# **VII EMR-PL Forum**

## 25-28 June 2024 University of Zielona Góra



Under the honorary patronage

Prof. dr hab. Wojciech Strzyżewski, the Rector UZ







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## COMMITTEES

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Mgr Ryszard Piotrowski - Member of the LOC, Webmaster, University of Zielona Góra

## **CONFERENCE PROGRAMME**

	<b>25.06.2024, Tuesday</b> (Venue: 4a Prof. Z. Szafrana Street, Building A-29)			
12:00 - 17:00	REGISTRATION (1st floor, Hall near Aula 106)			
17:00 - 17:30	OPENING CEREMONY (1st floor, Aula 106)			
	Chairwoman: <b>Dr hab. Maria Przybylska, Prof. UZ</b> (Zielona Góra), Chairwoman of the Local Organizing Committee (LOC) of the VII Forum EMR-PL;			
	Welcome address: <b>Dr hab. Piotr Pietrzyk, Prof. UJ</b> (Kraków), Chairman of the Polish Electron Magnetic Resonance (EMR–PL) Group;			
	<b>Prof. dr hab. Wojciech Strzyżewski</b> (Zielona Góra), the Rector UZ, Honorary Patronage of the VII Forum EMR-PL;			
	<b>Prof. dr hab. Andrzej Drzewiński</b> (Zielona Góra), Dean of the Faculty of Physics and Astronomy UZ;			
	<b>Dr hab. Bohdan Padlyak, Prof. UZ</b> (Zielona Góra), Chairman of the Local Organizing Committee (LOC) of the VII Forum EMR-PL			
	COMMEMORATIVE GROUP PHOTOS			
17:30 – 19:30	WELCOME RECEPTION (ground floor, cafeteria "Kuchnia u Macieja")			
	<b>26.06.2024, Wednesday</b> (Venue: 4a Szafrana Str. Building A-29, 1st floor, Aula 106)			
8:30 – 9:00	REGISTRATION (1st floor, Hall near Aula 106)			
	1st Oral session, Chairman: Dr hab. Maciej Witwicki, Prof. UWr			
9:00 – 9:40	C. Rudowicz, L. Mollabashi, S. Jalali-Asadabadi, M. Acikgoz, Z. Ghasemi-Dorcheh, R. Ebrahimi-Jaberi, M. Jalali-Asadabad, S. Rahimi, F. Jalali-Asadabadi			
	Interplay between spin Hamiltonian and crystal field Hamiltonian: DFT/ab initio and semiempirical modelling for Gd <sub>3+</sub> ions in PbTiO <sup>3</sup> and Tm <sub>3+</sub> ions in LiTmF <sub>4</sub> (Plenary Lecture 1)			
9:40 – 10:10	Maciej Marć , Wiktor W. Wolak, Andrzej Drzewiński, Stepan Mudry, Ihor Shtablavyi, <u>Miroslaw R. Dudek</u>			
	<i>Kittel's theory of ferromagnetic resonance for thin, flexible films with embedded magnetic nanostructures</i> (O-1)			
10:10 - 10:40	Jacek Sawka, Alina Bieńko, Anna Świtlcka, Roman Boča, Andrew Ozarowski			
	The impact of linker ligands on the structure dimensionality, magnetic anisotropy and slow relaxation processes of six-coordinate Ni(II) complexes (O-2)			
10:40 - 11:20	Bohdan Padlyak, Ihor Kindrat, Adam Drzewiecki, Ireneusz Stefaniuk			
	EPR spectroscopy of the Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> glasses co-doped with transition (Cu, Mn) and rare-earth (Eu, Sm) elements (review) (Plenary Lecture 2)			
11:20 - 11:50	COFFEE BREAK (ground floor, cafeteria "Kuchnia u Macieja")			

2nd Oral session, Chairman: Dr hab. Piotr Pietrzyk, Prof. UJ		
11:50 - 12:30	Maria Augustyniak-Jabłokow, Roman Strzelczyk, Ryhor Fedaruk	
	Methodology of EMR Investigations of the Graphene Related Carbon Materials (Plenary Lecture 3)	
12:30 - 13:00	Krzysztof Kruczała, Radim Beranek, Szymon Wierzbicki	
	Study of Catalytic Systems by Electron Paramagnetic Resonance Spectroscopy (O-3)	
13:00 - 13:30	Maciej Witwicki	
	Metal Cation Radical Complexes: From Environmental Pollutants to Functional Materials (O-4)	
13:30 - 15:00	LUNCH (ground floor, cafeteria "Kuchnia u Macieja")	
	3rd Oral session, Chairman: Dr hab. Ireneusz Stefaniuk, Prof. UR	
15:00 – 15:40	Dana Dvoranová, Zuzana Dyrčíková	
	The cw-Electron Paramagnetic Resonance Spectroscopy in Heterogeneous Photocatalysis (Plenary Lecture 4)	
15:40 - 16:10	Aneta Krasowska, Paweł Rejmak, <u>Piotr Pietrzyk</u>	
	From dioxygen to superoxide – EPR study of paramagnetic Zn <sup>2+</sup> -O <sub>2</sub> *- species in ZSM-5 zeolite and periodic DFT modelling (O-5)	
16:10 – 16:40	Kamila Sobańska, Piotr Pietrzyk	
	Identification of reactive oxygen species generated by the interaction of transition metal oxides and $H_2O_2$ (O-6)	
16:40 - 17:10	General Meeting of the Polish EMR Group	
17:10 – 17:40	COFFEE BREAK (ground floor, cafeteria "Kuchnia u Macieja")	
17:40 – 19:00	POSTER SESSION, Chairman: Prof. dr hab. Mirosław Dudek (1st floor, Hall near Aula 106)	
	<b>(P-1) <u>Zuzana Dyrčíková</u>, Miriama Malček Šimunková, Dana Dvoranová</b>	
	Photoinduced processes on modified titanium dioxide photocatalysts studied by indirect cw-EPR techniques	
	<b>(P-2) <u>Zuzanna Didjurgeit</u>, <u>Iga Sienkiewicz</u>, Adrianna Kędziora, Beata Kucharska, Bernadeta Dobosz</b>	
	Herbs with antioxidant and photosensitizing properties	
	<b>(P-3) <u>Vasyl Tataryn</u></b> , Bohdan Padlyak, Oleksiy Tataryn	
	System of digital scanning of the magnetic field for radiospectrometers of the "RADIOPAN" company (Poznań, Poland)	
	<b>(P-4)</b> Kacper Kut, Bogumił Cieniek, Ireneusz Stefaniuk, Grzegorz Bartosz, Izabela Sadowska-Bartosz	
	Effect of low concentrations of nitroxides on SH-SY5Y cells transfected with the Tau protein	
	(P-5) <u>Łukasz Dubiel</u> , Antoni Żywczak, Andrzej Wal, Ireneusz Stefaniuk	
	Electron magnetic resonance of Co-doped BaTiO3 ceramics at helium temperatures	

