ISBN: ί έήΖ ί ΫΩΖέ ί Ϊ ΧΖΧΨΖΩ

Cavtat, Croatia, 31 May – 3 June 2016

MEDITERRANEAN CONFERENCE
ON THE APPLICATIONS OF
THE MÖSSBAUER EFFECT
MECAME
CAVTAT 2016

In the Honour of Prof. Dr. Philipp Gütlich

BOOK OF ABSTRACTS

Edited by: Mira Ristić, Željka Petrović, Stjepko Krehula

MECAME 2016

2nd Mediterranean Conference on the Applications of the Mössbauer Effect

In the honour of Prof. Dr. Philipp Gütlich

Cavtat, Croatia

31 May to 3 June 2016

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Mira Ristić

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Logo designed by:
Tea Glušica

Published by:
Ruđer Bošković Institute, Zagreb, Croatia (2016)

Printed by:
ART STUDIO AZINOVIĆ d.o.o., Zagreb, Croatia

ISBN: 978-953-7941-12-3

WELCOME TO MECAME 2016!

On behalf of the Organising Committee, Programme Committee and International Advisory Board, we wish to welcome you at the 2nd Mediterranean Conference on the Applications of the Mössbauer Effect, MECAME 2016, which is taking place at Remisens Hotel Albatros, Cavtat, Croatia from 31 May till 3 June 2016.

MECAME 2016 is being organized in the honour of Prof. Dr. Philipp Gütlich (Johannes Gutenberg University, Mainz, Germany) to celebrate his eminent scientific contributions in the area of physical inorganic chemistry, especially in studies of dynamic electronic structure phenomena and magnetism of transition metal compounds, physical and chemical after effects of nuclear decay in coordination compounds, surface physics and chemistry, and industrial applications of Mössbauer Spectroscopy. Over the years, Prof. Dr. Philipp Gütlich and his research group greatly contributed to the development of different experimental techniques of Mössbauer spectroscopy (scattering methods, work with short-lived Mössbauer sources, time-integral and time-differential emission experiments). His additional contributions to the development of other complementary instrumental techniques should be also recognized. Prof. Dr. Philipp Gütlich has published more than 480 scientific publications (original research reports, review articles and book chapters), and co-authored and edited several books on the applications of Mössbauer spectroscopy in chemistry. Prof. Dr. Philipp Gütlich is a founder and the former editor-in-chief of the Journal *Comments on Inorganic Chemistry*. He made an incredible impact on many students and researchers from almost every continents of the world. We are very honoured that MECAME 2016 will bring together many of his former co-workers and students as well as many of his other colleagues all around the world. Presentations include the newest research about the application of Mössbauer spectroscopy in the chemistry and physics, materials science, nanotechnology, environmental and biological studies and use of synchrotron radiation for NRS and SR Mössbauer absorption experiments.

Cavtat, a small town located at the Adriatic coast overgrown by Mediterranean vegetation, clean sea water, and sandy beaches, will provide an enjoyable time to MECAME 2016 participants. The town has 2000 years long history and wherever you go you step on the remnants of the ancient settlements of Illyrian, Greek and Roman. The present look of the old part of Cavtat with the Rector's palace, Franciscan monastery, St. Nicholas' church, squares and city walls are preserved from the time of Republic of Dubrovnik. There is a born house of one of the greatest Croatian painters Vlaho Bukovac and the Mausoleum of the family Račić, the masterpiece of the great Croatian sculptor Ivan Meštrović.

We wish to all participants a successful conference and pleasant time in this charming town as well as in nearby Old City of Dubrovnik (the UNESCO world heritage site) and its beautiful surrounding Konavle.

Mira Ristić, Tetsuaki Nishida
and Virender K. Sharma

MECAME 2016 Chairs

ORGANIZATION AND SPONSORSHIP

MECAME 2016 is organized by the Ruđer Bošković Institute under auspices of Croatian Academy of Sciences and Arts, Department of Mathematical, Physical and Chemical Sciences.

MECAME 2016 is sponsored by PLIVA HRVATSKA d.o.o. and SCAN,d.o.o.

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Conference Programme *(only presenters are listed)*

Tuesday 31/05/2016

17:00 - 19:00 **Registration at Hotel Albatros**

20:00 **Welcome Reception at Hotel Albatros**

Wednesday 01/06/2015

09:00 - 09:15 **Opening Ceremony** (M. Ristić, T. Nishida, V.K. Sharma)

09:15 - 09:45 Hartmut Spiering: *Overview of the Scientific Achievements of Prof. Dr. Philipp Gütlich*

09:45 - 11:00 **Plenary & Invited Lectures** (Chairperson: T. Nishida)

09:45 - 10:30 Eckhard Bill: *Spectroscopy of Iron Complexes for Chemical Energy Conversion*

10:30 - 11:00 Dénes Lajos Nagy: *Poor Man's Big Bang: Lessons Learnt from After-Effect Studies with Mössbauer Emission Spectroscopy*

11:00 - 11:30 **Coffee Break**

11:30 - 13:00 **Invited Lectures** (Chairperson: E. Bill)

11:30 - 12:00 Yann Garcia: *Spin Transition Materials Based on Thermo and Photochromic Switches*

12:00 - 12:30 Jun Okabayashi: *Comparison between Mössbauer and X-ray Absorption Spectra in Novel Spin-Crossover Complexes*

12:30 - 13:00 Felix Tuczek: *Thermal and Optical Spin-State Switching of Surface-Adsorbed Iron Complexes*

13:00 - 14:30 **Lunch Time**

14:30 - 16:00 **Invited Lectures** (Chairperson: I. Felner)

14:30 - 15:00 Juliusz A. Wolny: *Nuclear Inelastic Scattering as a Tool for the Investigation of Spin Crossover Fe(II) Complexes*

15:00 - 15:30 Peter Adler: *Magnetic Phase Transitions in Iron Compounds with Composite Anionic Lattices Probed by Mössbauer Spectroscopy*

15:30 - 16:00 Vadim Ksenofontov: *Local and Itinerant Magnetism in Fe-based Superconductors*

16:00 - 16:30 **Coffee Break**

16:30 - 18:30 **Invited Lectures & Oral Presentations** (Chairperson: M. Reissner)

16:30 - 17:00 Vijayendra Garg: *Superparamagnetic Iron Oxide Nanoparticles (SPIONs) for Targeted Drug Delivery*

17:00 - 17:30 Victor Kuncser: *Magnetic Relaxation and Inter-Particle Interactions in Fe Oxide Nanoparticles for Bio-Medical Applications*

17:30 - 17:45 Marija Perović: *Magnetic Relaxation in Super Spin Glass Systems – Search for High Temperature Memory Effects*

17:45 - 18:00 Stanislaw M. Dubiel: *Magnetic and dynamic properties of a* σ-$Fe_{65.9}V_{34.1}$ *alloy*

18:00 - 18:15 Hakan Güngüneş: *Structural Investigation and Hyperfine Interactions of* $BaBi_xLa_xFe_{12-2x}O_{19}$ $(0.0 \leq x \leq 0.5)$ *Hexaferrites*

Thursday 02/06/2015

09:00 - 10:45 **Plenary & Invited Lectures** (Chairperson: D.L. Nagy)

09:00 - 09:45 Ralf Röhlsberger: *New Frontiers in Nuclear Resonant Spectroscopy: Applications from Nanomagnetism to X-Ray Quantum Optics*

09:45 - 10:15 Rolfe H. Herber & Israel Nowik: *Lattice Dynamics, Phase Transitions, Spin Relaxation and Valence Fluctuations in Ferrocenoids*

