

5 – 8 June 2018, Wrocław - Kudowa-Zdrój

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of Prof. Adam Jezierski, the Rector of University of Wrocław

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Welcome Address
The Fifth Forum EMR-PL,
Wrocław - Kudowa-Zdrój, 5 - 8 June 2018

Honoured Guests, Ladies and Gentlemen:

On behalf of the Council of the Polish EMR Group and the Local Organising Committee, co-chaired by Maria Jerzykiewicz and Julia Jezierska. (Faculty of Chemistry, University of Wrocław), I welcome you to the V Forum EMR-PL organized under the auspices of the Polish EMR Group. We all appreciate very much the hard work and organisational efforts of our colleagues in Wrocław, which have brought this Forum to fruition. On personal side, we may be all pleased that this Forum is held at such a nice setting of spa resort of Kudowa in the Sudety Mountains. It will certainly give us all a welcome respite from the hard work. I appreciate the great efforts of the Local Organising Committee to bring us here.

I believe that this Forum may play an important role in enhancing the strength of the EMR research groups in Poland. Continuing with the spirit of the 1st Forum in Rzeszów, 2nd in Huciska, 3rd in Kraków, and 4th in Poznań, this Forum is open to all participants 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 V Forum EMR-PL will satisfy most participants and provide ample opportunities to meet fellow researchers and to discuss various topics of interest.

For the second time we have invited as plenary speakers eminent EMR researchers from abroad: Prof. Ram Kripal, Head of the Electron Paramagnetic Resonance Group at Department of Physics, University of Allahabad, India, and two our compatriots working permanently in the USA: Professors Jerzy Krzystek and Andrzej Ożarowski, from National High Magnetic Field Laboratory, Florida State University, Tallahassee. We are grateful for accepting our invitation and hope that their participation will be beneficial to all colleagues.

I would also like to invite all participants, irrespective of their present status of membership in the Polish EMR Group, to join us at the General Meeting (GM) of the Society, to be held during the Forum. 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.

My sincere thanks go to Maria Jerzykiewicz and Julia Jeziarska, and all members of the Local Organising Committee, for their dedicated work to make the V Forum EMR-PL a successful meeting. Support from the Scientific Committee in nominating the invited speakers and maintaining the high standard of this Forum is also much appreciated. We are grateful to the Dean of the Faculty of Chemistry, Wrocław University, Professor Anna Trzeciak, for her support of the conference organization and financial assistance under the KNOW grants. Thanks are due to all speakers and participants, who by their attendance will help to make this Forum a great success.

I wish you all an enjoyable and stimulating experience at the Forum and in Wrocław/Kudowa-Zdrój. Thank you.



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*]

Tuesday, 5.06.2018

- 10.00 – 11.00 registration of the participants / Faculty of Chemistry,
University of Wrocław, ul. F. Joliot-Curie 14
- 11.00 – 11.45 visit to the main building of the University of Wrocław
- 11.45 – 13.00 transfer to Arboretum of the University of Wrocław in
Wojślawice
- 13.00 – 16.30 lunch and visiting of the arboretum
- 16.30 – 17.45 transfer to Kudowa Hotel in Kudowa-Zdrój
- 19.00 dinner followed by "get together"

Wednesday, 6.06.2018

- 8.00 – 8.50 breakfast
- Session 1. – Chairman: Czesław Rudowicz*
- 9.00 – 9.10 conference opening
- 9.10 – 9.55 **PL1: Ram Kripal**
"A Comprehensive Spectroscopic Study of Mn²⁺ doped PbS
nanocrystals"
- 9.55 – 10.15 **L1: Volodymyr Popovych**
"FMR Study of CdTe Single Crystals Implanted with High
Fluence of Cr ions"
- 10.15 – 10.35 **L2: Bohdan Padlyak**
"Features of EPR spectra in the V-doped borate glasses"
- 10.35 – 11.05 coffee break
- Session 2. – Chairman: Zbigniew Sojka*
- 11.05 – 11.50 **PL2: Ryszard Krzyminiewski**
"ESR study of functionalized nanoparticles with a magnetic
core"

- 11.50 – 12.10 **L3: Grzegorz Leniec**
"Site symmetries of cerium ions in BaWO₄ single crystals
codoped with sodium ions"
- 12.10 – 12.30 **L4: Ireneusz Stefaniuk**
"EMR study of ferromagnetic and antiferromagnetic
properties and structural data in CdCrTe alloy"
- 12.30 – 12.50 **L5: Marian Kuźma**
"Competition between ferro- and antiferromagnetic ordering
in metamagnetic Heusler alloys"
- 13.00 – 14.30 lunch

Session 3. – Chairman: Andrzej Ożarowski
- 14.30 – 15.15 **PL3: Zbigniew Sojka**
"Unusual powder EPR spectra"
- 15.15 – 15.35 **L6: Maria Jerzykiewicz**
"Application of EPR spectroscopy in soil sciences"
- 15.35 – 15.55 **L7: Bernadeta Dobosz**
"Super-hyperfine structure of spin labels in cells-
nanoparticles systems"
- 15.55 – 16.25 coffee break

Session 4. – Chairman: Szymon Łoś
- 16.25 – 17.10 **PL4: Czesław Rudowicz**
"Modeling spin Hamiltonian parameters for Fe²⁺ (S = 2)
adatoms on Cu₂N surface using microscopic spin Hamiltonian
approach"
- 17.10 – 17.30 **L8: Piotr Pietrzyk**
"Generation of Reactive Oxygen Species via Electroprotic
Interaction of H₂O₂ with ZrO₂ Gel"
- 17.30 – 17.50 **L9: Dariusz Man**
"Impact of vanadium(IV/II) complex on DPPC liposome
membranes: ESR method"
- 20.00 gala dinner

Thursday, 7.06.2018

8.00 – 8.50	breakfast
9.00 – 13.00	excursion to Błędne Skały and Kaplica Czaszek
13.00 – 14.30	lunch
14.30 – 15.30	meeting of the EMR-PL members
15.30 – 16.00	coffee break
16.00 – 19.00	POSTER SESSION
20.00	barbecue dinner

Friday, 8.06.2018

8.00 – 8.50	breakfast
	<i>Session 5. – Chairman: Piotr Pietrzyk</i>
9.00 – 9.45	PL5: Jerzy Krzystek "Terahertz Electron Paramagnetic Resonance"
9.45 – 10.05	L10: Ryhor Fedaruk "Coherent manipulation of electron qubits in pulsed EPR experiments with the bichromatic driving"
10.05 – 10.25	L11: Maria Augustyniak-Jablokow "Evidence for Long Spin Relaxation Times of Paramagnetic Centers in Graphene Oxide"
10.25 – 10.45	L12: Barbara Pytel "The application of EPR technique to study the influence of selected alcohols on dynamic parameters of lipid membranes"

PROGRAMME

- 10.45 – 11.15 coffee break
- Session 6. – Chairman: Jerzy Krzystek*
- 11.15 – 12.00 **PL6: Andrzej Ozarowski "**
 Comparison of Investigations on Mono and Polynuclear
 Complexes in High-Field and X-Band EPR"
- 12.00 – 12.20 **L13: Magdalena Kurdziel**
 "Innovative methods of starch modification studied by EPR
 method"
- 12.20 – 12.40 **L14: Szymon Łoś**
 "The Localization Phenomenon of Electric Charges on
 Reduced Graphene Oxide Flaks Seen by EMR and Impedance
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A Comprehensive Spectroscopic Study of Mn²⁺ doped PbS nanocrystals

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Key Words: Nanocrystals; chemical precipitation; X – ray diffraction; SAED pattern; optical properties; EPR.

ABSTRACT

Zero – dimensional Mn²⁺ doped PbS semiconductor nanocrystals have been synthesized by simple chemical routes. This work is an effort to dope one of the most studied semiconductor PbS nanocrystal system with one of the widely used transition metal dopant Mn²⁺ ion and describes new physical properties that have emerged following successful synthesis of these nanocrystals. The Mn: PbS nanocrystals have cubic structure (space Group *Fm3m*) and the average crystallite size lies between 5 nm to 10 nm as characterized by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) analysis. The structural properties of Mn: PbS nanoparticles are also studied by UV/Vis absorption spectrum and High Resolution Transmission Electron Microscopy (HRTEM). The quantitative chemical analysis of pure and Mn²⁺ doped PbS nanocrystals have been done with the help of Energy Dispersive Spectroscopy (EDS) spectra. The energy band gaps have been determined by UV/Vis absorption study with the help of Tauc Plot and are 5.30 eV, 5.27 eV, 5.22 eV and 4.70 eV for 0%, 0.05%, 0.26% and 0.52% Mn²⁺ doped PbS nanocrystals, respectively. The luminescence behaviour of the nanocrystals has been studied by photoluminescence (PL) spectra. The magnetic and electronic properties of Mn: PbS nanocrystals are studied using Electron Paramagnetic Resonance (EPR) spectra and the values of the electron g tensor, the second-rank axial zero- field splitting parameter *D* and the hyperfine parameter tensor *A* are calculated.

ESR study of functionalized nanoparticles with a magnetic core

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Key words: magnetite nanoparticles, TEMPO spin label, chemotherapeutics, nanoparticles focusing, rotating magnetic field, drug delivery

In recent years, nanotechnology has been developing very rapidly, bringing new materials for potential bioapplications. One of them are magnetic nanoparticles which can be applied both in medical diagnostics (e.g. contrast in magnetic resonance imaging) and therapy (as drug carriers). Especially beneficial is the use of nanoparticles for drug delivery in targeted therapies, e.g. in the treatment of cancer. Currently, chemotherapeutics are given to the bloodstream and only a small percentage of them reaches the tumor. The use of magnetic nanoparticles would make it possible to deliver the drug directly to the tumor without damaging the other organs and thus eliminating side effects.

In this paper the application of electron spin resonance for magnetic nanoparticles study was shown. Nanoparticles were functionalized with different drugs and spin labels and covered with chosen polymer to stay biocompatible. To deliver drugs to chosen location a new method, using a rotating magnetic field, has been developed. Additionally the application of ESR to control this delivery was shown.

Unusual Powder EPR Spectra

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Key words: EPR, powder, spectra, shape analysis

Specificity of EPR studies of nanomaterials is largely caused by their inherent heterogeneity and low local symmetry of the investigated paramagnets. The resultant EPR spectra are complicated by the fact that one is concerned with surfaces/interfaces, and that usually the investigated materials are in the form of powders. Thus, the proper interpretation of a variety of complicated EPR absorption patterns of such systems, as well as the extraction of magnetic interaction parameters therefrom, may pose challenging problems. This is because often the signals are superimposed and several parameters such as the g-tensor, fine (D-tensor) and hyperfine (A-tensor) interactions appear distributed giving rise to extra line broadening. The low site symmetry resulting in axes non-coincidence, appearance of extra lines, and smearing of strongly angle dependent lines restrains further the amount of the information extractable from the experimental spectra. As a result, a great deal of important molecular information about the investigated system is only available with the help of advanced computer analysis supported by quantum chemical calculations.

Various means can be employed to distinguish different EPR signals which compose the observed complex EPR absorption, and to extract the spin Hamiltonian parameters. The information derived from analysis of the spectra can be more rigorous if it is corroborated by computer simulation, and the system under study is labeled with isotopes of non-zero nuclear spin. In this contribution we focus the emphasis on specific machinery of the techniques applied to EPR studies in surface and nanomaterials chemistry, using selected case studies of shape analysis of untypical and complex EPR spectra.

Modeling spin Hamiltonian parameters for Fe^{2+} ($S = 2$) adatoms on Cu_2N surface using microscopic spin Hamiltonian approach

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Key words: crystal field (CF); zero field splitting (ZFS); microscopic spin Hamiltonian (MSH); magnetic anisotropy; Fe^{2+} adatoms on surfaces; $\text{Cu}_2\text{N}/\text{Cu}(100)$ and $\text{CuN}/\text{Cu}(100)$

Studies of transition metal atoms adsorbed on surfaces are gaining interest due to magnetic properties of $3d^N$ ($4f^N$) electrons, indicating that adatoms behave like magnets for potential, e.g. as memory storage applications. Scanning tunneling microscopy (STM), inelastic electron tunneling spectroscopy (IETS) [1,2], and recently EMR techniques [3] are employed. Crucial for description of adatoms is the spin Hamiltonian (SH) [4], especially zero-field splitting (ZFS) parameters (ZFSPs), which are often confused with single-ion anisotropy constants [5].

In this work we focus on Fe^{2+} ($S = 2$) atoms adsorbed on $\text{Cu}_2\text{N}/\text{Cu}(100)$ surface [1-3]. The 2nd-rank ZFSPs (D , E) are mostly considered, while only one 4th-rank ZFSP set is available [6]: B_k^q , $k = 2, 4$ (in the extended Stevens operators (ESO) notation [4]). Here we employ the package MSH/VBA [7] based on crystal field (CF) and microscopic spin Hamiltonian (MSH) theory, developed up to the fourth-order perturbation theory for $3d^4/3d^6$ ($S = 2$) ions within 5D approximation. The ZFSPs and Zeeman g -factors are calculated for Fe^{2+} ($S = 2$) adatoms adsorbed on $\text{Cu}_2\text{N}/\text{Cu}(100)$ for wide range of the microscopic parameters: spin-orbit (λ), spin-spin (ρ) coupling constants, and the crystal-field energy levels $^5D(\Delta_i)$. Since Δ_i are related with coordination and symmetry of adsorption sites, this approach enables studying magneto-structural correlations. The ρ -contributions and the 4th-rank ZFSPs are found important. Simulations of EMR spectra using *EasySpin* and the ZFSP set best matching experimental ZFSPs are carried out. In parallel poster presentations other aspects pertinent for this study are reported. The results enable comparison with ZFSPs obtained using density functional theory (DFT) methods.

