullerenes were in the focus of interest. An Organic Chemistry group under M. Maggini from Padova University collaborated with the EPR group, synthesizing various fullerene derivatives. Brustolon, Zoleo and Maniero characterized the radical anions of some fulleropyrrolidines by means of both cw- and pulse-EPR. The Corvaja group was focused on the study of C-60 derivatives covalently linked to a nitroxide radical. For these studies on the interaction of free radicals with excited triplet states, Corvaja shared with Prof. Seigo Yamauchi of Sendai (Japan) the 2001 Silver Medal of the International EPR/ESR Society. He also received the Gold Medal of the Magnetic Resonance Group of the Italian Chemical Society.

Pasimeni, with the help of the graduate student M. Ruzzi, independently developed a research program on the photophysics of fullerenic materials. He started many collaborations, those with M. Prato, an organic chemist in Trieste, and with D. Guldi, Erlangen, Germany, proving particularly fruitful. Pasimeni was particularly interested in the photoinduced ET in supramolecular systems involving fullerenes, as models for ET in photosynthesis. However, a tragic fate was awaiting him, and on February 11th 2001 he was killed in the very Department where he had worked with such passion and success. His last paper appeared five days later in Chemistry, a European journal.

Photoinduced ET for optoelectronic or photovoltaic applications continued to be a focus of the Corvaja group. Many graduate students and post-docs have contributed over the years, between them Franco, Toffoletti and Ruzzi; all of them are today (2016) staff members in the Padova EPR group. Corvaja retired in 2008.



Over the period 2003–2009, the Brustolon group, with Barbon, Maniero, Segre and the graduate student M. Bortolus, using TR-EPR and Echo EPR, studied the photoexcited triplets of oligothiophenes and other organic dyes in isotropic, anisotropic and confining matrices, in part in collaboration with P. Sozzani and A. Comotti, of Milano Bicocca University. In 2010 in collaboration with G. Zerbi and M. Tommasini (Politecnico of Milano), Brustolon and Barbon began a study on nanographites. In collaboration with B. Kahr, University of Washington, they studied by TR-EPR the photoexcited triplets in some Dyes Inclusion Crystals. After Brustolon's retirement in 2013, Barbon continued to study graphene-like materials in collaboration with M. Maggini. The dosimetry of ionizing radiations by echo EPR, begun by Brustolon, Zoleo and A. Lund of Linköping, Sweden is flourishing today (2016) in a collaboration with Barbon and M. Marrale of the University of Palermo. A further collaboration of Barbon with L. Weiner, Weizmann Institute, Rehovot, focuses on the use of nitroxides as a tool to study photoswitched electron transfer processes within proteins.

During the last years of her activity, Brustolon studied the application of EPR to Cultural Heritage (CH). Zoleo joined this field, characterizing relevant open-shell species in ancient paper, collaborating with scholars of the Humanities inside UNIPD. With geoscience groups, Zoleo dealt with CW and pulse EPR methods for archaeometric and datation on ancient materials. This research activity on EPR applications on CH is today one of the most fruitful in the EPR group in Padova.

From 2006 till her early retirement in 2013 the EPR research themes of Maniero were in the field of biological systems. With Bortolus, who worked as a post-doc in 2005–2006 in the spin-labeling EPR spectroscopy group of H. Mchaourab at Vanderbilt University in the US, she undertook CW and Pulsed EPR studies in the field of metallo-proteins, mitochondrial respiratory chain complexes, binding sites of the paramagnetic cofactors,

reduction level of the cofactors during ET processes, spin-labeled proteins and peptides in solution, and other biosystems. The most relevant collaborations were the long-standing one with L. C. Brunel and J. van Tol and with the group of C. Toniolo and F. Formaggio in DISC.

In the Photosynthesis group, Carbonera and Di Valentin recently extended the range of advanced EPR techniques (FT-EPR, pulse-ENDOR and time-resolved EPR, PELDOR) to metal centers, in particular those related to the hydrogenase maturation process. During the 25-years of research activity, Carbonera and Di Valentin have been involved in several research programs, and have undertaken many international collaborations, in particular with W. Lubitz, R. Hiller, E. Hofmann, P. Heathcote, C. Kay, K. Möbius, and R. Bassi.

Former Corvaja coworkers Franco, Ruzzi and Toffoletti have, since 2009, collaborated with R. Po of the ENI-Donagani Institute in Novara on TR-EPR and LEPR characterization of D-A films where D is a fullerene derivative and A are semiconducting polymers. Over the period 2000–2007 Franco used EPR methods to investigate the oxidative stress in biological fluids and cells, in collaboration with Department of Clinical and Experimental Medicine of UNIPD. In the Corvaja group he participated particularly in research on photoinduced spin dynamics, collaborating in particular with H. Levanon in Jerusalem, E. Goovaerts in Antwerp and K.M. Salikhov in Kazan. He became Associate Professor in 2015.

Ruzzi was appointed assistant professor in 2006. In collaboration with N. J. Turro, Columbia University, using both NMR and ENDOR, he investigated the nuclear relaxation and the para-H₂/ortho-H₂ interconversion in endofullerene H₂ molecule in systems as H₂@C₆₀. He is also working, together with Zoleo, on a research line on the magnetic behaviors of molecule-like gold nanoclusters in different redox states, in collaboration with F. Maran (DISC).

EPR in Pavia

(Antonio Fautitano, Armando Buttafava, Daniele Dondi and Fausta Martinotti)

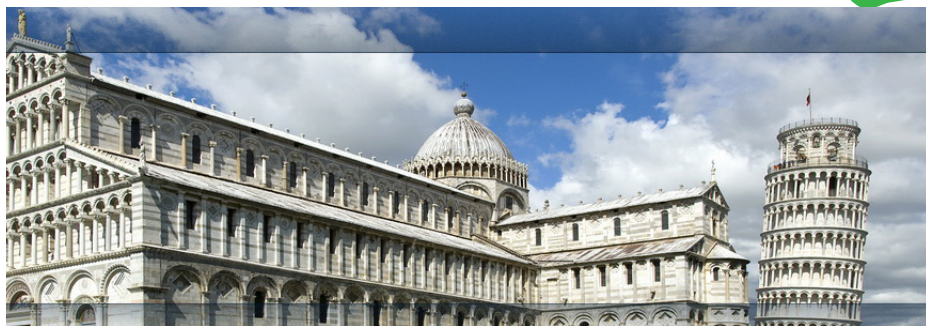
The EPR and Radiation Chemistry laboratory at the Chemistry Department of the University of Pavia was founded in 1968 (upon the initiative of the director M. A. Rollier) by A. Fautitano (group leader), F. Martinotti and A. Perotti, based on the experience gained during a two year training program at the Nuclear Engineering Department and the Chemistry Department of the Brookhaven National Laboratory (BNL, Upton N.Y.). The key instrumentation consisted of a Varian 4502 NMR/EPR spectrometer and a purpose-built 4 kCi Co-60 gamma source, while financial support came from ENI-SNAM Progetti. In 1972 A. Perotti left the group. In 1975 A. Buttafava joined the group, spending one-year training later in the lab of Prof. E. de Boer (Nijmegen, Holland). In 2005 D. Dondi joined the EPR group as a researcher after being awarded a PhD in photochemistry. After the retirements of Fautitano (2010) and Buttafava (2013), Dondi has become the leader of the EPR-Radiation Chemistry group.

The Pavia EPR group has participated in three national target projects (Progetti Finalizzati) and in the projects of relevant national interest (PRIN) in the field of free radical chemistry and radiation dosimetry. In 2005, Fautitano acted as national coordinator for a FIRB project on the Applications of Ionizing Radiations to Materials. Other vital resources have steadily been obtained from the collaboration with important industries (SNAM Progetti, Montedison-Solvay Solexis, Enichem, Pirelli).

On the international side, from 1989 to 1999, the group has participated in the institutional research collaboration with the Strathclyde University (Glasgow, UK) and the University of Lodz (Poland) on the theme "Radiation Chemistry and Physics of Solids". From 1999 to 2012, the group has played a key role in the management of the international post graduate Master in Nuclear and Ionizing Radiation Technology (TNRI, NIRT) under the Direction and coordination of Fautitano, Buttafava and A. Borio.

In Italy the group has pioneered the application of EPR spectroscopy in the field of radiation chemistry. Its research, reported through 136 papers in international journals, has involved four main themes.

A) Radiolysis mechanisms studies of low molecular weight organic compounds, carboxylic acids/urea clathrates, acyl chlorides, metal



complexes (metal carbonyls complexes, Ni(II) polyazamacrocyclic complexes, Pt(II) diolefins complexes, Al and Ti alkoxides), technological polymers and biomolecules playing a key role in the chemical bases of the radiobiological damage (DNA, nuclear proteins, chromatine, DNA/Pt(II) complexes).

B) EPR characterization of specific radical species, such as perfluoroalkoxy alkyl radicals, peroxy radicals, neutral free radicals and radical cations from polycyclic hydrocarbons with strained ring structure and radical cations from aromatic thioethers.

C) EPR investigation of solid state reactions initiated at room temperature by high energy irradiation, e.g. the kinetic and EPR study of the post-irradiation oxidation of isotactic polypropylene, the role of the ordered structures in the mechanism of radiolysis of oleic acid in the neat crystalline state and aliphatic esters in the state of urea clathrates. Further research is concerned with solid state polymerization of pure crystalline vinyl monomers (methacrylamide) and vinyl monomers in the state of clathrates (benzylmethacrylate), the modification of polymers for improving their mechanical properties, the introduction of reactive functional groups into polyolefine films to be used as solid electrolytes and the degradation of polymers to lower molecular weights for fine chemicals production.