10:15 - 10:45 Stewart J. Campbell: *Structural and Magnetic Properties of RMn_2X_2-type Compounds – Scope for Purpose Designed Materials*

10:45 - 11:15 **Coffee Break**

11:15 - 13:15 **Invited Lectures** (Chairperson: R. Röhlsberger)

11:15 - 11:45 Gerhard Wortmann: *Magnetism and Valence in the CsCl-Phases of EuO, EuS and EuSe at Extreme Pressures*

11:45 - 12:15 Ko Mibu: *Studies on Thin Iron-Oxide Films as Components for Spintronics Devices Using Conventional and Synchrotron-Radiation Mössbauer Spectroscopy*

12:15 - 12:45 Yoshio Kobayashi: *Chemical States of Localized Fe Atoms in Ethylene Matrices by Means of In-Beam Mössbauer Spectroscopy*

12:45 - 13:15 Satoshi Tsutsui: *Application of Synchrotron Radiation Mössbauer Spectroscopy to Samarium Compounds*

13:15 - 14:30 **Lunch Time**

15:00 **Conference Excursion**
Boat trip to Koločep Island, Dubrovnik sightseeing, dinner in Konavle village

Friday 03/06/2015

09:00 - 11:00 **Invited Lectures** (Chairperson: S.J. Campbell)

09:00 - 09:30 Frank J. Berry: *Manipulations of New Mineral-Related Materials*

09:30 - 10:00 Vladimír Šepelák: *Structural Disorder Phenomena in Nanostructured Oxides*

10:00 - 10:30 Junhu Wang: *Mössbauer Probed the Cationic Distribution of Spinel Oxides with Well Controlled Morphology as Electrocatalysts*

10:30 - 11:00 Yasuhiro Yamada: *Iron Films Deposited on Porous Alumina Substrates*

11:00 - 11:30 **Coffee Break**

11:30 - 13:00 **Invited Lectures** (Chairperson: L. Machala)

11:30 - 12:00 Virender K. Sharma: *Ferrites in Sustainable Energy and Environmental Remediation: Mössbauer Spectroscopy Characterization*

12:00 - 12:30 Michael Oshtrakh: *Mössbauer Spectroscopy of Hemoglobins and Ferritins: Recent Advances in Biophysical and Medical Research*

12:30 - 13:00 Paul A. Bingham: *Application of Mössbauer Spectroscopy to the Immobilisation of Radioactive and Toxic Wastes*

13:00 - 14:30 **Lunch Time**

14:30 - 16:00 Invited Lectures (Chairperson: V.K. Sharma)

14:30 - 15:00 Zoltán Homonnay: *Iron Oxide Nanoparticles for Plant Nutrition? - A Preliminary Mössbauer Study*

15:00 - 15:30 Nataliya Chistyakova: *Mössbauer Spectroscopy in Microbial Transformations of Iron-Containing Minerals*

15:30 - 16:00 Libor Machala: *Transformation Mechanisms of Ferrates - Impact on Their Application in Water Treatment*

16:00 - 16:30 Coffee Break

16:30 - 18:15 Oral Presentations (Chairperson: Z. Homonnay)

16:30 - 16:45 Tetsuaki Nishida: *Substitution of Ga_2O_3 and GeO_2 for Fe_2O_3 in Conductive Barium Iron Vanadate Glass*

16:45 - 17:00 Keito Osouda: *Electrical Conductivity and Local Structure of Aluminum-Containing Vanadate Glass*

17:00 - 17:15 Kosuke Sunakawa: *Local Structure and Magnetic Properties of Iron Phosphate Glass Prepared by Sol-Gel Method*

17:15 - 17:30 Alevtina Maksimova: *Mössbauer Spectroscopy of H, L and LL Ordinary Chondrites*

17:30 - 17:45 Károly Lázár: *Mobility of Iron Ions in Porous Ferrisilicates*

17:45 - 18:00 Adriana Lančok: Ferritin Nanoparticles in Biological Tissues

18:00 - 18:15 Alexander S. Kamzin: Mössbauer Studies of Magnetic Nanoparticles for Biomedical Applications

18:15 Closing Ceremony

20:00 Conference Dinner

POSTER PRESENTATIONS (Posters will be on display all the time during the conference)

P1 Shota Amagasa: *Mössbauer Study of Iron Carbide Nanoparticles Produced by Laser Ablation in Alcohols*

P2 Marko Bošković: *Animal Model Study of Magnetic Nanoparticles Biodistribution by AC Susceptibility*

P3 Hyunkyung Choi: *Mössbauer Analysis of the Mixed Olivines $LiFe_{0.9}Zn_{0.1}PO_4$*

P4 Serhiy Demeshko: *Spin State Versatility in a Series of Fe_4 [2×2] Grid Complexes: Effects of Counteranions, Solvent and Intramolecular Cooperativity*

P5 Israel Felner: *Lattice Dynamics, Phase Transitions and Spin Relaxation in $[Fe(C_5H_5)_2]PF_6$*

P6 Valentin Filippov: *Secondary Particles Precipitates in Be-Fe Alloys*

P7 Valentin Filippov: *The Phase Transformations in Intermetallic Phases in Zirconium Alloys*

P8 Valentin Filippov: *Precision of Iron the Solubility in Zirconium Alloys*

P9 Il'ya A. Gural'skiy: *Magnetic, Mössbauer and Structural Monitoring of Spin State Switch in Iron(II)-Pyrazine Cyanoheterometallates*

P10 Stjepko Krehula: *Synthesis and Properties of Indium-Doped Iron Oxides*

P11 Erno Kuzmann: *Mössbauer Study of pH Dependence of Iron Intercalation in Montmorillonite*

P12 Hiroyuki Nakamura: *Mössbauer Study of M-type Ca-La Ferrite Single Crystals*

P13 Naoki Nishida: *One-Pot Production of Copper Ferrite Nanoparticles by Chemical Method*

P14 Ivana Opačak: *The Precipitation of α-Fe_2O_3 Particles by Forced Hydrolysis of $FeCl_3$ Solutions in the Presence of Sodium Dodecyl Sulphate*

P15 Michael Reissner: *^{57}Fe Mössbauer Spectroscopy Analysis of Fe-Bearing Phases in the Manufacture of TiO_2 Pigment*

P16 Vlad Salomasov: *Iron Mössbauer Spectra Investigation of Nepheline Substrate Using for Preparing the Water Treatment Reagent*

P17 Sergii I. Shylin: *Spin Fluctuations in FeSe-Based Superconductors under Pressure*

PLENARY LECTURES

Spectroscopy of Iron Complexes for Chemical Energy Conversion

E. Bill

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Energy capture, conversion and storage in natural and technical systems is often based on chemical reactions of small molecules such as O_2, H_2, H_2O, CO_2, CH_3OH, or N_2. Since these are stable molecules they have to be activated for the corresponding reactions, e.g. by reduction with electrons from catalysts. Examples are the oxygen activation for chemical oxygenation, hydrogen atom transfer, or fuel cell-type applications, or splitting of water during photolysis. Evolution has provided efficient reaction mechanisms for such processes, which are mostly based on molecular complexes with transition metal ions. These concepts may be taken as blue prints for the design of efficient and versatile technical catalysts, but for comprehensive understanding we have to study the molecular structures as well as the electronic structures of the catalysts in detail. The latter can be achieved only with spectroscopy, and since iron is a key element in many cases, Mössbauer spectroscopy is in the focus of the research, usually in combination with other magnetic and optical techniques. In this contribution the electronic structure of iron catalysts for oxygen, nitrogen, and carbon dioxide activation will be addressed. The key intermediates in the reaction with oxygen and nitrogen are high-valent iron(IV) and iron (V) species with oxo and nitride ligands, supported by heme and various non-heme ligands. Deliberate tuning effects of the supporting ligand on d-electron energies and the reactivity of the compounds will be discussed. Iron – nitrosyl complexes can serve as model systems in this program, having interesting electronic properties in itself, in addition to their catalytic relevance. On the other hand, activation of carbon dioxide requires low-valent complexes, for which iron porphyrins in the formal oxidation state iron (0) and iron(I) are competent species. The electronic ground states of these systems have been explored in detail by using applied-field Mössbauer spectroscopy of trapped reaction intermediates and model compounds, with complementary information obtained from EPR and magnetic susceptibility measurements. Moreover, magnetic circular dichroism (MCD) spectroscopy was applied for exploring the excited orbital states of the compounds, which can explain more of their reactivity. The spectroscopic data are interpreted based on spin Hamiltonian analyses and quantum chemical calculations to obtain detailed descriptions of the catalytically active molecules.