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Terahertz Electron Paramagnetic Resonance

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Key words: single-ion magnets, HFEPR, Terahertz EPR, FIRMS

The recent wave of interest in single-ion molecular magnets based on transition metals and lanthanides/actinides coordination complexes has necessitated developing techniques that reliably measure the parameter of importance for characterizing their properties, namely magnetic anisotropy, also known as zero-field splitting (zfs) for transition metals, or crystal-field splitting (cfs) for lanthanides and actinides. Whereas for many metal complexes High-Frequency and -Field EPR (HFEPR), typically performed at sub-terahertz frequencies, has been fully adequate to determine zfs and cfs covering the range of approximately $1 - 20 \text{ cm}^{-1}$ (30 – 600 GHz), many of those that display single-ion magnet properties are characterized by so-called “giant anisotropy”. The term *giant anisotropy* is usually reserved for cases of zfs or cfs exceeding, often significantly so, the above numbers, often reaching 100 cm^{-1} (3 THz) and beyond. In such cases, increasing the EPR operating frequency into terahertz range is imperative. An overview of available and prospective techniques that make it possible will be presented together with recent applications originating from the MagLab using the technique known as Far Infra Red Magnetic Spectroscopy (FIRMS). These include at this point coordination complexes of Kramers ions cobalt(II) and rhenium(IV) (both $S = 3/2$) and non-Kramers species cobalt(III) and iron(IV) (both $S = 1$).

Comparison of Investigations on Mono and Polynuclear Complexes in High-Field and X-Band EPR

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Key words: high-field EPR, Mn(III) complex, binuclear systems, zero-field splitting

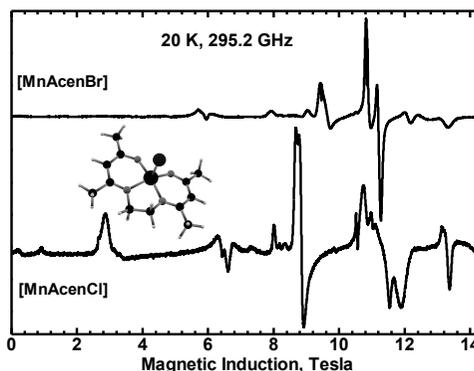
Transition metal ions with $S = 2$ ground state are typically characterized by large zero-field splitting parameters D and E , corresponding to the spin Hamiltonian

$$\hat{H} = \mu_B \mathbf{B} \{g\} \hat{\mathbf{S}} + D \left\{ \hat{S}_z^2 - \frac{1}{3} S(S+1) \right\} + E (\hat{S}_x^2 - \hat{S}_y^2)$$

D may be either positive or negative, relatively small (up to $\sim 6 \text{ cm}^{-1}$) in the case of Mn^{3+} , and often much larger for Fe^{2+} . Determination of the spin Hamiltonian parameters for such $S = 2$ systems has been frequently attempted using the X-Band EPR spectroscopy. The zero-field splitting between states $M_S = 2$ and $M_S = -2$ is small, of the order of $3E^2/D$, and thus may be accessible to X-Band EPR. The “forbidden” $\Delta M_S = 4$ transition appears in spectra close to the effective g value $g_{\text{eff}} = 4g_z$ and is the only feature to be seen. In contrast, many or all “allowed” $\Delta M_S = 1$ transitions are observed in the high-

field, high-frequency EPR. Several Mn^{3+} complexes, which have been studied in the past using X-Band EPR were synthesized and reinvestigated at high microwave frequencies and magnetic fields, and the spin Hamiltonian parameters were accurately determined, including their sign. While HF EPR shows profound differences between $[\text{MnAcenCl}]$ and $[\text{MnAcenBr}]$, virtually the same spin Hamiltonian parameters were found for both compounds from the X-Band spectra. The reasons for the X-Band EPR insensitivity to the zero-field splitting parameters in such cases will be discussed.

Many relatively simple transition metal complexes are inaccessible to X-Band EPR. This includes monomeric and binuclear Ni^{2+} systems, binuclear complexes of Mn^{2+} , Mn^{4+} , Fe^{3+} and even some copper dimers. High-Field EPR opens new possibilities in many areas. In addition to providing accurate spin Hamiltonian parameters, it also allows sign determination of the zero-field splitting, which is important in the theory of the metal-metal interactions in bi- and polynuclear complexes. Factors affecting the zero-field splitting in some binuclear systems will be discussed.



HF EPR spectra of Mn^{3+} complexes
recorded in frozen $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ solution.

NOTES

FMR Study of CdTe Single Crystals Implanted with High Fluence of Cr ions

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Key words: CdTe, Cr implantation, magnetic resonance, nanoprecipitates.

The samples for investigation were prepared from the CdTe single crystals, grown by the modified PVT method [1], both undoped and doped by iodine donors with dopant concentrations $N_I = 10^{18}$ and 10^{19} cm⁻³ in the initial charge. The samples in the form of thin platelets were implanted at high vacuum by 500 keV Cr⁺ ions with fluences 10^{16} , 10^{17} and 5×10^{17} cm⁻² [2]. Their magnetic properties were measured by EPR method using 9.43 GHz X-band Bruker FT-EPR spectrometer ELEXSYS E580 in a 100 – 300 K temperature range.

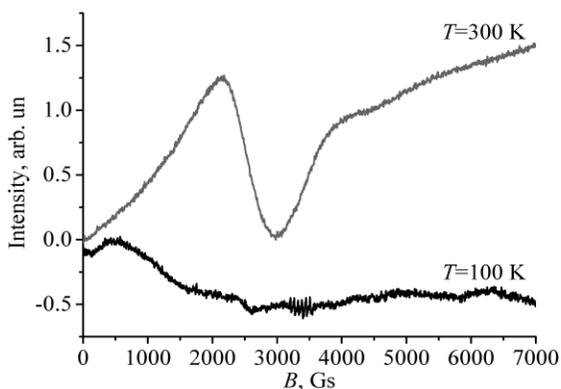


Fig. 1. EPR spectra of Cr-implanted CdTe:I ($N_I = 10^{19}$ cm⁻³) single crystal (fluence 5×10^{17} cm⁻²)

At room temperature the EPR spectrum consists of two components (Fig. 1). The first one with width $\Delta B_{pp} = 81.7$ mT is centered at $B_r = 261$ mT. A very broad ($\Delta B_{pp} > 1$ T) second line is attributed to the spins of the conduction electrons and it disappears at low temperatures. At the temperatures below 160 K the first line is of Callen shape, and it is associated with a super-paramagnetic state of Cr-related nanoclusters, which are usually formed in the as-implanted samples and are reduced by post-implantation annealing [3]. A

hyperfine structure at low temperatures, consisting of six features, is induced by spins of I nucleons.

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Features of EPR spectra of the V-doped borate glasses

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Key words: borate glasses; EPR; vanadyl; spin-Hamiltonian parameters; local structure.

The electron paramagnetic resonance (EPR) spectra of a series of the V-doped borate glasses with $\text{Li}_2\text{B}_4\text{O}_7$, LiKB_4O_7 , CaB_4O_7 , and LiCaBO_3 basic compositions containing 0.5 and 1.0 mol. % V_2O_5 were registered at $T = 300$ K and analysed. The results of EPR spectroscopy clearly show that the V impurity is incorporated into the network of investigated glasses, mainly, as isolated vanadyl (VO^{2+}) molecular complex centres with characteristic EPR spectra of the axial symmetry. The spin-Hamiltonian parameters (g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp}) of the VO^{2+} centres in glasses with $\text{Li}_2\text{B}_4\text{O}_7:\text{V}$, $\text{LiKB}_4\text{O}_7:\text{V}$, $\text{CaB}_4\text{O}_7:\text{V}$, and $\text{LiCaBO}_3:\text{V}$ compositions have been determined from their experimental EPR spectra. The simulated by us EPR spectra of the VO^{2+} axial centres in the investigated glasses perfectly coincides with the corresponding experimental EPR spectra. An additional broad asymmetric EPR signals, observed in the $\text{Li}_2\text{B}_4\text{O}_7:\text{V}$, $\text{LiKB}_4\text{O}_7:\text{V}$, and $\text{LiCaBO}_3:\text{V}$ glasses were assigned to the superposition of different combinations of pairs centres, coupled by magnetic dipolar and exchange interactions. The local structure of the VO^{2+} isolated and different pair centres in the network of investigated borate glasses are proposed. Optical absorption bands, which are observed in all investigated V-doped borate glasses, have been identified and interpreted in the framework of crystal field theory for the VO^{2+} molecular complex centres. The crystal field parameters and molecular bonding coefficients for the VO^{2+} centres in the investigated borate glasses were calculated and compared with corresponding referenced data for other V-doped borate glasses with the similar compositions.

Site symmetries of cerium ions in BaWO₄ single crystals codoped with sodium ions

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Keywords: sheelite, BaWO₄, structural refinement, EPR, roadmap, local symmetry

Barium tungstate crystals are interesting and relatively new medium for stimulated Raman scattering for applications in Raman shifters of laser radiation [1]. Good quality BaWO₄ crystals can be grown by Czochralski technique and doped with rare-earth ions. Doping with trivalent ions require charge compensation which may be provided, for example, by structural defects or proper codoping with alkaline metal ions. Crystals possess sheelite like structure with the space group $I4_1/a$.

Results of EPR studies of BaWO₄:Ce crystals and crystals codoped with Na are presented in this paper. EPR study was performed in the low temperature range 3K < T < 50 K for all three planes of single crystals. The EPR spectra were derived from cerium ions with a fictitious spin $S = 1/2$. The spin Hamilton (SH) parameters were determined. The values of SH parameters indicate the occurrence of paramagnetic centers in axial and low symmetry. The number of observed EPR lines depends on the selected plane. Based on the roadmap, we can determine that we have one center with axial symmetry and at least two centers with low symmetry. There are more centers with low symmetry than with axial symmetry. Temperature studies towards the three planes indicate very weak interactions between cerium ions. These interactions are interchangeable. The linewidth v.s. temperature revealed increasing exponential tendency with increasing temperature. It shows 1 phonon at the lower temperatures and Raman + Orbach effect at the higher temperatures. Exponential change of the ΔB could be connected with the spin-lattice relaxation processes involving excited states of Ce³⁺ ions.

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EMR study of ferromagnetic and antiferromagnetic properties and structural data in CdCrTe alloy

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Keywords: EMR, DMS, CdCrTe, Ferromagnetic properties

Dilute magnetic semiconductors (DMSs) are based on traditional semiconductors, but doped with magnetic impurities. Typically is manganese (Mn) or chromium (Cr) – II-VI semiconductor compounds, such as CdTe. DMSs doped with Cr are also attractive research object, because of their unique spintronics properties with possible technological applications [1]. In our work [e.g 2] we presented the results of the X-band electron magnetic resonance (EMR) measurements of Cr ions in CdTe bulk. We investigated Cd_{1-x}Cr_xTe alloy which were doped with different concentrations of chromium formed during the synthesis process. Crystals with different concentrations of chrome (up to x=0.08) were studied for a wide range of temperature. The crystalline structure of Cd_{1-x}Cr_xTe films were investigated by high resolution transmission electron microscopy (TEM) (Fig.1a). The observed ferromagnetic properties are correlated with changes induced by temperature and current (Fig.1b).

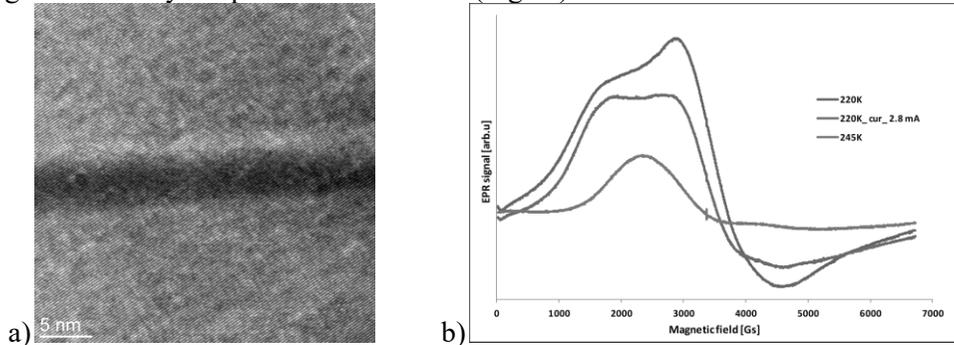


Figure 1.a) TEM image of crystalline structure of Cd_{1-x}Cr_xTe, b) EMR spectra of Cd_{1-x}Cr_xTe at different temperature with and without current flow.