D) EPR radiation dosimetry studies including modifications of the Alanine dosimeter and dosimetry using radiation produced gels.

Outside the radiation chemistry field, other EPR studies have addressed the mechanism of action of stabilizers, in particular of hindered amine light stabilizers (HALS), and the kinetic EPR determination of rate constants for free radicals reactions (H abstraction by aminyl radicals from HALS, self coupling of perfluorinated alkoxy alkyl peroxy radicals, the self coupling of polyolefines peroxy radicals), and, more recently pyrolysis, microwave induced reactions and photochemistry.

EPR in Pisa

(Luca A. Pardi, Massimo Martinelli and Dino Leporini)

The history of EPR “under the Leaning Tower” starts at the beginning of the 1970’s, stemming from the research on Multiple Quantum Spectroscopies developed at the Institute of Physics of the University of Pisa (F. Chiarini, M. Martinelli, S. Santucci, P. Bucci, 1972). They extended and applied the general theory, built on the application of

double quantization, to specific experimental techniques and, in particular, to magnetic resonance spectroscopies. Multiple irradiation spectroscopies are continuous wave (CW) methods based on multi-quantum processes that explore nonlinear properties of the magnetic systems at resonance. The original contribution in this field gave rise to the development of two related techniques, namely: Longitudinally Detected EPR (LODESR) and Doubly Modulated Electron Spin Resonance (DOMESR). These techniques allowed the investigation of the chemico-physical intricacies of a number of paramagnetic systems such as those with multiple superimposing signals (A. Colligiani, L. Andreozzi, A. Di Schino, M. Faetti, M. Giordano, D. Leporini, M. Martinelli, L.A. Pardi, S. Santucci and C. Umeton. 1985–2001). The study of the dynamics of supercooled liquid systems undergoing glass phase transitions was also a very active area of research at the Department of Physics in Pisa. In particular polymers and glass formers were investigated both from the theoretical and the experimental point of view through a variety of EPR techniques. In the late 1970’s and early 1980’s, innovative ESR techniques were also developed at the Department of Chemistry of the University of Pisa and used for the investigation of a variety of systems ranging from chemistry and biochemistry to the science of materials (A. Colligiani, C. Pinzino). These experimental activities later involved the Institute of Quantum Chemistry and Molecular Energetics (ICQEM) of CNR (National Research Council).

A High Field-High Frequency EPR facility (HF²-EPR) was established using university and CNR funds, within the research infra-structures of the IFAM-CNR, later IPCF-CNR. The HF²-EPR laboratory in Pisa, launched on May 26th 2000, was the first setup of this kind ever built in Italy and one of the few present in Europe. The experimental setup is based on a home built broadband spectrometer offering frequencies from 95–285 GHz and sweepable magnetic fields

up to 12 Tesla at 10 ppm homogeneity in a 1 cubic centimeter volume.

Thus one can investigate systems that are silent at conventional EPR frequencies (10 GHz), such as systems with large Zero Field Splittings, and high spin systems whose investigation at high frequency provides a deeper understanding of their magnetic properties (D. Gatteschi, C. A. Massa, L. A. Luca, M. Martinelli, L. Sorace, V. Bercu, F. F. Popescu, F. Di Benedetto, M. Romanelli 2001–2015). Further investigations of the molecular dynamics of polymers and glass formers were pursued exploiting the well known enhanced resolution of the HF²-EPR spectroscopy. (V. Bercu, D. Leporini, M. Massa, L.A. Pardi, S. Pizzanelli 2003–2015).

The HF²-EPR infrastructure team functioned as coordinator of the European Network named SENTINEL in the period from 2001 to 2005.

A thorough investigation of the opportunity offered by the CO₂ pumped FIR laser, as millimeter and submillimeter waves sources, was conducted in the laboratory before the adoption of solid state sources based on frequency locked Gunn diodes. In the first decade of the 21st Century the spectrometer was equipped with a quasi-optical bridge in order to fully exploit the expected gains in sensitivity at high fields and frequencies.

Several methodological developments were proposed in the field of millimeter and submillimeter waves. In particular, a branch of the research activity was devoted to the design and characterization of new kinds of resonating structures including the Whispering Gallery Mode Dielectric Resonators and the Non Radiative Resonators (G. Annino, M. Martinelli, M. Cassettari, M. Fittipaldi 2001–2005). This branch of research was conducted using a dedicated experimental setup based on the use of a Millimeter wave Network Analyser working in the GHz to THz frequency range (P Goy, 1999).

Extrinsic effects present in HF²-EPR were also investigated in order to determine the de-



tails of the line shape of macroscopic samples of paramagnetic systems in EPR experiments when using a radiation whose wavelength is of the same order of magnitude as the size of the sample. (D. Friselli, C. A. Massa, M. Martinelli, L. A. Pardi, I. Ricci 2005–2008).

EPR in Siena

(Rebecca Pogni and Riccardo Basosi)

EPR at the University of Siena started in 1967 with the pioneering work of E. Tiezzi, who during his stay at the University of Saint Louis, working with B. Commoner and S. Weissman, published, in BBA, the first Iron-nitrosyl complex EPR spectrum. When, in 1975, Tiezzi moved from Florence to the University of Siena, the magnetic resonance group (EPR and NMR) was established. The group was mainly involved in the combined application of magnetic resonance techniques to the analysis of model compounds of metal ion biological systems (Fe, Cu, Mn etc). In 1982–1984, R. Basosi, spent more than one year at the National Biomedical EPR center, Biophysics section (Milwaukee) guided by J. Hyde. In 1985 with the acquisition of a Bruker 200D-SRC spectrometer operating at X-band, Siena became independent of the facilities in Florence. Different bridges operating at various frequencies and new probes (loop gap resonators) were installed. In this context, an S-band bridge operating from 2–4 GHz was implemented in Siena. S- and X-band bridges were also acquired. The Multifrequency approach was exploited in particular in the study of paramagnetic systems in solution at room temperature combined with computer simulation of EPR spectra. The EPR group grew with the arrival of R. Pogni and a few years later of G. Della Lunga, M. C. Baratto, E. Busi and A. Sinicropi. About this time the Physico Chemical group of Siena, together with the Inorganic group of Florence, started the internationally known Chianti Workshop series on Electron and Nuclear Relaxation,

held in S. Miniato (Pisa). Around the same time an old Varian Q-band spectrometer was bought from ENI, while in the early 2000s the old X-band spectrometer was upgraded with the new Bruker Elexysis E-500 equipped with a liquid Helium apparatus ($T = 4\text{--}300\text{ K}$).

During the last 15 years the EPR research has been focused on the structural and catalytic mechanisms of oxidative enzymes (prevalently fungal peroxidases and laccases) with studies on the long range electron transfer process. The same systems have also been studied for their application to the biotechnological field with the detection of radical intermediates in the laccase-mediator systems, radical substrates and associated antioxidant activities. Another field of interest concerns the interaction of peptides with model membranes. Very recently a Q-band bridge has been implemented on the Elexys Bruker E-500 apparatus operating in CW at X- and S-band frequencies. A system for freeze-quench experiments is also available.

EPR in Torino

(Elio Giamello)

EPR spectroscopy in Torino started more recently than in other Italian Universities, when in the second half of the 1970s three Institutes of the University of Torino purchased an EPR spectrometer for studies in bio-inorganic chemistry and surface chemistry (an X-band Varian E-109). Meanwhile, two researchers, R.P. Ferrari and E. Giamello, saw the opportunity to exploit EPR spectroscopy in their own work. Ferrari, interested in biological and bio-inorganic chemistry, started to investigate the interaction of metal ions with DNA while Giamello spent six months in 1977 in Villeurbanne (Lyon) at the Institut de Recherches sur la Catalyse to become familiar with the applications of EPR to surface chemistry and catalysis. In 1984–1985 Giamello continued his training in the group of Michel Che at the University P. et M. Curie in Paris. This led to the institution of two EPR groups in Torino with research interests in distinct areas.

For the Ferrari group, the EPR research activity in bio-inorganic chemistry began with studies of Cu(II) complexes with DNA and on the interaction of Cu(II) and vanadyl ions with collagen, insulin and various amino acids. Ferrari was joined in 1993 by M. E. Ghibaudi, a graduate student. After an experience at the Mario Negri Institute for Pharmacological Research (Milano), she received her PhD in 1996 and from 1997 to 1999 worked as a post-doc in the Department of Cell and Molecular

Biology CEA-Gif sur Yvette (France). In the meantime, the biologist E. Laurenti joined the group after his PhD and a period at the Technical University of Denmark (Copenhagen). The main interest of the group was moving towards the characterization of the active sites of metal-proteins and to the study of their reaction products. Thanks to some national and international collaborations, the group focused on the characterization of both the Fe(III)-heme group in some peroxidases (zucchini, horseradish, lactoperoxidase) and the active site in multi-copper oxidases (tyrosinase and ascorbate oxidase). At the same time, investigations on the enzymatic activity were tackled involving the use of spin-trapping techniques to monitor the formation of semiquinone radicals deriving from catechols, catecholamines and estrogens. From 2000 the target was the characterization of the structure-function relationships of site-specific mutants in some bacterial peroxidases. Spin-labeling techniques also started to be used to study the folding/unfolding mechanisms of proteins and the interactions of polypeptides having pharmacological activity with polysaccharides and lipids. In recent years, after Ferrari's retirement the attention of the group turned to the area of bio-industrial applications with the preparation of mixed organic-inorganic heterogeneous catalysts, EPR being used primarily for the study of reaction mechanisms involving radical intermediates.

