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DEPARTMENT OF TECHNICAL PHYSICS FACULTY OF MECHANICAL ENGINEERING AND MECHATRONICS WEST POMERANIAN UNIVERSITY OF TECHNOLOGY IN SZCZECIN

POLISH EMR GROUP





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WELCOME ADDRESS

The Sixth Forum EMR-PL, West Pomeranian University of Technology (WPUT) in Szczecin, 19 – 22, September 2022

Honored Guests, Ladies and Gentlemen:

On behalf of the Council of the Polish EMR Group and the Local Organizing Committee (LOC) of the VI Forum EMR-PL, first I warmly welcome our Honored Guests:

- *Dr hab. inż. Jacek Wróbel, Professor of WPUT*, Rector of the West Pomeranian University of Technology in Szczecin we are most grateful His Magnificence for his support and Honorary Patronage.
- *Prof. dr hab. inż. Mirosław Pajor*, Dean, Faculty of Mechanical Engineering and Mechatronics, WPUT we sincerely thank the Dean for stepping in as Chairman of the LOC.
- *Professor dr hab. Niko Guskos*, Department of Technical Physics, WPUT, who was to chair the LOC in 2020/21 but due to delay caused by Covid pandemic has retired in the meantime, however, has greatly supported us as the Honorary Chairman of the LOC.

Next, in the same capacity, I welcome representatives of our valued sponsors:

Dr. Eric Xu, Director of Magnetic Resonance, CIQTEK company from Hefei, Anhui, China.

Dr Tomasz Czechowski, Research and Development Director, Novilet company in Poznań.

The companies they represent are developing and producing a range of EMR spectroscopy related instrumentation. We appreciate much not only the financial assistance received from our sponsors, but also the opportunity to learn about the available equipment. Later during the Opening Ceremony Dr Czechowski will deliver a presentation in person, whereas Dr. Eric Xu - online via video link, due time difference, on Tuesday morning.

On sad note, we would like to remember and honor Professor Ryszard Krzyminiewski, Faculty of Physics, Adam Mickiewicz University (AMU), Poznań, who passed away earlier this year. Professor Krzyminiewski co-chaired the Local Organizing Committee of the Fourth Forum EMR-PL held in Poznań, in June 2016. During the Opening Ceremony *Dr hab. Bernadeta Dobosz, Prof. UAM*, will present the scientific achievements of Professor Krzyminiewski and his contributions to the development of EPR/ESR spectroscopy at the AMU.

Last but not the least, in my capacity as the (*outgoing*) Chairman of the Polish EMR Group, I welcome all participants to the VI Forum EMR-PL.

Thanks are due to all Colleagues, who, at short notice, have decided to attend and thus helped greatly bringing this Forum back to life. I believe that, due to the presentations and posters, this Forum may play an important role in enhancing the strength of the EMR research groups in Poland. Continuing with the spirit of the previous Fora (1st in Rzeszów, 2nd in Huciska, 3rd in Kraków, 4th in Poznań, and 5th in Wrocław/Kudowa Zdrój), this Forum is organized under the auspices of the Polish EMR Group and is open to all persons involved in EMR basic research and applications. The main aims are to bring together EMR (EPR/ESR & FMR/AFMR) spectroscopists working in Poland as well as to promote and facilitate collaboration among the Polish EMR community. I am confident that the scientific program of the VI Forum EMR-PL will satisfy most participants and provide ample opportunities to meet fellow researchers and to discuss various topics of interest.

For the third time we have invited as plenary speaker an eminent EMR researcher from abroad. This time our **honored guest is Dr. Petr Neugebauer**, Central European Institute of Technology (CEITEC), Magneto-Optical and THz Spectroscopy Research Group, Brno, Czech Republic. We are grateful for accepting our invitation and hope that Petr's participation will be beneficial to all colleagues and it may also help forging stronger ties with the EMR communities in neighboring countries. This idea may be developed by the Chairman-Elect (see below).

Let me also say a few words about the Local Organizing Committee of the VI Forum EMR-PL.

I do believe that we all will appreciate the hard work and organizational efforts of our colleagues in Szczecin. Their dedication, the more valuable in view of the adverse conditions, have brought this Forum to fruition. It has turned out extremely difficult to revive the Forum after postponing first from 2020 to 2021 and then to 2022. It is enough to say that in June 2022, we have considered cancelling organization of the VI Forum in September this year in view of very low number of registered participants. Fortunately, finally we have made it, in spite of the uncertainties created by Covid pandemic, and the difficulties arising from the short time left to initiate formally the organization of Forum in early 2022. Therefore, in these circumstances we may feel lucky that we can meet again after the Covid related hiatus. This event would not have been possible without, I sincerely may say, the heroic efforts of the hard working LOC team.

Full list of the LOC members is included in the Book of Abstracts. In addition to the persons mentioned above as Honored Guests, special thanks go to staff from the Department of Technical Physics (DTP), WPUT:

Dr Danuta Piwowarska - Vice-Chairwoman,

Dr inż. Grzegorz Leniec – Secretary,

Dr Hubert Fuks - Member,

Dr hab. inż Paweł Berczyński, Prof. ZUT, Head of DTP – Member;

Prof. dr hab. inż. Rafał Rakoczy - Dean, Faculty of Chemical Technology and Engineering.

On personal side, I appreciate much consultations and support from *Dr hab. Piotr Pietrzyk, Prof. UJ*, Jagiellonian University, a special the LOC member. Note that at the last General Meeting of the Polish EMR Group, held during the 5th EMR-PL Forum in Wrocław/Kudowa Zdrój, June 7, 2018, at first I offered my resignation from the function of Chairman but in view the proposals from participants, I accepted to continue as Chairman for one more term. As a compromise solution, Piotr was unanimously elected as the Chairman-Elect of the Polish EMR Group. This fact turned out to very fortunate and provident. Due to outbreak of Covid my last term of office got extended for extra two years. I do believe that, after twelve years in the 'driver's seat', this is right time to pass the Chairman's duties to a younger colleague. I promise to actively support him in 'driving' further the Polish EMR Group in future, but then from a 'passenger seat'.

Notably, instead of celebrating the 10th Anniversary of establishing the Polish EMR Group during the VI Forum EMR-PL in Szczecin as planned in 2020, Piotr and myself, we have worked out an article: *The Polish EMR Group reaching maturity at 10th+ Anniversary*, published in EPR newsletter, 31/2, 6-8 (2021). Another sign, that against all odds induced by Covid pandemic, the Polish EMR community has been alive and kicking, is the account of our collective achievements and thriving activities over the years. With contributions from several colleagues, we have edited and co-authored another article: *History of electron paramagnetic resonance in Poland* – Part 1 appeared in EPR newsletter, 32/1, 8 - 9 & 12 - 13 (2022) and Part 2 in EPR newsletter, 32/2, 7 - 8 & 11 – 12 (2022).

We may be all pleased that this Forum is held this time in Szczecin. This provides an opportunity to those who visit this place for the first time to find out that it is an interesting and friendly city. Hope you will have a chance to do some sighting, especially to enjoy vistas not possible to see from the land during the planned boat trip.

I would also like to invite all participants to join us at the General Meeting of the Polish EMR Group, to be held during tomorrow evening. A whole range of topics of interest to the whole EMR community will be discussed. Hence, your votes and opinions are of great importance as they may shape the future course of events.

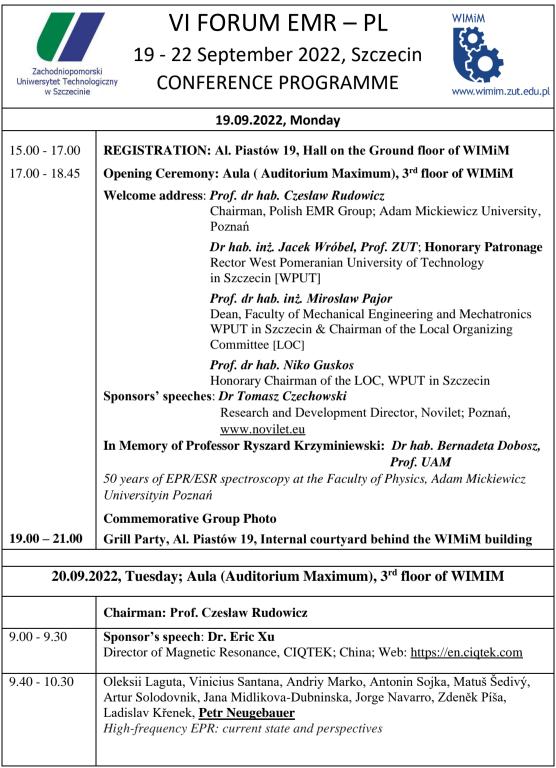
I wish you all an enjoyable and stimulating experience at the Forum and in Szczecin. Thank you.