	<b>(P-6) <u>Bogumił Cieniek</u>,</b> Ireneusz Stefaniuk, Magdalena Kulpa-Greszta, Anna Tomaszewska. Robert Pazik		
	EMR study of spinel multi-shell CoFe <sub>2</sub> O <sub>4</sub> nanoferrites		
	(P-7) <u>Ihor Kindrat</u> , Bohdan Padlyak, Adam Drzewiecki, Volodymyr Adamiv, Ihor Teslyuk, Bogumił Cieniek, Ireneusz Stefaniuk		
	EPR and optical spectroscopy of lithium tetraborate glasses doped with Tb and co-doped with Tb and Ag		
	<b>(P-8) <u>Iwona Rogalska</u>,</b> Bogumił Cieniek, <u>Ireneusz Stefaniuk</u> , Marta Ruszała, Jakub Grendysa, Anna Juś		
	Properties of Cd1-xMnxTe as a room temperature semiconductor radiation detector		
	<b>(P-9) <u>Danuta Piwowarska</u>, Niko Guskos, Konstantinos Aidinis,</b> Ewelina Kusiak-Nejman, Agnieszka Wanag, Antoni W. Morawski		
	Temperature dependence of EPR spectra in titanium dioxide modified with (3-aminopropyl) triethoxysilane (APTES)		
	<b>(P-10)</b> T. Jasiński, M. Drąg, <u>M. Kuzma</u>		
	Spin qubit pairs in DNA Hairpins – EPR methods of study		
	27.06.2024. Thursday		
	(Venue: 4a Szafrana Str. Building A-29, 1st floor, Aula 106)		
4th Oral session, Chairman: Prof. dr hab. Czeslaw Rudowicz, UAM			
9:00 – 9:20	Zbigniew Sojka		
	In Memory of Professor Krystyna Dyrek (Invited Lecture)		
9:20 – 10:00	Zbigniew Sojka		
	EPR and DFT Investigations into Reactive Oxygen Species Trapped on Surfaces and in Cages of Catalytic Relevance (Plenary Lecture 5)		
10:00 – 10:30	<mark>Krystian Mokrzyński</mark> , Andrzej Żądło, Grzegorz Szewczyk, Michał Sarna, Theodore G. Camenisch, Shosuke Ito, Kazumasa Wakamatsu, Tadeusz Sarna		
	The effect of oxidative degradation of Dopa-melanin on its basic physicochemical properties and photoreactivity (O-7)		
10:30 - 11:00	Katarzyna Zawada, Katerina Makarova, Małgorzata Korzeniowska nee Wiweger		
	Benchtop X-band EPR for in vivo studies of zebrafish - melanin radicals and nitroxyl spin probes (O-8)		
11:00 - 11:30	COFFEE BREAK (ground floor, cafeteria "Kuchnia u Macieja")		
	5th Oral session, Chairman: Prof. Dr hab. Zbigniew Sojka, UJ		
11:30 - 12:10	Alina Bieńko		
	Towards "better" molecular magnets. Correlation of structure and magnetic anisotropy (Plenary Lecture 6)		
12:10 - 12:40	Marian Kuzma, M. Bester, B. Cieniek, V. Popowich, I. Stefaniuk		
	Two-dimensional magnetism in a self-inercalated transition metal dichalcogenides (O-9)		

12:40 - 13:30	Free time before Conference excursion and Gala dinner		
13:30 - 15:00	LUNCH (ground floor, cafeteria "Kuchnia u Macieja")		
15:00 – 18:00	Bus and boat excursion to the "Winny Dworek" including tasting of local wines and cheeses		
18:00 - 20:00	Conference Gala Dinner in the restaurant at "Winny Dworek"		
20:00 - 21:00	Departure to Zielona Góra		
	28.06.2024, Friday (Venue: 4a Szafrana Str. Building A-29, 1st floor, Aula 106)		
6th Oral session, Chairman: Dr hab. Bohdan Padlyak, Prof. UZ			
10:00 - 10:30	Bernadeta Dobosz		
	Application of ESR spectroscopy in nanomedicine (O-10)		
10:30 - 11:00	Ireneusz Stefaniuk, Bogumił Cieniek, Agata Ćwik, Katarzyna Kluska, Idalia Kasprzyk		
	EPR case study - tracking long-lived free radicals in dandelion caused by air pollution (O-11)		
11:00 - 11:30	COFFEE BREAK (ground floor, cafeteria "Kuchnia u Macieja")		
11:30 - 12:00	CLOSING REMARKS AND CONCLUSION OF THE FORUM		
12:00 - 13:30	LUNCH (ground floor, cafeteria "Kuchnia u Macieja")		

### Categories & Duration of the presentations

1. Plenary: 40min (35 min + 5 min for discussion);

2. Invited: 40min (35 min + 5 min for discussion);

3. **Oral**: 30 min (25 min + 5 min for discussion).

NOTES:

\* Session Chairman are kindly requested to inform each presenter:

- about 10 min before the end of presentation that there are "10 min left including discussion";

– about 5 min before the end of presentation that "the remaining time should be devoted for discussion".

\* Presenters are kindly requested to 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.

### PLENARY LECTURES

## Interplay between spin Hamiltonian and crystal field Hamiltonian: DFT/ab initio and semiempirical modelling for Gd<sup>3+</sup> ions in PbTiO<sub>3</sub> and Tm<sup>3+</sup> ions in LiTmF<sub>4</sub>

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Z. Ghasemi-Dorcheh<sup>b</sup>, R. Ebrahimi-Jaberi<sup>b</sup>, M. Jalali-Asadabad<sup>b</sup>, S. Rahimi<sup>a</sup>, F. Jalali-Asadabadi<sup>b,d</sup>

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Key words: spin Hamiltonian theory; crystal field theory; modelling of SH and CF parameters; Gd<sup>3+</sup> doped in PbTiO<sub>3</sub>; Tm<sup>3+</sup> ions in LiTmF<sub>4</sub>; magnetization and susceptibility.

**Part (A) recaps** two approaches: the density functional theory (DFT)/ab initio and superposition model (SPM) analysis, for modelling of spin Hamiltonian (SH), including the zero-field splitting parameters (ZFSPs), and the crystal field Hamiltonian (CFH) parameters (CFPs).

**Part B1 presents** our studies<sup>1</sup> of **Gd**<sup>3+</sup> **ions in PbTiO**<sub>3</sub>: (i) structural changes in Gd<sup>3+</sup>-doped PbTiO<sub>3</sub> that are crucial for potential applications in photonics; (ii) DFT) optimization of structural data, which then serve as input for superposition model (SPM) analysis; (iii) computation of the formation energies of Gd<sup>3+</sup>: PbTiO<sub>3</sub> with and without O-vacancy to determine the stable composition; (iv) various structural models of Gd<sup>3+</sup>:PbTiO<sub>3</sub> used as input for SPM/ZFP modelling to analyze variations of ZFSPs from 5 to 780 K. The results were fine-tuned by matching with available experimental EMR data for Gd<sup>3+</sup> probes in PbTiO<sub>3</sub> nanoparticles. The combined DFT+SPM modeling provides reliable description of experimental data and confirms the plausibility of Gd<sup>3+</sup> entering Pb<sup>2+</sup> sites.

**Part B2 presents** our studies<sup>2</sup> of **Tm**<sup>3+</sup> **ions in LiTmF**<sub>4</sub>: (i) magnetic properties of LiTmF<sub>4</sub>, which promises applications in, e.g. MRI and spintronics; (ii) DFT/ab initio and SPM modeling of CFPs and the Zeeman *g*-factors; (iii) distinction between the complete (7 independent CFPs) and reduced (6 independent CFPs) approaches; (iv) computing the conserved CFP quantities predicted by the Noether theorem; (v) analysis of CF multiplet splitting in magnetic *B*-field as well as computing ionic magnetic moment and temperature dependencies of magnetic susceptibility. Our findings agree with experimental data thus indicating efficacy of the combined DFT+CFT+ $\Delta$ /SPM+CFT modeling.

**Part (C) elucidates** interplay between SH and CFH: (i) symmetry aspects: ascend of site symmetry of  $Gd^{3+}$  in PbTiO<sub>3</sub> from tetragonal type I to cubic at higher temperatures *verus* tetragonal type II S<sub>4</sub> site symmetry of Tm<sup>3+</sup> in LiTmF<sub>4</sub>; (ii) origin of the SH parameters, including ZFSPs and *g*-factors; (iii) the ZFS=CF and CF=ZFS confusion regarding these notions.