New Frontiers in Nuclear Resonant Spectroscopy: Applications from Nanomagnetism to X-Ray Quantum Optics

R. Röhlsberger

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The advent of high-brilliance, accelerator-driven light sources such as modern synchrotron radiation sources and X-ray lasers has stimulated a multitude of new experimental techniques. In this contribution I will review recent advances in two research fields: (a) the study of magnetic structure and dynamics in magnetic nanostructures [1] and (b) the establishment of x-ray quantum optics using nuclear resonances [2,3].

One of the most intriguing phenomena of quantum optics is electromagnetically induced transparency (EIT): Exposing a medium to intense laser light of a certain wavelength makes it transparent for light of a different wavelength for which it would be completely opaque otherwise. After its discovery several decades ago, EIT still receives enormous interest today because it allows to control optical properties at the level of single quanta of light and matter.

Recently, we have shown that phenomena like electromagnetically induced transparency can be observed in the regime of hard X-rays, using the 14.4 keV nuclear resonance of the Mössbauer isotope ^{57}Fe [1].

Embedding ensembles of Mössbauer nuclei in cavities and collectively exciting them with pulses of synchrotron radiation allows one to prepare superradiant eigenstates of resonant atoms. The radiative coupling of such ensembles in the cavity field can be employed to generate atomic coherences between different nuclear levels. This forms the basis for the new field of nuclear quantum optics in the regime of hard x-rays. Recently observed phenomena include slow light, Fano resonances, spontaneously generated coherences, and collective strong coupling of light and matter.

[1] L. Bocklage et al., Phys. Rev. Lett. 114 (2015) 147601.
[2] R. Röhlsberger et al., Nature 482 (2012) 199.
[3] J. Haber et al., Nature Photonics (2016) accepted.

INVITED LECTURES

Magnetic Phase Transitions in Iron Compounds with Composite Anionic Lattices Probed by Mössbauer Spectroscopy

P. Adler and M. Valldor

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High temperature superconductivity in oxocuprates and iron-based pnictides or selenides has been a frontier topic in solid-state research during the last decades. A common feature of both materials classes is a subtle interplay of superconductivity with magnetism. In case of oxocuprate superconductors it is well established that their antiferromagnetic parent compounds are Mott (or charge-transfer) insulators, but the situation is less clear in Fe-based systems. While non-superconducting iron pnictides with FeAs layers are frequently itinerant antiferromagnets with quite small magnetic moments ($< 1\ \mu_B$), certain iron selenides with FeSe layers are magnetic insulators with large moments of $\sim 3\ \mu_B$ which indicates a higher degree of electronic localization. In this talk we present studies on iron-based compounds with composite anionic lattices, namely selenide- and sulfide-oxides. Whereas in the prototype non-superconducting pnictides LnOFeAs separate FeAs and LnO layers occur, the compounds discussed here reveal highly anisotropic coordination spheres containing both chalcogenide ions. An example are spin-ladder-type alkaline-earth chalcogenide-oxides $AE\mathrm{Fe}_2Ch_2\mathrm{O}$ (AE = Sr, Ba, Ch = S, Se) the crystal structure of which is composed of $\mathrm{Fe}Ch_3\mathrm{O}$ units. These compounds show long-range magnetic order below $T_N \sim 220 - 260$ K [1,2] and are related to the spin-ladder type sulfide $BaFe_2S_3$, where recently pressure-induced metallization and the emergence of superconductivity were reported. Other examples that will be discussed contain $\mathrm{Fe}Ch_2\mathrm{O}_2$ or $\mathrm{Fe}Ch_4\mathrm{O}_2$ and $\mathrm{Fe}Ch_3\mathrm{O}_3$ units as building blocks. All these chalcogenide oxides are electronically well-localized Mott-type insulators containing high spin Fe^{2+} ($3d^6$) ions. Their Mössbauer spectra show the features of combined electric quadrupole and magnetic hyperfine interactions, which is typical for Fe^{2+}, and full Hamiltonian analysis was performed for the data evaluation (see Fig. 1 as an example). The Mössbauer spectra reveal local electronic and structural properties and provide detailed insights into the nature of the various magnetic phase transitions encountered in this class of materials. Finally we will discuss the complex selenide $[Cs_6Cl][Fe_{24}Se_{26}]$, which is related to the mineral bartonite. This material may be close to electronic itinerancy and its Mössbauer spectrum suggests a complex spin structure at low temperatures [3].

[1] M. Valldor et al., Eur. J. Inorg. Chem. (2014) 6150-6155.

[2] S. Huh et al., Eur. J. Inorg. Chem. (2015) 2982-2988.

[3] M. Valldor et al., Chem. Eur. J. 22 (2016) 4626-4631.

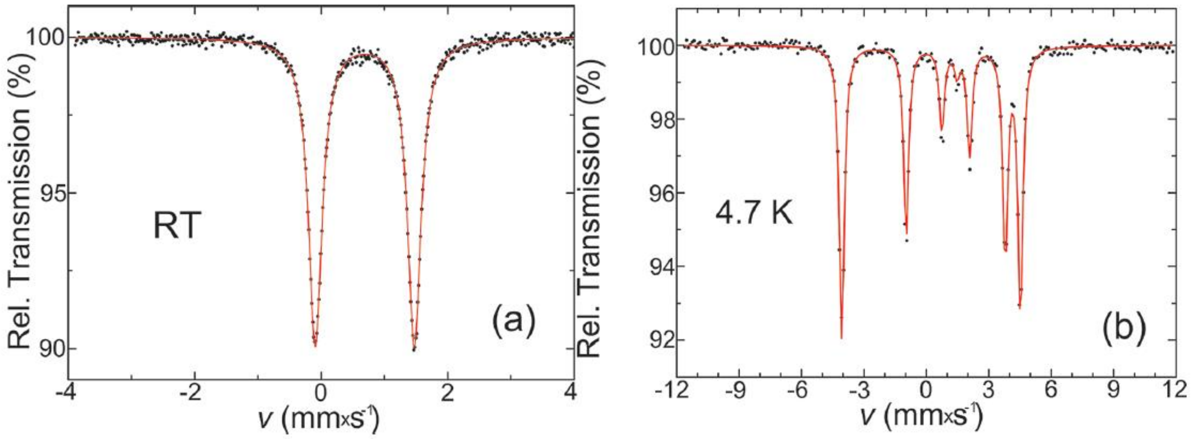

Fig. 1 (from Ref. [1]): Mössbauer spectra of $BaFe_2S_2O$ (a) at room temperature in the paramagnetic phase and (b) at 4.7 K in the magnetically ordered phase.