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Competition between ferro- and antiferromagnetic ordering in metamagnetic Heusler alloys

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Key words: NiMnIn Heusler alloys, magnetic resonance.

Metamagnetic Heusler alloys $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sb}_y$, $\text{Ni}_{50}\text{Mn}_{50-y}\text{Sn}_y$ and $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$ exhibit multifunctional properties such as shape memory effect, giant magnetoresistance, giant magnetocaloric effect, inverse magnetocaloric effect, giant magnetothermal conductivity[1]. These properties follow from interplay between structural and magnetic phase transitions.

The alloy $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$ is most interesting material for magnetostructural studies . On the termomagnetization curve , the alloy show a table –like peak with width from 250 – 290 K (for composition $y = 15.5\text{at.}\%$) and from 180-300 K (for $y = 10\text{at.}\%$) in the magnetic field of $H = 0.05\text{T}$ [2]. The sharp and pronounced increase of the magnetization at room temperature is described by Curie law and arises from magnetic transition from high temperature paramagnetic austenite phase (cubic $L2_1$) to the ferromagnetic phase at the same crystal structure. At lower temperatures around 260 K (for $y = 15.5\text{at.}\%$) and 230 K (for $y = 16 \text{ at.}\%$) the magnetization suddenly drops almost to the zero value .

The disappearing of magnetization is attributed to paramagnetic or antiferromagnetic ordering. In fact such paramagnetic- antiferromagnetic disorder below temperature M_f is likely to be imaged as an inhomogenous martensite paramagnetic phase consisting with superparamagnetic martensite particles and antiferromagnetic inclusions formed around the Mn ions in the Mn and In sites[3]. In the range temperature from martensitic transformation start (M_s) to the martensitic transformation finish (M_f), there coexist two crystallographic phases: austenite and martensite, therefore two magnetic phases coexist together as well. Unfortunately, the magnetization measurements do not give sufficient information on such mixed magnetic phases. In this paper we show how magnetic resonance measurements (EPR and FMR) can be interpreted for both mixed magnetic phases in a system. The measurements were done for $\text{Ni}_{50}\text{Mn}_{50-y}\text{In}_y$ ($y = 14.5$) ribbons [4].

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Application of EPR spectroscopy in soil sciences

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Key words: EPR, humic substances

In recent years, spruce and larch forests in Poland and Slovakia have been severely damaged by various factors (cutting off, wildfire and windthrow). Those events offered an opportunity to study the changes of the forest ecosystems. The presented results concentrate on the influence of forest destruction on soil profiles with special attention to application of EPR spectroscopy.

All the samples of humic acids extracted from the soils of the disturbed plots (forest were cut off, destroyed by windthrow or wildfire) exhibit lower radical concentrations of the semiquinone radicals than the reference samples. This effect was observed better for the samples of organic profiles than for mineral ones.

The decrease in radical content can be the result of several processes, such as the shifting of the semiquinones equilibria towards nonradical diamagnetic forms (hydroquinones or quinones) due to changes in the pH or to redox reactions. These processes may take place concurrently with the transformation of organic matter towards less aromatic structures, e.g. the reaction of the unpaired electron of a semiquinone with smaller molecules incorporated upon an environmental change. As a result, diamagnetic structures with a more aliphatic structure are formed. Another cause of the quenching of the radical can be its interaction with some metal ions (d-block like Cu(II), Fe(III), Mn(II)). However, in the present case no significant changes in metal ion concentrations were observed.

In order to identify the cause of the decrease in radical concentration the g-parameters were calculated and compared with data obtained from other spectroscopies (UV-Vis, ¹³C NMR, FT-IR). The lowest g-parameter characterized the control sample. This strongly suggests that the decrease in radical concentration in the humic acids from the soils exposed to the calamities is rather the result of a reduction in aromaticity and the incorporation of more oxygen-containing groups into the NOM structure. The matrix of the humic acid extracted from the environmentally affected areas has a more open and more reactive structure, whereby this organic matter is less stable than before the calamities.

Presented results prove that the EPR method can be very useful in structural studies of organic matter of soils.

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Super-hyperfine structure of spin labels in cells-nanoparticles systems

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Key words: TEMPO spin labels, yeast, magnetite nanoparticles, nanomedicine, drug carriers

Nanoparticles are studied as potential drug carriers in medical treatment. One of them are magnetite nanoparticles. They can be functionalized with different drugs and to stay biocompatible they are covered with a chosen polymer. Electron spin resonance is a method which has found a wide application in the study of physical properties of such materials. Additionally, if nanoparticles are functionalized with TEMPO spin label, not only the information about the core but also about their surface and its interaction with environment can be obtained. One of the stages in this type of study is research with using cells. Very interesting and important issue is how the nanoparticles interact with cells and if they attach to the cell membrane or enter the cell. It seems that using ESR, suitably functionalized nanoparticles and cells it is possible to answer this question.

In this work magnetite nanoparticles (core 20-40 nm) functionalized with a few types of TEMPO spin labels and covered with silan were studied using ESR. As a model cells yeast were used. It was found that the hyperfine structure in ESR spectrum of TEMPO depends on the temperature, the concentration of studied solution and type of attached spin label. This information can be useful in explaining how nanoparticles interact with cells.

EPR Insight into Generation of Reactive Oxygen Species via Electroprotic Interaction of H₂O₂ with ZrO₂ Gel

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Key words: EPR, HYSCORE, reactive oxygen species, superoxide, H₂O₂, metal oxides

Formation of reactive oxygen species (ROS) is of vital importance in catalytic oxidation chemistry. In this contribution we have shown that a non-redox system such as amorphous zirconium dioxide (ZrO₂) exhibits specific activation in ROS formation via H₂O₂ decomposition. Interaction between ZrO₂ and H₂O₂ in aqueous solution was investigated by means of EPR and HYSCORE techniques augmented with other physicochemical techniques (Raman, UV-Vis, FTIR, TG-MS, and XPS). This study involved a broad range of pH values and H₂O₂ concentration. Various reaction intermediates such as superoxide (O₂⁻) and hydroxyl (·OH) radicals as well as peroxide (O₂²⁻) species were identified. At pH below 5.3 the superoxide and hydroxyl radicals were generated simultaneously in large amounts with the peak concentration reached around the isoelectric point of the gel catalyst. In this pH region, the ZrO₂ gel exhibited the peroxidase-type activity, quantified by o-phenylenediamine assay. At pH > 5.3 formation of O₂²⁻ was accompanied by a substantial release of O₂ due to the pronounced catalase-like activity of ZrO₂. The role of electroprotic processes (an interfacial proton transfer coupled with an intermolecular electron transfer) in H₂O₂ decomposition and ROS formation was elucidated, and a plausible mechanism of this reaction, $\equiv\text{Zr}^+-\text{HO}_2^-(\text{surf}) + \text{H}_2\text{O}_{2(\text{aq})} = \cdot\text{OH}_{(\text{aq})} + \equiv\text{Zr}^+-\text{O}_2^-(\text{surf}) + \text{H}_2\text{O}$, was proposed. The surface of ZrO₂ covered with hydroxyl groups played a role of an ionic sponge, which influence the electroprotic equilibrium by capturing the charged reaction intermediates (superoxides). Unlike amorphous gel, crystalline zirconia exhibited only weak activity in production of ROS, and different mechanism was involved. The activity of the zirconia gel catalyst in ROS generation was quantified by measuring the Michaelis-Menten constant, which appeared to account for about 40% of the value characteristic of the Fenton-type oxides (Fe₃O₄, Co₃O₄).

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Impact of vanadium(IV/II) complex on DPPC liposome membranes: ESR method

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Key words: spin probes, liposomes, vanadium complex, membrane fluidity

Vanadium is used in technology, for example, in metallurgy, but is also a component of living organisms. Vanadium was observed in all animal cells, but its biochemical function has not been definitively identified. EPR spectroscopy enables tracking the influence of vanadium compounds on changes in membrane dynamics. The effect of vanadium complex (V (IV/II)) on the liposome membranes formed of synthetic lecithin (DPPC) was presented in this paper. Liposomes were formed during the sonication of DPPC lecithin in an aqueous medium. The concentration of the vanadium compounds, was changed from a range of 0% to 7% in a molar ratio to the lecithin. The EPR technique was used to examine the fluidity of membranes using three spin probes (TEMPO, 16DOXYL stearic acid methyl ester, stearic acid 5DOXYL methyl ester), penetrating different regions of the membrane. The TEMPO probe penetrates the interface space water-lipid and allows to designate partition parameter F. The probe 16DOXYL is located in the middle of the lipid bilayer and allows to designate rotational correlation time τ , while the probe 5DOXYL gives information of membrane fluidity from the region under space the polar head groups and allows to designate the order parameter T. The results of research allow the following conclusions:

- The changing of membrane fluidity was observed, as a function of admixture concentration.
- Was also observed a significant difference in effect on the membranes, of vanadium complex V(II) relative to V(IV).
- Significant differences in the action of complexes on the membranes, are to be related probably, to the much stronger reactivity of the V(IV) complex than the V(II) complex.

Coherent manipulation of electron qubits in pulsed EPR experiments with the bichromatic driving

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Key words: pulsed EPR; Rabi oscillations; spin decoherence; bichromatic field

The decay of Rabi oscillations provides direct information about coherence of two-level spin systems (qubits). When observed in EPR experiments, it is often *shortened* by spatial inhomogeneity of the microwave (MW) field amplitude in a bulk sample. In order to suppress this undesired loss of coherence, we propose an additional dressing of spin states by a weak longitudinal continuous radiofrequency (RF) field [1]. Our calculations of the Rabi oscillations for the Gaussian, cosine and linear distributions of the MW amplitude show that the maximum suppression of the inhomogeneity-induced decoherence is achieved at the so-called Rabi resonance when the radio-field frequency is in resonance with the Rabi frequency of spins in the MW field. The manifestations of such suppression in the published EPR experiments with the bichromatic driving are discussed. At the Rabi resonance, the decay time of Rabi oscillations in the inhomogeneous MW field can be increased by an order of magnitude as compared to the single MW excitation (see Fig. 1). The proposed method could open new possibilities for separating the contributions of relaxation mechanisms from those due to the inhomogeneous driving in spin decoherence.

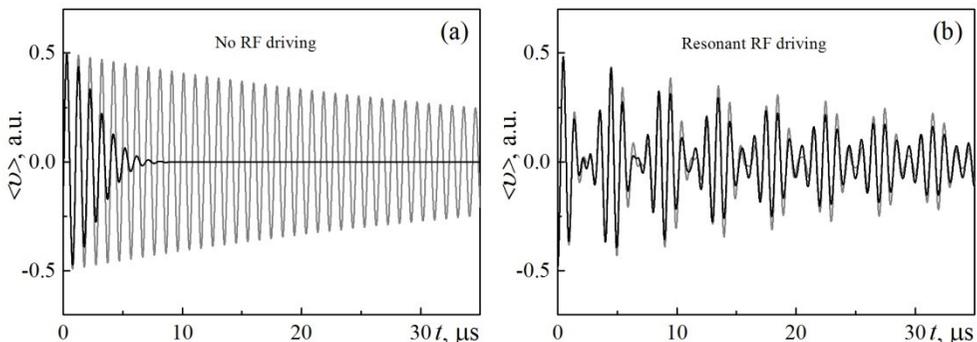


Fig. 1. Rabi oscillations in the homogeneous (grey lines) and inhomogeneous (black lines) MW field without (a) and with the resonant (b) RF driving.

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Evidence for Long Spin Relaxation Times of Paramagnetic Centers in Graphene Oxide

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Key words: graphene oxide; long spin relaxation times; electron paramagnetic resonance; rapid passage; hydrogen-related defects

Our study of graphene oxide (GO) by means of CW EPR reveals the presence of centers with the spin-lattice relaxation time longer than 1 μs at room temperature. That is the first observation of such long relaxation time in GO. The existence of the slowly relaxing center is evidenced by the out-of-phase EPR observed at the phase 90° relative to that of the magnetic field modulation. This signal appears when the conditions of slow-passage through resonance are violated, i.e. when the rate of change of the magnetic field due to sweep of the external magnetic field and/or to magnetic field modulation is faster than the electron spin relaxation rate. In this case the spin response lags the modulating field and the first-harmonic out-of-phase signal is generated under microwave power saturation. An observation of the out-of-phase signal reveals that the spin-lattice relaxation time T_1 of this paramagnetic center is longer than $1/\omega_f$ (1.6 μs at 100 kHz), where ω_f is the modulation frequency. We show that this type of centers can be attributed to the isolated unfunctionalized carbons in the highly functionalized regions of GO. The room temperature dependence of the EPR signal intensity on microwave power indicates the presence of the second type of paramagnetic centers with shorter relaxation time. However, such dependence observed at 4.2 K shows that the relaxation times of both types of centers are long enough to saturate the EPR signal. The centers of the second type demonstrate the Curie-Weiss temperature dependence of the unsaturated signal intensity, interact with each other via conduction electrons and are therefore localized in the graphene-like regions of the GO layer. We find also that the adsorption of air and water molecules on the GO surface decreases the degree of saturation due to shortening the spin-lattice relaxation time of paramagnetic centers. These findings are supported by the preliminary pulsed EPR study of the GO sample in air giving at 120 K $T_1 \cong 500 \mu\text{s}$ and $T_2 \cong 30 \text{ ns}$ for the center in the highly functionalized regions.