Acknowledgements: Poznań Supercomputing and Networking Centre Grant #353.

<sup>&</sup>lt;sup>1</sup> M. Açıkgöz, et al. Physical Chemistry Chemical Physics, 25 (2023) 3986–4004.

<sup>&</sup>lt;sup>2</sup> L. Mollabashi, et al., submitted in March 2024 to Physical Review B.

## EPR spectroscopy of the Li2B4O7 glasses co-doped with transition (Cu, Mn) and rare-earth (Eu, Sm) elements (review)

Bohdan Padlyak<sup>a,b</sup>, Ihor Kindrat<sup>a</sup>, Adam Drzewiecki<sup>a</sup>, Ireneusz Stefaniuk<sup>c</sup>

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Key words: Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> glass; EPR; Cu<sup>2+</sup> ions; Mn<sup>2+</sup> ions, Sm<sup>3+</sup> ions; spin-Hamiltonian parameters.

The Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Cu,Eu glass containing 1.0 mol.% CuO and Eu<sub>2</sub>O<sub>3</sub> impurities as well as Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Mn,Sm glass containing 1.0 mol.% MnO<sub>2</sub> and Sm<sub>2</sub>O<sub>3</sub> impurities were obtained by high temperature melting technology and detailed studied by XRD, EPR, optical absorption, and photoluminescence methods [1,2]. Parameters of the local structure (interatomic distances and coordination numbers) for studied glasses were derived from experimental XRD data analysis.

The EPR and optical absorption, emission, photoluminescence excitation show that the Cu impurity is incorporated into the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> glass as Cu<sup>2+</sup> (3*d*<sup>9</sup>) and Cu<sup>+</sup> (3*d*<sup>10</sup>) ions. The Cu<sup>2+</sup> ions (electron spin S = 1/2) in the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Cu,Eu glass show typical EPR spectrum of axial symmetry with characteristic 4-component hyperfine structure caused by nuclei of <sup>63</sup>Cu (natural abundance – 69.17 %, nuclear spin, I = 3/2) and <sup>65</sup>Cu (30.83 %, I = 3/2) isotopes The precise spin Hamiltonian parameters ( $g_{||}, g_{\perp}, A_{||}, A_{\perp}$ ) and peak-to-peak first derivative linewidths of the hyperfine components ( $\Delta H_{pp}^{||}$  and  $\Delta H_{pp}^{\perp}$ ) for Cu<sup>2+</sup> ions at T = 295 K in the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Cu,Eu glass were obtained by best fitting of the simulated EPR spectrum to the experimental spectrum.

The EPR and optical spectroscopy (absorption, luminescence excitation, emission, decay kinetics) show the presence of  $Mn^{2+}(3d^5)$  and  $Mn^{3+}(3d^4)$  impurity ions in the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Mn,Sm glass. The  $Mn^{2+}(3d^5)$  ions (electron spin S = 5/2) in the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Mn,Eu glass show an isotropic EPR spectrum with a characteristic 6-component hyperfine structure caused by nuclei of the <sup>55</sup>Mn isotope (natural abundance – 100 %, I = 5/2). Parameters of all observed EPR spectra of the Mn<sup>2+</sup> centres in Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Mn,Eu glass were determined at T = 295 K. By EPR spectroscopy in the studied glass were identified three types of the Mn<sup>2+</sup> centres: single Mn<sup>2+</sup> (1) centres in the strongly distorted sites (ratio of rhombic and axial constants,  $|E/D| \le 1/3$ ), single Mn<sup>2+</sup> (2) centres in the sites with almost cubic symmetry ( $D \cong 0$ ,  $E \cong 0$ ) as well as Mn<sup>2+</sup> pairs and small clusters coupled by magnetic dipolar and exchange interaction, respectively.

**Acknowledgments.** This work was supported by the Ministry of Education and Science of Ukraine (research project No. 0122U001833, realized in the Vlokh Institute of Physical Optics, Lviv, Ukraine).

### References

[1] B.V. Padlyak, I.I. Kindrat, V.T. Adamiv, Y.O. Kulyk, I.M. Teslyuk, A. Drzewiecki, I. Stefaniuk, Mater. Res. Bull. 167 (2023) 112432.

[2] B.V. Padlyak, I.I. Kindrat, V.T. Adamiv, A. Drzewiecki, I. Stefaniuk, Mater. Res. Bull. 175 (2024) 112788.

## Methodology of EMR Investigations of the Graphene-Related Carbon Materials

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Key words: EMR techniques; carbon materials; sample preparation; lineshape; vacuum Rabi oscillations.

Carbon nanomaterials are of interest for new technologies and applications. Therefore their properties are intensively studied using various methods. Because many of these materials contain paramagnetic centers (PCs), electron magnetic resonance (EMR) can be an effective method for studying them. The continuous wave (CW) EMR spectra of carbon materials are usually simple and consist of one or two overlapping Lorentzian lines differing only in linewidth, with *q*-factor close to that of a free electron. These simple spectra make it difficult to extract useful information about the properties of the studied materials and sometimes even to identify PCs. Some additional difficulties are caused by electrical conductivity of these materials manifesting in the Dysonian distortion of the resonant line and decreasing a quality factor of resonator. Moreover, it was recently shown that high spin concentration of PCs with a narrow EMR line can result in distortions of the CW EMR spectrum due to a cavity quantum electrodynamics effect called a vacuum Rabi splitting. Temperature dependencies of CW spectra expand the possibilities of extracting useful information. Additional EMR techniques, such as pulsed EMR, are also needed to overcome difficulties in studying these materials. However, our experience has shown that recording CW EMR spectra of carbon materials, due to their specific properties, requires special attention. The first challenge is proper preparation of the sample, which, generally, should be small, diluted in diamagnetic media and be subjected to vacuum before measurement. These requirements result from the properties of the material and the physical phenomena accompanying magnetic resonance.

In this report, the impact of such phenomena as the skin effect, vacuum Rabi splitting, or microwave heating on the EMR spectra is discussed. As a result, a protocol for sample preparation and EMR measurements is proposed. We believe that this will provide repeatable and reliable results.

### The cw-Electron Paramagnetic Resonance Spectroscopy in Heterogeneous Photocatalysis

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Key words: photocatalysis; indirect EPR techniques; photoinduced electron transfer; reactive oxygen species.

The heterogeneous photocatalysis represents one of the effective methods within the Advance Oxidation processes (AOPs). The crucial role here plays hand in hand the material of photocatalyst, and harvested light. The Achilles' heel of most utilized metal oxides (titanium dioxide or zinc oxide) as photocatalysts is their absorption in the UV region, so currently the main goal is preparation of photocatalytic material active upon solar light exposure. The metals/non-metals doing/decorating or modification with other semiconductors have been proposed as promising way to improve the absorption in the visible region and charge carrier separation. Charge transfer processes upon photoexcitation of nanocrystalline photocatalysts initiate the generation of paramagnetic species and radical intermediates, the nature and quantity of which are determined not only by the photocatalyst properties, but also by the physicochemical factors affecting the light absorption by the photocatalyst, the quantity and nature of adsorbed species, desorption of products or the interface properties. Here the cw-electron paramagnetic resonance (EPR) spectroscopy is of utmost importance for their detection. The EPR measurements at low temperatures (e.g., 100 K) have potential to detect and identify the paramagnetic centers/defects in studied samples formed via synthetic/postsynthetic treatment and trapped charge carriers (electron/hole) produced by photoexcitation of photocatalyst. Although EPR provides direct detection of free radicals, in photocatalytic investigations utilization of indirect techniques, such spin trapping, spin scavenging, oxidation of sterically hindered amines or photoreduction, is often applied. The evaluation of the photocatalytic activity of individual metal oxide structures is based on the nature and quantity of reactive radical intermediates generated in the irradiated semiconductor dispersions obtained by in situ EPR spectroscopy. Proper choice of suitable experimental conditions is crucial for their successful application in heterogeneous semiconductor systems and can help to gain a comprehensive picture of the photoinduced processes undergoing upon light exposure of the photocatalyst in suspensions.