Manipulations of New Mineral-Related Materials

F.J. Berry

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We have recently reported on the synthesis of new inorganic materials with structures derived from the mineral schafarzikite of composition $FeSb_2O_4$ [1]. We have also demonstrated the power of Mossbauer spectroscopy for the examination of changes in oxidation states resulting from cationic substitution and for the investigation of complex magnetic interactions in these types of materials [2,3]. We have now developed this work and report here on the unusual oxidation of these types of materials and also on the synthesis of other compounds with structures derived from the related minerals known as versiliate and apuanite. We will also demonstrate how Mossbauer spectroscopy has proven to be an important technique for elucidating fundamental properties in these types of materials.

[1] M.J. Whittaker, R.D. Bayliss, F.J. Berry, C. Greaves, J. Mater. Chem. 21 (2011) 14523-14529.

[2] R.D. Bayliss, F.J. Berry, B.P. de Laune, C. Greaves, O. Helgasson, J.F. Marco, M.F. Thomas, L. Verjara, M.J. Whittaker, J. Phys.: Cond. Matter 24 (2012) 27601-27607.

[3] F.J. Berry, B.P. de Laune, C. Greaves, M.J. Whittaker, M.F. Thomas, J.F. Marco, Hyperfine Interactions 226 (2014) 544-552.

Application of Mössbauer Spectroscopy to the Immobilisation of Radioactive and Toxic Wastes

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Developing materials and methodologies for the safe handling, treatment, storage of radioactive and toxic wastes continues to be an issue faced by many countries. Mössbauer spectroscopy can be a key technique to support research and development of new materials in this field, for example in the development of new glassy or ceramic host matrices for the immobilisation of specific waste types. Mössbauer spectroscopy is particularly well-suited to this field because Mössbauer-active isotopes (chiefly ^{57}Fe) are sufficiently abundant in many wastes and / or host materials; allowing us to probe the oxidation state/s, magnetic ordering, local atomic structure and crystallinity of a wide range of materials containing these isotopes in sufficient abundance. Here are presented examples and case studies of the successful application of Mössbauer spectroscopy to problems in the field or radioactive and toxic waste immobilisation.

Structural and Magnetic Properties of RMn_2X_2-type Compounds – Scope for Purpose Designed Materials

J.L. Wang[1,2], S.J. Kennedy[3,2], M. Hofmann[4,2] and S.J. Campbell[2]

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[2] *School of Physical, Environmental and Mathematical Sciences, UNSW Canberra, Australian Defence Force Academy, Canberra, ACT 2610, Australia*
[3] *European Spallation Source ERIC, Tunavägen 24 Medicon Village, 223 63 Lund, Sweden*
[4] *Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstrasse 1 D-85748 Garching, Germany*
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Rare earth (R) transition metal (T) compounds based on RT_2X_2 (metalloid X = Ge, Si) with the body centred tetragonal $ThCr_2Si_2$-type b.c.t. structure (S.G. I4/mmm), are among the most intensively studied series of intermetallic compounds over past and recent decades [e.g. 1, 2]. These compounds form a layered structure with atoms stacked along the *c* axis in the sequence -R-X-T-X-.

Compounds with T = Mn attract particular interest due to the magnetic moment carried by the Mn atoms and the presence of strong magneto-elastic coupling. Another significant feature is the wide solubility ranges for the R, T and X atoms leading to extensive series of ternary and pseudoternary compounds of the type $R_{1-y}R'_yT_2X_2$, $RMn_{2-x}T_xX_2$ and $R_{1-y}R_yMn_2\ X_{2-x}X'_x$. The strong dependence of the magnetic exchange interactions on intra-planar Mn-Mn distances and, to a lesser extent, on inter-planar Mn-Mn distances together with the scope for magnetic moment on the R atoms, leads to a complex array of magnetic states. This in turn leads to a wide range of physical behaviours and properties, including a variety of magnetic ordering, superconductivity, mixed valence, Kondo and heavy fermion behaviour [e.g. 3].

The role of interatomic correlations between magnetic phases and the origin of the two phase regions which have been shown to exist in these pseudoternary compounds have attracted attention recently [2], as has the role of magnetostructural coupling in governing the magnetocaloric behaviour of these compounds [e.g. 4, 5]. A brief overview of the magnetic and structural behaviour of these pseudoternary Mn-based compounds will be presented. Attention will be paid to the role that Mössbauer effect spectroscopy and neutron scattering studies have played in resolving aspects of their fascinating behaviours including delineation of phase diagrams (e.g. $PrMn_{2-x}Fe_xGe_2$) and unravelling magnetocaloric properties.

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Mössbauer Spectroscopy in Microbial Transformations of Iron-Containing Minerals

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One of the possible ways of iron mineral formation is an extracellular reduction of amorphous Fe (III) oxides and hydroxides by the group of microorganisms that was found in the 1980's and named dissimilatory iron-reducing bacteria [1, 2]. Microbial activity plays a key role in the biogeochemical cycling of Fe in aquatic and terrestrial environments. Studies of properties of nanomaterials, which are obtained as a result of microbial synthesis is one of the most important problem. The microbial synthesis may be carried out in conditions that are close to natural one. These nanoparticles as the products of such type synthesis can be used as carrier for target drug delivery. Microbial transformations of iron-containing minerals such as synthesized ferrihydrite, magnetite, phyllosilicates biotite and glauconite were studied by Mössbauer spectroscopy methods. Alkaliphilic bacterium *Fuchsiella ferrireducens* used synthesized ferrihydrite as an electron acceptor. It was found that during the strain growth with the ethanol in the cultivation medium siderite and magnetically ordered phase (a mixture of hematite and maghemite) formation was observed. Nanoparticles of magnetically ordered phase were also formed. In the presence of acetate the formation of siderite is presented but the magnetically ordered phase is virtually not formed. The dissimilatory bacteria transfer electrons on the surface of iron-containing mineral. Therefore iron reduction process strongly depends on the ratio between quantities of bacterial cells and particles of minerals because electron concentration on the particles surface depends on the bacterial cells quantity. The experiment in which different ratios between quantities of cells and particles of minerals were realized by different flask orientation was carried out. The samples were obtained as a result of iron reduction of ferrihydrite with concentrations 10, 45, 100 мM by bacterium *Geoalkalibacter ferrihydriticus.* The Mössbauer spectra of superparamagnetic particles were fitted with many state superparamagnetic relaxation model by program SpectrRelax [3]. Our study showed that the change in the number of cells per particle lead to a change in the size of the formed particles, as well as changes of the ratio between the siderite and magnetite content in the samples. Mössbauer studies of bacterium *G. ferrihydriticus* growth in a medium containing synthetic magnetite showed that for the first passages of culture from ferrihydrite the reduction of Fe^{3+} atoms was observed with formation of siderite. In the following passages the bacterial reduction ability vanished. Mössbauer study of kinetic experiments with glauconite and *Carboxydocella thermautotrophica* revealed two stages of bacterial growth. At first stage up to the 78 hours from the incubation the strain oxidized CO. After that, when CO was fully exhausted bacterium started to reduce Fe^{3+} atoms from glauconite with formation of siderite.