The application of EPR technique to study the influence of selected alcohols on dynamic parameters of lipid membranes.

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Key words: DPPC liposomes, ESR spin probe method, alcohols.

The effect of five selected alcohols: methanol, ethanol, propanol, butanol, and pentanol, on the dynamic properties of liposome membranes formed of synthetic lecithin DPPC was presented in this paper.

Liposomes are good lipid bilayer models suitable for investigation of the impact of biological active substances of biological and model membranes. Majority of substances used in the technology, pharmaceutical and cosmetic industry can significantly modify properties of membranes which – in some cases – can cause unexpected negative side effects. Therefore, it is so important to investigate an impact of different types of substances (e.g. commonly used alcohols) on a biological membranes and its lipid models. The variety of available alcohols makes them widely applicable as a solvent in pharmaceutics, the textile industries and chemical processes. EPR spin probe method was used to determine the dynamic properties of the liposome membranes.

Liposomes were formed during the sonication of DPPC lecithin in an aqueous medium. The concentration of lecithin in the sample was 10 μM . A spin probe in a concentration of 0,001 M the liposome water dispersion. The EPR technique made use of two spin probes penetrating the different areas of the membrane. TEMPO probe penetrates the interphase water–lipid (partition parameter F) and the 16-doxyl stearic acid methyl ester probe locates in the middle of the lipid bilayer (rotational correlation time τ). The concentration of the alcohols compounds changed in the range of 0% to 2,6% in a molar ratio to the aqueous medium. For the study there was chosen alcohols in homologous series: methanol CH_3OH , ethanol $\text{C}_2\text{H}_5\text{OH}$, propanol $\text{C}_3\text{H}_7\text{OH}$, butanol $\text{C}_4\text{H}_9\text{OH}$, and pentanol $\text{C}_5\text{H}_{11}\text{OH}$.

The results of our research, based on the analysis of changes of spin probes spectroscopic parameters, showed the following conclusions:

- the change of membrane fluidity, as a function of admixture concentration, was dependent on the type of additives;
- the changes of dynamic parameters for given alcohol were similar to the liquidity interphase water-lipid as the depth of the bilayer;
- methanol, ethanol and propanol, decrease the fluidity of the membrane in the liquidity interphase water-lipid and depth of the bilayer;
- butanol, and pentanol increase the fluidity of the membrane in the liquidity interphase water-lipid and depth of the bilayer;
- in all studies butanol, and pentanol showed the least activity.

Innovative methods of starch modification studied by EPR method

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Key words: barley starch, oat starch, ozone treatment, stable radicals, UV irradiation

Starch is one of the renewable plant products used as food and as a raw material in many industries. Its properties often need adaptation to specific technological requirements. This is accomplished by various modifications of starch by physical, enzymatic and chemical methods. Starch oxidation is the most widely used one. The commercial production of such starch usually obtained by treatment with chemical oxidizing agents generates unwanted residues of used oxidants and products of their reduction. The necessity of purifying such material and the disposal of waste creates the environmental hazards can lead to impurities in final product and makes the processes more costly. Hence, the idea of application of ozone and UV radiation as substitutes of traditional oxidants in modification of starch arose. In the light of the literature data it appears that there is no properly elaborated theory of the impact of UV radiation, as well as ozone on the starch material.

Two cereal starches, oat and barley, before and after ozone, UV, thermal treatment and chemical oxidation were investigated by XRD, EPR and FTIR. Some physicochemical properties of studied samples were also measured. Native starches differed in their crystallinity, chemical content and the amount of stable radical species. The lower content of amorphous amylose in oat starch, as well as the presence of amylose-lipid complexes caused the more ordered structure of oat starch. However, the number of radicals detected by EPR in native oat starch was higher than in barley one. All modification led to strong changes in all physicochemical parameters of starches. With increasing degree of oxidation (the highest upon UV and the lowest upon thermal treatment) the depolymerization of starches, connected with their crystallinity decrease, was observed (the highest in heated starches and the lowest for UV treated). Simultaneously, the amount of stable radicals increased, the most noticeably upon UV and thermal treatment. The process was more effective in barley starch. On the basis of detailed analysis of EPR spectra the carbon centered character of radicals and the mechanism of their formation was proposed, supported by data obtained from other used analytical methods.

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The Localization Phenomenon of Electric Charges on Reduced Graphene Oxide Flaks Seen by EMR and Impedance Spectroscopy

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Key words: localization phenomenon, graphene, EMR, impedance, conductivity

The EPR is excellent technique to study the localization phenomenon on various systems. However, in carbon porous materials due to conducting properties and complex electronic states on the system surface in spectra there are seen only single line, which are not follow the Curie law. To look deeper into the charge carrier behavior at surface we applied the impedance spectroscopy measurements. The careful analysis of the impedance spectra reveals some additional details concerning the charge dynamics at the graphene surface. There were find two scattering centers. This is supporting the EPR deconvolution into different electronic states present on the carbon surface. The careful analysis of the impedance spectra allows also for a more precise description of the variable range hopping of charge transport in complex scheme connections between graphene flaks of thermally reduced graphene oxide sample. The dynamic of current carriers movement is government by resistivity step, ΔR and characteristic jump time, τ . This two parameters determine the capacitance of each scattering processes present in the system. Based on knowledge of accumulated current carriers can be ascertained the charge sign involved in dissipative action. Both holes and electrons are responsible for conductive properties. The carriers polarity is depended on the temperature change. What's more the localization length showing the distance from which charges are excited to take a part in conducting properties can be calculated as well. This study reveals that in the system holes can be easily delocalized and they are played the crucial role in the conductive properties. In higher temperature scope the strong holes delocalization result in stronger electrons localization and opposite relation is observed during temperature drop. The not conservation of the Ohm's law by the system is due to attractive interaction between holes and electrons as well.

NOTES

Electron magnetic resonance of ZnCoO thin films embedded with metal Ag/Au nanoparticles

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Keywords: EMR, ZnO, Curie temperature, nanoparticles

Zinc oxide (ZnO) is a well-known inexpensive semiconductor with perspective for various applications [1]. It is important that some of the Zn can be substituted by magnetic transition metal ions to form a metastable solid solution. Especially interesting is doping of ZnO with Co since both Zn^{2+} and Co^{2+} ions has near identical ion radius [2]. In present paper we report on studies of $Zn_{0.8}Co_{0.2}O$ thin film fabricated by pulsed laser deposition, with Ag and Au nanoparticles (NPs) embedded on ZnO structure synthesized by homogeneous nucleation technique.

Electron magnetic resonance (EMR) measurements were carried out (Fig. 1.), spectrum lines were fitted with the Dyson function and hence the line parameters were obtained: peak-to-peak line width, and the resonance field. The temperature dependence of EMR was determined and the Curie temperature of $Zn_{0.8}Co_{0.2}O$ was obtained.

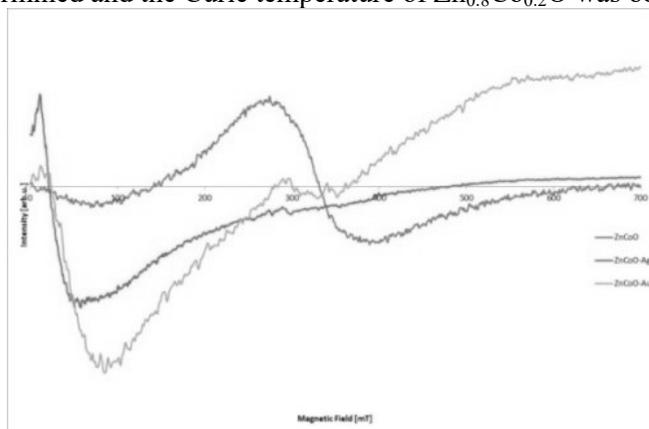


Figure 1. EMR spectra of ZnCoO (blue), ZnCoO/Ag (red) and ZnCoO/Au (green), obtained at 180K, the y axis has been rescaled to obtained the similar intensities

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Electron Paramagnetic Resonance Study of $\text{AgGaGe}_{3-x}\text{Si}_x\text{Se}_8$ Silicon-Doped Chalcogenide Single Crystals

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Key words: EPR, AGGSiSe, semiconductor, silicon compounds

Silicon-doped chalcogenide single crystals $\text{AgGaGe}_{3-x}\text{Si}_x\text{Se}_8$ (AGGSiSe) were obtained by solid state phase growth of equimolar amounts of AGSe and SiSe_2 at 970 K during 24 h. This compound is isostructural: space group $I-42d$, $a=0.59041$ nm, $c=1.0499$ nm, $Z=1$ and he has energy band gap equal to 2.30 eV. They have been reported as promising materials for nonlinear and piezoelectric physical properties [1].

In our work we presented the results of the X-band electron paramagnetic resonance (EPR) measurements of the AGGSiSe system. The investigation were performed in the whole concentration range with $x=0.03$; 0.05; 0.1; 0.2. The EPR measurements at temperature range from 95 K up to 350 K using the X-band ELEXSYS Bruker E 580 spectrometer were performed. The obtained representative EPR spectra are shown in Fig. 1.

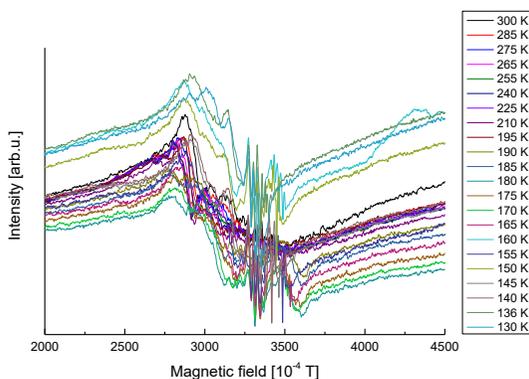


Fig. 1. EPR spectra of $\text{AgGaGe}_{3-x}\text{Si}_x\text{Se}_8$ ($x=0.1$) at different temperature.

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EMR study of ferromagnetic and antiferromagnetic properties and structural data in CdCrTe alloy

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Keywords: EMR, DMS, CdCrTe, Ferromagnetic properties

Dilute magnetic semiconductors (DMSs) are based on traditional semiconductors, but doped with magnetic impurities. Typically is manganese (Mn) or chromium (Cr) – II-VI semiconductor compounds, such as CdTe. DMSs doped with Cr are also attractive research object, because of their unique spintronics properties with possible technological applications [1]. In our work [e.g 2] we presented the results of the X-band electron magnetic resonance (EMR) measurements of Cr ions in CdTe bulk. We investigated Cd_{1-x}Cr_xTe alloy which were doped with different concentrations of chromium formed during the synthesis process. Crystals with different concentrations of chrome (up to x=0.08) were studied for a wide range of temperature. The crystalline structure of Cd_{1-x}Cr_xTe films were investigated by high resolution transmission electron microscopy (TEM) (Fig.1a). The observed ferromagnetic properties are correlated with changes induced by temperature and current (Fig.1b).

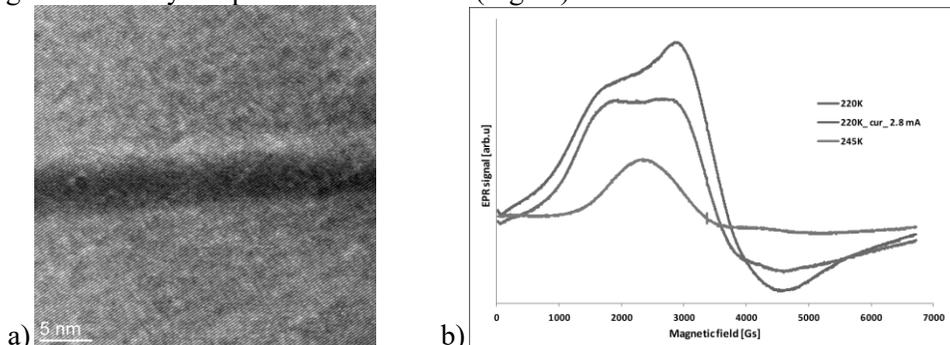


Figure 1. a) TEM image of crystalline structure of Cd_{1-x}Cr_xTe, b) EMR spectra of Cd_{1-x}Cr_xTe at different temperature with and without current flow.

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The effects of protonated heterocyclic cations on structural, EPR and magnetic properties of $[\text{CuCl}_4]^{2-}$ anions

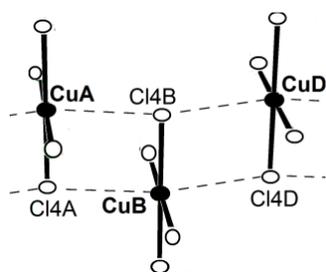
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The crystal structure, EPR and magnetic susceptibility measurements were undertaken to study the effect of organic cations: 4,4'-bipiperidinium, trans-2,5-dimethylpiperazinium and 3-amino-2-chloro-5-methylpyridinium on the structural and magnetic properties of the $[\text{CuCl}_4]^{2-}$ anions in the cationic-anionic complexes **1**, **2** and **3**, respectively. The $[\text{CuCl}_4]^{2-}$ anions, providing the same donor set of Cu(II) coordination sphere, are exceptionally suitable for observing the influence of the anions geometry on their **g** tensors. The EPR spectral studies revealed a characteristic decrease of the anisotropy of axial **g** tensor components (from $\Delta g = g_{\parallel} - g_{\perp} = 0.305$ for **1** to 0.243 for **2** and 0.185 for **3**) with the change of geometry of $[\text{CuCl}_4]^{2-}$ anions from pseudo-tetrahedral for **1** to elongated octahedral for **2**, where the anion by itself is square planar (Scheme), and to square planar for **3**.