Midan

Czesław Rudowicz

Chairman, Polish EMR Group [established at URz in Rzeszów, 2010] Founder President, Asia-Pacific EPR/ESR Society [established at CityU in Hong Kong, 1997]

CONFERENCE PROGRAMME



10.30 - 11.10	Ryhor Fedaruk, Maria A. Augustyniak-Jabłokow, Roman Strzelczyk,
	Antonio Barbon Vacuum Rabi splitting and Rabi oscillations in EPR of glass-like carbon
11.10 - 11.50	COFFEE BREAK
11.50 - 12.30	Ireneusz Stefaniuk , Czesław Rudowicz, Dawid Marcinkowski, Ariel Adamski, Maciej Kubicki, Violetta Patroniak, Tomasz Ślusarski, Muhammed Açıkgöz, Mirosław Karbowiak, Adam Gorczyński, Maria Korabik <i>CW and pulsed EMR spectra of Cu2+ ion in potential molecular nanomagnets</i>
12.30 - 12.55	Krystian Mokrzyński, Michał Sarna, Theodore G Camenisch, Tadeusz Sarna <i>Photoreactive and antioxidative properties of natural melanin pigments</i>
12.55 - 13.20	Agnieszka Drzał, Martyna Elas Electronic paramagnetic resonance in the non-invasive monitoring of the tumor microenvironment
13.20 - 14.50	LUNCH
	Chairman: Prof. Petr Neugebauer
14.50 - 15.30	Muhammed Açıkgöz, Ram Kripal, Madan Gopal Misra, Awadhesh Kumar Yadav, Paweł Gnutek, <u>Czesław Rudowicz</u> Semi-empirical modeling of crystal field and zero field splitting parameters for Mn ²⁺ ions doped into tetramethylammonium tetrachlorozincate crystal
15.30 - 16.10	Maria A. Augustyniak-Jablokow, Roman Strzelczyk, Ryhor Fedaruk, Krzysztof Tadyszak, Karolina Jurkiewicz Triplet States in Glass-like Carbon
16.10 - 16.35	<u>Roman A. Strzelczyk</u> , Susanna Ciuti, Antonio Barbon A new tool for EPR data analysis in the study of photoexcited triplet states
16.35 - 17.00	COFFEE BREAK
17.00 - 18.30	POSTER SESSION
18.30 - 19.30	GENERAL MEETING OF THE POLISH EMR GROUP
20.00 - 23.55	CONFERENCE BANQUET, Venue will be announced at Registration.
	21.09.2022, Wednesday; Aula , 3 rd floor of WIMiM
	Chairman: Prof. Maria A. Augustyniak-Jabłokow
9.00 - 9.40	Bartosz Mozgawa, Filip Zasada, Kinga Góra-Marek, Chengyang Yin, Zhen Zhao, Piotr Pietrzyk, Zbigniew Sojka Molecular insights into the SCR reaction mechanism catalyzed by Cu and Ni, metallozeolites - EPR/HYSCORE, 2D COS IR and DFT investigations
9.40 - 10.05	Bernadeta Dobosz, Ryszard Krzyminiewski, Klaudia Kotarska, Eliza Gunia, Grzegorz Schroeder, Joanna Kurczewska <i>Interactions between TEMPO-functionalized magnetic nanoparticles and cells</i>

10.05 - 10.30	Kamila Sobańska, Łukasz Wolski, Piotr Pietrzyk
	<i>EPR</i> detection of reactive oxygen species on mixed metal oxides in the presence of hydrogen peroxide
10.30 - 10.55	Bartosz Mozgawa , Filip Zasada, Monika Fedyna, Kinga Góra-Marek, Piotr Pietrzyk, Zbigniew Sojka <i>EPR study of copper active sites in Cu-SSZ-13 zeolites - application in selective</i> <i>catalytic reduction of NOx with ammonia</i>
10.55 - 11.25	COFFEE BREAK
	Chairman: Prof. Zbigniew Sojka
11.25 - 11.50	Krzysztof Kruczała, Marek Bucki Study of plastic objects aging processes by means of EPR spectroscopy
11.50 - 12.15	Bohdan V. Padlyak , Ihor I. Kindrat, Yurij O. Kulyk, Adam Drzewiecki, Yurij S. Hordieiev, Victor I. Goleus, Radoslaw Lisiecki <i>Local Structure, EPR and Optical Spectroscopy of Complex Lead-Silicate Glass, Doped with Copper</i>
12.15 - 12.40	V.D. Popovych , L. Dubiel, I. Stefaniuk, B.Cieniek, M. Kuzma Anisotropic effects of EPR spectrum of the Cr_3Te_4 macro-defects embedded in the CdTe single crystalline matrix
12.40 - 13.05	Maciej Witwicki Semiquinonato Complex of diamagnetic metal cations: experimental and computational EPR studies
13.05 - 15.00	LUNCH
16.00 - 18.00	BOAT TRIP, Details will be announced at Registration.
	22.09.2022, Thursday; Aula, 3rd floor of WIMiM
	Chairman: Prof. Ireneusz Stefaniuk
9.00 - 9.40	Adam Ostrowski, Waldemar Bednarski, Izabela Malinowska, Marta Kowalkińska, Anna Zielińska-Jurek ESR photochemical measurements of new photocatalysts for water treatment by spin-trapping method
9.40 - 10.05	Barbara Pytel. Dariusz Man Impact of selected selenium compounds on dynamic properties of model membranes - electron paramagnetic resonance study
10.05 - 10.30	M. Kuzma , V.D. Popovych, S. Zhou, G. Luka, I. Stefaniuk, B. Cieniek Anisotropic hyperfine interaction in CdTe:I single crystals implanted with chromium
10.30 - 11.10	COFFEE BREAK

11.10 - 11.35	Yi-Shin Chen, Zhen Bao, Wen-Tse Huang, Agata Lazarowska, Natalia Majewska, Sebastian Mahlik, <u>Grzegorz Leniec</u> , Slawomir M. Kaczmarek, Hsiao-Yu Huang, Chun-I Wu, Di-Jing Huang, Ru-Shi Liu <i>Unusual EPR spectra and temperature behaviour of Mn</i> ²⁺ <i>ions in organic-</i> <i>inorganic hybrid manganese halides.</i>
11.35 - 12.00	Niko Guskos, Agnieszka Sienkiewicz, Ewelina Kusiak-Nejman, Agnieszka Wanag, Antoni W. Morawski, <u>Danuta Piwowarska</u> EPR investigation of APTES-TiO ₂ under artificial solar light
12.00 -12:30	CONFERENCE CLOSING
12:30-14:00	LUNCH

Categories & Duration of the presentations:

- * **Plenary**: 45 min + 5 min for discussion
- * **Invited**: 35 min + 5 min for discussion
- * **Oral:** $20 \min + 5 \min$ for discussion.

Session Chairmen are kindly requested to inform each presenter:

- 1) about 10 min before the end of presentation that there are *"10 min left including discussion"*;
- 2) about 5 min before the end of presentation that "*the remaining time should be devoted for discussion*".

Please upload the file with your presentation into the conference computer before the start of a given session, unless you intend to use your own notebook.

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IN THE MEMORY OF PROFESSOR RYSZARD KRZYMINIEWSKI

<u>Bernadeta Dobosz</u>

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Prof. dr hab. Ryszard Krzyminiewski – a physicists, was born in 1948 in Poznań.

From the beginning of his scientific work, he was involved in spectroscopic research, especially of biologically active substances, using electron spin resonance (ESR) – PhD in 1979: "Electron spin resonance of nucleic acid (RNA) components irradiated with gamma rays". Professor was also interested in issues related to medicine. He led to the creation of a new specialization at the Faculty of Physics of the Adam Mickiewicz University - medical physics, transformed in 2012 into a field of study.



In his scientific work, Professor developed two topics: advanced analysis of biosignals (ECG and pulse wave) and functionalized nanomaterials as drug carriers in targeted therapy. The greatest scientific achievements of Professor include participation in the construction of ESR spectrometers and the first ENDOR spectrometer in Poland, development of several computer softwares for advanced analysis of ESR spectra, development of the NURSE-ECG and HSR-PW methods (advanced analysis of ECG and pulseoximetry records), implementation of the medical telemonitoring system MONTE, as well as the development of the method

of functionalized magnetic nanoparticles focusing (MNF-3D) and the application of the ESR method to control the processes of such nanoparticles endocytosis into cells.

In 2021 Professor Krzyminiewski celebrated the 50th anniversary of his professional work.

Prof. dr hab. Ryszard Krzyminiewski died on May 18, 2022 at the age of 74.

LECTURES

Letrure 1 - Plenary Lecture

High-frequency EPR: current state and perspectives

Oleksii Laguta, Vinicius Santana, Andriy Marko, Antonin Sojka, Matuš Šedivý, Artur Solodovnik, Jana Midlikova-Dubninska, Jorge Navarro, Zdeněk Píša, Ladislav Křenek, and <u>Petr Neugebauer</u>

Central European Institute of Technology, Magneto-Optical and Terahertz Spectroscopy Group, Brno University of Technology, Purkynova 123, 61200 Brno, Czech Republic.