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## EPR and DFT Investigations into Reactive Oxygen Species Trapped on Surfaces and in Cages of Catalytic Relevance

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Key words: EPR; DFT; oxygen activation; zeolites; oxides.

The chemistry of oxygen species at heterogeneous surfaces and interface has attracted a wide attention over the years owing to its vital relevance for thermal catalysis, photocatalysis, electrocatalysis and materials science as well for development of mimetic systems. Due to the peculiar properties associated with its triplet,  ${}^{3}\Sigma_{g}$ , ground state that hinders the reactivity, dioxygen molecules are usually activated on catalytic surfaces by a sequence of gradual reduction and dissociation steps  $O_{2(g)} \rightarrow O_{2(a)} \rightarrow O_{2^{-}(ads)} \rightarrow O^{2^{-}(ads)} \rightarrow O^{2^{-}(ads)} \rightarrow O^{2^{-}(lattice)}$ , where various surface reactive oxygen species (surface ROS), ranging from electron-poor (electrophilic) to electron-rich (nucleophilic), of distinctly different reactivity and proton affinity appear. Among them the paramagnetic  $O_{2^{-}(ads)}$  (S = ½) and  $O^{-}(ads)$  (S=1/2) species are EPR active. The catalytic role of the surface is to provide oxygen in a specific activated state, which permits a new reaction pathway of lower activation energy to take place. Many experimental and theoretical investigations have been devoted to detailed elucidation of these activation processes, starting from the early stages of  $O_{2^{-}}$  formation via an interfacial electron transfer until final incorporation of the resultant  $O^{2^{-}}$  ion into the oxide lattice. Massive and porous oxide systems containing isolated, clustered or periodically extended transition metal ions belong to the most active materials for heterogeneous activation of dioxygen.

This paper reports on the activation of dioxygen on transition metal ions dispersed inside the nanopores of the zeolites and on transition metal oxides exemplified by metallozeolites, supported systems containing andspinels (Ni/MFI, Fe/MFI, Cu/MFI, Cu/CHA VO<sub>2</sub>/BEA, (MoO<sub>x</sub>/SiAO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Co-MgO). Experimental EPR investigations using isotopically enriched O-17 and O-18 dioxygen were corroborated by DFT modeling to provide a detailed molecular and phenomenological description of heterogeneous activation of dioxygen. Reversible and irreversible pathways of interfacial electron transfer activation of O<sub>2</sub> were identified. Molecular resolution approach was used, in turn, for an indepth insight into the ET events. In this context charge and the spin density redistribution along the  $\pi$ ,  $\sigma$ , and  $\delta$  orbital channels in the course of oxygen activation by transition metal centers were analyzed be means of the extended transition state - natural orbitals for chemical valence approach (ETS-NOCV). Congruent and incongruent charge and spin density flows were identified to contribute jointly to the activation of the attached dioxygen species. Their individual energetic relevance was quantified, which allowed for explaining the oxygen binding and activation mechanisms with unprecedented accuracy. Computational spectroscopy allowed for molecular interpretation of the ROS spectroscopic EPR parameters, and their structure sensitivity.

### Towards "better" molecular magnets. Correlation of structure and magnetic anisotropy

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Key words: magnetic anisotropy; SMM; SIM; HFEPR; FIRMS.

The theoretical and experimental study carried out in recent years allowed to determine the properties that guarantee SMM or SIM type behavior, which are: high spin state S, large magnetic anisotropy with both a negative ZFS parameter D (easy-axis anisotropy) and an easy-plane anisotropy (D > 0), as well as the formation of a significant energy barrier (increasing with S and D). These properties lead to bistable systems, showing the longer the relaxation times, the higher the energy barrier. However, since the specific conditions for the occurrence of SMM and SIM are not easy to achieve in practice, and the blocking temperatures of the molecular magnets obtained so far oscillate in a low range, our activities focused on finding a path of "tuning" the values of magnetic parameters. The correlation of the magnetic study with the crystal and molecular structure is the basis for the control of the synthesis and properties of the obtained magnetic materials, and ensures a change in magnetic anisotropy as a result of rational changes in structural anisotropy. However, achieving a high D value requires understanding how to adjust the geometry of the compound to obtain a significant contribution of spin-orbital coupling to magnetic anisotropy. The results of our research work conducted for a series of Co(II) complexes with the different N- donor ligands, its derivatives and halide or pseudohalide linkers show that the modulation of the geometry of the system is possible by modifying structural factors: substituent replacement in the ligand, disturbance of the ligand field strength, introduction of anionic ligands (Scheme 1). The presence of high magnetic anisotropy affecting a significant increase in the energy barrier in the obtained materials was additionally confirmed by high-field EPR (HFEPR) studies in the frequency range of 100-650 GHz supported, due to the large splitting of energy levels, by the innovative FIRMS (Far-Infrared Magnetic Spectroscopy) method consisting in on terahertz frequency sweeps and measurement of radiation absorption as a function of frequency. Our research shows also that not only the negative sign of the D parameter is not a necessary condition to observe relaxation processes, but also no or almost negligible zfs effect or high ground state spin. An example we reported the field induced slow magnetic relaxation in Cu(II), Mn(II) and Cr(III) complexes.



## Kittel's theory of ferromagnetic resonance for thin, flexible films with embedded magnetic nanostructures

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Key words: ferromagnetic resonance; thin film; magnetic nanoparticles; magnetic nanowires.

The intensive development of flexible magnetoelectronics is leading to the appearance of new materials in the form of non-magnetic flexible polymer matrices with embedded densely packed magnetic nanoparticles. These nanoparticles form various types of nanolayers, magnetic nanowires and other magnetic agglomerates forced by the restricted geometry of the thin film, in which magnetic dipole interactions become important. These interactions can be controlled by elastic deformations of the polymer matrix [1]. The densely packed magnetic nanoparticles can be obtained using the physico-chemical methods of 2D printing by forcing the self-assembly of nanoparticles into various types of spatial structures. The example can be magnetic nanowires [2,3]. Magnetic interactions present in the confined geometries significantly affect the ferromagnetic resonance condition. In this research, we show how Kittel's theory [4] can be adapted to describe magnetic resonance in such systems.

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## The impact of linker ligands on the structure dimensionality, magnetic anisotropy and slow relaxation processes of six-coordinate Ni(II) complexes

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Key words: Single-Molecule Magnets (SMM); Single-Chain Magnets (SCM); Magnetic anisotropy; Slow Magnetic Relaxation; Ni(II) complexes.

The search for new functional materials which show magnetic properties typical of molecular magnets (SMM) or single magnetic ions (SIM) such as long relaxation times, spontaneous magnetization below the critical temperature and the ability to tunnel the quantum magnetization has been a challenge for scientists for many years. However, even if suitable condition have been met the obtained compounds still exhibit too low blocking temperature. For this reason, the purpose of our research is finding a path of "tuning" the values of magnetic parameters through structure correlation and magnetic anisotropy, which is measured by the zero field splitting parameter in a zero magnetic field (D). There are many proposed examples of such mechanisms in the literature for Co(II) compounds, while such relationships for Ni(II) ions (with two unpaired electrons and characteristic magnetic anisotropy) are still relatively unknown. Considering the above we present the study of structure and magnetic properties of two Ni(II) complexes with 2.6-bis(pyrazol-1-yl) pyridine ligands and different linker ligands: azide and dicyanoamide about formulas  $[Ni_2(pypz)_2(\mu_{1,1}-N_3)_2(N_3)_2]\cdot 2H_2O$ and [Ni(pypz)(dca)(H<sub>2</sub>O)]<sub>n</sub>·n(dca). The use of various pseudohalide ligands allowed for fine-tuned the magnetic anisotropy and relaxation dynamics by controlling the ligand field strength and symmetry of the crystal field. The presence of high magnetic anisotropy affecting a significant increase in the energy barrier in the obtained materials was additionally confirmed by high-field EPR (HFEPR) measurement in the frequency range of 100-650 GHz due to the large splitting of energy levels. The AC susceptibility of complex  $[Ni_2(pypz)_2(\mu_{1,1}-N_3)_2(N_3)_2]\cdot 2H_2O$  indicates multiple relaxation processes, analyzed via the Debye model, revealing parameters indicative of Raman and direct relaxation processes.