The magnetic exchange interactions between $[\text{CuCl}_4]^{2-}$ anions in the complexes evidently resulted from crystal packing structure dependent on the organic cations and water of crystallization (W) which modify the geometry of

a) Cu-Cl...Cl-Cu contacts in **1-3**, b) Cu-Cl...W...Cl-Cu bridge in **1** and **3**, c) dichloride bridge in dinuclear units formed in the chain structure of **2** (Scheme), d) π - π stacked pyridine rings in **3**. In **2** and **3** all these

magnetic exchange pathways occurred on relatively long distances leading to a weak and comparable antiferromagnetic exchange; their intra- and intermolecular interactions are similar, corresponding to $J = -1.6 \text{ cm}^{-1}$, $J' = -0.5 \text{ cm}^{-1}$ and $J = -1.8 \text{ cm}^{-1}$, $J' = -0.4 \text{ cm}^{-1}$, respectively, where $H = -JS_A S_B - zJ' \langle S_z \rangle S_z$. For **1** the closer Cu-Cl...Cl-Cu contacts cause the stronger exchange interactions in agreement with $J = -8.48 \text{ cm}^{-1}$, $J' = -3.32 \text{ cm}^{-1}$.

Acknowledgements.

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Cobalt(II) complexes based upon 2,6-bis(pyrazol-1-yl)pyridine ligand and pseudohalido coligands showing slow magnetic relaxation.

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Three pentacoordinate $[\text{Co}(\text{pypz})\text{X}_2]$ complexes, where *pypz* is a tridentate ligand 2,6-bis(pyrazol-1-yl)pyridine and $\text{X} = \text{Cl}^-$ (**1**), NCS^- (**2**) or NCO^- (**3**), were synthesized and characterized by the results of X-ray structure, magnetic and EPR studies. The DC magnetic data showed a sizable magnetic anisotropy, which was confirmed by high-field HF EPR measurements. Well-resolved high-field EPR spectra of high spin cobalt (II) were observed over the microwave frequency range 100–650 GHz [Fig.1]. The spin Hamiltonian parameters g , D and E , were determined from simulations of the powder patterns. The zero-field splitting in compounds **1** and **2** is very large and even with frequencies as high as 600 GHz no transitions between the Kramer's doublets can be observed. Only the transitions within the lower Kramer's doublet are seen. The experimental spectra of both complexes could be simulated with axial g tensor components, a very large positive D value and different E/D ratios. The higher E/D ratio of 0.295 in for **2** compared to 0.078 in **1** is associated with the lower symmetry of **2**, as it is lacking the twofold axis. To determine the exact D value for **1** (40.92 cm^{-1}) the FIRM method was used. Knowledge of the zero field splitting parameters and their signs is crucial in interpreting the SMM or SChM behavior. The AC susceptibility data revealed a slow magnetic relaxation under small applied DC field with two (for **1** and **3**) or three (**2**) relaxation modes.

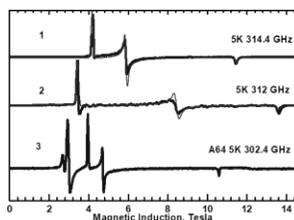


Fig.1. EPR Spectra of a complexes **1-3** at 5K and 302 - 314 GHz.

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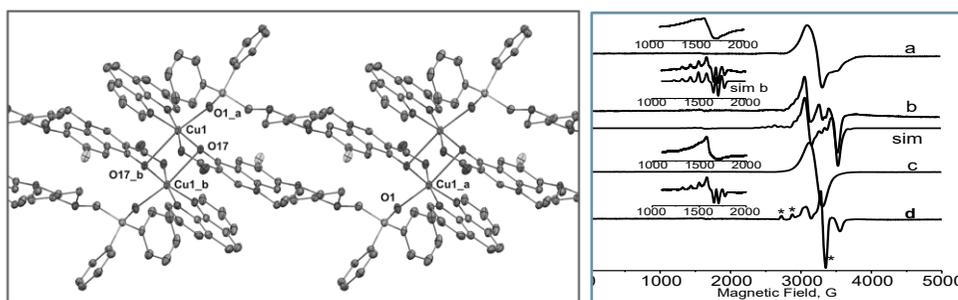
Phosphine derivatives of selected fluoroquinolones and their Cu^I and Cu^{II} complexes.

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Here we present copper(I) iodide and copper(II) complexes with diphenylphosphinomethyl derivatives of two fluoroquinolones (ciprofloxacin and norfloxacin) and with neocuproine (Cu^I) or phenanthroline (Cu^{II}) auxiliary ligands. The synthesized compounds ([Cu^I-PCp], [Cu^I-PNr], [OPCp-Cu^{II}]⁺ and [OPNr-Cu^{II}]⁺) were characterized by elemental analysis and MS as well as by the NMR, EPR and IR spectroscopies. X-ray techniques were used to determine the crystal and molecular structures of [Cu^I-PCp]·CH₂Cl₂·CH₃CN and [OPCp-Cu^{II}]NO₃·3H₂O.



Left: X-ray structure of [OPCp-Cu^{II}]⁺ Right: The EPR spectra of powder and water frozen solution of [OPNr-Cu^{II}]⁺ (6a and 6b, respectively) and [OPCp-Cu^{II}]⁺ (6c and 6d, respectively) together with the theoretical (simulated, sim b) spectrum giving the best fitting of the experimental spectra for S=1 (due to Cu-Cu-exchange interaction) and spin Hamiltonian parameters $g_{||} = 2.27$, $g_{\perp} = 2.06$; $A_{||} = 85$ G, $A_{\perp} = 20$ G, $|D| = 0.043$ cm⁻¹; g tensor was rotated versus D tensor around Y axis by 18° for both complexes. The 7 lines of hyperfine splitting for $\Delta m_s = 2$ low field lines is an unequivocal proof that the Cu(II) unpaired electrons are coupled with two copper nuclei, each having $I = 3/2$.

All complexes exhibited high cytotoxicity against two cancer cell lines (A549 - human lung adenocarcinoma and CT26 - mouse colon carcinoma) significantly higher than unmodified fluoroquinolone antibiotics, the phosphines and their chalcogenide derivatives as well as cisplatin. Apoptosis, observed at a great predominance, was induced by all studied complexes. Importantly, it was concluded that Cu^I complexes were much more active than those with Cu²⁺, despite their highest efficacy to produce reactive oxygen species, participating in overall cytotoxicity.

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N-oxide Surfactants as Multifunctional Materials

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Key words: antioxidants, surfactants, N-oxides, radical scavenging, DFT

Due to ability to form aggregates, the surfactants are widely used in design of nanocarriers for bioactive compounds. For this reason, great effort is devoted to the search for new non-toxic and biocompatible surfactants, which in addition to the stabilizing effect, should exhibit additional functionalities. This work is continuation of our studies on the properties and behavior of N-bis,3,3'-(dimethylamino)propyl]alkylamide N-oxides [1]. We report here the results of comprehensive studies on antioxidant activity of these surfactants di-N-oxides. For this purpose EPR technique was applied, in which the disappearance yield of the EPR spectrum of standard radical DPPH (1,1-Diphenyl-2-picrylhydrazyl) due to its reduction (scavenging) by the surfactants (antioxidants) is monitored [2]. It is known that antioxidants can prevent cardiovascular and neurodegenerative diseases by neutralizing reactive oxygen species generated by oxidative stress in the cells. Hence, the N-oxide surfactants with antioxidant properties may find wide applications as ingredients in the cosmetic, pharmaceutical and food industries. Our results indicated an effectiveness of radical scavenging by di-N-oxides, what proved their ability to neutralize the short-lived radicals of oxidative stress. The kinetic of the scavenging processes was also measured and analyzed. The application of computational methods, DFT and ab initio, allowed to propose the molecular mechanism of the reactions and their energetic effects. Antiradical properties were tested on model of emulsion system showing that di-N-oxides significantly protect the emulsion lipids against induced peroxidation.

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A new 2D Framework based on 2,3'-bipyridine-2',3-dicarboxylate copper(II) units: synthesis, structure and characterization.

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Key words: coordination polymers, copper(II), crystal structures, TGA, magnetic properties, EPR and fluorescent properties.

Aminocarboxyl ligands can act as precursors of metal coordination polymers. Coordination polymers (CPs) are a thriving class of functional solid-state materials that have attracted much attention due to their potential use in various key applications, among them storage/separation, catalysis, molecular magnetism and non-linear optics. The use of Berghoff autoclave allows for a one-pot synthesis of pure crystalline magnetic materials. Control of pressure and temperature in this setup ensures stable synthesis conditions and its reproducibility. A new ligand 2,3'-bipyridine-2',3-dicarboxylic acid monohydrate and a new copper(II) 2D coordination polymer $[\text{Cu}(2,3'-2',3\text{-bpdc})\text{H}_2\text{O}]_n$ (2,3'-2',3-bpdc = deprotonated bipyridinedicarboxylic acid) were synthesized in Berghoff autoclave and characterized by X-ray diffraction studies, IR spectra, elemental analysis, EPR, luminescence spectra and TGA. Magnetic properties show weak antiferromagnetic coupling of the metal ions in the copper compound. These interactions are most likely assisted by hydrogen bonds. The proposed pathway is illustrated in the Figure below, displaying the closest Cu...Cu distances.

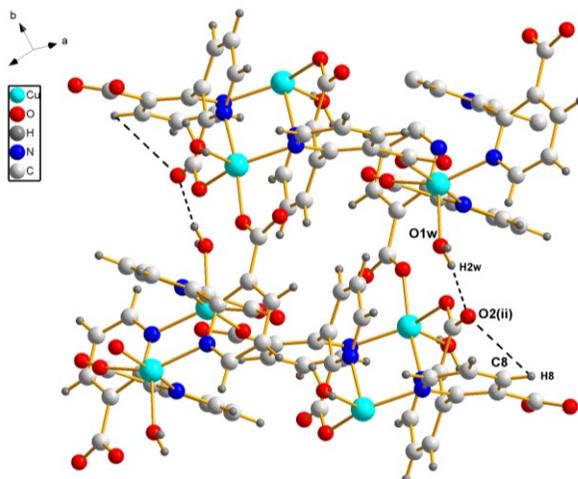


Figure 1: Proposed pathway of the magnetic interactions in the studied coordination polymer ($\text{Cu-COO}\cdots\text{H}_2\text{O}\cdots\text{H}_2\text{O-Cu}$).

Activity of Intrazeolitic Palladium Species in CH₄ and NO Abatement – Test Reactions and EPR Insight into the Nature of Active Centers

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Key words: zeolite, palladium, EPR, nitric oxide, deNO_x

Palladium-containing zeolites or bimetallic palladium zeolites are known to activate methane molecules and other diatomic gas-phase molecules of environmental importance (CO, NO). In this contribution we examined interaction of NO/CH₄ with Pd and Ce sites inside ZSM-5 and Y matrices.

Metal-exchanged zeolites were obtained via subsequent ionic exchange in aqueous solutions. Initially obtained Pd-zeolites were reduced in H₂ in order to recover the sorption capacity of the zeolite matrix, and then ionic exchange with a cerium salt was carried out. XRF analysis was used for determination of chemical composition of the materials. Formation and identification of Pd nanocrystals was followed with TEM measurements. In situ adsorption experiment were carried out by means of EPR and FTIR measurements.

It was found that palladium in Y and ZSM-5 zeolites exhibited versatile redox chemistry. All possible valence states were identified (Pd(III), Pd(II), Pd(I), Pd(0)). Formation of surface adducts with NO was investigated with EPR and IR techniques. Reaction with NO resulted in an EPR signal with a characteristic hyperfine structure. It originated from the coupling with the magnetic moment of nucleus ¹⁰⁵Pd (22.3%, *I* = 5/2). In addition, in the case of interaction with Pd(I), the superhyperfine structure could be observed, which was assigned to two nuclei of nitrogen (¹⁴N, *I* = 1) coming from dinitrosyl species Pd⁺(NO)₂. While in the case of Pd(I) they were formed by simple addition reaction ${}^2\text{Pd} + 2{}^2\text{NO} = {}^2\{\text{Pd}^+(\text{NO})_2\}$, for the oxidized centers reactive adsorption was observed, which led first to a reduction of Pd³⁺ to Pd²⁺ and Pd⁺, and subsequent formation of the paramagnetic mono- Pd²⁺NO and dinitrosyls Pd⁺(NO)₂.