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Spin Transition Materials Based on Thermo and Photochromic Switches

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Iron(II) spin crossover (SCO) complexes continue to attract a great deal of interest with focus centred on gaining a full understanding of their magnetic, optical, structural and vibrational properties [1] to developing smart sensors and spintronic devices. In this frame, SCO nanomaterials have emerged as a new class of materials for investigation, considering nanostructuration processes and size reduction effects [1]. Although sophisticated techniques can be used for the preparation of SCO nanoparticles, we have introduced a biomembrane as a soft and green support for deposition of SCO micro and nanocrystals, which were used for printing on various supports. More recently, we investigated the SCO properties of hybrid nanomaterials made of MCM-41 including 1D Fe(II) 1,2,4-triazole coordination polymers. This later class of SCO materials, whose spin states can be switched by light [2], afforded the first 1D chain with 1,2,4-triazole ligands displaying a two-step spin conversion, as well as a SCO material displaying a 60 K hysteresis loop centered at room temperature [3]. These compounds were discovered in the frame of our general investigation of a new range of porous metal organic frameworks. Indeed, using a ditopic 1,2,4-triazole-tetrazole ligand, we recently isolated a mononuclear iron(II) high-spin neutral complex, with coordinated water molecules. The situation becomes intriguing when the complex is screened for sensing abilities for a series of chemicals. Indeed, the complex detects methanol among alcohols and hydrochloric acid among the acid series. The sensing process, which involves a spin state change for the methanol case, is visually detectable, fatigue-resistant, selective, and reusable, as demonstrated by both ^{57}Fe Mössbauer and diffuse reflectance spectroscopies.

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Superparamagnetic Iron Oxide Nanoparticles (SPIONs) for Targeted Drug Delivery

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Superparamagnetic iron oxide nanoparticles have been and still are of scientific research interest because of their biomedical applications. Drug delivery systems have improved for the medical applications of drug particulates. Drugs loaded superparamagnetic nanoparticles can be guided towards a certain location by magnetic field gradient. Such drug systems have significant advantages such as: (i) the ability to target specific locations in the body; (ii) the reduction of the quantity of drug needed to attain a particular concentration in the vicinity of the target; and (iii) the reduction of the concentration of the drug at non-target sites minimizing severe side effects. To achieve these benefits, the nanoparticles have to be engineered for the functionality, biocompatibility and the efficiency. Nonagglomeration of nanoparticles and reduction or still better eliminate its toxicity are some of unsolved issues. Magnetic iron oxide (Fe_3O_4/γ-Fe_2O_3) nanoparticles were synthesized using co-precipitation method. These nanoparticles were characterized using XRD, Raman, Mössbauer, photoacoustic spectroscopy and vibrating sample magnetometer. The growth of the nanoparticles was confined by the zeolite resulting to fine superparamagnetic particles. XRD and Raman spectra show the presence of only cubic iron oxide (Fe_3O_4/γ-Fe_2O_3). The identification of the specific phase of iron oxide was achieved by photoacoustic measurement. It shows the pure iron oxide consists of magnetite (Fe_3O_4). Increase in zeolite concentration leads to decrease in particle size of iron oxide and the phase tends towards maghemite (γ-Fe_2O_3). The thermal stability of the nanoparticles was enhanced by nucleating the nanoparticles in the zeolite template. The onset temperature of agglomeration due to thermal treatment of iron oxide/zeolite composites was 250 K higher compared to pure magnetite. TG-DTA shows the surface to H_2O interaction energy increase as zeolite content increases. This indicates that the binding energy of negatively charge drugs would be higher as zeolite is introduced along with magnetic iron oxide. These nanoparticles exhibit magnetization which can be stimulated by an external AC magnetic field for the controlled release of the attached drug.

Lattice Dynamics, Phase Transitions, Spin Relaxation and Valence Fluctuations in Ferrocenoids

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Temperature dependent Mössbauer Effect (ME) spectroscopy has developed into a sensitive technique to elucidate the metal atom dynamics in organometallic solids, especially those of iron and tin [1]. In the present review we focus on the information which can be extracted from such ME studies related to the metal atom motion, the anisotropy of this motion, the spin relaxation rate in paramagnetic compounds, valence fluctuations in some compounds and the nature of numerous phase transitions in these solids. In particular, we have investigated the motional anisotropy on parent ferrocene $[(C_5H_5)_2Fe]$ and related structures involving ring substitution in the η^5-C_5H_5 moieties and in bucky ferrocenes [2]. We have observed the consequences of the onset of ring rotation in octa- and nona-methyl ferrocene and the influence of this ring rotation on the temperature dependence of the recoil-free fraction of the metal atom [3]. In the presence of a large quadrupole splitting (~ 2.5 mm sec^{-1}) in the diamagnetic compounds, we have been able to ascertain the vibrational anisotropy (parallel and perpendicular to the major symmetry axis) in a number of ferrocenoid solids and relate this to the local molecular structures involved. Using the application of an external magnetic field, we have shown that the sign of the quadrupole interaction in paramagnetic compounds is negative in contrast to its value in the diamagnetic precursors [4]. We have also been able to show that paramagnetic species such as the ferricinium salts, Fc^+A^-, where A^- is BF_4^-, PF_6^- and AsF_6^-, their spins relax by an Orbach process [5]. The relaxation rate is effectively independent of the nature of A^-. Finally, we have elucidated the valence fluctuations in a di-iron boron compound with valence trapping at low temperatures yielding a de-trapped transition as T increases [6].

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Iron Oxide Nanoparticles for Plant Nutrition? - A Preliminary Mössbauer Study

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Agriculture is getting into the focus of interest of research as the World's population is increasing despite strong countermeasures applied in certain countries. To handle this situation, food production is a key question and its success highly depends on how it is possible to grow healthy plants. For high quality crop and efficient production, optimal nutrition for the plants is a necessity, and in case of bad quality soil, missing nutrients should be supplied by fertilizers.

One of the most important micronutrient for plants is iron. Shortage of iron hampers chlorophyll formation in the leaves, results in slow growth and finally the plant may die.

Uptake of iron by plants from the soil is known to proceed by two strategies and it has been studied by us using Mössbauer spectroscopy [1,2]. These strategies assume dissolved iron(III) which either forms a complex to be able to get through the cell membranes of the root, or are first reduced to iron(II) than transferred into the cytoplasm in this form.

Since storage of iron in cells is usually realized in the form of ferritin whose iron-bearing core resembles very much to a ferrihydrite/iron(III) oxide/oxyhydroxide nanoparticle, one may consider plant nutrition supply in the soil directly by iron-based oxide or oxyhydroxide and magnetite/maghemite nanoparticles.

In our research, we have prepared iron(III) oxyhydroxide (Fig. 1) and magnetite/maghemite nanoparticles to use them as possible nutrition source. The first plant growth experiments indicate successful iron uptake from ferrihydrite nanoparticles, and the mechanism of the uptake is being subject of ongoing studies.

We are reporting here on the preparation and characterization of these nanoparticles intended to be used for nutrition purpose, using Mössbauer spectroscopy and other methods.