## Study of Catalytic Systems by Electron Paramagnetic Resonance Spectroscopy

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Key words: photocatalyst; spin trap; zeolites; oxygen reduction reaction.

Electron paramagnetic resonance (EPR) spectroscopy is a method of choise to study species with unpaired electrons, such as transition metal cations, reactive oxygen species (ROS), adsorbed radical



anions, and defects, which are often involved in catalytic reactions. In this talk, some examples of the application of EPR to the study of heterogeneous catalytic systems will be presented. The in situ measurements performed with a micro-AEMFC placed in the cavity of the EPR spectrometer allowed the detection of \*OOH and \*OH radicals on the cathode side and \*H radicals on the anode side (Fig. 1). The presence of such radicals indicates that ROS play an important role in the degradation mechanism of the anion-

conducting polymers [1]. In the case of the photocatalysts, it was possible to determine the location of VO<sup>2+</sup> (Fig. 2) and Cu<sup>2+</sup> ions in the TiO<sup>2</sup> matrix and to follow the evolution of the redox center during the catalytic reactions. EPR measurements showed that both cocatalysts enhance



the activity of the catalysts, but the mechanism of enhancement is

different in both cases [2]. EPR spectroscopy provides evidence for the highly dispersed state of ceria throughout the zeolite matrix and the presence of superoxide radicals [3].

The examples presented here illustrate the great power of EPR in studying the catalytic system as well as the mechanisms of catalytic reactions.

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## Metal Cation Radical Complexes: From Environmental Pollutants to Functional Materials

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Key words: radicals; EPR; high-field EPR; DFT; ab initio.

Radicals are atoms or molecules with an unpaired electron in an orbital with dominants or p character. Although typically unstable, their stability can be enhanced through steric protection, spin density delocalization or coordination with metal cations, allowing for the isolation of radicals as pure compounds.

Environmentally persistent free radicals (EPFRs) are pollutants that may contribute to health problems. Most studies focus on EPFRs from combustion, but we demonstrated, using multifrequency EPR spectroscopy, that EPFRs can also form from natural polyphenols exposed to heavy metal ions like Pb(II) and Hg(II). Our relativistic DFT computations revealed these radical species are semiquinonato complexes of heavy metal ions.

Radical species have applications in material science. We isolated a stable semiguinonato complex of aluminum from 1,2-dihydroxybenzene and characterized it using multifrequency cw-EPR spectroscopy and computational techniques (DFT and DLPNO-CCSD). Additionally, we synthesized complexes of Al<sup>3+</sup>, Gd³⁺, Dy<sup>3+</sup> Co<sup>2+</sup>, and with а redox-active pincer ligand 0,N,O derived from 3,5-di-tert-butylcatechol for single-molecule magnet (SMM) applications. These complexes with the O,N,O ligand, which can exist in various oxidation states (Fig. 1), were analyzed using X-ray crystallography, multifrequency EPR, SQUID measurements and detailed theoretical calculations (fractional occupation number weighted electron density and CASSCF/NEVPT2).

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Fig. 1. Oxidation states of the pincer O,N,O ligand used in this study

## From dioxygen to superoxide – EPR study of paramagnetic Zn<sup>2+</sup>-O<sub>2</sub><sup>•-</sup> species in ZSM-5 zeolite and periodic DFT modeling

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Key words: EPR; DFT; superoxide; oxygen activation; spectra simulations; ZSM-5.

The activation of dioxygen  $O_2$  molecules may involve either electron or energy transfer processes. The latter implies redox transformation leading to reactive oxygen species (ROS). One such species,  $O_2^{\bullet-}$  superoxide radical anion, plays a vital role in catalysis, environmental chemistry, and biochemistry. One of the possible ways to generate these radicals is  $O_2$  adsorption on low-valent transition-metal ion centers dispersed in porous materials, such as zeolites. Herein, we present an EPR spectroscopic and theoretical analysis of an excellent example of a system defined by monovalent  $Zn^+$  ions.

This work aims to refine the experimental EPR studies involving the adsorption of isotopically labeled  ${}^{17}O_2$  on  $Zn^+$  exchanged MFI zeolite obtained by chemical vapor deposition. EPR measurements provided geometric constraints for the observed superoxide species, while periodic DFT modeling detailed its structure and electronic properties. The geometry optimization was performed at the DFT level for periodic models of MFI, containing a single  $Zn^+$  ion (Fig. 1) and  $Zn^+-Zn^{2+}$  pair, where oxygen adsorption can lead to the formation of  $O_2^{\bullet-}$ . Several possible zinc-superoxide adducts were computationally studied. Large cluster models were subsequently cut from these structures and used for calculating EPR g and A tensors.



Fig. 1. (a) DFT-optimized structure of side-on Zn<sup>2+</sup>-O<sub>2</sub><sup>•-</sup> with two magnetically equivalent oxygen nuclei, and (b) EPR powder spectra for 17-O enriched adsorption complex (b)

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## Identification of reactive oxygen species generated by the interaction of transition metal oxides and $H_2O_2$

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Key words: reactive oxygen species; radicals; hydrogen peroxide; advanced oxidation processes.

From the point of view of catalytic and environmental chemistry, reactive oxygen species (ROS) are extremely important entities containing oxygen atoms in unusual oxidation states or dioxygen in the excited state. These include hydroxyl radicals (\*OH), superoxide anions  $(O_2^{-*})$  or singlet oxygen ( $^{1}O_2$ ). ROS can be produced by the Fenton reaction using hydrogen peroxide and photocatalytic processes. Due to the high oxidizing activity of organic pollutants and non-toxicity, they are increasingly used in advanced oxidation processes, which makes them an alternative to commonly used, chemically supported methods of biological and mechanical purification. In fact, AOPs can be used as the last step in the water purification when contaminant concentrations are at a low level. This aspect is there beneficial because the efficiency of AOP processes can be controlled by selecting an appropriate catalyst that enables the formation of significant amounts of strongly oxidizing radicals.

The aim of this work is the identification of reactive oxygen species generated during hydrogen peroxide activation on transition-metal oxides and the relation between composition of the catalyst (type of transition metal, presence of an admixture) and it's activity in oxidation of model organic wastewater pollutants. The materials used in this study (Zr and Nb amorphous oxides and their composites with CeO<sub>2</sub>, CuO nanocrystalline phases) were selected in such a way that they enable the formation of ROS via the Fenton and electroprotic mechanisms. In the first step, they were characterized by X-ray diffraction (XRD) and Raman spectroscopy to confirm their structure. EPR spectroscopy, especially measurements using the 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) spin trap and 2,2,6,6-tetramethyl-4-piperidone (TEMP) oxidation, was used to identify paramagnetic ROS such as hydroxyl radicals and singlet oxygen, respectively. In addition, the activity of the catalysts in methylene blue, rhodamine B, and ciprofloxacin degradation as a test reaction was investigated. The obtained results showed synergy between the adsorption of pollutant molecules on the surface of the catalysts and the activity in the formation of ROS and their ability to undergo degradation reactions. Catalysts that generate the largest amount of \*OH radicals have the greatest activity in the degradation processes. This is because hydroxyl radicals are responsible for the degradation of dyes.