Since the 1980's Giamello's group research activity has been focused on EPR characterization in surface chemistry and in heterogeneous catalysis. After the year spent in the M. Che group in Paris, Giamello continued CW-EPR studies of the chemistry of oxide systems with a special focus on surface reactivity. The Torino group cooperated with the other Italian EPR groups in the 1986 Summer School in Pra Catinat (TO) that was crucial for the foundation of GIRSE, formally established one year later during the Bressanone meeting. In 1991 an Irish graduate student, D. Murphy, currently professor at Cardiff University (UK), joined the group. Another PhD student, M. C. Paganini, after a post-Doc period in Twente and at the Technical University in Munich, became Assistant Professor in 1999. A few years later M. Chiesa joined the group, after his PhD at the Cardiff University (2002). S. Livraghi obtained his PhD in 2007. Nowadays M. C. Paganini and M. Chiesa are Associate Professors while S. Livraghi is Research Assistant. Several other PhD students and post-doc joined the group over the years.



To go beyond a trivial and “analytical” use of EPR, common in particular in heterogeneous catalysis literature, the Torino group developed a rigorous methodological approach to the treatment of CW-EPR data, obtained with efficient simulation programs of EPR powder spectra. The main research subject since the 80’s has been the characterization of paramagnetic reaction intermediates at the surface of poly-crystalline metal oxides. These are often radical ions formed by electron transfer from the solid to the adsorbed molecule. The superoxide ion (O_2^-) has been one of the most important surface radicals investigated by the group, together with CO_2^- , CO^- , CNO_3^- and N_2^- radical anions, observed for the first time on a solid surface. Early in its history, the group collaborated with various national groups (Forzatti in Milano, Busca in Genova, Zecchina, Morterra in Torino) dealing with surface chemistry and heterogeneous catalysis.

In the early 90’s the group was involved in the study of surface defects of ionic oxides based on trapped electrons, the so-called surface color centers, and was able to show how the paramagnetic (one-electron) surface color centers on alkali earth oxides are not associated with true surface vacancies. They are stabilized at particular morphological locations of the surface including single ions having low coordination and high Madelung potential. The electron does not occupy an atomic orbital but is stabilized by a strong local electrostatic field. Their EPR spectra show hyperfine interactions with the surrounding nuclei providing information on their position. These studies showed that the surface color centers belong to the family of the electrides, ionic compounds characterized by electrons playing the role of anions. In this research field in the early 90’s the Torino EPR group began a longstanding collaboration with the group of Computational Chemistry active in the University of Milano Bicocca led by G. Pacchioni and including C. Di Valentin. The use of computation, in particular of hyperfine

coupling constants, is crucial in complex systems such as the real solid surfaces.

From 2000–2010 the study of model ionic oxides gradually gave way to that of the photoactive semiconducting oxides, in order to exploit solar light for energetic or chemical purposes. The field of photoactive oxides has been dominated by titanium dioxide starting from the observation of water photosplitting in a photo-electrochemical cell (Fujishima, 1972). The afore-mentioned experiment led to research into artificial photosynthesis and on the photocatalytic abatement of pollutants. Titanium dioxide has a strong limitation due to the necessary use of UV light for the initial photoexcitation. At the beginning of 2000 an intense worldwide search was being undertaken concerning the ability of nitrogen impurities in TiO_2 to generate absorption of visible light. The Giamello group, in collaboration with Pacchioni’s group, provided an important contribution to the understanding of this system showing how the nitrogen intra-band states act as intermediate levels in the promotion of valence band electrons to the conduction band. Since 2010 this idea has inspired subsequent work of the group, aimed to employ doped wide band gap oxides in photocatalytic systems called third-generation photocatalysts.

The equipment of the EPR groups in Torino, that for nearly thirty years was based on CW spectrometers, was enriched in 2010 by a pulsed machine working in both X-band and Q-band modes. The research in pulse-EPR, developed in particular by M. Chiesa, who had become familiar with the technique in the laboratory of S. van Doorsleer in Antwerp, is now producing very interesting results. Recent work concerns transition metal ions in various catalytic systems based on mesoporous matrices (aluminophosphates) and heterogeneous catalysts for the polymerization of olefins (Ziegler-Natta catalysts). The EPR approach, thanks to the use of hyperfine spectroscopies (pulsed ENDOR and HYSCORE), allows the investigation

of complex systems by monitoring the weak hyperfine interactions in the surrounding of a (paramagnetic) catalytic center.

A brief history of GIRSE

GIRSE (Gruppo Italiano di Risonanza di Spin Elettronico) was founded in 1987, during an EPR school organized in Prà Catinat, a tiny and secluded mountain village where most of the Italian EPR community for the first time was confined long enough to give birth to friendships and collaborations bound to last for life. The founders were EPR spectroscopists from universities and CNR laboratories (Padova, Bologna, Firenze, Torino, L’Aquila, Milano, Sassari, Ancona, Pisa, Siena, Roma, Palermo), and from ISS (Roma). GIRSE had, and still has, a twofold mission: diffusing the knowledge of EPR spectroscopy in Italian research groups while stimulating the application of EPR methods in physics, chemistry, biology and medical sciences.

While GIRSE was the second EPR group to be founded in Europe, it was the first interdisciplinary EPR national group independent of established scientific societies, the already existing British EPR Group being a subgroup of the RSC. Up to the present day, GIRSE has organized nine national meetings in Italy, the last two in collaboration with the French and Spanish groups. It has also held five national EPR schools covering both basic principles and advanced techniques. GIRSE is now chaired by D. Carbonera, who has been preceded as President by M. Brustolon, A. Alberti, A. Sotgiu, G. F. Pedulli and E. Giamello.

Non-formality and interdisciplinarity are key-features of GIRSE that has prompted researchers in other countries to set up similar associations. There are presently 14 national EPR groups in Europe, and all are members of the informal federation EFEPR (European Federation of EPR) that was created in 1991 during a conference in Padova jointly organized by GIRSE and the British EPR group. A steering committee was initially set up, and in the following year EFEPR was formed. Klaus Möbius was elected as its first President and was succeeded by Marina Brustolon, Daniella Goldfarb, Etienne Goovaerts, Graham Smith and Sabine van Doorsleer. EFEPR has been an important driving force for the development of EPR methodologies in Europe, with its ten international meetings and seven Summer Schools on Advanced EPR.



List of EPR groups for which detailed accounts are not available

- University of Bari “Aldo Moro”, Chemistry Department: Francesco Ciminale. Topics: structure and reactivity of organic radicals.
- University of Bologna, Dept. of Industrial Chemistry: Claudio Zannoni, Alberto Arcioni. Topics: EPR in liquid crystals.
- University of Bologna, Dept. of Organic Chemistry: Ludovico Lunazzi, Giuseppe Placucci. Topics: Organic free radicals and radical ions.
- University of Catania, Dept. of Chemical Sciences: Raffaele Bonomo. Topics: EPR of transition metals complexes.
- University of L'Aquila, Dept. of Health Sciences: Antonello Sotgiu, Marcello Alecci, Silvia Colacicchi. Topics: ESR Imaging.

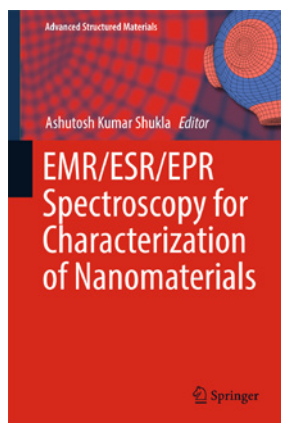
- University of Palermo, Dept. of Physics and Chemistry: Roberto Boscaino, Franco Gelardi, Simonpietro Agnello. Topics: Spin dynamics and SiO₂-nanomaterials. Ignazio Ciccarello, Maria Li Vigni, Aurelio Agliolo Gallitto; High-Tc superconductivity. Maria Brai, Antonio Bartolotta, Maurizio Marrale. Topics: Radiation dosimetry and discrimination of radiation quality for various applications (such as clinical radiation therapy, industry and food irradiation).
- University of Calabria, Dept. of Physics, Arcavacata di Rende: Luigi Sportelli, Rosa Bartucci. Topics: application of pulse EPR to Biophysics.
- University of Ferrara, Dept. of Chemistry: Orazio Traverso, Andrea Barbieri. Topics: EPR of inorganic materials

- University of Modena, Dept. of Biochemical Sciences: Aldo Tomasi. Topics: Application of ESR to Medicine.
- University of Rome “Tor Vergata”: Alessandro Desideri, Giuseppe Rotilio. Topics: application of ESR to biological systems.
- University of Sassari, Dept. of Chemistry and Pharmacy: Mario Branca, Giovanni Micera. Topics: ENDOR of ion pairs in solution.
- Institute of Biomolecular Chemistry, CNR, Catania: Mario C. Foti. Topics: Reactivity of Organic free radicals.
- Institute of Molecular Sciences and Technologies, Milano: Alessandro Ponti. Topics: Advanced pulse EPR methods.
- Istituto di Struttura della Materia, CNR, Roma: Donato Attanasio. Topics: EPR characterization of ancient marble quarries via Mn(II).