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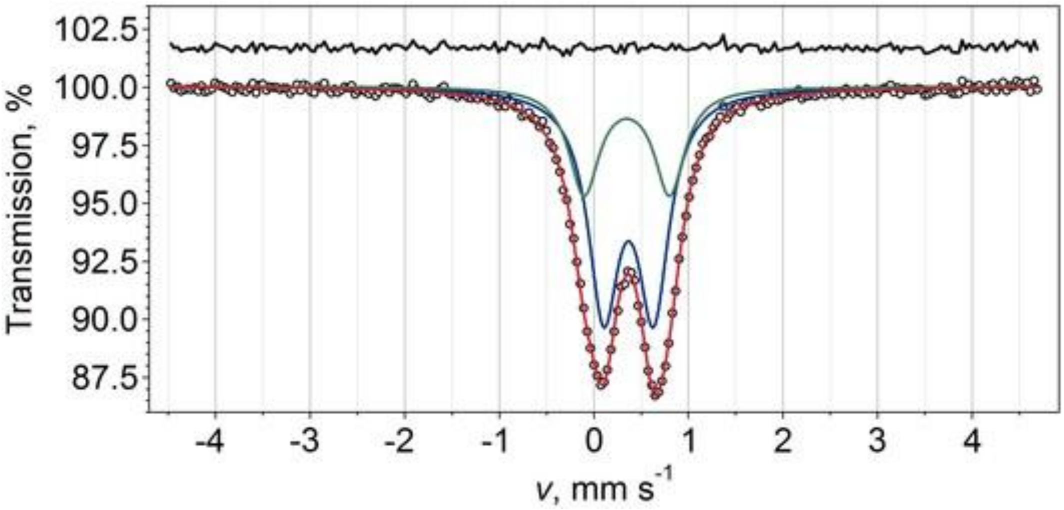

Fig. 1 Room temperature Mössbauer spectrum of nano ferrihydrite.

Chemical States of Localized Fe Atoms in Ethylene Matrices by Means of In-Beam Mössbauer Spectroscopy

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The in-beam Mössbauer spectroscopy using a short-lived ^{57}Mn ($T_{1/2}$ = 1.45 m) implantation in solids is the simple system to investigate the chemical states and final lattice positions of isolated Fe atoms produced after the nuclear decay. We have studied the chemical states and reaction products of isolated Fe atoms in gas matrices of Ar, Xe, and CH_4. In ^{57}Mn implantation into a CH_4 matrix, it was found that the chemical species of $Fe(CH_4)_2^+$ were produced, as derived from DFT calculations and the Mössbauer parameters [1]. In this study, the in-beam Mössbauer spectrum of ^{57}Mn implantation into a mixed gas matrix of C_2H_4 and Ar was performed. It was expected to determine the exotic chemical products after the reaction of Fe^{n+} ions with C_2H_4 molecules. The experiment was carried out at the heavy-ion medical accelerator (HIMAC) at the National Institute of Radiological Science. A mixture gas matrices of C_2H_4 and Ar (C_2H_4:Ar = 3:7) were agglutinated on a metal plate cooled down to 16 K using a pulsed-tube- type He refrigerator. A ^{57}Mn beam was produced by the nuclear projectile fragmentation reaction between a primary ^{58}Fe beam (E = 500 MeV/nucleon) and a production target of ^{9}Be. The ^{57}Mn particles were separated by an in-flight RI beam separator. Then, after optimizing and slowing-down the energy of the ^{57}Mn particles, they stopped at an adequate depth in the C_2H_4/Ar matrix sample. A parallel-plate avalanche counter (PPAC) was employed to detect the internal conversion electrons emitted after resonant absorption of the Mössbauer γ-rays [2]. The in-beam Mössbauer spectra of ^{57}Mn implantation into C_2H_4 matrix was measured at 16 K. The spectrum was well fitted as the primary approximation with four components of a singlet and three doublets, as shown in Fig. 1. The singlet of δ = –2.04(2) mm/s was assigned to be the excited state of Fe^+ ($3d^74s^0$) surrounded by Ar atoms, and the doublet of δ = –0.30(6) mm/s and ΔE_Q = 0.85(1) mm/s was assigned to be Fe^+ ($3d^64s^1$) in the ground state, as were determined in our previous report about the atomic configurations of ^{57}Fe in Ar matrix [3]. The other two components were considered to be attributable to the reaction products of isolated ^{57}Fe atoms with C_2H_4 molecules. These components were discussed with DFT calculations and the obtained Mössbauer parameters. This work was supported by JSPS KAKENHI Grant Number 25410062.

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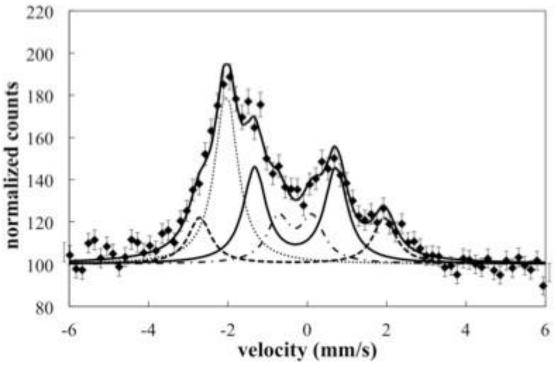

Fig. 1 In-beam Mössbauer spectra of ^{57}Fe obtained ^{57}Mn implantation in C_2H_4/Ar matrix measured at 16 K. The isomer shift is given relative to Fe metal at room temperature.

Local and Itinerant Magnetism in Fe-based Superconductors

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Many experimental facts provide evidence that antiferromagnetic spin fluctuations can mediate superconductivity acting as “glue” for Cooper pairs in Fe-based superconductors. Our Mössbauer studies of FeSe intercalated with Li/NH_3 spacer layers with a superconducting transition temperature of T_C = 43 K support this idea [1]. They demonstrate that simultaneously with superconducting transition in ^{57}Fe Mössbauer spectra appears a magnetic subspectrum of dynamic nature. In this regard, this novel superconductor with its high T_C could be considered as a clue compound for the understanding of the principal mechanisms of superconductivity in Fe-based superconductors. From Mössbauer measurements follows that the intensity of the magnetic fraction scales with a transition curve when passing to the superconducting state. From other hand, conductivity measurements demonstrate that T_C decreases with increasing pressure. Taking into account this fact, a detailed Mössbauer study of FeSe intercalated with Li/NH3 under pressure was performed using the ^{57}Fe-Synchrotron Mössbauer Source (SMS) at measuring line ID18 at ESRF. Pressure measurements with SMS revealed that both the amount of magnetic fraction and the frequency of the hyperfine magnetic field fluctuations do follow the variation of T_C with pressure. They prove that the superconducting pairing in FeSe-based superconductors is mediated by the antiferromagnetic spin fluctuations. From other hand, existence of static non-compensated magnetic moments is incompatible with superconductivity. In the series of ^{57}Fe-SMS measurements we performed also pressure studies of Cu-doped FeSe superconductor (20% ^{57}Fe-enriched $Fe_{0.97}Cu_{0.04}Se$). Doping of small amounts of Cu into the FeSe matrix suppresses superconductivity and introduces local static moments at the Fe sites, evidenced by glassy magnetic interactions. Application of pressure leads to restoration of superconductivity in Cu-doped FeSe. High-pressure studies of non-supercondctive $Fe_{0.97}Cu_{0.04}Se$ using the SMS revealed that this occurs because of the suppression of the static spin-glass state. Only nano-scale phase separation of insulating vacancy-ordered antiferromagnetic and metallic non-magnetic FeSe-similar domains provides conditions for coexistence of static magnetism and superconductivity [2,3].