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## The effect of oxidative degradation of Dopa-melanin on its basic physicochemical properties and photoreactivity

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Key words: eumelanin; oxidative degradation; bleaching; singlet oxygen; photoprotection; phototoxicity.

Melanin, particularly eumelanin, is commonly viewed as an efficient antioxidant and photoprotective pigment. Nonetheless, the ability of melanin to photogenerate reactive oxygen species and sensitize the formation of cyclobutane pyrimidine dimers may contribute to melanin-dependent phototoxicity. The phototoxic potential of melanin depends on a variety of factors, including molecular composition, redox state, and degree of aggregation. Using complementary spectroscopic and analytical methods we analyzed the physicochemical properties of Dopa-melanin, a synthetic model of eumelanin, subjected to oxidative degradation induced by aerobic photolysis or exposure to 0.1M hydrogen peroxide. Both modes of oxidative degradation were accompanied by dose-dependent bleaching of melanin and irreversible modifications of its paramagnetic, ion- and electron-exchange and antioxidant properties. Bleached melanin exhibited enhanced efficiency to photogenerate singlet oxygen in both UVA and short-wavelength visible light. Although chemical changes of melanin subunits, including a relative increase of DHICA content and disruption of melanin polymer induced by oxidative degradation were considered, these two mechanisms may not be sufficient for a satisfactory explanation of the elevated photosensitizing ability of the bleached eumelanin. This study points out possible adverse changes in photoprotective and antioxidant properties of eumelanin that could occur in pigmented tissues after exposure to high doses of intense solar radiation.

## Benchtop X-band EPR for *in vivo* studies of zebrafish - melanin radicals and nitroxyl spin probes

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Key words: zebrafish, melanin radicals, spin probes, membrane fluidity, *in vivo* model.

*In vivo* studies rarely utilized X-band EPR due to the small size of X-band resonators and the relatively high power required to detect EPR signals, which rendered them unsuitable for most often used laboratory animals such as mice or rats.

Zebrafish (*Danio rerio*) is a small tropical fish with genome sharing over 70% similarity with humans. Relatively easy husbandry, ease of genetic modifications, fast development, and the close mirroring of processes in humans make zebrafish an attractive substitute for other vertebrate models, particularly in biomedical research. Among the wide range of applications, zebrafish are used as a model for cancer, neurodegenerative diseases and ageing, i.e. processes where free radicals play an important role.

To allow an *in vivo* detection of free radicals in living zebrafish embryos and larvae we designed specially-shaped glass and quartz capillaries. When used together with eSpect+, they allow the measurement of X-band EPR spectra while ensuring the embryos and larvae survival.

One of applications of this approach is the detection of a single line EPR spectrum corresponding to eumelanin free radicals naturally forming in zebrafish. The signal is visible in pigmented zebrafish embryos and is absent in the *albino* line, which has a naturally occurring mutation in the *slc45a2* gene that blocks melanin synthesis. Similarly, fish in which pigment formation has been chemically inhibited by phenylthiourea also lack the signal.

Melanin has very diverse roles and functions in various organisms, yet in most species it gives coloration to skin or eyes, and protects from UV radiation. It is also postulated that it plays an important role in melanoma progression. When oxidized, melanin forms radicals, which could be detected with EPR spectroscopy. This application could be expanded by xenotransplanting human melanoma cells into zebrafish embryos giving new opening for melanoma studies.

When using zebrafish model and specially-shaped capillaries together with eSpect+, standard X-band EPR spectrometers can have other *in vivo* applications. The EPR parameters could be used to calculate membrane order parameters and, thus, give direct information about fluidity/rigidity of the membrane *in vivo*. For this purpose, we studied both hydrophilic and lipophilic spin probes. As a result, we were able to detect changes in the membrane fluidity in pigment-free mutant or chemically treated fish.

## Two-dimensional magnetism in a self-inercalated transition metal dichalcogenides

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Key words: 2-D magnetism; chromium tellurides; ferromagnetic resonance.

The layered structure of dichalcogenides  $Cr_{1+\delta}Te_2$  facilitates their epitaxial growth with thickness down to 1.2 nm which is equivalent to 2-unit cell thickness of monolayers [1]. In such monolayers, the magnetic anisotropy counteracts spin fluctuations, thereby providing the samples for exploring magnetic properties in the 2D limit. The  $\delta$  parameter of non-stoichiometry tunes considerable phase transitions in this material. We focus attention on  $Cr_2Te_3$  ( $\delta = 0.33$ ) and  $Cr_3Te_4$  ( $\delta = 0.5$ ) samples (see Fig. 1) for which the Curie temperature approaches a room temperature what is unprecedented opportunity in the field of spintronics.



Fig. 1. Model of  $Cr_{1+\delta}Te_2$  crystal

The measurements of ferromagnetic resonance in Cr<sub>2</sub>Te<sub>3</sub> crystals reveal two types of magnetic transitions. The first at 295 K relates to quasi isolated two–dimensional monolayers with crystal structure of the NiAs type. The second one, at 210 K, follows from bulk ferromagnetism.

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## Application of ESR spectroscopy in nanomedicine

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Key words: iron oxide nanoparticles; polymers; yeast cells; cancer cells; targeted therapy.

Despite the development of technology, the diagnostics of many diseases, including cancer, at an early stage and thus the possibility of curing them is still a challenge for medicine. The solution to this problem may be the use of nanomaterials, which, due to widespread interest and extensive research, are gaining increasingly better parameters. Properly prepared nanoparticles can improve the effectiveness of radiotherapy (radiosensitizers) as well as protect healthy tissues and cells (radioprotectors). Functionalized with various drugs (nanodrugs) can be used in targeted therapy, which will also improve the effectiveness of treatment while reducing the dose of the drug. The potential effectiveness of such a solution is influenced by many factors, related to both the properties of the material itself and the purpose of its use (e.g. tumor environment). Such studies are performed using cell lines and tissue models.

Iron oxide and polymer nanoparticles were investigated using electron spin resonance spectroscopy (ESR). The measurements were performed on a Bruker ESR spectrometer EMX-10, operating in the Xband (9.4 GHz). The nanoparticles were functionalized with nitroxide probes, TEMPO derivatives. The research used yeast cells as a model organism and selected cancer cell lines. Cell proliferation was monitored under a microscope. The received results show the wide possibility of using the ESR technique in nanomedicine and also indicate what should be particularly noted in this type of research.

## EPR case study - tracking long-lived free radicals in dandelion caused by air pollution

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Keywords: Taraxaum sp.; dandelion; free radicals; air pollution; EPR.

Particulate air pollution is one of the global environmental pollutants. Studies indicate that a new type of pollutant from mainly fossil fuel combustion and automobile exhaust emissions should be considered, i.e. environmentally persistent free radicals (EPFRs). These radicals are ubiquitous in the environment, have a long life span, and are capable of producing harmful reactive oxygen species (ROS). Dandelion is a plant that is often used for biomonitoring.

The samples were collected in 2020 and 2021 in spring and late summer on rain-free days. The material used for the study was roots, leaves, flower stalks and inflorescences of Taraxaum sp., and was collected from 6 sites with 3 plants each. The air pollution of particulate matter with PM10 and PM2.5 fractions was also measured using a DustTrak II analyzer. The content of EPFRs in dandelions was studied using the electron paramagnetic resonance (EPR) method. Two types of radicals were considered, for values of g factor < 2.0030 associated to C-centered radicals, and for g factor > 2.0030 associated with a mixture of O- and C- centered radicals. Relationships between components were also determined for each part of the plant. The leaf was selected as the most appropriate part of the plant for the measurement of carbon-derived EPFRs radicals. The g<sub>ef</sub> value (Fig. 1) and the total number of spins were performed. The results obtained from the EPR measurements and air pollution were analyzed and relationships between location, season, and EPR results were found.