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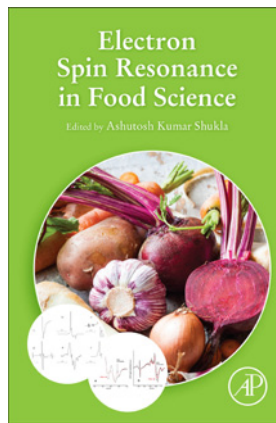
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EMR/ESR/EPR Spectroscopy for Characterization of Nanomaterials
A.K. Shukla (Ed.)
Series: Advanced Structured Materials,
Vol. 62; 1st ed. 2017, XI, 179 pages, 96
illustrations, 35 illustrations in colour.
Printed book. Price (Hardcover):
86,99 € | £64.99 | \$99.00; 93,08 € (D) |
95,69 € (A) | CHF 96.00

The subject matter of this book is the application of EMR/ESR/EPR spectroscopy for characterization of nanomaterials. Initial chapters deal with nanomaterials and

their classification. Characterization of metallic nanoparticles, metal oxide nanoparticles and rare earth impurity doped nanoparticles from the (ESR) spectrum parameters are covered in the chapters that follow. A special feature of the book is EMR/ESR/EPR spectroscopic characterization of nanoparticles which are important due to their bactericidal and anticancerous properties. Strength of continuous wave (CW) is explained with the help of suitable examples. The book focuses on applications and data interpretation avoiding extensive use of mathematics so that it also caters to the need of young scientists in the life science disciplines. The book includes a comparison with other spectroscopic characterization methods so as to give an integrated approach to the reader. It will prove useful to biomedical scientists and engineers, chemists, and materials engineers in student, researcher, and practitioner positions.



Electron Spin Resonance in Food Science
Editor: Ashutosh Kumar Shukla
Publisher: Elsevier
No. of pages: 156
Language: English
©Academic Press 2017
Published: 22.12 2016
Imprint: Academic Press
Paperback ISBN:
9780128054284
Price: \$130,00

This book covers in detail the ESR identification of the irradiation history of food products and beverages to investigate changes that occur during storage, besides aiming to improve hygienic quality and extend the shelf-life with least tempering in their nutritional profile. The title includes ESR applications in drug control and safety with a section on drug-polymer interaction in context of packaging films. ESR imaging applications are also covered in a separate chapter. International regulations relevant to irradiated food items are also included. Book is designed to serve as a complete reference on application of ESR spectroscopy in Food Science research. Special focus is on applications and data interpretation avoiding extensive use of Mathematics so as to cater the need of young scientists from different disciplines.

Erwin Louis Hahn (1921–2016)



Erwin Hahn, the discoverer of the spectroscopic echo has passed away. Everyone involved magnetic resonance or nonlinear optical spectroscopy knows about the echo. Even medical doctors with just basic MRI knowledge do. Erwin had the great fortune of discovering the echo. When receiving the Russel Varian Prize 2004 in Lille at the joint meeting of the 17th EENC and the 32nd Congress AMPERE, he reminisced “Certainly if I had not discovered the spin echo displaying the first free induction decay signal after a pulse as well, it would have been discovered by someone else quite soon”. Although best known for the echo, Erwin Hahn has contributed several other seminal discoveries to our standard repertoire of day-to-day science in addition to the spin echo (*Phys. Rev.* **80**, 1950, 580), for example, cross-polarization together with Sven Hartmann (*Phys. Rev.* **128**, 1962, 2042) and self-induced transparency with S. L. McCall (*Phys. Rev.* **183**, 1969, 457; *PRL* **18**, 1967, 908). Moreover, among others he worked on such diverse topics as liquid-state NMR and scalar couplings in micro-tesla magnetic fields, detection of sea-water motion by nuclear precession, electron-spin-envelope modulation, nuclear spin noise, coherent Raman beats, spin-echo serial storage memory, and enhancement of surface NMR by laser-polarized noble gases.

Erwin Hahn was a modest man with a brilliant, sharp mind and a wonderful sense of humor. He regularly attended the Congresses AMPERE and the Gordon Conferences on Magnetic Resonance where one could discuss with him at ease and would always learn from him, be it science or be it being human. Whatever echo remains, it bears his smile.

Bernhard Blümich
President of the Groupement AMPERE

* * *

The recent passing of Erwin Hahn, Father of the spin echo, causes us to pause to stop and reflect about what magnetic resonance, in general, and EPR in particular, owe to this remarkable and dynamic individual.

Important tributes to Erwin on his 90th birthday from those who knew him well may be found in *EPR Newsletter* (21/2, 2011). These are: To Erwin Hahn on his 90th Birthday by George Feher (p. 5) and Hans Wolfgang Spiess (p. 5). Then there is Erwin @ 90 by his Berkeley colleagues, Dmitry Buder and Jean-Claude Diels (pp. 6, 7). Finally there is a lengthy tribute, Erwin L. Hahn, Scientist, Mentor, Friend by Alex Pines. Collectively, these provide fascinating insights and observations concerning Erwin's contribution to magnetic resonance as well as something of the dynamic person that he was! There is no need to repeat them here.

In a previous *EPR Newsletter* (13/1-2, 2003) I talked about the 041 Coffee Club in the Clarendon Lab in Oxford during the early 1960's. To recap, Lab 041 was originally Brebis Bleaney's lab but had been taken over by my doctoral supervisor, Bill Hayes. The 041 Coffee Club however continued and around 10.30 each morning about 20 people would come to our lab, often staying for an hour or so! I previously mentioned that a regular visitor each morning during my first year, 1961-2, was John van Vleck from Harvard. What I did not mention then was that Erwin Hahn was another visitor to the Clarendon who sometimes came to 041 for coffee, while on sabbatical from Berkeley with Prof. Nicholas Kurti and the Low Temperature Group. Actually, looking back, I think we doctoral students were all somewhat more in awe of him than we were of van Vleck!

I did not meet Erwin again until 1994 during AMPERE in Kazan. Until I looked up photos from that Conference, I had forgotten that my friend Sung Ho Choh from Korea and I spent a very pleasant hour or two

talking with him during the conference boat trip (see photo). On that occasion he reminisced about his sabbatical in Oxford with Kurti's group where his task was to use NMR to measure microkelvin temperatures during nuclear adiabatic demagnetisation experiments. That work resulted in an outstanding and very thorough piece of work, not published until 1965, by Walstedt (Hahn's student), Hahn, and Froidevaux and Geissler from Oxford [*Proc. Roy. Soc.* A284, 499].

Then the following year, 1995, during ISMAR at Sydney University, I had the privilege of sitting opposite Erwin and his wife at the Conference Banquet. As we talked for about two hours about many things, he again waxed eloquent about his 1961-2 sabbatical in Oxford, and coming to the 041 Coffee Club. His recollection of people whom he met in 041 was remarkable.

There is no doubt that Erwin Hahn played a foundational role in magnetic resonance. He will always be remembered for the discovery of, and explanation for, spin-echoes [*Phys. Rev.* **80**(1), 580, 1950]. I am still awed by that paper in its completeness and elegance and by the insightfulness of the amazing figures prepared without the benefit of modern computer graphics! Here is a comment I discovered on the internet that reminded me of another major contribution. “Hahn also discovered gradient echoes that occurred when a gradient field was reversed described in this paper. He even went further to show how velocity could be measured based on gradient induced phase shifts, the foundation of modern phase-contrast MRI.” Hahn's paper appeared in *J. Geophys. Research* [**65**, 776, 1960].

Erwin made a major foray into EPR territory through the work of his student, Larry Rowan, and in collaboration with Bill Mims, which took pulsed magnetic resonance to a new level. This first observation of ESEEM was reported by Rowan, Hahn and Mims in *Phys. Rev.* **137**, A61, 1965.

I can think of no better way to gain insight into Erwin's scientific career up to the mid-80's than by reading the extensive 1986 interview for the APS that may be found by navigating the following URL: www.aip.org/history-programs/niels-bohr-library/oral-histories/4652

When one realises that Erwin's Radar work during WWII involved microwave pulses, it is perhaps not surprising that he thought of doing NMR with RF pulses. Thus there is more to the story than revealed in the classic 1950 paper. Here Erwin also reflects on his work in optics, inspired to some extent by his discoveries in NMR.



Readers of the Newsletter will have enjoyed Erwin's Einstein tidbits in *EPR Newsletter* 15/1, 14, 2005, about meeting Einstein.

Erwin received many honours among them Membership of the US National Academy, Foreign Membership of the Royal Society of London and Fellowship of IES.

I feel privileged to have had the opportunity, on two occasions, to have been able to talk with him at length.

A tribute from Charles Slichter, who overlapped with Erwin for a few months at the University of Illinois in 1949, appears below.

John Pilbrow
Melbourne, Australia,
January 16th, 2017

Erwin and Charlie: The First Three Years

I am honored by the invitation from Laila Mosina and John Pilbrow to take part in the celebration of the life of Erwin Hahn. He is one of the most admired, most honored, and indeed beloved scientists in the history of magnetic resonance.

In 2011, the *EPR Newsletter* celebrated Erwin's 90th birthday with several delightful articles from admirers, most of whom were much younger than Erwin. I am only two years younger and have known him since we were both graduate students. We have been friends for 68 years.

We began studies for our PhD's using magnetic resonance about a year after Pur-

cell, Pound, and Torrey in Cambridge and Bloch, Hansen, and Packard in Stanford had announced the discovery of nuclear magnetic resonance (Cambridge) or nuclear induction (Stanford). Their discoveries in early 1946 followed closely on the end of the Second World War in August 1945.

Erwin and I had the remarkable experience of entering a brand new field of science when it was still possible to know personally almost all of the other workers in the field. In this short note, I tell about those early years that culminated in the discovery of J-coupling by Erwin and his student Maxwell (from the study of ^1H spin echoes), and simultaneously but independently by Herb Gutowsky, Dave McCall, and me (from study of splittings of NMR steady state spectra by coupling between ^{19}F and ^{31}P nuclei), and finally in the award of the Nobel Prize to Felix Bloch and Edward Purcell in 1952.

Erwin attended Juniata College as an undergraduate, majoring in Chemistry, but he found as he progressed that his interests were shifting towards Physics. So on graduation in 1943, he transferred to Purdue to work with the physicist Karl Lark-Horowitz. In 1944, he lost his deferment and was drafted by the Navy. He was assigned to the Radio Technician's program from which he emerged with the rank "technician's mate" and was assigned teaching radar and sonar. This gave him experience with pulse signals.