For the reactions with CH₄ and CH₄/NO mixture, the concentration profiles recorded for H₂-reduced catalysts (Pd nanoparticles as major active phase) showed that onset of CH₄ oxidation in O₂ was already located below 300°C, while decomposition of NO alone produced N₂ and N₂O only above 300°C. Reactions with NO+CH₄ and NO+CH₄+O₂ showed that NO reduction competed with CH₄ oxidation and the temperature windows for both these processes diverge. This apparent misfit of the temperature windows could be diminished by introducing cerium components which helped in binding nitrogen oxide.

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Interaction of O₂ with Electron Rich and Poor Transition-Metal Ions and Formation of Superoxide Species Inside Zeolite Channels

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Key words: superoxide, powder EPR spectrum, zeolite, electron transfer

Heterogeneous activation of dioxygen leading to the formation of surface electrostatic (O₂⁻, O₂²⁻, O⁻, O²⁻) and covalent (TMI(dⁿ)=O^{z-}) species is one of the key process in catalysis, including photo- and electrocatalysis. In this contribution we focus on 1e⁻ reduction of O₂ molecule over selected model zeolitic systems. The research aims at elucidation of a type of geometry of the superoxo adducts, as well as their electronic and magnetic structure studied by means of electron paramagnetic resonance (EPR) spectroscopy and density functional theory (DFT) modeling. As the active centers we chose electron-rich (Zn^I, Ni^I) and electron-poor (V^{IV}) transition-metal cations exchanged into the channels of high-silica zeolites.

Zinc(I) cations were loaded into zeolite channels by chemical vapor deposition of metallic Zn onto H-ZSM-5: Zn⁰_(g) + H⁺_(zeol) = Zn⁺_(zeol) + 1/2H_{2(g)}. The EPR spectrum of the Zn⁺(4s¹)/ZSM-5 is composed of an isotropic signal with $g_{\text{iso}} = 1.998$. Reaction of the Zn⁺ZSM-5 with O₂ (295 K) resulted in appearance of a new rhombic signal with g -tensor value of $g_{zz} = 2.061$, $g_{xx} = 2.003$, $g_{yy} = 2.010$, assigned to a superoxide anion. Structure identification of the adduct was assured by using ¹⁷O-enriched molecular oxygen ($I = 5/2$). The resulting signal of doubly-labelled Zn²⁺(¹⁷O-¹⁷O)⁻ adduct is composed of 11 lines ($|A_{xx}| = 7.7$ mT, $|A_{yy}| = 0.6$ mT, $|A_{zz}| = 0.6$ mT) which demonstrates that both oxygen nuclei are magnetically equivalent.

For the nickel and vanadium systems, Ni(I) and VO₂ centers were tested toward O₂ adsorption. Interaction of both types of centers resulted in EPR signals due to the superoxide radicals bound to the metal cores. In case of VO₂ direct attachment to the V core is confirmed by hyperfine splitting due to $I = 7/2$ nuclear spin. The observed spin-Hamiltonian parameters are: $g_{xx} = 2.0054$, $g_{yy} = 2.0113$, $g_{zz} = 2.0239$, $|A_{xx}| = 0.54$ mT, $|A_{yy}| = 0.68$ mT, and $|A_{zz}| = 0.98$ mT. In the case of Ni(I) centers, apart from EPR identification, analysis of the charge and spin-density redistributions carried out by means of DFT-NOCV method for the Ni²⁺-O₂⁻ adduct showed that three distinct channels of the spin and charge density flow of π , σ , and δ symmetry act cooperatively in the formation of the superoxo O₂⁻ species.

As a result, Zn(I), VO₂, and Ni(I) represent three distinct types of 1e⁻ donor centers: σ -donor, π -donor, and δ -donor, respectively, capable of formation of intrazeolite superoxide species.

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**Ab initio calculations of EPR spin-Hamiltonian parameters
– DFT-guided molecular interpretation of spectral parameters**

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Key words: DFT, EPR, computational spectroscopy, simulation, EPR tensors

Molecular interpretation of EPR spectra parameters of low symmetry paramagnetic surface species within powder systems requires combination of computer simulations of spectra for the real systems [1] with relativistic quantum chemical calculations of \mathbf{g} , \mathbf{A} , \mathbf{Q} and \mathbf{J} magnetic tensors. DFT has become a first choice methodology for this kind of modelling. Thus, an adequate choice of (a) an exchange-correlation potential, (b) the base functions, (c) the relativistic corrections to wave function (ZORA, Pauli, DKH), (d) an approximation of a spin-orbit (SO) operator, (e) a technique of calculation of the magnetic parameters (one- or two-component method) or full relativistic four-component calculations (only for small molecular systems) is essential [2].

In this contribution DFT calculations of EPR tensors for selected intrazeolitic systems (nickel and copper adducts) are presented. Geometry optimization of zeolitic clusters was performed with Gaussian09, whereas \mathbf{g} - and \mathbf{A} -tensors were calculated with ORCA. Magnetic couplings diagrams for \mathbf{g} -tensors were prepared with one-component method based on Pauli Hamiltonian implemented in ADF.

It has been concluded that \mathbf{g} -tensor components are more sensitive to the type of an correlation-exchange functional than a basis set, with the hybrid functionals being preferred. As for the SO approaches, the ZORA and SOMF gave virtually the same results with minor advantage over Pauli method. The discrepancy between calculated and experimental results depends on the spin density redistribution within a paramagnetic complex. In case of metal-centred radicals the results are found to be more sensitive to the choice of basis set, and the g_{ii} and A_{ii} values are more divergent from the experimental counterparts as compared to the ligand-centred radicals.

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Site symmetries of cerium ions in BaWO₄ single crystals codoped with sodium ions

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Keywords: sheelite, BaWO₄, structural refinement, EPR, roadmap, local symmetry

Barium tungstate crystals are interesting and relatively new medium for stimulated Raman scattering for applications in Raman shifters of laser radiation [1]. Good quality BaWO₄ crystals can be grown by Czochralski technique and doped with rare-earth ions. Doping with trivalent ions require charge compensation which may be provided, for example, by structural defects or proper codoping with alkaline metal ions. Crystals possess sheelite like structure with the space group $I4_1/a$.

Results of EPR studies of BaWO₄:Ce crystals and crystals codoped with Na are presented in this paper. EPR study was performed in the low temperature range 3K < T < 50 K for all three planes of single crystals. The EPR spectra were derived from cerium ions with a fictitious spin $S = 1/2$. The spin Hamilton (SH) parameters were determined. The values of SH parameters indicate the occurrence of paramagnetic centers in axial and low symmetry. The number of observed EPR lines depends on the selected plane. Based on the roadmap, we can determine that we have one center with axial symmetry and at least two centers with low symmetry. There are more centers with low symmetry than with axial symmetry. Temperature studies towards the three planes indicate very weak interactions between cerium ions. These interactions are interchangeable. The linewidth v.s. temperature revealed increasing exponential tendency with increasing temperature. It shows 1 phonon at the lower temperatures and Raman + Orbach effect at the higher temperatures. Exponential change of the ΔB could be connected with the spin-lattice relaxation processes involving excited states of Ce³⁺ ions.

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Glassy state NMR of quadrupolar nuclei

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Key words: EFG tensor, NMR, quadrupolar interaction, disordered solids, glasses

Precise fitting of powder NMR spectra of quadrupolar nuclei requires powerful computers. Necessity of integration over all orientations of crystalites makes the spectrum have not analytical representation. In addition the use of well known models [1] in connection with good accuracy of NMR measurements causes that perfect fit cannot be done every time. The reason for this may be of various types - from some unspecified apparatus errors to inaccuracy of the physical model. For example for glasses, which are composed of randomly oriented clusters, we often do the same as for powders. However every cluster in that case have random environment and differs from other clusters not only orientation but can be slightly deformed. Such random deformation should be included in high precision measurements.

The basic problem in this situation is to determine distributions of parameters describing considered interactions. Especially for quadrupolar interaction, Czjzek [2] first found joint distribution of electric field gradient (EFG) tensor components of randomly packed atoms in amorphous materials. This model was later developed by Maurer [3] to describe deformed structures mostly preserving local order.

This work presents calculation of joint distribution of quadrupolar coupling constant and asymmetry parameter of EFG tensor in solids with local disorder for slightly deformed charge system. In this work, in contrast to Czjzek and Maurer models the calculation was made directly from the disturbance of the initial electric charge system surrounding the quadrupolar nucleus without using approach based on EFG tensor invariants.

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Influence of paramagnetic defects on a spin-lattice relaxation of ^{13}C nuclei in nanodiamonds

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Keywords: nanodiamonds, ^{13}C NMR, spin-lattice and spin-spin relaxation

Nanodiamonds reveal noticeable amount of paramagnetic defects, such as unpaired electrons on dangling bonds and paramagnetic nitrogen P1 centers. The interaction between nuclear and electron spins creates an effective additional channel for the nuclear spin-lattice relaxation and strongly accelerates it. We report on a nuclear magnetic resonance (NMR) study of nanodiamonds. Our measurements of the ^{13}C nuclear spin-lattice relaxation rate R_1 of the diamond core carbons show stretched exponential magnetization recovery and 3 orders of magnitude increase in R_1 in comparison with the natural diamond, attributed to the interaction of nuclear spins with unpaired electron spins. We obtained ^{13}C spin-lattice (R_1) and spin-spin (R_2) relaxation rate dependence on magic-angle-spinning (MAS) rate in highly purified synthetic nanodiamonds. Noticeable slowdown of both relaxation processes and reduction of nuclear spin diffusion coefficient D with increasing MAS rate was obtained and attributed to suppression of nuclear spin diffusion by MAS. We developed a theoretical approach that describes the MAS rate dependence of R_1 , R_2 and D , allows quantitative analysis of the data and shows good compliance with the experiment. Impact of defects induced by milling of micron-sized synthetic diamonds was studied by magnetic resonance techniques as a function of the particle size. EPR and ^{13}C NMR study of highly purified synthetic micro- and nano-diamonds was done for various fractions separated by sizes. Noticeable acceleration of ^{13}C nuclear spin-lattice relaxation with decreasing particle size was found and showed to be caused by the contribution to relaxation coming from the surface paramagnetic centers induced by samples' milling. The developed theory of the spin-lattice relaxation for such a case shows good compliance with the experiment. Our NMR data are presented along with the EPR findings.

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Preparation and analysis of graphene oxide aerogels

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Key words: aerogel, graphene oxide, reduced graphene oxide, freeze drying

Aerogels are porous solid state foams with predominantly opened pore structure. The difference between dried in ambient conditions hydrogel (xerogel) and aerogel is in the maintained pore structure of the foam. We have prepared graphene oxide water suspension with Hummers method (EDS, C:57%, O:43%, C/O = 1.33). During hydrogel preparation using autoclave hydrothermal synthesis (2h, 180°C) we have observed partial oxygen reduction, the C/O ratio increased to 2.35 (Fig. 1(left)). Applying freeze drying to a fast frozen in liquid nitrogen hydrogel allowed removing water molecules without damaging the pore structure what resulted in an aerogel formation. The bulk density of aerogel is around 2.5 mg/cm³, and specific surface (BET) is 130 m²/g (Fig. 1).

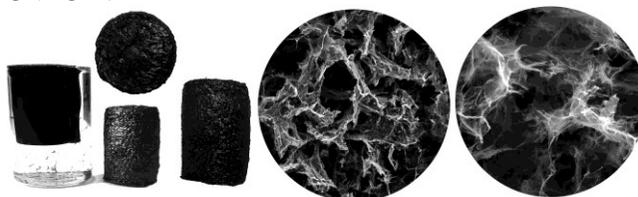


Fig. 1 Graphene oxide (from left): hydrogel, aerogel photographs (top and front), SEM micrographs (300x, 1500x).

Obtained partially reduced GO aerogel exhibits two component EPR signal where the narrow line is visible in helium temperatures till 150 K and in higher temperatures the broader line gains an intensity (Fig. 2).

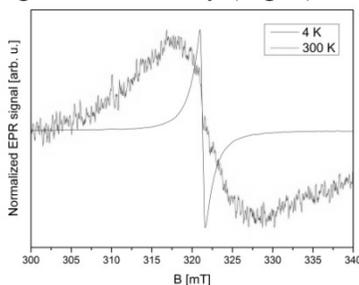


Fig. 2 EPR signal for partially reduced GO recorded at 4K and 300K.

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EPR and magnetometry of mixed phases in $\text{FeVO}_4\text{-Co}_3\text{V}_2\text{O}_8$ system

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Key words: Vanadates, magnetic susceptibility, electron paramagnetic resonance, iron group ions

Magnetic properties of five $n\text{FeVO}_4/(1-n)\text{Co}_3\text{V}_2\text{O}_8$ composites obtained in reactions between FeVO_4 and $\text{Co}_3\text{V}_2\text{O}_8$ (with the composition index $n = 0.54, 0.50, 0.40, 0.30$ and 0.20) have been investigated by dc magnetometry and magnetic resonance spectroscopy. The composites contained two phases: one having lyonsite-type structure and the other $\text{Co}_3\text{V}_2\text{O}_8$. Temperature dependence of dc magnetic susceptibility of these samples showed the Curie-Weiss paramagnetic behaviour with a strong antiferromagnetic (AFM) interaction in the high-temperature range and transition to AFM phase at $T_N = 6$ K. For all composites the magnetic hysteresis loop in isothermal magnetisation was registered indicating the existence of a ferromagnetic component. Samples $n = 0.54$ and 0.50 displayed a large coercive field and remanent magnetisation in contrast to the other three samples. EPR spectra of studied samples showed a broad asymmetric line that could be decomposed on two lorentzian lines. Temperature dependence of the spectral parameters (resonance field, linewidth, integrated intensity) of these components were studied in high-temperature range ($T > 90$ K). The observed spectra were attributed to different $\text{Fe}^{3+}/\text{Co}^{2+}$ spin clusters in a lyonsite-type structure facilitating magnetic frustration.