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From its discovery, electron paramagnetic resonance (EPR) is a constantly developing technique following technological advances in generating and detecting microwaves, creating strong magnetic fields, and fast digitalization, among others. In the talk, I will discuss developments in the field of high-frequency EPR (HFEPR) with a special focus on experiments in the frequency domain compared to the traditional field domain EPR. I will report on the recent development of a highfrequency rapid scan electron spin resonance (FRASCAN) spectrometer at the Brno University of Technology. The basic principle of frequency rapid scan will be explained and compared to conventional methods. I will present significant progress in the experimental determination of Zeeman diagrams (frequency vs. field EPR maps) and discuss the advantages of HFEPR for investigating high-spin systems, particularly single-molecular magnets (SMMs). Besides, we dedicate a section to discuss the advances in the studies of the cyclotron resonance in thin-films and modern solid-state materials like graphene (graphite). Furthermore, the importance of HFEPR for dynamic nuclear polarisation (DNP) is discussed. At last, I will demonstrate the possibility of accessing very short relaxation times (ns) by implementing rapid frequency scans, emphasizing the power of frequency domain EPR. This technique allowed to perform, for the first time, multi-frequency relaxation studies in a single spectrometer at frequencies above 100 GHz.



FRaScan Spectrometer.

- O. Laguta, A. Sojka, A. Marko, and P. Neugebauer: "Rapid scan ESR: a versatile tool for the spin relaxation studies at (sub)THz frequencies", <u>Appl. Phys. Lett.</u> <u>120, 120502 (2022)</u>
- A. Sojka, M. Šedivý, A. Lagiň, A. Gabriš, T. Láznička, V. T. Santana, O. Laguta, P. Neugebauer, "Sample Holders for Sub-THz Electron Spin Resonance Spectroscopy", IEEE T. Instrum. Meas., 71, 8002812 (2022)
- 3. O. Laguta, M. Tuček, J. van Slageren, P. Neugebauer: "Multi-frequency rapidscan HFEPR" J. Magn. Reson. 296, 138–142 (2018)
- P. Neugebauer, D. Bloos, R. Marx, P. Lutz, M. Kern, D. Aguila, J. Vaverka, O. Laguta, C. Dietrich, R. Clérac and J. van Slageren: *"Ultra-broadband EPR spectroscopy in field and frequency domains", Phys. Chem. Chem. Phys.*, 20, 15528-15534 (2018)
- D. Bloos, J. Kunc, L. Kaeswurm, R. L. Myers-Ward, K. Daniels, M. DeJarld, A. Nath, J. van Slageren, D. K. Gaskill and P. Neugebauer: "*Contactless millimeter wave method for quality assessment of large area graphene", 2D Mater.* 6, 035028 (2019)

Lecture 2

Vacuum Rabi splitting and Rabi oscillations in EPR of glass-like carbon

<u>Ryhor Fedaruk</u>¹, Maria A. Augustyniak-Jabłokow², Roman Strzelczyk², Antonio Barbon³

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Keywords: vacuum Rabi splitting; Rabi oscillations; glass-like carbon; triplet states

Two types of coherent phenomena such as a vacuum Rabi splitting and Rabi oscillations can be observed in EPR of carbon-related materials. In particular, high spin concentration of $10^{19} - 10^{20}$ spin/g in some carbon materials including glasslike carbons (GLCs) results in very intense and narrow EPR signals. The EPR signals of these materials are usually presented by a single line and it difficult to identify paramagnetic centers (PCs). It was recently shown that high concentration of PCs can result in distortions of the CW EPR line spectrum due to a cavity quantum electrodynamics effect called a vacuum Rabi splitting. This effect arises from the strong coupling between electron spins and photons in the microwave cavity and is also called a vacuum Rabi oscillation when it is observed in a time domain. This weak effect for a single spin is enhanced by a factor of for an ensemble of spins and can be observed when the number of polarized spins in the cavity is substantially larger than the number of microwave photons. These conditions can be realized in the CW EPR of GLCs, especially at low temperatures, and distortions due to the vacuum Rabi splitting can make measurements of the real line impossible. On the other hand, at a strong pulsed microwave field when, resonant interactions between the field and spins can result in another effect, Rabi oscillations (transient nutations). Besides a free induction decay (FID) and a spin echo, these strong-field-induced oscillations of magnetization are used in pulsed EPR to study relaxation processes or for identification of quantum transitions. The vacuum and strong-field-induced Rabi oscillations have different properties. In some cases, including GLCs, these two types of oscillations can be realized and used to study such features of PCs that is difficult to measure by other EPR techniques.

In the present paper, we demonstrate the vacuum Rabi splitting in the CW EPR spectrum of GLCs and use its sample-size dependence to define conditions for undistorted registration of EPR spectra and for the absolute determination of the number of spins in a sample. The strong-field-induced Rabi oscillations as well as FID were applied for measuring relaxation times and identifying a type of EPR line broadening. We find that the Rabi frequency in our sample is 1.34(2) times higher than this frequency of PCs in the reference sample () indicating the presence of triplet states.

Lecture 3

CW and pulsed EMR spectra of Cu²⁺ ion in potential molecular nanomagnets

<u>Ireneusz Stefaniuk^{a*}</u>, Czesław Rudowicz^b, Dawid Marcinkowski^b, Ariel Adamski^b, Maciej Kubicki^b, Violetta Patroniak^b, Tomasz Ślusarski^b, Muhammed Açıkgöz^c, Mirosław Karbowiak^d, Adam Gorczyński^b Maria Korabik^d

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Keywords: Electron magnetic/paramagnetic resonance (EMR/EPR); Continuous wave (CW) and pulsed EMR spectroscopy; Spin Hamiltonian; Molecular nanomagnets (MNMs).

Molecular nanomagnets (MNMs) are extensively studied because of a variety of potential applications, e.g. molecular spintronics, quantum information processing, or sensing. Our earlier work [^[i]] describes the synthesis, structural and magnetic properties, cw-EPR, theoretical modeling of spin Hamiltonian (SH) parameters. The effect of structural changes on slow magnetic relaxation for the mononuclear octahedral copper complex (compound 1 $[Cu(C_{17}H_{21}N_5O_4)(CH3OH)][ClO_4]_2$, compound 2 $[Cu(C_{19}H_{25}N_5O_4)(H_2O)(CF_3SO_3)_2])$ were also analyzed. Here, we present new results of continuous wave (CW) and pulsed EMR studies in a wide temperature range (5 K-300 K) and extended analysis of the EMR line parameters using the EasySpin program. Measurements of the relaxation times: T1 and T2* were carried out using pulsed EMR in helium temperatures. The measured T1 and T2* relaxation times using pulsed EMR are, for example, at a temperature of 15K: component 1, T1 = 593 ns and $T2^* = 580$ ns and component 2, T1 = 599 ns and $T2^*$ = 576 ns. When the temperature is lowered, the relaxation times increase, whereas an increase in temperature causes a decrease in the value of the relaxation times. This enables comparative analysis of the relaxation mechanisms based on CW and pulsed EMR data.

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Lecture 4

Semi-empirical modeling of crystal field and zero field splitting parameters for Mn²⁺ ions doped into tetramethylammonium tetrachlorozincate crystal

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Keywords: Electron magnetic/paramagnetic resonance (EMR/EPR); Optical spectroscopy and crystal field Hamiltonian; Spin Hamiltonian and zero-field splitting; Superposition model analysis

Superposition model (SPM) analysis is useful for semi-empirical modeling of the crystal field parameters (CFPs) as well as the zero-field splitting (ZFS) parameters (ZFSPs). We utilize SPM for Mn²⁺ ions doped into tetramethylammonium tetrachlorozincate, $[N(CH_3)_4]_2$ ZnCl₄ (TMATC-Zn) crystal. Local structural data for the prospective Mn²⁺ sites are determined considering possible lower symmetry cases. The model calculations are carried out for the two substitutional options for dopant Mn^{2+} ions in TMATC-Zn: substitutional and interstitial sites, which have been invoked in literature. The aim is to discriminate between the two competing options. This is achieved by using the SPM predicted CFPs and ZFSPs for the dopant Mn²⁺ ions to determine the CF energy levels and the ZFSPs and then comparing the modelled results with those obtained by optical and EMR spectroscopy, respectively. First, SPM is employed to predict CFPs, which serve as input for the perturbation theory expressions to calculate the conventional 2^{nd} -rank ZFSPs (D, E) at orthorhombic sites. Then, the SPM/CFPs are used as input for the CFA package to calculate the CF energy levels within the 3d⁵ configuration and re-analyze available optical spectra. Independently, SPM is employed to predict all 2nd- and 4th-rank ZFSPs from structural data. Correlation of optical and EMR spectroscopy data increases modeling reliability. Comparison of the predicted ZFSPs (D, E) with experimental ones and consideration of the magnitudes of distortions yielding good matching, enables discriminating between the two substitutional options. It is shown that interstitial sites are more suitable than substitutional sites for Mn²⁺ ions in TMATC-Zn, in agreement with the experimental EMR presumptions. Our results reveal the importance of combining two separate methods to determine more

reliably the most likely site for substitution of paramagnetic ions. This study also tests the range of applicability of CF theory and SPM analysis for Mn^{2+} ions in TMATC-Zn crystals and prepares grounds for consideration of the properties of molecular nanomagnets containing Mn^{2+} ions.