When the war ended, he applied to Purdue, but they lacked the funds to give him support. He then applied to the Physics Department

at the University of Illinois and was admitted as a research assistant.

After a year of exploration of Particle Physics, he decided to switch to a more "table top science" area and at the suggestion of Professor James Bartlett, began study of the papers by Felix Bloch about NMR, as a possible thesis area. Since no Illinois faculty member was knowledgeable about nuclear magnetic resonance, Erwin was on his own. With the help of an electrical engineering student, Howard Knoebel, and stimulated by his knowledge of radar, Erwin assembled an NMR apparatus suitable for pulsed NMR studies of transient phenomena in liquids. He showed that when a spin system that is in thermal equilibrium is excited by a single short RF pulse, a signal is produced that decays at a rate determined either by natural relaxation processes, or by the degree of inhomogeneity of the static magnetic field. This decaying NMR signal is called "The Bloch decay". He also showed how to measure the spin-lattice relaxation time, T_1 , using pulse excitations at a succession of times. In June 1949, he completed a thesis and was awarded a PhD. In essence, he had completed a thesis with almost no help from an advisor.

When the war started in December 1941, I was a freshman at Harvard, majoring in physics. The Department put us through an accelerated program in circuit theory and electronics. In the spring of 1943, I left college at the suggestion of my advisor J. H. Van Vleck, to join a war project headed by the Chemist E. Bright Wilson, at the Underwater Explosive Research Lab of the Woods Hole Oceanographic Institution, building and repairing electronic apparatus used to record pressure-time curves resulting from underwater explosions. At Woods Hole I met several people who later became important in the field of magnetic resonance: George Frankel, Bill Schneider, and Al Redfield (at that time a high school senior).

In January 1946, I returned to college to finish my undergraduate studies. I entered grad school in the fall of that year.

My thesis advisor was Edward Purcell. I was his third student. His first student, Nico Bloembergen, was just finishing when I started with Purcell. His second student, George Pake, had a year to go. For his thesis George had studied ^1H resonance of water of hydration in solids and found the famous "Pake doublets" arising from the dipolar coupling between the two hydrogen atoms in a water molecule. He showed that he could measure proton-proton distances in water of hydration. ►

He then turned to a problem suggested to Purcell by the Chemist George Kistiakowsky whom Purcell encountered one day at lunch in the Faculty Club. Kisty was excited by hearing of Pake's result and suggested to Purcell that Pake try to determine the structure of the molecule diborane: B_2H_6 . Kisty sent his student Herb Gutowsky to help. They did not succeed in finding its structure, but they studied H-H distances and also molecular rotations of several hydrocarbons. The work taught Herb about NMR. Both George and Herb received PhDs in June 1948. George went to Washington University in St Louis and Herb to the Chemistry Department at Illinois. (On their departure, their NMR apparatus, which was next door to mine, was taken over by Raymond Andrew, a Commonwealth Fellow from England. We got to know each other well.)

For my thesis I did electron spin resonance studies of crystal splittings and spin lattice relaxation times in ionic crystals, a topic suggested by Professor Van Vleck.



In January 1949, I had been offered a position with the rank of instructor in the Physics department of the University of Illinois by its head, Wheeler Loomis, who knew Purcell from wartime service at MIT's Radiation Lab. Loomis had been the second in command at the lab and Purcell a staff member working under I. I. Rabi. Loomis recognized the importance of the discovery of nuclear magnetic resonance, so he wanted a Purcell student. He came to Cambridge to recruit.

A major attraction of Illinois for me was that Loomis had recruited Frederick Seitz from Carnegie Tech to assemble a group of Solid-State Physicists. Seitz was famous because of his book "Modern Theory of Solids". Since the transistor had recently been discovered by Bardeen and Bratain and by Shockley. I felt that the field of Solid State Physics would be ripe for study by magnetic resonance. I accepted Loomis's invitation.

Like Erwin, I finished my thesis in June 1949. In September I moved to Urbana to take up my faculty position at the University of Illinois. Erwin welcomed me. We had actually met a few months earlier when he came on a visit to Cambridge at the suggestion of Loomis to see the NMR apparatus in Purcell's lab.

I found that Erwin had made an amazing discovery that summer that he called "spin echoes". He was studying NMR signals (the "Bloch decays") on an oscilloscope that followed a short excitation pulse. His samples were liquids like water or glycerine. If an initial pulse had been followed by a second identical pulse at a sufficiently short time T later, a second Bloch decay appeared, but to his surprise a third signal also appeared spontaneously at a time $2T$ after the first pulse. He called third signal a "spin echo".

Typically with the magnets we had, the decays of the "Bloch decays" arose because the static magnetic field was inhomogeneous, causing the precessing nuclei to get out of step with one another following an initiating pulse. So the system must be acting as though the spin alignment "unwound", causing a decaying signal. When there were two pulses the second pulse must somehow be acting to make them rewind to some state approximating the starting configuration, producing the echo at $2T$.

With Purcell, I had not been doing pulse excitation studies of electron spins, nor had I studied Bloch's papers, so I was totally mystified by Erwin's finding. He told me that he had found that use of the equations in Bloch's paper enabled him to explain his

result if he assumed the Bloch decay arose because of the spread in precession rates from magnet inhomogeneity. Erwin had a hand-waving explanation of the result but I could not follow it. Erwin wrote Purcell to announce his finding, and Purcell responded with warm congratulations and with a very simple graphical method that would give the echo. Erwin gives Purcell's graphical explanation in his first paper. (It was several years before Carr and Purcell invented the 90-180 echo sequence that makes the explanation of an echo simple).

For his PhD thesis, Erwin had studied the decay of the NMR following excitation by a single pulse, the so-called Bloch decay. To persist a long time, the magnet must have a highly uniform field over the sample. In the Bloch decay, the signal faded out because spins in different parts of the sample got out of phase since they had different precession rates. Evidently the echo represented a recovery of a signal that decayed and thus the pulses enabled one to undo the effects of the inhomogeneity of the magnetic field. This was a hugely exciting result since magnet inhomogeneity was a major frustration since it concealed details that contained important information.

There were two other remarkable discoveries that Erwin's data also revealed.

By moving his sample to different positions in the magnet gap, Erwin could change the duration of the Bloch decay. But in addition, if the magnetic field gradient was big enough, the signal decayed precipitously. He concluded that the molecules of the samples he was studying were diffusing spatially in the inhomogeneous field of his magnet, so that a given molecule might be at a different value of magnetic field when the echo appears than it occupied at the time of the first excitation pulse.

Fascinated by this result, I worked out the theory of the effect of diffusion in the inhomogeneous static magnetic field on T dependence of echo amplitude and showed it to Erwin. He included it in a footnote in his paper on spin echoes, and kindly acknowledged my help. I have in retrospect realized that I should have asked Erwin whether he would like me to work out the theory before doing so. In effect I "stole" some of his data by failing to ask him first.

The second surprising result he called "the slow beat". It occurred in molecules like CH_3CH_2OH possessing more than one type of H site. Its manifestation was a rather complicated pattern of echo amplitude as a

function of the time between pulses. Instead of being a simple exponential decay, there was a more intricate envelope whose origin was a mystery.

Erwin had many friends. One, Sid Drell, who had been a Princeton undergraduate, also got a PhD at Illinois in June 1949. Both Sid and Erwin were talented violinists and both played in the University of Illinois orchestra. Erwin was married and, by then, had a son. Sid and I were both bachelors. We often ate meals together at the University Union Building across the street from the Physics Building, then returned to the Physics Building for the evening. We became close friends.

In the spring of 1950, Erwin learned that he had been awarded a prestigious post-doctoral fellowship sponsored by the National Research Council. He chose to use his fellowship at Stanford with Felix Bloch.

Erwin left for Stanford in the early spring where he set up a new NMR apparatus and began work with Bloch. Thus started a rich association. Not only was Bloch an amazing scientific advisor but he and Erwin became deep friends. Erwin found that Bloch was an accomplished pianist. They enjoyed playing music together.

At Stanford, Erwin acquired a graduate student, D. E. Maxwell, with whom he pursued the explanation of the “slow beats”.

When I had arrived at Illinois, I had found that there was, in addition to Erwin, a new magnetic resonance student, Dick Norberg, who had been attracted to NMR by Erwin’s work. Dick had just built a second NMR ap-

paratus. He had been an undergraduate at DePaul University, a small college in Greencastle, Indiana. During the war, he had been a weather officer in the Air Force. He was a bit older than me. He became my first student.

In the fall of 1949, Dick enrolled in the Seitz’s course about the theory of solids. Following a lecture on the effect of adsorption of H by Pd metal, Dick came to me to propose that he study the ^1H NMR of the H-Pd system for a thesis. Dick undertook this project with a very ingenious method of using the Pd sample as the wire of the NMR coil. Dick employed steady state, pulsed, and spin echoes to obtain rich results such as demonstrating that the H atoms were diffusing in the Pd wire and measuring the rate of diffusion. This was the first application of spin echoes by anyone other than Erwin.

In 1951, Al Overhauser came to Illinois as a post doc to do experiments with Professor James Koehler on the effect of radiation on the mechanical properties of solids. He became interested in our magnetic resonance studies because for his PhD thesis at Berkeley he had calculated the spin lattice relaxation time of conduction electrons in metals. He attended the seminar Dick gave on his H-Pd results. That night, stimulated by Dick’s talk, he invented dynamic nuclear polarization (the “Overhauser effect”). So this is an indirect but real stimulus resulting from “Erwin at Illinois”.