Parallel Field Mode in EMR (EPR) Spectroscopy of Transition Ions: Survey of Applications and Theoretical Background

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Key words: EMR (EPR) spectroscopy; parallel field configuration; Kramers ions vs non-Kramers ions; group theory; selection rules

Historically, at first electron magnetic resonance (EMR/EPR) measurements were confined to the perpendicular field configuration, i.e. the mode with the oscillating field \mathbf{B}_1 perpendicular to the static field \mathbf{B}_0 ($\mathbf{B}_1 \perp \mathbf{B}_0$) [1, 2]. This configuration could standalone provide EMR/EPR signals originating from both Kramers and non-Kramers ions, i.e. the half-integer and integer spin systems, respectively [3-5]. Due to the advent of high-field and high-frequency EMR techniques (HF²-EMR) [6], multi-oriented measurements became more widely achievable.

In this work we focus on the advantages of the parallel field mode ($\mathbf{B}_1 \parallel \mathbf{B}_0$) [1-5]. To this end an extensive literature survey is under progress. Availability of versatile software packages, e.g. *EasySpin* [7], and advances in multi-oriented EMR [8,9], facilitate novel applications of parallel field mode. This project includes analysis of perpendicular and parallel field oriented spectra for identifying certain species (radicals, intermediate species), processes (catalysis, reaction mechanism) or even discrimination of impurities in sample [4,10,11]. Our survey indicates that comparison of distinct fingerprint regions in EMR spectra of Kramers and non-Kramers ions is often used for analysis of bioprocesses [11]. The compounds surveyed include systems with non-interacting transition ions [4] as well as exchange-coupled systems [5]. EMR studies utilizing parallel field mode are categorized and pertinent EMR related data, including zero-field splitting (ZFS) parameters, are systematically tabularized. Furthermore, group theory [12] is employed to expose distinct spectroscopic behaviour of integer and half-integer spins systems in parallel/perpendicular field mode. The relevant selection rules [12] are reviewed to provide explanation for specific characteristics of the parallel field mode for systems with integer spin $S \geq 1$.

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Maximum rhombicity of zero-field splitting (ZFS) terms in EMR spectroscopy: Is the rhombicity ratio $E/D = 1/3$ achievable?

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Key words: effective spin Hamiltonian (SH) theory; zero field splitting (ZFS); rhombicity ratio; orthorhombic standardization; transition ions; DFT/ab initio methods

Orthorhombic spin Hamiltonians are ubiquitous in electron magnetic resonance (EMR) studies [1,2], yet their intricate features are sometimes not fully understood [3,4,5,6]. For orthorhombic zero-field splitting (ZFS) terms, the rhombicity ratio for the second-rank ZFS parameters (ZFSPs): $\lambda \equiv E/D$ can always be limited to the range (0, 1/3) [3]. Moreover, non-standard ZFSP sets ($|\lambda| > 1/3$) cannot be directly compared with standard ones ($0 \leq |\lambda| \leq 1/3$). These features enable orthorhombic standardization of ZFSPs [3-6]. Non-standard ZFSP sets should be transformed into a proper axis system using standardization transformations [3-7]. Applications to non-standard ZFSP sets [4-6] amply show importance of standardization.

In this work we focus on the question: is the rhombicity ratio $E/D = 1/3$ achievable in real ion-host systems? To this end an extensive literature survey is under progress. The ZFSP sets with $|\lambda|$ very close to 1/3 are categorized and systematically tabularized. The survey indicates that the convention $0 \leq |\lambda| \leq 1/3$ is widely utilized in EMR studies, so tacitly - most often without providing any explanation or references. Several cases of non-standard ZFSP sets as well as those with $|\lambda| = 1/3$ have also been identified. The former sets yield large rhombicity, however, after standardization using computer package CST [7], it turns out to be only apparent. Implications of the maximum rhombicity $|\lambda| = 1/3$ for interpretation of experimental EMR spectra and theoretical calculations based on density functional theory (DFT) or ab initio methods are analyzed. Structural implications of (i) orthorhombic standardization [4] and (ii) $|\lambda| = 1/3$ [6] are considered. Our study enables discriminating between the valid cases of maximum rhombicity and possible computer artifacts. The present results will also be utilized in ongoing studies of adatoms on surfaces, single molecule magnets and single ion magnets.

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Origin of the Ground Kramers Doublets for $\text{Co}^{2+}(3d^7)$ Ions with the *Effective Spin* $3/2$ Versus the *Fictitious 'Spin'* $1/2$

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Key words: Electron magnetic resonance (EMR), Crystal/ligand field (CF/LF), Zero-field splitting (ZFS), Single molecule magnets (SMM), Co^{2+} ions

The electron magnetic resonance (EMR) spectra of various single crystals doped with $\text{Co}^{2+}(3d^7)$ ions with the electronic spin $S = 3/2$, which yields nominally the *effective* $\tilde{S} = 3/2$, are often interpreted using the spin Hamiltonian with the 'spin' S ($S' = 1/2$), including only the Zeeman and hyperfine structure tensors \mathbf{g} and \mathbf{A} [1]. In a number of papers the origin of the observed ground Kramers doublet state, to which the so called 'spin' $S' = 1/2$ is ascribed, is not specified.

In this work the possible mechanisms leading to such distinct ground $\text{Co}^{2+}(3d^7)$ states are overviewed in terms of the underlying crystal field energy level schemes. The crucial concepts of the *effective* spin \tilde{S} and the *fictitious* 'spin' S' (that in fact does not represent the true spin) are clarified. The distinction between these concepts helps clarifying the terminological confusion encountered in literature. Specific cases of assignments of the ground states and options for the origin of the 'spin' $S' = 1/2$ are considered in order to obtain better understanding of the local environment around the Co^{2+} ions in various host crystals. Additional motivation for the wider study of $\text{Co}^{2+}(3d^7)$ ions in crystals exhibiting various local symmetry sites arises from realization that since these ions exhibit a variety of behavior, from the *effective* spin $\tilde{S} = 3/2$ with very large or moderate zero-field splitting (ZFS) to the fictitious 'spin' $S' = 1/2$. This offers potential applications ranging from the Co^{2+} compounds maybe suitable as high-pressure probes for high-magnetic-field and high-frequency EMR measurements [2] to single-molecule magnets (SMM) and single-ion magnets (SIM) [3]. As a case study we investigate: (i) the polarized optical absorption and EMR spectra of Co-doped beryls and chrysoberyl [4], (ii) EMR spectra of Co^{2+} ($S' = 1/2$) ions in PbMoO_4 and YAlO_3 [5,6]. The calculations are carried out using the crystal field analysis (CFA) package [7], which enables the complete diagonalization within the whole $3d^N$ configuration for arbitrary symmetry. The lowest energy levels and corresponding wave-functions enable identifications of the particular observed ground Kramers doublet states.

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Calculations of zero-field splitting parameters for $3d^N$ adatoms adsorbed on surfaces - comparative analysis of different approaches

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Key words: magnetic anisotropy; zero field splitting (ZFS); microscopic spin Hamiltonian (MSH); crystal/ligand field (CF/LF); Fe^{2+} and Mn^{2+} adatoms; DFT/ab initio methods

Transition metal atoms adsorbed on insulating surfaces gained interest due to perseverance of magnetization resulting from $3d^N$ electrons. Scanning tunneling microscopy (STM) and inelastic electron tunneling spectroscopy (IETS) experiments show that these systems behave like magnets for potential applications, e.g. as memory storage. The appearance of magnetization is explained based on single-ion anisotropy, which is described by zero-field splitting (ZFS) parameters (ZFSPs).

Systems of most interest are Fe^{2+} atoms adsorbed, e.g. on $Cu_2N/Cu(100)$ or $CuN/Cu(100)$ surfaces [1,2]. In a parallel presentation [3] we report predictions of ZFSPs for Fe^{2+} adatoms using the package MSH/VBA [4] based on conventional crystal field (CF) and microscopic spin Hamiltonian (MSH) theory, developed up to the fourth-order perturbation theory (PT) for $3d^4$ and $3d^6$ ions with spin $S = 2$ within the 5D approximation. Here we reconsider ZFSPs reported in literature obtained using density functional theory (DFT) methods, as well as our own DFT results, to complement our MSH/VBA calculations [3]. DFT results enable mapping of the physical energy levels to those of effective ZFS Hamiltonian $S.D.S$ thus yielding the conventional D and E ZFSPs. Analysis of the second-order PT expressions used within DFT methods is also provided. Applicability of such expressions for $Mn^{2+}(3d^5)$ adatoms [5] is considered from the point of view of MSH theory. The present comparative study is aimed at bridging the gap between DFT methods and CF/MSH ones. . The present results will also be utilized in ongoing studies of adatoms on surfaces, single molecule magnets and single ion magnets.

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Relationships between Zero-Field Splitting Parameters for Adatoms on Surfaces and Magnetic Anisotropy Quantities: Comparative Survey

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Key words: magnetism; zero field splitting (ZFS); microscopic spin Hamiltonian (MSH); magnetic anisotropy energy (MAE); transition metal 3d^N adatoms

The zero field splitting (ZFS) parameters (ZFSPs) ubiquitous in EMR have recently been widely employed in studies of magnetic properties of adatoms on surfaces. Magnetic anisotropy (MA), i.e. tendency of the total magnetic moment (M) to point along preferential directions, is crucial for potential technological applications. For bulk systems, MA is quantified by the magnetic anisotropy energy (MAE), i.e. the dependence of the system's internal energy on the direction of M . Several problems emerge at the interface between spin Hamiltonian [1] and MA/MAE theories [2] making quantification of MA in terms of measurable quantities controversial, especially when moving from bulk magnetic systems to adatoms [3]. Since intrinsic magnetic moments of adatoms could constitute building blocks for, e.g. magnetic storage and qubits for quantum computing, proper understanding of MA/MAE becomes important.

In this work, we consider density functional theory (DFT) methods [4] used to quantify MA/MAE as well as to extract ZFSPs. For this purpose we have surveyed qualitative and quantitative definitions of MA/MAE used in DFT studies of adatoms. Our survey indicates that frequently, relationships between ZFSPs for adatoms and MA quantities are improperly presented. Importantly, concepts regarding the origin of ZFS Hamiltonian and definitions of fundamental quantities: magnetic moments, magnetization, and MA/MAE, are frequently imprecise or simply missing. This may lead to confusion, not only at semantic level, but also to detrimental consequences, e.g. wrong numerical results for the quantities derived theoretically or experimentally. Possible implications of imprecise association of ZFSPs to MA/MAE, in the context of the transition from bulk systems to adatoms, are discussed for the benefit of EMR practitioners. The present results will be utilized in ongoing studies of single molecule magnets and single ion magnets.

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Determination of 2nd- and 4th-rank zero-field splitting (ZFS) parameters from ZFS energy levels for effective spin $\tilde{S} = 2$ systems

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Key words: Electron magnetic resonance (EMR); zero field splitting (ZFS); spin Hamiltonian (SH); Fe²⁺ adatoms on surfaces; DFT/ab initio methods

A remarkable group of systems studied by EMR (EPR) techniques is formed by the 3d⁴ and 3d⁶ ions exhibiting an orbital singlet ground state with the effective spin $\tilde{S} = 2$ at orthorhombic sites [1,2,3]. Conversion relations have recently been derived to enable comparison of the 2nd-rank zero-field splitting (ZFS) parameters (ZFSPs) determined based on the fictitious spin $S' = 1$ and effective $\tilde{S} = 2$ approaches [3]. This has enabled analysis of high-frequency EMR data for Fe²⁺ ions in forsterite and comparison of ZFSPs (D , E) for $S' = 1$ and $\tilde{S} = 2$ [3].

In this work considerations [3] are extended to 2nd- and 4th-rank ZFS terms in \tilde{H}_{ZFS} . We present analytical method for extracting ZFSPs for $\tilde{S} = 2$ systems: conventional (D , E) or in Stevens operators notation (B_k^q) [4], from data on ZFS energy levels. The major difficulty is that the number of observed EMR transitions is at most 4. Since the number of ZFSPs is two (only 2nd-rank) or five (2nd- and 4th-rank), systems of equations are either under- or over- determined. Hence several variants have to be investigated yielding alternative solutions.