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Magnetic Relaxation and Inter-Particle Interactions in Fe Oxide Nanoparticles for Biomedical Applications

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The remarkable new phenomena observed in magnetic nanoparticulate structures derive from the interplay between the intrinsic properties of the components, finite size effects and interphase/interparticle interactions. The magnetic response of the system is strongly related to such peculiar magnetic phenomena and gives support for a large variety of biomedical applications. Issues related to the magnetic response of complex systems consisting of different types of Fe oxide nanoparticles (composites, multifunctionalized, ferrofluids) designed to achieve both target-specific diagnostics and therapeutics are emphasized together with proposed theoretical and experimental solving items. Specific characterization methodologies based on temperature and field dependent Mössbauer spectroscopy and SQUID magnetometry deserving an adequate magnetic characterization of the nanoparticulate systems in respect to phase composition, local and long-range magnetic structure, intra- and inter-particle magnetic interactions and mainly to the magnetic relaxation phenomena are underlined. The critical problem of the material dependent characteristic time τ_0 in a Neel type relaxation is also considered, due to its significant influence on the relaxation time. It is proven that a reliable value can be derived with accuracy only by combining dynamic methods of significantly different time windows, as for example a.c. susceptibility and Mössbauer spectroscopy, or by exploiting temporal dependencies of magnetization. Effects of inter-particle interactions (matrix mediated or dipolar) are also discussed. A specific attention is provided to the effects of inter-particle (dipolar type) interactions on the magnetic relaxation effects in magnetic fluids of different volume fractions. New methodologies for the correct evaluation of the specific absorption rate (SAR) from real experimental data taking into account also environmental loss factors are proposed. The whole range of heat transfer mechanisms involving large size distributions and strong inter-particle interactions are discussed as function of some relevant temperature-dependent physical parameters such as Neel and Brownian relaxation times.

It has been proven both experimentally and by micromagnetic simulations that the direct effect of the inter-particle dipolar interaction is not only an increased particle anisotropy energy but also a decrease of the characteristic time constant τ_0, with direct influence on the efficiency of the heat transfer during potential hyperthermia treatments.

Transformation Mechanisms of Ferrates - Impact on Their Application in Water Treatment

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Ferrates are a general name for compounds with the iron in higher oxidation states, i.e. Fe(IV), Fe(V) and Fe(VI). In recent years, the ferrates attract increased attention due to their potential for water treatment and environmental remediation technologies. Ferrates alone can transform under high temperature [1,2], humid air [3] or in water. These transformation processes limit the applicability of ferrates from the point of view of storage and effectiveness of their oxidative reactions with other species in water. Kinetics and mechanism of ferrates transformation depend on many parameters such as temperature, humidity of air, presence of CO_2 in air, presence of inorganic buffering ions in water. ^{57}Fe Mössbauer spectroscopy has been applied as a powerful experimental technique for studying the transformation mechanisms under various physicochemical conditions. The both ex-situ and in-situ approaches were used. The transformation mechanisms in liquids were studied by Mössbauer spectroscopy of frozen solutions. While thermal decomposition of potassium ferrate(VI) leads to reduction of Fe atoms ending by the formation of $KFeO_2$, the transformation of ferrates in solution is based on the both reduction of Fe atoms and charge disproportionation caused by electron transfers. Kinetics and transformation of ferrate(IV), ferrate(V), and ferrate(VI) differ significantly. An example of Mössbauer spectrum, which was obtained by a transformation of sodium ferrate(IV) in ethanol, contains components related to Fe(III), Fe(IV), Fe(V), and Fe(VI) together (Fig. 1). Examples of successful degradation of iodide, phosphates, and arsenic from water by using of ferrates will be presented from the view of the application of Mössbauer spectroscopy.

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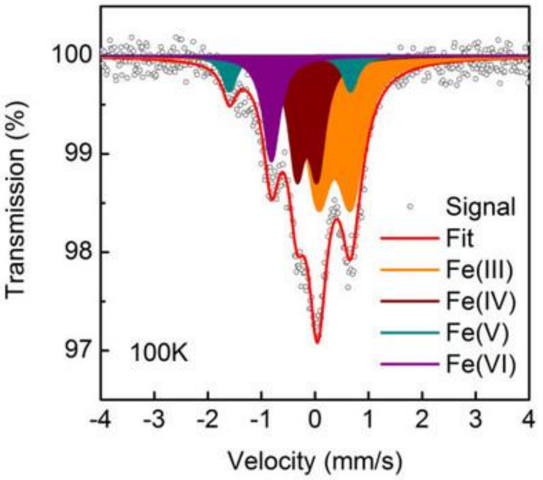

Fig. 1 Mössbauer spectrum of the solution frozen after 300 s of reaction of Fe(IV) in ethanol.

Studies on Thin Iron-Oxide films as Components for Spintronics Devices using Conventional and Synchrotron-Radiation Mössbauer Spectroscopy

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The needs to investigate local magnetic properties of very thin magnetic layers and their interfaces often appear in the field of magnetic recording and spintronics. Mössbauer spectroscopy, which can detect local electronic states around nuclei, can be a powerful tool for these purposes. When Mössbauer spectroscopy is applied to thin films or nanostructures prepared on thick substrates, conversion electron Mössbauer spectroscopy with a radioactive source is usually used in laboratories. With this method, however, it is relatively difficult to perform measurements at special sample conditions, such as at very low temperatures and in magnetic fields. Besides, more and more sensitivity has been required for very thin films and patterned nanostructures prepared on substrates. Synchrotron-radiation Mössbauer spectroscopy has made it easy to measure Mössbauer spectra of thin films in low and high temperatures [1], under external magnetic field [1], and under electric current flow [2]. It has also become possible to study the direction of magnetic moments (parallel or antiparallel) using circularly polarized synchrotron-beams [3]. Thus synchrotron-radiation Mössbauer spectroscopy is a promising method which makes Mössbauer spectroscopy more attractive for researchers in magnetic thin films and nanostructures. In this presentation, examples of the studies on magnetic thin films using conventional conversion electron Mössbauer spectroscopy and synchrotron-radiation Mössbauer spectroscopy are demonstrated. The samples introduced here are exchange-coupled Fe/Fe_3O_4 bilayer films and impurity-doped α-Fe_2O_3 films. These are well-known old materials with a lot of published Mössbauer studies, but the studies on thin films of these materials revive as a promising ingredient for novel magnetic recording and spintronics. The Mössbauer spectroscopy here is a powerful tool to study buried interfaces, very thin antiferromagnetic films, and so on.

Acknowledgment:
The studies on spintronics-related oxide films were performed under the collaborations with Dr. H. Yanagihara (Univ. Tsukuba), Dr. E. Kita (Univ. Tsukuba), Dr. T. Nozaki (Tohoku Univ.), Dr. M. Sahashi (Tohoku Univ.), and Dr. M. A. Tanaka (Nagoya Inst. Tech.). The synchrotron radiation experiments were performed in collaboration with Dr. T. Mitsui (JAEA) and M. Seto (Kyoto Univ.) at the beam lines BL11XU, SPring-8.

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Poor Man's Big Bang: Lessons Learnt from After-Effect Studies with Mössbauer Emission Spectroscopy