A short time later Herb came over from Chemistry to tell me about results from studying the NMR signal of ^{13}Na in powders of

Na metal. With Pake he had become familiar with the fact that the NMR line width of molecules that are rapidly reorienting as in liquids were narrowed from their width if the reorientation was frozen out. He found a similar “line narrowing” for the ^{23}Na line width in solid metallic Na for temperatures above 170 K all the way up to Na melting point at about 373 K. He proposed that the motion must be diffusion of the Na atoms and obtained the activation energy from the temperature dependence of his data. Above about 200 K, the real line width could not be measured because it was obscured by the magnet inhomogeneity. Dick and I realized that we could get rid of the magnetic broadening by using spin echoes, hence could extend Herb’s data all the way to the melting point of Na. Herb loaned us a sample. We used spin echoes to measure the Na atomic diffusion rate from 100 K to its melting point. Another “Erwin enabled” discovery.

In August 1950, Herb told me that he and his student Hoffman had been studying frequency dependence of the ^{19}F resonance on the chemical formula of the molecule containing the ^{19}F atom. This information was called the “chemical shift”. They had found that in diatomic molecules, the ^{19}F resonant frequency correlated with the difference in electronegativity of the two atoms of the molecule. Norman Ramsey had published a general theory of chemical shifts for use in his molecular beam experiments. Using it, I came to the conclusion that for an F_2 molecule the shift arose from the admixture



International Conference on Double Resonance and Multiple Quantum Transitions, Paris, July 1958. Left to right: W. E. Lamb, N. F. Ramsey, R. V. Pound, B. Bleaney, C. J. Gorter, E. L. Hahn, J. H. Van Vleck, A. Abragam.

of the excited anti-bonding state into the ground state by the static magnetic field, causing there to be electric currents flowing in the valence electrons induced by the static magnetic field. (This analysis is published in my 1953 paper with Herb's student Apollo Saika.) This meant that the chemical shift arose because there were currents flowing in the electron cloud of the F atom. For a negative ^{19}F ion, a closed shell, there is no current hence no chemical shift from this mechanism. Using this model, we were able to obtain a quantitative explanation of Herb's results.

In April 1951, Herb and his student Dave McCall, studying liquid phosphorous halides, found that there were multiple ^{19}F and ^{31}P NMR absorption lines with separations indicating magnetic coupling between the two species. Their paper to *Physical Review* was received April 16, 1951. Each individual line was narrow as expected for rapidly re-orienting liquid molecules. Similar surprising results had been reported by Raymond Andrew, and also by Proctor and Yu. Herb and Dave came to me to discuss these results. The direct dipolar coupling between the nuclear spins is zero when averaged over the molecular orientations of a molecule in a liquid, so another mechanism was needed to explain such splittings. In September we submitted a paper to *Physical Review* based on the idea that currents flowing in the electron cloud such as suggested to explain chemical shifts might be the explanation. The interaction would be formally a dot product ($I_F \cdot I_P$) coupling between the nuclear spins

since for the rapid molecular rotations would produce a spherically uniform coupling. Our paper was received at *Physical Review* September 10, 1951.

Herb suggested that this coupling might explain Erwin's slow beats. So my student Ed McNeil studied the ^{19}F spin echo signals of BrF_5 and IF_5 , indeed finding signals similar to Erwin's.

Meanwhile, Hahn and Maxwell had studied ^1H slow beats in a number of different molecules. From these they found the explanation for the slow beats. It was identical to our explanation. They likewise proposed a dot product coupling with a coefficient they denoted as J . Their paper was received at *Physical Review* on October 31, 1951 so our two groups essentially used different routes to get the same important result that a new spin-spin coupling exists between atoms that are chemically bonded to each other.

Erwin sent a copy of his paper to Purcell. Purcell went to Norman Ramsey, and together they came up with a different mechanism than Herb, Dave, and I had used to get the dot product coupling. Since these materials were all diamagnetic, we did not look for a mechanism that involved electron spins. The mechanism we suggested depended on orbital currents induced in the electron cloud by the nuclear spins. Ramsey and Purcell proposed that nuclear spins of each atom would induce a polarization of its own electron spin. Since the chemical bond implies an exchange coupling between the electron spins, the total energy will depend on the relative nuclear

spin orientations. Purcell and his student Herman Carr verified this theory by observing the ^1H and ^2D NMR spectra of HD.

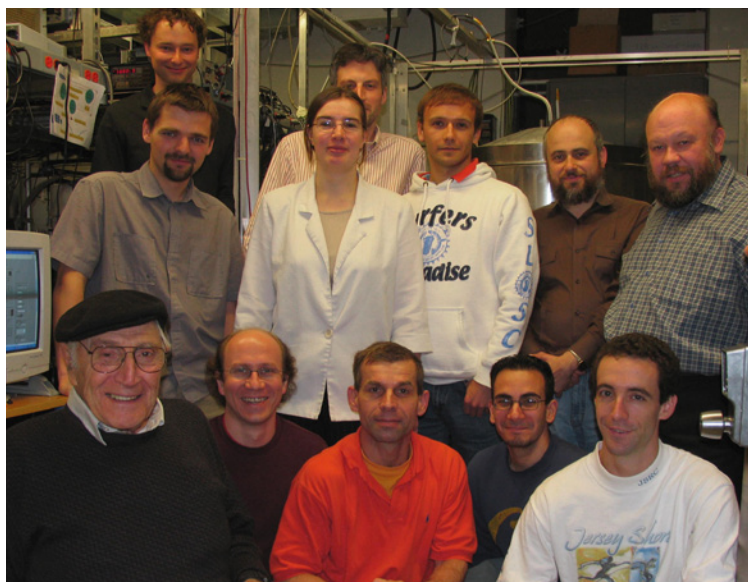
The coupling soon acquired the name "J-coupling." It is very important in the use of NMR in Chemistry for determining the structure of molecules because it shows what atoms are bonded to each other. Subsequent to the Ramsey, Purcell and Carr, Purcell papers, Hahn and Maxwell and Gutowsky, McCall, and I published further papers in 1953 incorporating the Ramsey/Purcell theory in their data analysis.

In this short paper, I have simply touched on the beginnings of Erwin's career, illustrating the immediate impact of his discovery of spin echoes in opening new fields of science in Physics and Chemistry.

In 1952, Purcell and Bloch were awarded the Nobel Prize in Physics. In his Nobel Prize lecture Purcell described several discoveries made possible by NMR. The final one he describes and uses to illustrate the exciting future prospects of nuclear magnetism is the J coupling in the HD molecule.

With Erwin at Berkeley and me in Urbana, we did not see each other often. I looked forward to chances to get to Berkeley. Gordon Conferences provided another chance that I treasured. There I could see Erwin, surrounded by admirers, as he regaled them with his repertoire of stories about science or other matters.

Charles P. Slichter



Erwin Hahn and his colleagues.



Charlie Slichter, Erwin Hahn, and Dick Norberg at a Gordon Conference.



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The 55th Annual Meeting of the Society of Electron Spin Science & Technology (SEST2016)

November 10–12, 2016, Osaka, Japan

www.sci.osaka-cu.ac.jp/~sest2016

The 55th Annual Meeting, SEST2016, was held from November 10 to 12, 2016 at Media Center, Osaka City University, Osaka, Japan. The SEST meeting has been organized in mid-Autumn every year at various cities in Japan, empowering communication with all SEST members and local people in the Society of Electron Spin Science and Technology. The society includes a wide variety of scientific fields from fundamental to application in the electron spin mediated sciences. The total number of the participants in SEST 2016 was 228, including 86 graduate/undergraduate students. There were 52 oral and 78 poster presentations in addition to 4 invited lectures from overseas: Prof. Konstantin Ivanov (International Tomography Center, Russia), Prof. Chris Kay (University College London, UK), Prof. Valery Khramtsov (West Virginia University, USA), and Prof. Gunnar Jeschke (ETH Zürich, Switzerland).

The SEST2016 started with the competition of the SEST Excellent Presentation Awards for young scientists. The Awards went to Mr. Fumitoshi Ema (Kobe Univ.), Mr. Akihiro Shimizu (Osaka City Univ.), and Dr. Hideyuki Takahashi (Kobe Univ.) under the review by Award Committee.

SEST also offers the student poster awards. This year the poster awards were won by the following six graduate students: Mr. Yuya Ishikawa (Fukui Univ.), Mr. Kohei Ozeki (Nagoya Univ.), Ms. Mayuko Kuno (Osaka Univ.), Mr. Kunito Fukuda (Gunma Univ.), Mr. Naoya Murata (Kyoto Inst. Tech.), and Mr. Toshiki Mogi (Saitama Univ.).

In the afternoon of November 11, there was a general meeting of SEST with the awards ceremony. The SEST Award went to Prof. Yoshio



SEST2016 Excellent Presentation Award winners. Left to right: F. Ema, K. Sato, H. Takahashi, A. Shimizu.

Teki (Osaka City Univ.) for his achievement entitled “Studies of Spin Alignment and Spin Science in π -Conjugated Organic Spin Systems”. The SEST Young Investigator Awards went to Prof. Shoko Okazaki (Sojo Univ.) for her theme entitled “Basic Study for Application to the Medical Field of the Electron Spin Resonance” and Prof. Masaki Horitani (Northwestern Univ.) for his theme entitled “Advanced Magnetic Resonance Studies on Metalloproteins”.