Acknowledgments: RK is grateful for support by Head, Department of Physics, University of Allahabad, U.P. 211002, India. C. Rudowicz acknowledges partial support from the internal research grant from the Faculty of Chemistry, Adam Mickiewicz University.

Lecture 5

Triplet States in Glass-like Carbon

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Keywords: glass-like carbon; shungite; triplet states; conduction electrons; forbidden transitions

Glass-like carbons (GLCs) are a large group of disordered carbon materials whose properties vary depending on the precursor and on the temperature and time of the high temperature treatment (HTT). Predominantly sp^2 bonded GLCs are comprised of an isotropic entanglement of graphenic nanostructures and are non-graphitizable. Similar properties are shown by shungite, a natural GLC. Synthetic GLCs are accompanied by high concentration of paramagnetic centers which strongly depends on HTT and reach maximum in 700-900 °C.

Paramagnetism of GLCs was studied by magnetic susceptibility and EPR focused on the impact of HTT on the intensity of the EPR signal. Despite a high density of PCs and strong EPR signals in GLCs, there is a surprisingly small number of articles on the EPR study of these materials and the origin of the observed PCs remains unknown. Because of an apparently simple EPR spectrum of these disordered and inhomogeneous materials, it is difficult to identify these PCs, in particularly, without low-temperature studies. Additional difficulties are caused by electrical conductivity manifesting in the Dysonian line and decreasing quality factor of resonator. Moreover, high spin concentration of GLCs can result in distortions of the EPR signal due to the strong coupling between electron spins and the microwave cavity. The temperature dependences of the EPR signals in GLCs were investigated in the limited range of 103-473 K and their low-temperature properties are unknown until now.

We report EPR studies of GLCs performed in the temperature range 4.2-300 K. To obtain a true dependence of the EPR line intensity (*I*), we carefully chose the form and mass of samples, microwave power and take into account temperature-induced changes in the resonator quality factor due to electrical conductivity. Contribution of localized and delocalized electrons in our samples can be distinguished using temperature dependences of *IT*. Subtracting of the Pauli paramagnetism gives temperature-dependent *IT*. We conclude that the ground state is nonmagnetic and the magnetic one is an excited state and the observed paramagnetism is due to triplet state. This hypothesis is supported by a weak signal from "forbidden" transitions ($\Delta m_s=2$) in the spectrum of GLC revealed in the half-field region.

Lecture 6

Molecular insights into the SCR reaction mechanism catalyzed by Cu and Ni metallozeolites - EPR/HYSCORE, 2D COS IR and DFT investigations

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Keywords: NOx, selective catalytic reduction, spectroscopy, molecular modeling

Activation of NH₃, NO, O₂ and HC which are the prime reactants of the SCR reaction is essentially controlled by their capacity of forming specific bonds with the intrazeolite Cu and Ni cations characterized by various location, coordination and valence states. Spectroscopic studies allow for explicit insight into the molecular mechanism of the activation of those reactants, which is essential not only for a phenomenological description of their capture, but also for a more in-depth understanding of the elementary events constituting the SCR reaction. Mechanistic investigations into the elementary steps of selective catalytic reduction of NO on Cu and Ni zeolites using NH₃ and C₂H₄ as reductants, respectively, were performed by application of the EPR/HYSCORE and the 2D COS IR spectroscopies, corroborated with DFT and first principles thermodynamic (FPT) modeling. It was shown that several types of the active centers, such as single bare cations, hydroxylated cations and dual μ -oxo M²⁺–O^{2–}–M²⁺ species, are involved in this reaction, yet acting in a distinctly different fashion. In the case of the HC-SCR reaction over NiZSM-5 the unique electronic and magnetic structure of the nitrosyl intermediates was ascertained by EPR, HYSCORE and IR and studies, and next substantiated by the DFT/GGA and CASSCF calculations. The electrophilic vs nucleophilic nature of the ligated NO^{δ +} appears crucial for its successful insertion into the >C=C< bond and for subsequent N–N bond formation. Selective catalytic reduction occurs along the nitrate/ammonia and NOx/cyanide routes, which are controlled by the reversal of partial charge on the nitrogen from positive in N^{$\delta+$}O into negative in N^{$\delta-$}H₃ or –CN^{$\delta-$}/–N^{$\delta-$}CO. In the case of the NH₃-SCR reaction over CuSSZ-13 and Cu/NiSSZ-13 catalysts the NH₃ binding plays the key role in the low temperature, formation of nitrates in the medium temperature and ammonia retention an acid Bronsted sited at high temperature. EPR and 2D COS IR studies made possible to identify the reaction intermediates and to follow their transformation routs into desired dinitrogen. The Ni-O-Cu bridges are beneficial for decrease of the undesired NH₃ oxidation, whereas higher thermal stability of the Ni-NH₃ complexes is helpful for the intrazeolite NH₃ retention. The FPT modeling provided a requisite thermodynamic background for understanding the SCR reaction course.

Acknowledgements

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Lecture 7

ESR photochemical measurements of new photocatalysts for water treatment by spin-trapping method

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Keywords: ESR photochemical measurements, photocatalysts, free radicals, spin-trapping, PBN

Free radical species plays an important role in the photodegradation of environmental pollution (including different pharmaceuticals) and their removal from water and wastewater. Titanium(IV) oxide is one of the commonly used photocatalyst, however, in a technological process, there are several problems with cyclic utilization of the powdered nano-TiO₂ particles suspended in the treated water. Recently, magnetic photocatalysts have appeared in which TiO₂ is deposited on the surface of various types of ferrites, enabling easy separation of the photocatalyst from the system after the purification process [1].

Photoexcitation of TiO₂ (and other photocatalysts) can create a valence band hole h_{vb}^+ and e_{eb}^- pair. In the presence of water molecules or hydroxide ions, the positive holes can generate hydroxyl radicals. Moreover, under aerobic conditions superoxide radicals are created, which can be transformed to hydrogen peroxide or hydroxyl radicals [2, 3].

Electron spin resonance (ESR) is one of the most sensitive methods for free radicals detection. Unfortunately, superoxide or hydroxyl radicals have too short a lifetime to detect such radicals directly by ESR. In order to obtain a more stable adduct, that could be detected and identified by ESR, we used PBN (N-tert-Butyl- α -phenylnitrone) as a spin trap for short-lived radicals.

We have performed photochemical (ESR) measurements of an aqueous suspension of the chosen photocatalysts used in water purification processes. The suspensions were UV irradiated ($l_{max} = 365$ nm) directly in the ESR resonator with

the light power of about 70 mW/cm². ESR spectra have shown that the short-lived hydroxyl radicals were trapped on PBN.

Our ESR photochemical experiments were performed under aerobic and hypoxic conditions. The higher intensity of trapped hydroxyl radical ESR spectra recorded under aerobic conditions, clearly shown that both superoxide and hydroxyl species can be created during the UV irradiation.

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ORAL and POSTERS

Oral 1

Photoreactive and antioxidative properties of natural melanin pigments

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Keywords: natural melanins, photodegradation, photoreactivity, photoprotection, phototoxicity, skin

Photoreactivity of melanin has become a major focus of research due to the postulated involvement of the pigment in UVA-induced melanoma. Melanins in human skin are frequently exposed to solar radiation that can modify the photoprotective properties of pigments and potentially elevate the risk of phototoxic reactions mediated by the photoreactive behavior of pigments. In this research, we examined the photoreactive and antioxidant properties of natural melanin pigments isolated from hair samples obtained from donors of different skin phototypes (I, II, III, and V) and subjected to 400 nm photodegradation. Their paramagnetic properties were determined using X-band and W-band electron paramagnetic resonance (EPR) spectroscopy. Photodegradation of the pigments was monitored using X-band EPR and UV-VIS spectrophotometry. EPR oximetry was used to analyze oxygendependent photoprocesses mediated by melanin pigments. Photoproduction of superoxide anion was determined by EPR spin-trapping using DMPO as a spin trap. Time-resolved near-infrared phosphorescence was employed to measure quantum yield of singlet oxygen photogeneration. DPPH EPR assay was used to determine the one-electron reduction capacity of the photodegraded pigments. Biological implications of the presence of photodegraded pigments were studied in cultured cells. MTT assay was used to determine the viability of human epidermal keratinocytes (HaCaT cells) exposed to native and photodegraded melanins of different phototypes in the dark and after irradiation with light from a solar simulator. Changes in the mitochondrial membrane potential, one of markers of apoptosis, were determined using JC-10 assay. Accumulation of lipid hydroperoxides (LOOH), as a result of light-induced toxicity of natural melanins was measured by iodometric assay. The obtained results revealed that photodegradation of the hair melanins

substantially decreased their antioxidant properties and enhanced their photoreactivity, particularly the melanins ability to photogenerate singlet oxygen. These melanin changes enhanced phototoxic potential of the pigments, which could play a role in the contribution of melanin in UVA-induced melanoma.