Fig. 1. Average  $g_{\text{ef}}$  values for the leaf for the position and intake periods

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### **POSTER PRESENTATIONS**

## Photoinduced processes on modified titanium dioxide photocatalysts studied by indirect cw-EPR techniques

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Key words: photocatalysis; spin trapping; photoinduced electron transfer; reactive oxygen species.

Heterogeneous photocatalysis, as one of the advanced oxidation processes (AOPs), is an exciting strategy in the lowering of an increasing stress on the environment due to expanding needs of civilization place. The key restriction so far has been the selection of the right photocatalyst, as existing semiconductor photocatalysts are mostly employed when exposed to UV light. The target is expansion of their photocatalytic effectiveness into the visible region and preparation of the sunlight-driven photocatalyst. Different approaches from several semiconductor materials have already been presented. Composite photocatalysts are formed by doping with metallic and nonmetallic portions, resulting in the production of complexes with interfacial charge transfer (ICT). Based on a mixture of quantum chemical calculations and prior experiments, the development of ICT complexes looks to be a viable avenue. The combination of organic molecules (e.g., taxifolin, salicylic acid derivatives) on the surface of the semiconductor allows photoinduced charge carriers to be transferred from the organic molecules to the semiconductor photocatalyst, preserving their potential and potentially leading to the formation of reactive oxygen species that participate in degradation reactions. Spectroscopic methods such as cw-EPR and UV-Vis-NIR spectroscopy allow a unique view of ongoing processes in various systems. Thanks to indirect EPR techniques such as spin trapping with 5,5-dimethyl-1-pyrolline N-oxide (DMPO), spin scavenging with 4-hydroxy-2,2,6,6tetramethylpiperidin-1-oxyl (Tempol) or photoreduction via reduction semi-stable radical cation of 2,2'-azinobis-(3-ethylbenzthiazolin-6-sulfonate) is possible to utilize the photocatalytic properties of nanomaterials in various environments. Based on the results so far, it can be said that compared to the pure semiconductor photocatalyst, the photocatalytic efficiency in the visible region has improved [1-5].

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### Herbs with antioxidant and photosensitizing properties

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Key words: photosensitizers; herbs; antioxidants; photodynamic therapy; TEMPO.

Photosensitization is a process that increases the skin's sensitivity to sunlight. It may be caused by active compounds contained in medicinal plants. This mechanism is also used in photodynamic therapy (PDT), which involves the use of photosensitizers activated by light of an appropriate wavelength. Photodynamic therapy is used in the treatment of various diseases, including skin cancer. Many photosensitizing herbs also have antioxidant properties, making them interesting from a medical perspective. The aim of the study was to assess the antioxidant properties of selected photosensitizing herbs using the electron paramagnetic resonance (EPR) technique. The study included chamomile, horsetail, goldenrod, and lovage. The EPR technique enabled the registration of spectra, based on which changes in the concentration of free radicals over time were measured. The results of the EPR analysis confirmed that all tested herbs have the ability to scavenge free radicals, with varying degrees of effectiveness. The conducted research highlights the potential of these plants as natural antioxidants, but their photosensitizing properties require further research in the context of use during photodynamic therapy.

## System of digital scanning of the magnetic field for radiospectrometers of the "RADIOPAN" company (Poznań, Poland)

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Key words: RADIOPAN company; EPR; modernization; digital NMR magnetic field unit; sensitivity.

In order to provide high resolution and sensitivity EPR spectrometers are quite bulky devices, because they use large magnets to ensure the homogeneity of magnetic field in the investigated sample. The EPR spectrometers have been manufactured since the discovery of the EPR phenomenon until to the present time by different producents. It is natural that some part of the electronic equipment of old EPR spectrometers are physically and technically obsolete. Whereas the magnet itself and the microwave bridge remained practically unchanged up to now.

Modernization of the "RADIOPAN" EPR spectrometers firstly was solved by using a digital magnetic field scan unit, described in [1]. The proposed in [1] magnetic field scan unit linearly changes magnetic field and measures its value. Such solution allows significantly expand technical capabilities of the "RADIOPAN" EPR spectrometers, but does not use their construction features. In our opinion during modernization of the EPR spectrometers must be maximally taking into account their construction features.

All "RADIOPAN" EPR spectrometers contain NMR magnetometer of high quality, which can be used for precise magnetic field measurements. and to carry out the field sweeping by using the same standard magnet current amplifier to the input of which is applied a voltage corresponding to desired value of the magnetic field. Thus, the magnetic field values can be directly read from the NMR unit of the "RADIOPAN" EPR spectrometer that allows to record the magnetic resonance signal with high resolution.

Proposed modernization of the "RADIOPAN" EPR spectrometer of the SE/X-2544 type was realized in the Institute of Physical Optics (Lviv, Ukraine).

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## Effect of low concentrations of nitroxides on SH-SY5Y cells transfected with the Tau protein

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Key words: antioxidant; glutathione; nitroxides; oxidative stress; reactive oxygen species; SH-SY5Y cells

Nitroxides, stable synthetic free radicals, are promising antioxidants, showing many beneficial effects both at the cellular level and in animal studies. However, the cells are usually treated with high millimolar concentrations of nitroxides, which are not relevant to the concentrations that could be attained in vivo. This study aimed to examine the effects of low ( $\leq 10 \mu$ M) concentrations of three nitroxides, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), 4-hydroxy-TEMPO (TEMPOL) and 4-amino-TEMPO (TEMPAMINE), in pure chemical systems and on SH-SY5Y cells transfected with the human tau protein (TAU cells), a model of chronic cellular oxidative stress, and transfected with the empty plasmid (EP cells). All nitroxides were active in standard antioxidant-activity tests except for the 2,2'-azinobis-(3-ethylbenzthiazolin-6-sulfonate) radical (ABTS\*) decolorization assay. Nitroxides reduced Fe<sup>3+</sup>, inhibited autoxidation of adrenalin as well as pyrogallol, and oxidation of dihydrorhodamine123 by 3-morpholino-sydnonimine (SIN-1). TEMPO protected against fluorescein bleaching from hypochlorite, but TEMPAMINE enhanced the bleaching, apparently due to chloramine formation. Nitroxides showed no significant cytotoxicity and were reduced by the cells to nonparamagnetic derivatives. They decreased the level of reactive oxygen species, depleted glutathione, and increased mitochondrial-membrane potential in both types of cells, and increased lipid peroxidation in TAU cells. These results demonstrate that even at low micromolar concentrations nitroxides can affect the cellular redox equilibrium and other biochemical parameters.

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## Electron magnetic resonance of Co-doped BaTiO<sub>3</sub> ceramics at helium temperatures

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Key words: BaTiO<sub>3</sub>; perovskite; multiferroics; Co-doping.

Multiferroics are the subject of intensive studies due to their potential applications in microelectronic or optoelectronic devices. The BaTiO<sub>3</sub> perovskite is very interesting due to its multifunctional properties, such as its piezoelectric and ferroelectric [1].

In this poster, we present the results of electron magnetic resonance (EMR) studies on the Co-doped  $BaTiO_3$  ceramics for the  $BaTiO_3$ :Co sample with different cobalt content. The EMR spectra were performed at the 6 – 100 K temperature range.

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## EMR study of spinel multi-shell CoFe<sub>2</sub>O<sub>4</sub> nanoferrites

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Keywords: nanoferrites; spinels; EMR; ferrites; magnetic properties.