Two mini-symposia were, as usual, organized during the SEST meeting. One was organized by Profs. Toshiaki Arata (Osaka Univ.) and Hiroyuki Mino (Nagoya Univ.), focusing on “Electron Spin Science of Protein Molecules Working in Life”. Biologically oriented topics were presented and discussed. Invited speakers were in the following; Prof. Toshimichi Fujiwara (Osaka Univ.), Prof. Chojiro Kojima (Yokohama National Univ.), Prof. Masahiro Shirakawa (Kyoto Univ.), Prof. Yasufumi Umena (Okayama Univ.), and Prof. Mitsuo Shoji (Univ. of Tsukuba). Another symposium was organized by Prof. Makoto Negoro (Osaka

Univ.). The topics were oriented to “Electron Spin Quantum Information Science”. The following speakers introduced the advanced sciences to gain attentions after the brief introduction by Prof. Negoro; Prof. Yasuhiro Tokura (Univ. of Tsukuba), Prof. Norikazu Mizuochi (Kyoto Univ.), Prof. Yuimaru Kubo (OIST), and Prof. Kazunobu Sato (Osaka City Univ.).

The society of SEST has been established in 2002 by unifying various Japanese communities related to electron magnetic resonance spectroscopy. The society covers wide research topics on not only magnetic resonance but also electron spin science from fundamental to applied sciences; physics, chemistry, biology, pharmacy, medicine, dosimetry and other areas.

Next SEST2017 will be held in early November in Tokyo. You are cordially invited to the forthcoming SEST2017. Please join SEST2017, discussing a wide variety of electron spin science.

Kazunobu Sato, Chair, SEST2016
Professor, Graduate School of Science
Osaka City University

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**Annual International Conference
“Modern Development of Magnetic
Resonance-2016” (MDMR2016)**
October 31 – November 4, 2016
Kazan, Russia

In November 2016, Kazan welcomed participants from the Russian Federation (Moscow, Novosibirsk, Kaliningrad, Krasnoyarsk, Nizhny Novgorod, Chernogolovka), Germany, Israel, Italy, and the United States in order to discuss achievements and new tendencies in applications of magnetic resonance within the Annual International Conference “Modern Development of Magnetic Resonance” dated to the Zavoisky Award 2016 ceremony. Professor Michael Bowman (University of Alabama, Tuscaloosa, USA) and Professor Arnold Raitsimring (University of Arizona, Tucson, USA) shared the Zavoisky Award 2016.

The conference was organized by the Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, the Academy of Sciences of the Republic of Tatarstan, and the Kazan Federal University under the auspices of the Groupement AMPERE. The conference demonstrated the increasing interest in magnetic resonance studies in diverse fields of science. It included six plenary lectures, nearly thirty invited talks and nearly the same number of oral talks within the following sections: Chemical and biological systems; Strongly correlated electron systems; Low-dimensional systems and nano-systems; Theory of magnetic resonance; **Modern methods of magnetic resonance**; Other applications of magnetic resonance; Perspective of Magnetic Resonance in Science and Spin-Technology, and within the workshop “Spin-Based Information Processing”.

The conference was opened with plenary lectures. The lecture “Electron spin resonance



From left to right: Aleksei Kalachev, Rinat Mamin, Violeta Voronkova, Laila Mosina, Kev Salikhov, Valerii Tarasov.

on the border between para- and ferromagnetism: quantum versus classical” was given by V.A. Atsarkin, and T. Takui presented the lecture “Molecular spin technology for quantum computers and quantum information processing”. The plenary lecture of J. H. Freed was devoted to overcoming insufficient signal strength in ESR using new wavelet denoising methods, while H. Ohta in his lecture discussed recent developments and future perspectives of multi-extreme THz ESR. On November 2nd, there were two other plenary lectures: “New Porphyrin Molecules with Möbius-Strip Topology as Studied by Modern Magnetic Resonance Methods” by K. Möbius and “Why EPR Will Save the World?” by K. Salikhov.

This year much attention was attracted by reports devoted to the spin-based information processing, which were given in the framework of the special workshop and were basically related to quantum information science. Lead-

ing experts in the field, P. Bertet, J. Morton, J. Majer, M. Tobar, D. Suter, A. Tyryshkin, to name a few, reported on different aspects of EPR research of quantum information systems, e.g., spin qubits based on donors in silicon, hybrid quantum systems – coupling color centers to superconducting cavities, high-Q and novel cavity structures for photon-spin strong coupling, magnetic resonance at the quantum limit and beyond, etc. Without doubt, this conference was marked by a significant event, namely, the celebration of the 80th birthday of Prof. Kev M. Salikhov.

The financial support of the Government of the Republic of Tatarstan, Russian Academy of Sciences, Russian Foundation for Basic Research, and BrukerBioSpin is gratefully appreciated.

A. A. Kalachev
Chairman of the MDMR2016



At the opening of the conference.



Takeji Takui presents his plenary lecture.

Turning Right or Wrong into Sure or Unsure

Chapter Two

Because of the heavy use of multiple choice tests for determining student progress, its common to find students thinking about their results as “right” or “wrong”. In teaching students what research is and how to analyze their results, I find this the most difficult barrier to overcome.

One of the unpleasant side effects of pencil and paper tests is that students do not rely on their own abilities to learn new information and evaluate its authenticity. Thus, the most common question from a student first encountering an EPR spectrum of a sample they chose is “Is this right”?

When I taught general chemistry labs, I loved helping the students to attain a better understanding of what they were doing and why they were doing it. I hated grading the labs because the grading rubric did not allow for much consideration of what the student actually did. Students did not get a chance to repeat their results (there wasn't time) and so, on the basis of one experiment, a student's results were evaluated on what they should have gotten. They were either right or wrong.

I've always had a hard time explaining a “wrong” result obtained by experimentation. Even if they don't follow the instructions, they get some kind of result, and if the result doesn't make sense, it can point to where the student made a mistake. The student learns something new. But, in the

crush of high school or college chemistry, this self-evaluation rarely happens. Thus, a student expects their result to be right or wrong rather than an outcome based on what they actually did.

Students with high grades often expect to be right because they can follow directions and have been rewarded for it. How, then, does one move a student from “right” or “wrong” to “sure” or “unsure”?

When students are consumers of knowledge, they do not have to take responsibility for the data. In a classroom environment, students are fed information that they are required to both memorize, synthesize, and integrate with previous information. But what happens when a student is working in a field where they have little to no prior knowledge? What does a result mean in this context?

In my experience, it is when a student is faced with a result (a squiggly line on the screen) about which they know nothing, and I won't tell them if the answer is “right”, that they then begin to think about what it means to get a result where no one knows what the result should be. This is often the make or break point for a student in the SMART Center. If they cannot handle the uncertainty of not knowing if their result is “right” or “wrong” and they cannot step back sufficiently to think about what to do next, they are unlikely to proceed much further in research. They do not have the confidence or self-reliance to believe that


they can resolve the situation and move forward. Even something simple like repeating the experiment several times can be a deal-breaker. However, if the student is comfortable with uncertainty and is willing to think about how to learn more about what they are doing, they are on their way to developing a research project. They are learning to move from “unsure” to “pretty sure”, which is about the best a scientist can do.

These students are primed to learn more about the methodology and sample preparation so that they can reproduce their results. Sample size and placement, instrument settings, sample temperature, now take on an important role in determining the shape and size of the spectrum. Students now begin to develop an eye for the experimental details that make the difference between being unsure and pretty sure of their results. They are beginning to take ownership of their data. They are becoming producers of knowledge.

I think this is the most critical function of the SMART Center. Its' students may or may not become scientists and spectroscopists, but, no matter what path they decide to follow, they will have learned that information can be questioned and that information can be refined and changed. Imaging a world where everyone had that ability.

Dr. Reef (Philip D., II) Morse,

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POSITIONS

Research Specialist Senior Position at West Virginia University

The Department of Biochemistry is searching for a Research Specialist Senior, with a strong background in RF/MW engineering experience. This position is available immediately and will be in the In Vivo EPR Multifunctional Magnetic Resonance center, Department of Biochemistry, Health Sciences Center, West Virginia University in Morgantown, WV. The selected candidate will assist Dr. Tseytlin in designing and manufacturing electron paramagnetic resonance (EPR) spectrometers and imagers. The position will be for one year in length, with a possibility of extension. The duties and responsibilities for this position are: designing, manufacturing, assembling, and experimental testing of EPR spectrometers and imagers. Applicants must hold a minimum of Master's Degree (or foreign equivalents) in Electrical Engineering, Physics or a related field and two years of experience, or a combination of education and experience. Qualifications must be met by time of appointment. All interested, qualified can-

didates should apply to jobs.wvu.edu with a cover letter of interest and current CV.

West Virginia University is an Equal Opportunity/Affirmative Action Employer and the recipient of an NSF ADVANCE award for gender equity. The University values diversity among its faculty, staff and students, and invites applications from all qualified individuals, including minorities, females, individuals with disabilities and veterans.

Postdoc in optical nuclear magnetic resonance, joint Los Alamos/UNM, USA

The quantum nanophotonics and biosensing lab at U. of New Mexico (PI: Victor Acosta) and the atomic magnetometer/NMR/MRI labs at Los Alamos National Lab (PI: Igor Savukov) seek a motivated postdoctoral candidate for a joint UNM/LANL project. The successful candidate will work on a highly multidisciplinary project that combines new techniques in optical nuclear polarization using NV centers in diamond nanostructures with low-field and optically-detected NMR/MRI. The goal is to develop a microfluidic platform operating at room temperature and low magnetic field which can deliver biochemical analytes with a nuclear polar-

ization exceeding that possible using large superconducting magnets and/or cryogenic temperatures.

While working on the project, the postdoc will:

- Apply quantum mechanics, nanophotonics, and biochemistry to emerging new fields.
- Learn semiconductor nanofabrication techniques in world-class cleanrooms (CHTM, CINT).
- Work with partners in academia, national labs (LANL, Sandia), and industry (ODMR Tech).