Acknowledgments

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Electronic paramagnetic resonance in the non-invasive monitoring of the tumor microenvironment

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Keywords: EPR imaging, oximetry, cancer, microenvironment

The composition of the tumor microenvironment varies depending on tumor types, but characteristic features include immune cells, stromal cells, blood vessels, and extracellular matrix. Tumor microenvironment is thought not only to be silent bystander but also to actively promote the progress of cancer. In the course of tumor growth, tumor cells and components of the tumor microenvironment develop dynamic relationships that support cancer cell survival, local invasion, and metastatic dissemination. We have used non-invasive imaging in preclinical models to characterize tumor oxygen level, redox state, and vascular structure.

Metastatic and non-metastatic tumors E0771 tumors show significant differences in their vascular system, tumor oxygenation, and tumor redox state. Results from EPR oximetry, EPR redox imaging, and Doppler ultrasound were in agreement with immunohistochemistry and Western blot data showing enhanced oxidative stress, microvascularization, and EMT markers in more invasive tumors. These changes were accompanied by a slower growth rate, increased vascularization, and indications of oxidative stress in more aggressive tumors.

In a different model of orthotopic breast cancer, 4T1 we demonstrated that ultrasoundsensitive oxygen microbubbles are an effective way to increase tumor oxygenation for several minutes and enhance effectiveness of radiotherapy. Furthermore, EPR oximetry and oxygen imaging but not photoacoustic imaging were able to precisely monitor the effects of this hyperoxic therapy.

The use of LiNc-BuO-based microspheres allows to image oxygenation of orthotopic glioblastoma GL-261 tumors. It is a non-invasive way to access absolute oxygen concentration in tumors not accessible by most oximetric methods. Implantation of a probe together with cancer cells makes the measurements not reliable on coregistration with other modalities because the signal comes only from the area of the tumor.

EPR redox mapping and oximetry, especially in combination with other noninvasive imaging methods, provide a powerful window into tumor microenvironment.

A new tool for EPR data analysis in the study of photoexcited triplet states

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Keywords: time-resolved EPR, photoexcited triplet states, simulation, magneto-photo selection,

Studies of photoexcited triplet states by EPR are complicated by spin relaxation times being comparable with lifetimes of the triplet states. This fact influences both acquisition of the spectra and acquisition of the time traces. A specific analysis of the data is therefore required, and commonly available EPR software not always can take into account all relevant aspects.

We developed a new software toolbox oriented to the data analysis of commonly used EPR experiments for photoexcited triplet states with population of either zerofield states or Zeeman states (charge-recombination triplets). A user-friendly graphical interface helps with the input of the Hamiltonian parameters and the experimental parameters for a selection of experiments.

Our software can reproduce the entire 3D time-resolved EPR (TREPR) spectra obtained from frozen glassy solutions by taking into account anisotropic relaxation processes¹ as well as in the presence of librational motion. The anisotropy of the decay of the triplet levels to the ground state is also considered.

In addition, it can be used to simulate spectra influenced by magnetophotoselection effects (MPS) which can be exploited for the determination of the orientation of the transition dipole moment in samples without the need of working with macroscopically oriented matrices².

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Interactions between TEMPO-functionalized magnetic nanoparticles and cells

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Keywords: TEMPO, magnetic nanoparticles, drug delivery, yeast cells, cancer cells

Magnetic nanoparticles are good candidates for drug carriers. They can be functionalized with various drugs. Using a magnetic field of appropriate geometry it is possible to control their movement. An important issue is their effect on cells and interactions with them.

Electron spin resonance (ESR) is a method successfully applied to study nanomaterials, including iron oxide nanoparticles. In our research, using ESR, we developed a method of studying the interactions between such nanoparticles and cells, both normal and cancer.

In this work the application of ESR method in monitoring the endocytosis of TEMPOfunctionalized magnetic nanoparticles into yeast and chosen cancer cells is shown. The impact of chosen physical factors on this process is discussed.

EPR detection of reactive oxygen species on mixed metal oxides in the presence of hydrogen peroxide

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Keywords: reactive oxygen species, hydrogen peroxide, mixed oxides, radicals, advanced oxidation processes

The formation of reactive oxygen species (ROS) through the decomposition of hydrogen peroxide is associated with a cascade of reactions that involve redox-active centers of Fenton-like catalysts or acid-base surface functional groups, which mediate electroprotic reactions. Such two functions can be utilized by combining two types of oxide, redox-active crystalline oxides and nonredox amorphous oxides, into one material.

The aim of this work is the identification of reactive oxygen species (ROS) generated during hydrogen peroxide activation on mixed transition-metal oxides and the investigation of mechanism of this activation process. The selection of the studied systems (Zr, Nb, Hf amorphous oxides and their composites with CeO₂, Co₃O₄, CuO nanocrystalline phases) will allow for insight into processes analogous to the Fenton mechanism, electron transfer processes, and electroprotic processes. Identification of ROS was carried out with spectroscopic techniques such as EPR, Raman, and UV-Vis. The paramagnetic species were identified by measuring oxides after the reaction with hydrogen peroxide (in situ measurements in quartz tubes in controlled atmosphere) as well as during the reaction with H₂O₂ using of 5,5dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trap. In such conditions, the shortlived radical species react with a spin trap to form a stable adduct. The measurements were carried out with varying pH values for the mixed oxides that differ in isoelectric point values and with different positions of the conductive and valence band edges. The formation of radical species was followed further by colorimetry using substrates specific for the peroxidase activity (OPD). The surface-stabilized diamagnetic ROS were tested by Raman spectroscopy.

The mechanistic study, based on the spectroscopic identification of H_2O_2 decomposition products, was carried out to identify and differentiate between catalase- and peroxidase-like reactivity of the tested materials.

Acknowledgments

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EPR study of copper active sites in Cu-SSZ-13 zeolites - application in selective catalytic reduction of NOx with ammonia

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Keywords: Cu-SSZ-13, SCR, Catalysis, NOx, Zeolites

Selective catalytic reduction of NO_x using ammonia (NH_3 -SCR) is one of the most prominent branches of automotive (diesel) exhaust treatment in environmental catalysis. In particular copper-exchanged small-pore zeolites, such as synthetic chabazite (SSZ-13), are already being implemented in commercial systems. However, despite excellent conversion rates and high hydrothermal stability, the exact mechanism of the reaction is not fully understood.

In this work EPR spectroscopy has been used to great extent as an analytic tool to gain insight into the nature and reactivity of copper active sites in the zeolite. The reduction of copper during temperature programmed ammonia desorption (NH₃-TPD), can be directly investigated through the acquisition of CW-EPR spectra of Cu^{2+} (d⁹) ions (**Fig. 1. a**). However, the resultant reduced forms can also be probed, through the usage of gaseous NO, with whom they form paramagnetic Cu⁺-NO[•] adducts (Fig. 1. **b**). When exposed to oxygen, they can transform into various species of nitrate/nitrite. Speciation of copper obtained from computer simulation can be used for scaling the results of thermodynamic calculations (periodic DFT + first principle thermodynamics) to match the experimental findings of other methods (TPD, TPSR, IR), as well as providing proof that predicted forms of NO_x species are formed on Cu sites under the conditions of SCR and SCO processes.

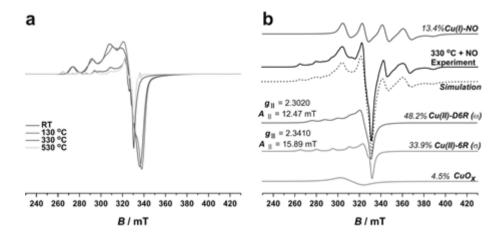


Fig. 1. Thermal evolution of EPR signal for Cu-SSZ-13 + NH_3 system (**a**) and deconvolution of EPR spectra obtained after reaction at 300 °C and adsorption of NO (**b**).