A ferrites are a ceramic material made up of iron oxide with a metallic element. Ferrite-type compounds described with the general chemical formula  $AFe_2O_4$ , where the metal cation A can be commonly represented by the  $Zn^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{2+}$ , etc. are a fairly broad subgroup of inorganic materials belonging to the larger spinel family, which are depicted by the cubic crystal structure assigned to the Fd<sup>-</sup>3 m (No. 227) space group.

Nanoferrites have been prepared 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  $N_2$ . The results of the X-band electron magnetic resonance measurements of CoFe<sub>2</sub>O<sub>4</sub> nanoferrites were obtained for a wide temperature range (Fig. 1). We can observe complex interactions in the materials being studied. By modifying the composition of the materials it is possible to control the magnetic properties (ferromagnetism-antiferromagnetism-ferrimagnetism).



Fig. 1. Temperature dependence of EMR spectra of the CoFe<sub>2</sub>O<sub>4</sub>-Co-Mn-Zn core/shell nanoferrites

## EPR and optical spectroscopy of lithium tetraborate glasses doped with Tb and co-doped with Tb and Ag

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Key words: lithium tetraborate; Tb<sup>3+</sup> ions; Ag<sup>+</sup> ions; Ag nanoclusters; photoluminescence; energy transfer.

The spectroscopic and luminescent properties of the Tb-doped and Tb-Ag co-doped lithium tetraborate ( $Li_2B_4O_7$  or  $Li_2O-2B_2O_3$ ) glasses containing 1.0 mol.% Tb\_2O\_3 and 2.0 mol.% AgNO\_3 are detailed studied using electron paramagnetic resonance (EPR), optical absorption, and photoluminescence (emission, excitation, decay kinetics, quantum yield) techniques.

The EPR spectra of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Tb glass show signals related to paramagnetic Tb<sup>4+</sup> ( $4f^7$ ,  $^8$ S<sub>7/2</sub>) centres in sites with strong rhombic distortion [1,2] and Fe<sup>3+</sup> ( $3d^5$ ,  $^6$ S<sub>5/2</sub>) non-controlled impurity ions. In the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:Tb,Ag glass besides Fe<sup>3+</sup> ions are observed EPR signals of Ag<sup>0</sup> ( $4d^{10}5s^1$ ) and Ag<sup>2+</sup> ( $4d^9$ ) ions as well as signal of Tb<sup>4+</sup> centres in sites with weak rhombic distortion [1,2].

The optical absorption spectra of the investigated glasses show narrow and very weak 4f - 4f absorption bands related to  $Tb^{3+}$  ( $4f^8$ ,  $^7F_6$ ) ions. The luminescence emission spectra of the both investigated glasses show numerous narrow emission bands corresponding to the  $^5D_4 \rightarrow ^7F_J$  (J = 6 - 0) and  $^5D_3 \rightarrow ^7F_J$  (J = 5 - 3) transitions of  $Tb^{3+}$  ions. The decay kinetics of the most intense emission band of  $Tb^{3+}$  ions at 541 nm ( $^5D_4 \rightarrow ^7F_5$  transition) is characterised by a lifetime slightly longer than 2.6 ms. The luminescence emission spectra of the Tb-Ag co-doped glass show two broad weakly-resolved emission bands in the violet-green spectral range related to Ag<sup>+</sup> ( $4d^{10}$ ,  $^1S_0$ ) ions and nonplasmonic Ag nanoclusters ( $Agm^{n+}$  centres). The decay kinetics of these bands is non-monoexponential, characterised by an average lifetime in the  $\mu$ s time range. An enhancement of the  $Tb^{3+}$  luminescence intensity and quantum yield was observed in the Tb-Ag co-doped Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> glass. The energy transfer from Ag<sup>+</sup> ions and Ag nanoclusters to  $Tb^{3+}$  ions was discussed. Silver co-doping is a promising approach to improve the luminescent properties of  $Tb^{3+}$  ions in borate glasses.

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### Properties of Cd<sub>1-x</sub>Mn<sub>x</sub>Te as a room temperature semiconductor radiation detector

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Keywords: EMR; CdMnTe; MBE; radiation detector; DMS.

The unique features, such as giant Zeeman splitting and bound magnetic polaron (BMP) due to the strong exchange interaction between the magnetic moments of the magnetic ions and the spins of band electrons, of diluted magnetic semiconductors (DMS) have opened the doors for spintronic device applications. In our work, we presented the results of the X-band electron magnetic resonance (EMR) measurements of  $Cd_{1-x}Mn_xTe$  doped with different concentrations of manganese (x – 0.034; 0.046, 0.0112, 0.023, 0.041; measured by XRF method) studied for a wide temperature range.  $Cd_{1-x}Mn_xTe$  have been prepared by molecular beam epitaxy (MBE), to which the end conditions of growth on (100) low-symmetry surface of a substrate had to be first established. Growth processes were performed in the Riber Compact 21 MBE system using the standard MBE growth mode. The crystal structure was evaluated by means of the high-resolution X-ray diffraction technique (HXRD). Using PANalytical's "Amass" program, numerical simulations were conducted to ascertain the composition and thickness of the layers.  $Cd_{1-x}Mn_xTe$  samples are inspected by optical microscopy immediately after unloading from the growth system. In particular, the Nomarski contrast imaging

mode is typically utilized, as it offers high resolution and clarity relative to other imaging modes when inspecting thin film samples.

We observed two groups of lines: originating from manganese (330 mT) and a low-field microwave absorption line (LFMA). In addition, we observe a line from other paramagnetic centers (e.g. defects). The subject of our analysis is the line originating from manganese and its dependence on concentration.



Fig. Temperature dependence of EPR spectra of  $Cd_{1-x}Mn_xTe$  (D353C13, x=0.034)

## Temperature dependence of EPR spectra in titanium dioxide modified with (3aminopropyl) triethoxysilane (APTES)

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Keywords: EPR measurements; APTES-modified TiO2.

Titania nanocomposites modified with 500 mM (3-aminopropyl) triethoxysilane (APTES) were prepared using the solvothermal method (180 °C for 4 h), followed by calcination at higher temperatures (800-1000°C). Modifying titania with APTES has been found to lead to enhanced photocatalytic properties compared with unmodified TiO<sub>2</sub> calcined at the same temperatures. This was attributed to the effective slowing down of the phase transition from anatase to rutile. Electron paramagnetic/ferromagnetic resonance measurements showing EPR spectra from oxygen defects in all nanocomposites (Fig. 1) were strongly dependent on the calcination temperature. Additional resonance lines appeared from magnetic agglomerates whose intensity increased with increased calcination temperature.



Fig. 1. Temperature dependence of the EPR spectra for nanocomposite of the TiO<sub>2</sub>-4h-180°C-500mM- 900°C in the temperature range 90<T<295 K

## Spin qubit pairs in DNA Hairpins – EPR methods of study

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Deoxyribonucleic acid (DNA) is the well-known biological molecule on which the genetic information of all living organisms from plants to viruses, bacteria to animals and humans is encoded. DNA not only encodes the necessary information for all cells, but also plays an essential role in the formation of all proteins and enzymes for these cells. Synthetically obtained short DNA chains (from a few to several pairs of nucleotides) are called Hairpin DNA (H-DNA) because of the characteristic shape of such a double DNA chain (Fig. 1).



Fig.1. Hairpin DNA.

A peculiar application of H-DNA could be to use this molecule as material for the construction of A a qubit, i.e. the basic unit in a quantum computer corresponding to a bit in classical computers. There are several proposals for the construction of a qubit (e.g. nitrogen defects in diamond). However, a qubit constructed from DNA would have an advantage over the others because it has a well-defined initial state.

In this paper, we will review the basic methods using EPR spectroscopy to study and characterise photogenerated biradicals in DNA Hairpins. Continuous wave methods as well as pulsed methods in the X-band will be analysed.

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