The position will initially be based in Albuquerque, NM at the UNM lab. There the work will be focused on developing the NV hyperpolarization apparatus. Then the postdoc will transition to conducting NMR/MRI experiments at LANL to characterize and optimize its performance.

A PhD in Physics, Chemistry, Optical/Electrical/Chemical/Biomedical Engineering, or a related field is required. Experience in spin physics, biophysics tool development, and/or quantum optics is desired. Experience in magnetometry, semiconductor nanofabrication, and/or solid-state color centers is also helpful. Compensation is commensurate with

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experience and is expected to increase when work transitions to LANL. Candidates with very strong publication records will have an opportunity to apply to highly competitive LANL fellowship programs. More information is available on our webpage. Interested candidates, please send Cover letter (describing research interests and career goals) and CV (with complete publication record) to Victor Acosta (vmacosta@unm.edu) and Igor Savukov (isavukov@lanl.gov). UNM and LANL are equal opportunity employers.

Postdoctoral Fellow

The Magnetic Resonance Spectroscopy group at Rensselaer Polytechnic Institute (RPI) is conducting cuttingedge research in the fields of solar energy transduction in natural and artificial systems and the development of novel materials and solar technologies. By performing fundamental and applied research, we work on sustainable solutions for major challenges facing energy and the environment. RPI is committed to the training of future scientists and engineers and is one of the oldest science and engineering universities in the United States. We are looking for a Postdoctoral Fellow for advanced multi-frequency pulsed electron paramagnetic resonance (EPR) spectroscopy of natural and artificial systems.

Your tasks

- Operation and further development of pulsed EPR spectroscopy experiments (including ENDOR, HYSCORE and transient EPR spectroscopy)
- Performance of experiments on redox proteins, metal oxides and thin films
- Analysis and numerical simulation of experimental data
- Presentation of scientific results at national and international conferences
- Publication of scientific results in international journals
- Scientific collaboration with graduate and undergraduate researchers at RPI

Your profile

You are a flexible team member able to work independently on different projects. You have completed your PhD in chemistry or physics and have experience with pulsed EPR spectroscopy. A good command of various software tools enables you to analyze pulsed EPR spectra readily. You have active interest in experimental work with good practical skills and enjoy working in an interdisciplinary team. Your broad knowledge in physical chemistry and spin physics is a valuable asset to understanding the results of complex experiments. Good communication skills in English are required.

For further information please contact:

Prof. K. V. Lakshmi

Department of Chemistry and Chemical Biology and The Baruch '60 Center for Biochemical Solar Energy Research Rensselaer Polytechnic Institute

Troy, NY 12180

e-mail: lakshk@rpi.edu

lakshmi@baruch60center.org

phone: (518) 698 7976

Please send your application materials to Prof. K. V. Lakshmi through e-mail correspondence.

Cryogenic EPR Postdoctoral Position

A postdoctoral position is available immediately for a collaborative project between Professor Cory's lab at The Institute for Quantum Computing (IQC) and a local startup. The project uses superconducting resonators and Optimal Control Theory (OCT) to increase the sensitivity of pulsed electron spin resonance at cryogenic temperatures. The goal of the project is to also demonstrate applications to molecularly thin samples. This program is expected to reveal new and interesting results of EPR of biochemical processes.

The successful applicant should have an advanced degree (PhD) in chemistry, biochemistry or physics with significant experience in EPR of biomolecules.

The appointment will be for two years with the possibility of renewal. The salary is competitive and commensurate with experience, ranging from \$55,000 to \$70,000. Women and minorities are encouraged to apply.

Apply to grum.teklemariam@highqlp.com.

Research Scientist (Postdoctoral associate)


The Institute of Macromolecular Chemistry AS CR, v.v.i. seeks a postdoctoral associate / research scientist to join the Laboratory of electron paramagnetic resonance of polymer systems (EPR)

Requirements: University degree and PhD in the field of chemistry, physical chemistry or physics / Practical experience with the method of electron paramagnetic resonance (EPR) / Knowledge of and working experience with polymers and EPR imaging will be an advantage / Stays abroad will be an advantage / Good knowledge of English language / Good publication activity / Independence, reliability. Details about research work can be obtained from RNDr. Petr Štěpánek, DrSc., stepanek@imc.cas.cz

Candidates should submit a structured CV emphasizing experience relevant to the advertised position, a motivation letter and a list of publications and other results to e-mail: fenc@umch.cz HR department tel. (420) 296 809 385.

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Please Contact: Phil Barker pba02985@bigond.net.au or pbarker@uow.edu.au to receive user logbook and publications list.

Postdoctoral Associateships in Magnetism at NIST

We offer postdoctoral opportunities in magnetism at the National Institute of Standards and Technology in Boulder, Colorado, USA. Annual salary is \$65,600 plus benefits. Appointments are for two years. Application deadlines are 1 February and 1 August annually (but inquire earlier).

The application process is competitive. Typical successful applicants have a strong research background and academic record. Letters of reference and an original research proposal are required.

U.S. citizenship and a background investigation are required (no exceptions).

www.nist.gov/pml/electromagnetics/magnetism

EPR Specialist Position at Johns Hopkins

Postdoctoral or specialist (staff) position is available immediately to study membrane proteins at the Johns Hopkins University School of Medicine in Baltimore, Maryland, USA. We study conserved membrane enzymes with implications for human health (see Nature Chem Biol 8:759, eLife 1:e00173, and Nature Rev Micro 7:411), and are generously funded by the National Institutes of Health (NIH) and the Howard Hughes Medical Institute (HHMI). The project uses site-directed spin labeling (SDSL) with nitroxide probes to

study the dynamics, distance measurements, and saturation kinetics with CW-EPR methods. The applicant must have at least 3 years of prior experience in SDSL, EPR, spectrum simulations, and distance measurements as evidenced by publications. Experience with membrane proteins is preferred but not essential. Position will come with generous salary and benefits, depending on experience and record of achievement. Interested applicants please send detailed CV and contact information for 3 references to rosanna@jhmi.edu.

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Please send resume, cover letter and salary requirements to brukey.jobseprfse0620@bruker-biospin.com

EQUIPMENT

Wanted: Badly needed certain parts of, or even a complete Bruker X-Band microwave unit from the mid-seventies, the one which came with the Bruker B-ER 420 system. Particularly, the klystron heating and protection board, B-E-Z 10. Please contact Prof. Dr. Wolfgang

E. Trommer, Department of Chemistry, TU Kaiserslautern, P.O.Box 3049, D-67653 Kaiserslautern, Germany. E-mail: trommer@chemie.uni-kl.de.

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Please contact techepr03@gmail.com for availability and pricing.

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Please contact: Richard W. Quine, e-mail: rquine@du.edu, phone: 1-303-871-2419

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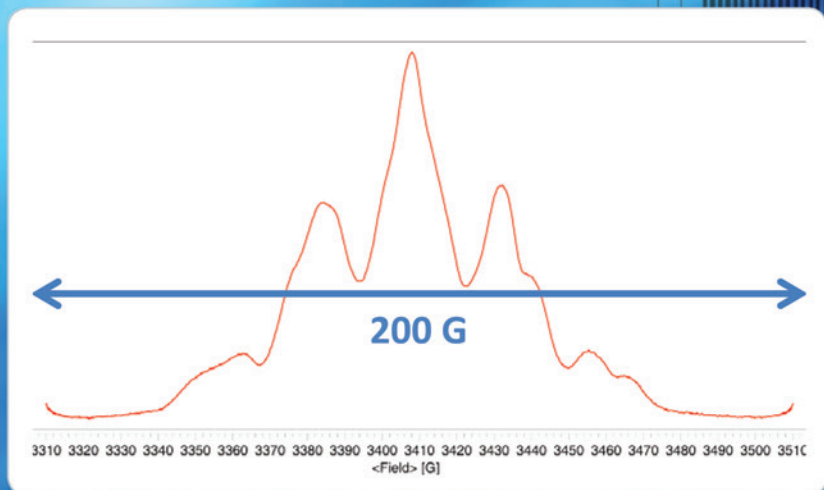
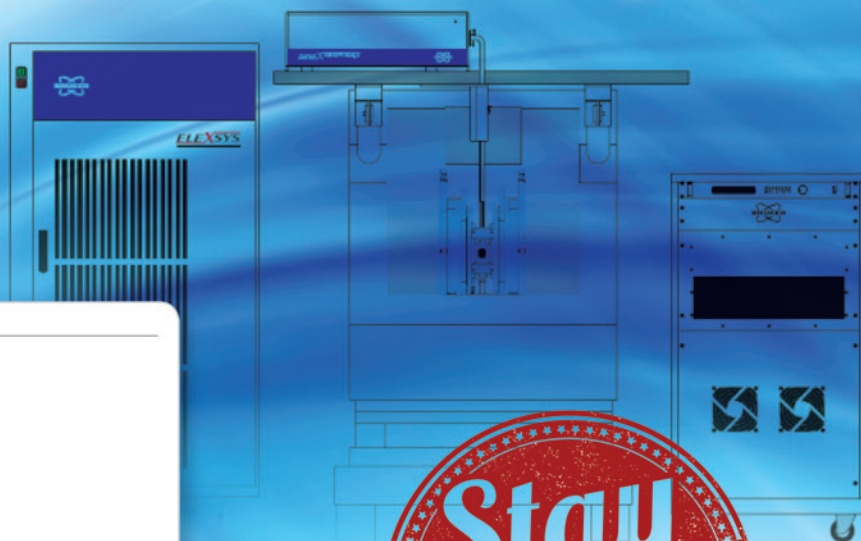
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