Study of plastic objects aging processes by means of EPR spectroscopy <u>Krzysztof Kruczała</u>, Marek Bucki

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Keywords: EPR, PVC, radicals, plastics, polymer degradation

Plastics are based on approximately fifty polymer types, however, the most used are polyethylene, polypropylene, polyethylene terephthalate as well as poly(vinyl chloride). They are present in all areas of our daily lives [1] and can be found almost everywhere: in kitchen appliances, fabrics, cars, and more. So, it is no surprise that they have also been applied in the field of art and architecture, enriching the artistic expression of modern art. When industrially manufactured plastics were designed for mass-scale production of items for relatively short-term use, in the case of museum objects the desired lifetime should be extended to centuries [2]. The aging of polymeric materials and the destruction of objects is a big problem for modern art viewers and curators. The research aimed to find a correlation between chemical degradation and a gradual loss of the original mechanical properties, which threatens the very survival of the objects. The early degradation processes can be detected by EPR spectroscopy due to the exceptional sensitivity of EPR methods for the detection of radical species [3]. The degradation process of PVC includes the formation (Fig 1A) of the radicals which can be detected by EPR (Fig. 1B). The short-living radicals might react with the stabilizer (e.g. Tinuvin 770) often present in commercially available plastics giving long-living species which allow investigating the degradation and local viscosity (Fig 1C)

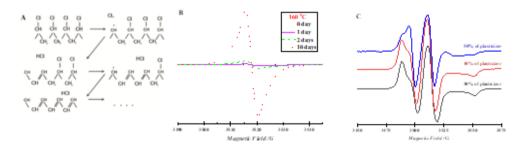


Figure 1. Scheme of PVC degradation (a), CW EPR spectra of the carbon (b), and nitroxide radicals formed during PVC thermal degradation.

Acknowledgments.

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Local Structure, EPR and Optical Spectroscopy of Complex Lead-Silicate Glass, Doped with Copper

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Keywords: Cu-doped lead-silicate glass; EPR; UV – Vis absorption; photoluminescence; decay kinetics.

The glasses with 0.521PbO-0.371SiO₂-0.068ZnO-0.027K₂O-0.013BaO basic composition, doped with CuO (or PbSiZnKBaO:CuO), were obtained by standard glass melting technique using technological conditions for lead-silicate glasses, developed in the Ukrainian State University of Chemical Technology (Dnipro, IR The EPR, XRD, transmission, Ukraine) [1]. optical absorption. photoluminescence and its decay kinetics in the PbSiZnKBaO:CuO glass were studied. The observed characteristic EPR spectra of the Cu^{2+} (3d⁹, ²D_{5/2}) and Fe³⁺ $(3d^5, {}^6S_{5/2})$ paramagnetic ions were adequately described using the spin Hamiltonian formalism. Average interatomic distances and coordination numbers for main structural units, SiO₄ and PbO_n (n = 3 - 6), as well as Pb-Pb and Pb-Si interatomic distances in the network of studied glass were determined from radial distribution functions. The IR transmission spectrum of studied glass in the 400 - 4000 cm⁻¹ range was registered and interpreted. Observed broad absorption band, peaked near 870 nm, was ascribed to the ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ transition of the Cu²⁺ centres. Using analysis of the fundamental absorption edge the optical band gap and Urbach energy of the studied glass were evaluated. Photoluminescence (excitation and emission) spectra and decay curve of the Cu^+ ($3d^{10}$, 1S_0) centres in the PbSiZnKBaO:CuO glass were

registered and interpreted. The PbSiZnKBaO:CuO glass upon UV photoexcitation also demonstrates broad intense emission band, peaked about 575 nm. This emission band with fast decay kinetics was assigned to intrinsic band-to-band recombination luminescence. The CIE chromaticity diagram for Cu⁺ and intrinsic emission bands in the studied glass was built and discussed.

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https://doi.org/10.1016/j.mseb.2022.115655

Anisotropic effects of EPR spectrum of the Cr₃Te₄ macro-defects embedded in the CdTe single crystalline matrix

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In heavily doped CdTe:Cr single crystals, obtained by the modified PVT technique, we reported the presence of second phase defects in the form of needles or polygons, which were identified nano-thick platelets of Cr_3Te_4 lying in the {111} planes of the host matrix [1, 2]. Since Cr_3Te_4 and some other chromium tellurides are ferromagnetic at RT, such a composite material may show properties enabling its use for spintronic devices [3]. Continuing our previous work [2], thorough investigations of the angular dependence of the EPR lines, which originated from the ferromagnetic state of Cr_3Te_4 defects, were performed in the present communication.

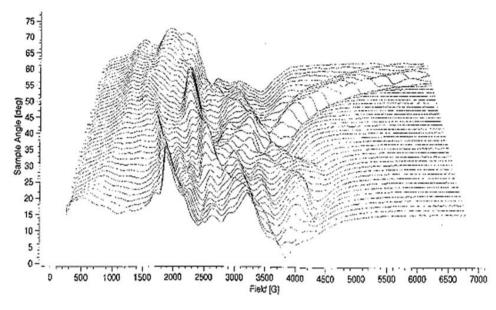


Fig.1. Angular dependence of FMR spectrum of CdTe:Cr sample at RT.

EPR spectrum of highly doped CdTe:Cr is complex below the Curie temperature of Cr₃Te₄ (Fig.1), which is from 315 to 345 K according to the literature data [4]. The rotation axis of the investigated sample was aligned along the direction in the zinc-blende CdTe lattice. Thus, the defects grown in (111) or ($^{-1}$ - $^{-1}$ -1) planes of CdTe were "in plane" oriented. Due to the two-dimensional geometry of the defects (which are, in fact, thin layers), the ferromagnetic lines from the defects do not change their position significantly due to the rotation of the constant field **B**. Contrary, those defects placed in the crystal planes of ($^{-1}$ 11), (1 -11), ($^{-1}$ -11), ($^{-1}$ -1), ($^{-11}$ -1) are near "out of plane" orientation and their positions are changed noticeably with the resonance field. The above lines can be easily discerned in the spectrum at the high magnetic field, and the shape anisotropy of Cr₃Te₄ defects can be calculated from the angular dependence of the resonance field for these lines.

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Semiquinonato Complex of diamagnetic metal cations: experimental and computational EPR studies

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Keywords: radicals, EPR, DFT, ab initio, EPFR

Environmentally persistent free radicals (EPFRs) are a new class of environmental pollutants. These toxic species could be partly responsible for some of the health problems. Most of the studies conducted to understand the origin and nature of EPFRs have focused primarily on nanoparticles or engineered nanomaterials during combustion. Using 9.7, 34 and 406 GHz EPR spectroscopy, we demonstrated that EPFRs can be generated from natural polyphenols when they are exposed to heavy metal ions like Pb(II) and Hg(II). Our relativistic DFT computations reviled that these radical species are semiquinonato complexes of the heavy metal ions. However, radical species can be tamed for use in material science. We isolated a semiquinonato complex of aluminium, derived from 1,2-dihydroxybenzene, as an amorphous and porous solid that exhibits very good stability under ambient conditions. As shown in Figure 1, EPR spectroscopy was used in concert with computational techniques (DFT and DLPNO-CCSD) to characterise its molecular and electronic structure,

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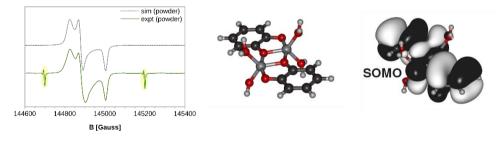


Figure 1. Solid-phase 406 GHz EPR spectrum of the semiquinonato Al³⁺ complex and its DFT-predicted molecular model along with the singly-occupied molecular orbital (SOMO).

Impact of selected selenium compounds on dynamic properties of model membranes - electron paramagnetic resonance study.

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Keywords: EPR method, spin probes, model membrane, liposome, selenium compounds

The cell membrane is a mechanical, selectively permeable barrier that separates the interior of the cell from its surroundings. It is one of the essential structural and functional elements of cells. The proper condition of the membranes, determines the proper functioning of the body's cells.

In scientific work, models of biological membranes are very often used. When amphiphilic lipids are introduced into water, they spontaneously aggregate into liposomes. To produce structures made of bilayers, sonication can be used. Advantages of using model membranes include: the lipids of which they are composed can be precisely composed; the environment in which the system is located can be precisely controlled and altered; selected chemical compounds can be introduced into the membranes, and their effects on the structural and dynamic properties of the membrane can be analyzed.

Electron paramagnetic resonance spectroscopy allows the study of systems containing unpaired electrons. Its applicability is enhanced by the use of spin probes, which allow the study of non-paramagnetic compositions. The EPR technique is used to observe changes in the structural and dynamic properties of model membranes, as it best illustrates the dynamics of membranes in real time, while being a non-invasive and highly sensitive technique. It also makes it possible to study a specific substance in the presence of other, unidentified compounds.

Selenium is an element necessary for the proper functioning of the human body. However, selenium compounds used above certain concentrations are toxic to living organisms. Both the carcinogenic and anti-cancer properties of selenium are being studied. Since it acts on both diseased and healthy cells, work is underway to assemble selenium compounds into liposomes. By providing targeted transport of active substances, liposomes protect healthy tissues, reducing the side effects of its action. The effectiveness of selenium depends on the method of administration, the dose used and the duration of the experiment, among other factors. But above all, it depends on the chemical form of this metalloid, since they have different biological properties.

The purpose of this study, was to investigate the effects of sodium selenite and sodium selenate (Sigma Aldrich), depending on their concentration, on the fluidity of membranes of liposomes made from DPPC (Sigma Aldrich) and lecithin extracted from egg yolk. Electron paramagnetic resonance (EPR) technique was used for the study. In the study, spin probes used were: TEPMO (Sigma Aldrich) and 16-DOXYL (Sigma Aldrich). Analysis of spectroscopic parameters, provided information on changes in the dynamic properties of the studied membrane, occurring under the influence of changing concentrations of selenium compounds.