Our analytical solutions are applied for Fe²⁺ ($\tilde{S} = 2$) atoms adsorbed on CuN surface using the spin excitation energies, i.e. ZFS energy level values, obtained within various density functional theory (DFT) approaches [5]. The theoretical values differ from the experimental ones [6]. To unravel possible sources of this discrepancy, the ZFSPs are extracted from DFT data [5] for various variants. Analysis of the results indicates significant role of the 4th rank ZFSPs. It turns out that neglecting the 4th rank ZFSPs strongly affects so-obtained values of the 2nd-rank ZFSPs. Our method enables extraction of ZFSPs from experimental ZFS energy level values as well as theoretical ones. The present results will also be utilized in ongoing studies of Fe²⁺ ($\tilde{S} = 2$) ions in forsterite and related crystals, single molecule magnets and single ion magnets.

This work was supported by NSC (NCN) grant no. 2016/21/B/ST4/02064.

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Magnetic phase transition and exchange bias in $\text{Ni}_{50}\text{Co}_5\text{Mn}_{35.5}\text{In}_{14.5}$ Heusler alloy

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Key words: Ni-Co-Mn-In, magnetic phase transition, exchange bias, melt spinning, EMR

The highest interest in Ni-Mn based Heusler alloys has focused on gallium alloys. However, off-stoichiometric Ni-Mn-In in certain composition range, have similar properties to Ni-Mn-Ga. What is more, indium is significantly cheaper than gallium, what makes Ni-Mn-In attractive for future practical application. Co-doped alloys have received much attention in recent years, due to their magnetic and structural properties. The Curie temperature and the martensitic transition temperatures are shifted to higher temperatures and, in some compositions, structural phase transition disappear with Co addition. Additionally, the brittleness of Ni-Mn-In can be reduced by Co addition.

In this research, the magnetic properties of a $\text{Ni}_{45}\text{Co}_5\text{Mn}_{35.5}\text{In}_{14.5}$ ribbons were investigated by electron magnetic resonance (EMR) and vibrating sample magnetometry (VSM). The shift of hysteresis loop, which was observed in the sample, suggests the existence of exchange bias effect.

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Optimization of peracetic acid homolysis for the degradation of atrazine and bisphenol with spin trap ESR

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Key words: atrazine, BPA, spin trapping, Fenton, DFT

Bisphenol A (BPA) and atrazine are widely spread xenoestrogens with the reported adverse effect on the human and fish health. BPA is used in the production of food packages, PVC, thermal receipts etc. Atrazine is herbicide which used to kill grassy and broadleaf weeds, and it is often found contaminating water supplies. BPA degradation is based on the reaction with the OH radical. Whereas atrazine is removed from drinking water with granular activated carbon, ozone oxidation, reverse osmosis or ion exchange. Despite of various available degradation methods there is still need for easy, high-performance and safe method suitable for the degradation of different types of xenoestrogens in drinking water and groundwaters.

We showed previously the high efficiency of the peracetic acid (PAA) homolysis catalyzed by MnO_2 for the degradation of phenol. In this work we optimize the PAA/ MnO_2 system for the effective degradation of BPA and atrazine. We have applied ESR spin trapping and UV-vis spectroscopy to monitor degradation reactions of organic compounds. DFT calculations (at B3LYP/6-31G(d,p) and MO6X/6-311+G(d,p) levels of theory) were used to identify the energetically preferred reaction paths, intermediate products and radicals.

Atrazine and BPA degradation under MnO_2 /PAA homolysis have led to additional reaction paths (with CH_3 , $CH_3COO\cdot$ and $CH_3CO\cdot$ radicals) to those observed under most widely used advanced oxidation processes such as the Fenton reaction (with OH-radical only). On the other hand, ESR spin trapping showed that in the first 10 minutes of the reaction the active degradation of atrazine and BPA occurred. Also, the ESR results suggested that C- and O-centered radicals played important role in the atrazine and BPA degradation. Monitoring of the reaction with UV-Vis was suitable for the BPA degradation, whereas it was not effective in case of atrazine, as the absorption of atrazine and its products strongly overlapped. Based on DFT calculation, application of MnO_2 /PAA system for BPA and atrazine degradation could lead to the formation of less xenoestrogenic compounds than the products of BPA and atrazine degradation with OH radicals only.

The research was supported by National Science Centre (NCN grant 2013/11/D/NZ7/02346) and ICM grant G14-6.

Using X band EPR for the studies of the oxidative stress in the zebrafish embryos *in vivo*

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Key words: *in vivo* EPR, spin traps, spin probes, zebrafish, toxicity

Oxidative stress is associated with various diseases e.g. cardiovascular diseases, neurodegenerative diseases or cancer. It is often induced by the overproduction of reactive oxygen species, including hydroxyl or peroxy radicals. EPR allows to study various radicals using dedicated spin probes and spin traps. The majority of EPR *in vivo* studies concentrate on rat and mice models to which 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) spin probe and 2-methyl-N-[(1-oxido-4-pyridinyl)methylene]-2-propanamine-N-oxide (POBN), alpha-phenyl N-tertiary-butyl nitron (PBN) or 5,5-dimethyl-pyrroline N-oxide (DMPO) spin traps were applied. However, studies using such animal models are expensive and time consuming. Zebrafish embryos are known to be a good preliminary model due to their fast development, possibility for direct observation of developmental stages and the ease of genetic modifications. Moreover, fish can be treated by adding tested compounds directly to fish water, and their response to treatments often recapitulates this what is observed in higher vertebrates,

In this work we explored the use benchtop X band EPR for the studies of zebrafish embryos *in vivo*. We optimized the procedure of treating embryos with the spin agents as well as EPR measurement parameters. We tested the toxicity of TEMPOL, 3-carbamoyl-PROXYL and DMPO, POBN, PBN. The concentrations up to 5mM of DMPO, POBN and 3-carbamoyl-PROXYL could be used for the short time (30 min before experiment) treatment of the zebrafish embryos. Whereas lower concentrations could be used for the long-time exposure from 5 hour post fertilization embryos. A clear ESR signal was observed for spin probe systems (3-carbamoyl-PROXYL and TEMPOL) from the 1 mM concentration after the thorough rinsing of the fish with E3 medium buffer. 3-carbamoyl-PROXYL (as a spin probe) and DMPO (as a spin trap) could be used for the studies of oxidative stress in zebrafish *in vivo*, however further studies are needed. The adaptation of the spin probe/spin trap ESR systems for zebrafish could contribute to further studies of mechanisms of various diseases associated with the oxidative stress.

The variation in the antioxidant activity of *Aronia melanocarpa* cultivated in Poland due to geographical region and collection time

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Key words: *Aronia melanocarpa*, antioxidants, DPPH-EPR, maturation, anthocyanins

Bioactive compounds of aronia berry (*Aronia melanocarpa*) have very strong antioxidant properties. Consumption of aronia juice or supplementation of the extract has been shown to lower blood pressure and regulate cholesterol levels in patients with hypercholesterolemia, as well as to mitigate oxidative stress (in animal models). This effect is ascribed to a high content of polyphenols, including anthocyanins and hydroxycinnamic acids. However, the variation in antioxidant properties and chemical composition of aronia berries could be significant. For example, the amount of anthocyanins in 1 kg of fruits varies from 3 to 6.3 g. Thus, the aim of this project has been to determine the variation of antioxidant properties as well as of content of anthocyanins and hydroxycinnamic acids in aronia berries due to geographical region and the time of harvesting. The antioxidant properties of studied samples have been determined using the DPPH-EPR test. The amounts of anthocyanins and chlorogenic acids have been analyzed using spectrophotometric and chromatographic methods.

The location of a plantation has a significant influence on the bioactive compounds content and antioxidant properties of *Aronia melanocarpa* fruit.

The antioxidant properties in aronia berries from all regions was the highest in green fruits, then a drop was observed as fruits started to ripe, followed by a slow increase at the end of August. A very similar pattern was noticed for the content of hydroxycinnamic acids during the maturation of fruits. The increase at late summer was detected in the case of the anthocyanin content as well.

This study has been performed as a part of the 2015/17/B/NZ7/03089 project financed by the Polish National Science Center.

Radicals initiated in selected amino acids and collagen by gamma-rays

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Keywords: amino acids, collagen, EPR spectroscopy, radicals, gamma-rays

The research was carried out as a part of strategic project that concerns the creation of biological dressing from human skin. One of the main stages in the preparation of allogeneic tissue grafts for medical applications is radiation sterilization that ensures effective elimination of pathogens from grafts. Unfortunately, ionizing radiation carries the risk of damage to the proteins structure. The goal of our researches was to find out what changes are made in the collagen structure based on the observation of its basic residues - amino acids.

The research technique was electron paramagnetic resonance (EPR) spectroscopy. For the studies we chose three representative amino acids, which are important in maintaining proper collagen structure: glycine, L-proline and hydroxyproline. The amino acids were irradiated in a Co-60 source with a 10 kGy dose at 77 K (collagen) or at ambient temperature (amino acids) in an air atmosphere. In the second case the measurements were performed for 15 months to observe conversion of the radicals over time.

Immediately after irradiation glycine shows a strong triplet which has been assigned to the radical formed after deamination. However, after a month of storage, other radicals were revealed, stable even after a year. We observed in the low and high magnetic field lines that probably originate from the radical formed upon hydrogen atom abstraction from methylene group, which also seems to be a primary product. However, directly upon irradiation, the intensive spectrum of the first radical covers the weaker signal.

Irradiated L-proline shows the signal in the form of triplet that has been attributed to the radical center interacting with two beta protons of the methylene group. The radical decays after a few months without initiating any other paramagnetic species.

Hydroxyproline after irradiation demonstrates a very rich spectrum. The signal observed has been attributed to the product of decarboxylation preceded by electron loss. The radical is converted into the more stable successor showing a broad spectrum of unidentified product.

The collagen spectra recorded under cryogenic conditions demonstrated poorly resolved signals being the superposition of several lines some of which belong to the backbone of macromolecule.

ESR and FTIR investigation of oxygen basicity in Ce/MCF and Nb/MCF materials

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Key words: Nb, Ce/MCF materials; NO adsorption; FTIR; ESR; acidity - basicity

Niobium and cerium dopants of mesoporous cellular foams, MCF, have been recently considered as promoters enhancing the basicity of amino-organosilanes anchored to the supports. Therefore, we aimed at getting a deeper insight into the acid-base properties of MCF modified with Nb or Ce species and also by both metal species together. A special focus was put on the properties of oxygen atoms coming from cerium and niobium oxide loaded on the MCF. Oxygen ions in CeO₂ are mobile when compared with the Ce cations that determine basic/redox properties of ceria, whereas Nb₂O₅ is known as acidic metal oxide. However, niobium source loaded on MCFs is transformed upon calcination to niobium included into the silica skeleton and in this way generates different oxygen species than those in the metal oxides. In this study we used NO as a probe molecule for testing the basicity of oxygens coming from metal species loaded on MCF. After adsorption of NO the samples were studied by FTIR and ESR spectroscopies. NO adsorption at 293 K on monometallic samples followed by heating at different temperatures led to the formation of adsorbed radical species observed in ESR spectra which exhibited different shapes for Ce/MCF and Nb/MCF. According to [1] the ESR signal of NO adsorbed on Ce/MCF can be assigned to low mobile NO radical species (N' type), whereas the spectrum of NO adsorbed on Nb/MCF is characteristic of mobile species (N type). Signal of N type species corresponds to weakly adsorbed NO showing higher mobility and is characterized by broader line width. Thus, the ESR spectra of NO adsorbed on Ce/MCF confirmed the presence of oxygen defect holes which stabilized chemisorbed NO. The high mobility of NO was observed when chemisorption occurred on LAS (Lewis acid sites) in Nb/MCF. For bimetallic samples both, mobile and stable NO radicals were observed. NO adsorption combined with FTIR and ESR spectroscopy allowed estimation of the presence of defects in ceria loaded on MCF, mobility and oxidative properties of oxygen in both modifiers and strength of chemisorption on active centers.

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Search for single ion magnets (SIM) - structural and EPR studies of Ln-based SIM compounds

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Key words: Electron Paramagnetic Resonance (EPR), magnetism, single molecule magnets (SMM), Gd³⁺ ions

This presentation outlines preliminary results and perspectives of our ongoing studies [1,2] of single molecule magnets (SMM) and single ion magnets (SIM), specially based on lanthanides (4f) ions [3-6]. Over the past fifteen years or so, studies of such systems have become an important sub-area of molecular nanomagnets. The major driving force has been their exceptional promise in applications such as ultra-high-density data storage, spintronics, and quantum information processing [3].

A number of newly synthesized Ln-based SIM compounds with N₂O-donor Schiff base ligand are currently undergoing investigations using X-band EPR spectroscopy. This includes [Ln₂(C₁₅H₁₂N₄O₂)₃(NO₃)₃], where Ln = Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺ and Gd³⁺. So far only one sample containing Gd³⁺ metal ion has yielded strong EPR spectrum with overlapping signals revealing complicated structure of spin transitions at the g-factor of 1.98. Guided by available magnetism and EPR studies, we expect Gd³⁺ ions to have spin S = 7/2 [3-7]. Subsequently, temperature and magnetic field dependences of VSM magnetic susceptibility in the range of 2 K - 400 K and from -9T to 9T were performed revealing paramagnetic properties of this system. Our Gd³⁺ complex crystallizes in P-1 space group and the ligand arises as a result of salicylic aldehyde condensation and 2-(1-methylhydrazinyl)benzoxazole, where the metal ion has coordination number of 9.

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