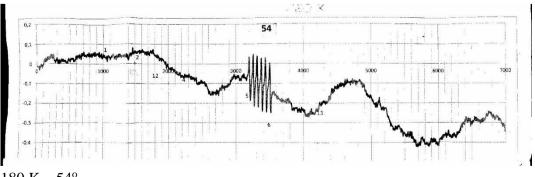
Anisotropic hyperfine interaction in CdTe:I single crystals implanted with chromium

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The iodine doped CdTe crystals offer unique electronic properties. The single crystals CdTe:I were grown from vapour phase. We have implanted (110) oriented samples with Cr^{2+} ions with energy of 500 keV and fluence of 5×10^{17} cm⁻¹. The SRIM simulations [1] revealed a projected implantation range $R_p = 335,4$ nm along with longitudinal straggling $\sigma = 150.5$ nm. Thus, on the surface of the sample a thin layer of CdTe:I doped with Cr was formed. The concentration of Cr in the layer was not uniform: the maximal concentration was 0. 83 at%. at the depth 320-400 nm.

The EPR spectra were obtained using Bruker Elexyys E580 spectrometer in the X band (9,4 GHz). The angular dependence of epr spectrum was carried out at the temperature of 180 K. The spectrum (see Fig.1) shows hyperfine structure (HF) at particular orientations of crystal in respect to the magnetic field. The HF spectrum consists of six lines of equal intensity. We attribute the spectrum to the hyperfine coupling of Cr ions with iodine nuclides (I = 5/2).



180 K 54°

Fig.1. The hyperfine epr spectrum of CdTe:I single crystals implanted with Cr.

The angular EPR spectrum was measured in the "out of plane" orientation of the sample. Nor the gravity position $B_r = 335.5$ mT of the multiplet, not its width ΔB = 30.0 mT does not change with the angle in the plane perpendicular to the (110) surface. However, the HF multiplet disappears completely for particular orientations of the sample. Anisotropic hyperfine interaction is addressed.

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Unusual EPR spectra and temperature behaviour of Mn²⁺ ions in organic-inorganic hybrid manganese halides

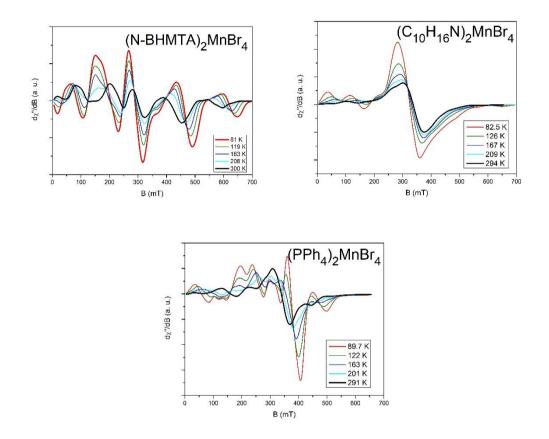
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Organic-inorganic hybrid metal halides are attracting attention in the research field due to their bright light emission, tunable photoluminescence wavelength and convenient synthesis method. The formula is $A_m B_n C_i$, where A stands for organic cation, B for metals and C for halides. The compounds we investigated were (N-BHMTA)₂MnBr₄, (C₁₀H₁₆N)₂MnBr₄ and (PPh₄)₂MnBr₄. Luminescent Mn²⁺ complexes have attracted more attention than others due to less toxicity compared to lead complexes, much more abundant storage compared to rare earth elements and greater stability compared to tin complexes. The luminescence spectrum depends on the geometry of the nearest neighbouring Mn²⁺ ions (XRD studies), the crystal field (optical studies) and the deformation of the nearest neighbouring Mn²⁺ ions (EPR studies).

 Mn^{2+} ions are extensively studied by EPR technique due to the characteristic EPR signal observable over the full temperature range (also at room temperature). In high symmetry, we observe a sextet of EPR lines originating from the hyperfine interaction of Mn^{2+} ions. In low symmetries we can observe up to 5 sextets of EPR lines depending on the distortion of the nearest neighbourhood of the Mn^{2+} ions. Strong pair interactions of Mn^{2+} ions are characterised by a single broad EPR line. In our complexes, we observe five broad EPR lines over a wide range of magnetic

induction up to 600 mT. In addition, the EPR signal changes significantly with temperature for all three complexes (figs).



I present the results of magnetic studies using the EPR technique and with a SQUID magnetometer.

EPR investigation of APTES-TiO2 under artificial solar light

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Keywords: EPR measurements, APTES-modified TiO2

The samples TiO_2 modified with of 3-aminopropyltriethoxysilane (APTES - TiO_2) nanomaterials with improved photocatalytic activity under artificial solar light (ASL) irradiation with different calcination temperature was synthesized. The EPR spectra were obtained at room temperature showed an intense resonance line from defects related to conducting electrons with g_{eff} value equal from 2.0028 to 2.0026 and 1.9052 for temperatures 800, 900 and 1000 °C, respectively, while for pure calcined TiO₂, these ERP lines were not observed (Fig.1). An intense EPR signal was observed from localized magnetic moments originating from oxygen defects. By increasing the calcination temperature, the intensity increased significantly to the calcination temperature of 800 C. Where the most effective photocatalytic process was obtained. Above, this signal decreased sharply. Probably at higher temperatures, an increase in electrical conductivity occurs. As a result of the skin effect process, the penetration depth of the microwave is reduced.

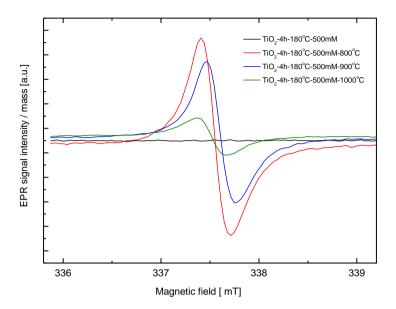


Fig.1. The EPR spectra at RT of the uncalcined TiO₂-4h-180°C-500mM, and annealed TiO₂-4h-180°C-500mM-800°C, TiO₂-4h-180°C-500mM-900°C and TiO₂-4h-180°C-500mM-1000°C.

Poster 1

The low-field microwave absorption in EMR spectra for Ni₅₀₋ xCo_xMn_{35.5}In_{14.5} ribbons

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Keywords: LFMA, Heusler alloys, Ni-Co-Mn-In. ribbons

In some materials, microwave absorption can be tuned by a very low magnetic field, and in that case, this effect is known as low-field microwave absorption (LFMA) [1]. This phenomenon was explored in different magnetic materials such as amorphous ribbons, nanoparticles, nanowires, and thin magnetic films [2].

In our prior work on the electron magnetic resonance (EMR) of $Ni_{50}Mn_{35.5}In_{14.5}$ annealed ribbons [3], we observed the LFMA signal for the first time in the Ni-Mnbased family. We also examined Ni-Co-Mn-In alloys with different cobalt content for the occurrence of the LFMA signal and confirmed the resonant character of this signal for Ni-Co-Mn-In alloys. In this poster, we discuss the unpublished EMR date of $Ni_{50-x}Co_xMn_{35.5}In_{14.5}$ ribbons and present a review of LFMA.

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Poster 2

EMR study of PLD growth zinc oxide and carbon nanocomposite thin films

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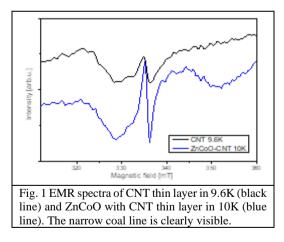
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Keywords: carbon nanotube, zinc oxide, EMR, PLD, DMS, CNT

Since the discovery of fullerenes and carbon nanotubes, there have been many technological developments in the field of nanocarbon materials [1]. Multi-walled carbon nanotubes (CNT) are nanostructures with many potential applications [2,3]. Furthermore, zinc oxide (ZnO) is a well-known inexpensive material with perspective for applications [4,5]. Some of the Zn ions can be substituted by magnetic transition metal (TM) ions to form a metastable solid solution.



In this paper, we have grown and studied the properties of CNT and Co-doped ZnO with CNT thin films produced by the pulsed laser deposition (PLD) method. The target for the deposition technology was made of CNT and $Zn_{1-x}Co_xO$ with CNT pressed powder. The dimensional parameters of the nanotubes were 6-10 nm by 2 μ m. Electron magnetic resonance (EMR) measurements of thin films were performed. The asymmetric resonance lines with Dyson shape were observed. EMR

lines were compared between pure CNT, CNT thin layer, and ZnO with CNT thin layer. We observed the separation of the line coming from CNTs. We also observed that the PLD method transfers the structure of the target (carbon nanotubes) to the layer and results in the incorporation of carbon into the structure of ZnO.

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Poser 3

X- and Q-band EMR study of Zn_{1-x}Mn_xFe₂O₂ fabricated using nonhydrolytic approach

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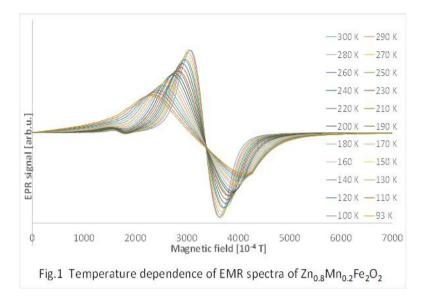
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Keywords: EMR, ferrites, SEM, XRD, magnetic properties

Abstract

In our work, we presented the results of the X- and Q-band electron magnetic resonance (EMR) measurements of Zn_{1-x}Mn_xFe₂O₂ doped with different concentrations of manganese (x - 0, 0.2, 0.5, 0.8, 1) studied for a wide temperature range. Zn_{1-x}Mn_xFe₂O₄ ferrites have been prepared by using a non-hydrolytic approach through thermal decomposition of the respective zinc, manganese and iron acetylacetonate complexes in a benzyl alcohol at 200 °C under a protective atmosphere of N₂. The crystal structure was evaluated by means of the powder Xray diffraction technique (XRD), while the cell parameters were calculated using Rietveld refinement. The particle size and morphology were estimated by transmission electron microscopy (TEM), whereas the element ratio was evaluated using the SEM-EDS technique. The size of the ferrite particles was found to be around 6 nm with a very narrow distribution and a spherical morphology in all cases. The synthetic approach chosen allowed doping control of ZnFe₂O₄ with a wide range of manganese cation concentrations. For some samples, two component lines of EMR spectra were observed. A clear separation of the EMR spectra lines was observed at low temperatures in the Q band. In addition, the line parameters were analyzed as a function of temperature. Curie temperature was determined for the tested samples.



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Poster 4

Ferrofluid-coated electromagnetic field-assisted bioreactor for biomass production

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Keywords: electromagnetic filed; ferrofluid; magnetic properties; bioreactor; bioengineering; biomass

Biotechnological manufacturing of bioproducts often requires high biomass concentration. Bacteria cultivation processes are still being optimised following novel technologies and technical upgrades in bioreactors. The application of electromagnetic fields (EMFs) is one of the recent trends in bioprocessing. The main goal in most biotechnological processes is to enhance the productivity of biomass. It may be achieved in several ways, e.g., using new or modified organisms or strains; optimising the operation strategies; developing cell immobilisation techniques or novel types of bioreactors. One of the most crucial factors to achieve an effective bioprocess is a bioreactor. Most biomass production and productivity studies have only focused on applying commercial bioreactors without looking for new methods or approaches to intensify biomass production. No previous study has investigated a ferrofluid-coated electromagnetic field-assisted bioreactor for biomass production. Therefore, this study aimed to investigate the modulating effects of ferofluid coat (without direct contact with cells) on the operation of a novel type of bioreactors during biomass production in model bacteria. Ferrofluids are stable colloidal suspensions of magnetic particles in either polar or non-polar base fluid (e.g., water, transformer, engine oils, or ethylene glycol). In the case of this experimental work, the magnetite was obtained by the coprecipitation method. The several analyses were performed to analyse the phase composition (X-ray diffraction, Infrared spectroscopy) and assess the mean grain size, structure (scanning and transmission electron microscopy, Scherrer method), and magnetic properties (Electron paramagnetic resonance, Superconducting Quantum Interference Device) of the particles. The obtained particles were applied for the production of the ferrofluid suspension (2 g/L) in a 50 mL Falcon-type tube. Then, smaller tubes were placed inside the bigger tubes through the hole in the cap matching the diameter of the smaller tube. These tubes were placed in the EMF-assisted bioreactor in order to carry out the biomass production (Escherichia coli and Staphylococcus aureus).

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Poster 5

The Impact of Hydration and Dehydration on the Mobility and Location of Ibuprofen Molecules in the Voids of Ultra-Stable Zeolite Y

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Keywords: <u>mesoporous zeolites</u>, <u>confinement effect</u>, <u>guest-host systems</u>, nuclear magnetic resonance (NMR), X-ray diffraction (XRD)

Mesoporous dealuminated zeolites are used as hosts for ibuprofen. This drug experiences high mobility when confined in mesopores, which is largely dependent on the water content. Zeolites are materials that are naturally hydrated under ambient conditions. Nitrogen adsorption and X-ray diffraction (XRD) show that the samples with the content of ibuprofen up to 38% have the guest phase residing only in mesopores. ¹H and ¹³C MAS NMR studies of samples in ambient conditions, after dehydration, and in hydration prove the impact of water for increased mobility of ibuprofen. Increased mobility of the introduced phase was also detected for samples with no water content. It was ascribed to ibuprofen located outside mesopores, which experiences a prolonged time of cooling to room temperature. This phenomenon is important for all the future uses of the melting method in guest–host systems and the future use of zeolites for biomedical applications.

Poster 6

Overexpression of the tau protein induces oxidative stress in SH-SY5Y cells. Protection by 4-amino-TEMPO and nitroxide-containing nanoparticles.

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Key words: tau protein, oxidative stress, 4-amino-TEMPO, nitroxide-containing nanoparticles,

Tau protein is a microtubule-associated protein, predominantly expressed in the neurons, involved in the microtubule assembly and associated with the proper functioning of the cytoskeletal network. Abnormally phosphorylated tau protein is the principal component of neurofibrillary tangles, accumulating in the brain especially in Alzheimer's disease, a disease accompanied by oxidative stress. The aim of this study was to examine whether overexpression of the tau protein leads to changes in the redox status of SH-SY5Y cells.

SH-SY5Y cells transfected with the human 4-repeat tau isoform, hTau40, subcloned into pcDNA3.2/V5/DEST, and cells transfected with the empty vector were provided by Dr. M. Fahnestock (McMaster University) and grown in the presence of 250 μ g/ml G418.

The level of reactive oxygen species was elevated in tau-overexpressing cells as compared with cells transfected with the empty vector (by $15\pm6\%$ when estimated by 2',7'-dichlorodihydrofluorescein (DCFDA) and by $119\pm19\%$ when estimated with dihydroethidine). The level of protein aggregates and of glutathione was increased in the tau-overexpressing cells by $71\pm36\%$ (apparently overproduction of glutathione to compensate for oxidative stress). The tau-overexpressing cells were more sensitive to hydrogen peroxide but more resistant to 6-hydroxydopamine, 4-amino-TEMPO and nitroxide-containing nanoparticles than cells transfected with the empty plasmid The doubling time of tau-overexpressing cells was significantly slowed down (65 vs 34 h). These results indicate that overexpression of the tau protein imposes oxidative stress on the cells resulting in the growth impairment.

The nitroxide 4-amino-TEMPO and nitroxide-containing nanoparticles mitigated oxidative stress in tau-overexpressing cells, decreasing the level of ROS. These synthetic antioxidants seem promising for in vivo applications, the more that they are able to penetrate the brain-blood barrier, as demonstrated by EPR measurements of their transport through a model of this barrier.

This study was performed within the Project SONATA BIS 6 2016/22/E/NZ7/00641 "Nanomolecular antioxidants: biological basis of targeted therapy of neurodegenerative diseases" financed by the National Science Centre of Poland.

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Mapping the Redox State in the extracellular and intracellular space

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Finding new types of biomarkers for different diseases

Possible knowledge transfer from preclinical to clinical

Assessment of Blood-Brain-Barrier functioning

Monitoring of drug delivery mechanisms

Pharmacokinetics study

Verification of the therapy outcome

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- Resonance frequency: 1150 MHz

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- Detection methods: Continuous Wave (CW) with multiharmonic analysis and Rapid Scan (RS)









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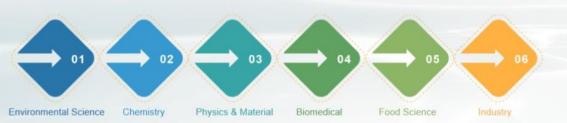
Benchtop EPR

Electron Paramagnetic Resonance Spectrometer EPR200M

Technical Details

Parameter	Value
Frequency Range	9.2-9.9GHz
ield Modulation Amplitude	10 Gauss
Agnetic Field Range	6500 Gauss (Max)
Magnetic Field Uniformity in he Sample Area	Better than 50mG
Detection Signal-to-Noise Ratio n Continuous-Wave Mode	Better than 600:1
Absolute Spin Sensitivity	5×10 ⁹ spins/(G√Hz)

Applications





Electron Paramagnetic Resonance Spectrometer





EPR200-Plus

- 1D magnetic field scanning
- 2D magnetic field-microwave power scanning
- 2D magnetic field-modulation amplitude sweep
- 2D magnetic field-time scanning
- Variable temperature experiments
- Irradiation experiments

X-Band Continuous Wave Electron Paramagnetic Resonance Spectrometer





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