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The electron capture (EC) of ^{57}Co feeds the 136.5 keV excited state of ^{57}Fe. The daughter iron ion has a hole in the K or L shell that recombines on the 10^{-14} s scale. This may happen by the emission of X-rays or of Auger electrons. In the latter case, further vacancies are created in the electron shell leading to highly ionized Fe ions. As a rule, within much less than 10^{-9} s, the surrounding crystal lattice returns to thermal equilibrium. Conventional Mössbauer experiments show the charge and spin state of the nucleogenic atom in the time range of about 2×10^{-8} s < t < 10^{-6} s after the EC, corresponding to the 1.41×10^{-7} s lifetime of the 14.4 keV level populated 1.3×10^{-8} s after the EC. Due to the fast relaxation, anomalous lattice states cannot be observed in the Mössbauer spectrum. In contrast to this, the electrons may or may not be thermalized by the time window of the Mössbauer measurement depending on the properties of the system. Therefore, in a Mössbauer emission experiment showing directly non-equilibrium states in the 2×10^{-8} s < t < 10^{-6} s range, one may indirectly look for signatures of precursor states and processes getting, thereby, closer and closer to the moment of the EC. Reviewing these studies from the past four decades is the subject of the present contribution. Under favourable conditions, short-lived (10^{-10} s < t < 10^{-8} s) electronic excitations and their relaxation processes not directly contributing to the spectrum can be studied in detail. Examples are long-lived low-energy electronic excitations of Fe^{3+} ions after the EC of ^{57}Co observed in ^{57}Co-doped LiNbO$_3$ and LiTaO$_3$. The initial populations of the Zeeman-split sublevels of the $^6A_{1g}$ ground state of Fe^{3+} ions are different and depend on the relative direction of the magnetic field relative to the crystallographic *c*-axis [1]. Analysis of the radiationless transition probabilities within the precursor states allowed for determining the properties of those states in much detail. A great variety of after effects could be observed in ^{57}Co-doped MgO by Tuczek et al. Non-equilibrium population of the spin states was investigated by the Mainz group using the coincidence technique. Aliovalent charge states are formed 10^{-14} s < t < 10^{-10} s after the EC when the electron hole in the inner K or L shell moves outward via radiative (X-ray) or non-radiative Auger-processes. Processes in this early stage can be indirectly monitored by correlating the quantity of aliovalent ions with the concentration of acceptors and donors in the vicinity of the nucleogenic atom. The crucial parameter of the model of competing acceptors is the electron-capture distance of the traps. A study on Mg- and Fe-doped LiNbO$_3$ shows that this distance is as low as (2.7±1.4) nm clearly showing that the main actors of the process are the 600 eV rather than the 6 keV Auger electrons [2]. A slightly modified version of the same model fairly well describes the formation of aliovalent Fe^{1+} in ZnSe [3].

Comparison between Mössbauer and X-Ray Absorption Spectra in Novel Spin-Crossover Complexes

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Transition-metal complexes bridged by ligand molecules have attracted much attention for their cooperative interaction by changing their spin states between low-spin (LS) and high-spin (HS) states, which brings the interesting physical and chemical phenomena. Controlling of ligand fields by changing coordination polymers is also one of the most fascinating subjects in molecular magnetism. Here, we focus on the two-dimensional Hoffman-type spin crossover (SCO) complexes such as $Fe(pyridine)_2Ni(CN)_4$ [1] and Fe(4*halogen*-py)$_2[Fe(CN)_2]_2$ [2]. The SCO phenomena in Fe^{2+} ($3d^6$) sites can be detected by several methods such as Mössbauer, X-ray absorption, EPR, IR, UV/vis spectroscopies and magnetic susceptibility measurements. Because the structural changes with the increase of the bond distances between metal and ligands of 0.01-0.025 nm bring the transitions between HS to LS states, both electronic states and bond distances have to be probed explicitly by the element-specific analyses. We performed the x-ray absorption fine structure (XAFS), extended XAFS (EXAFS), and Mössbauer spectroscopy for these SCO compounds depending on temperature through the HS-LS transitions.

Temperature-dependent spectral changes include the thermal broadening, in general. Debye-Waller factors have to be considered in the analyses of both Mössbauer and XAFS spectra. The structural form factor is written as functions of temperature and Debye temperature , which represents the viscosity of the molecules, and is analysed by the fitting of the spectral area of Mössbauer spectra. Analysis of XAFS spectra also depicts the Debye-Waller factor. These analyses reveal that is estimated to be approximately 100 K from the spectral fitting of both HS and LS states for these complexes.

In the presentation, I will discuss the temperature-dependent electronic structures of SCO complexes by means of XAFS and Mössbauer spectroscopy.

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Mössbauer Spectroscopy of Hemoglobins and Ferritins: Recent Advances in Biophysical and Medical Research

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Hemoglobins and ferritins are two vitally important iron-containing proteins. Hemoglobins (tetrameric and monomeric) are responsible for molecular oxygen transport and storage. Ferritins are iron storage proteins. There are a large variety of these proteins with corresponding variations of protein structure and functions during the course of evolution. In case of some molecular diseases, structure and functions of these proteins can be changed reflecting pathological processes. The ^{57}Fe as a natural label in these proteins could reflect some changes in the structure of local microenvironment related to the functional features of hemoglobins and ferritins. Therefore, ^{57}Fe Mössbauer spectroscopy is a useful probe for these proteins to study in the normal and pathological processes. We applied Mössbauer spectroscopy with a high velocity resolution to study several normal tetrameric and monomeric hemoglobins with different molecular structure and functions as well as hemoglobins from several patients with blood malignancy. Revealing variations in Mössbauer parameters were related to such small structural differences in these hemoglobins. Study of ferritin and its analogous demonstrated anomalous temperature dependences of some Mössbauer parameters with temperature decrease down to 90 K permitted us to consider heterogeneous iron core model for the fit of Mössbauer spectra of ferritins and its analogues in the paramagnetic state. Different content of ferritin-like iron was observed in spleen and liver tissues from several patients with blood system malignancy as well as some structural variations in the ferritin iron cores in spleen and liver were suggested for pathological cases.

Acknowledgements

This work was supported in part by the Ministry of Education and Science of the Russian Federation (Project No. 2085).

Magnetic Relaxation in Super Spin Glass Systems – Search for High Temperature Memory Effects

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Magnetic memory effect is among the most intriguing phenomena encountered in the magnetic materials with the broken ergodicity. In general sense, ergodicity becomes ‘broken’ as a consequence of disorder and/or frustration (due to competition/mixture in interactions) in magnetic systems. Magnetic relaxation time scale of such systems becomes comparable with the observation time over which properties are measured, leading to the appearance of nonequilibrium dynamics and unusual magnetic relaxation phenomena such as aging, rejuvenation or memory effects. In particular, the origin of these phenomena in nanoparticle systems is due to the effect of interparticle interactions which depends on particle concentration and degree of agglomeration. In addition, the strength of interparticle interactions in nanoparticle system strongly depends on chemical composition and morphology (size, shape and structure of nanoparticles) and can be successfully tuned by a proper choice of the synthesis method as well as variation of different chemical parameters during the synthesis process. In comparison to canonical spin glasses or other glassy systems, the additional advantage of nanomaterials stems from the fact that memory effects can be observed at higher temperatures. Recently, it was showed that memory effect could be used for storing digital information into material, i.e. as a thermal memory cell [3], in which a bit of digital information was successfully stored by pure thermal manipulation. Thermal inscription of information employed a specific temperature-time procedure, which involved continuous cooling with isothermal waiting time periods in the absence of any externally applied magnetic or electric fields. Used materials showed transition to a glassy state at relatively low temperatures, thus restricting the usage of such cell to temperatures below 40 K. The application of magnetic nanoparticles with high freezing temperatures could provide the basis for the development of thermal memory cells that operates at higher temperatures. Presentation of experimental results of our group will comprise reports on the synthesis of several strongly interacting nanoparticle systems that showed memory effects above 80 K. Recent studies were based on the investigation of poorly crystalline iron oxide nanorods, obtained by thermal decomposition of iron oxalate precursor [1], while earlier works were focused on the glassy behaviour of mixed valence manganite obtained by mechanochemical milling [2] as well as strongly interacting maghemite particles. Novel efforts are focused toward the synthesis of large monodomain FeCo and FeCoNi nanoparticles, with the spin glass like transition at much higher temperatures. Memory effects and magnetic aging in the above listed nanoparticle systems were thoroughly investigated by employing SQUID magnetometry in specific experimental procedures and protocols, in both DC and AC magnetic fields.

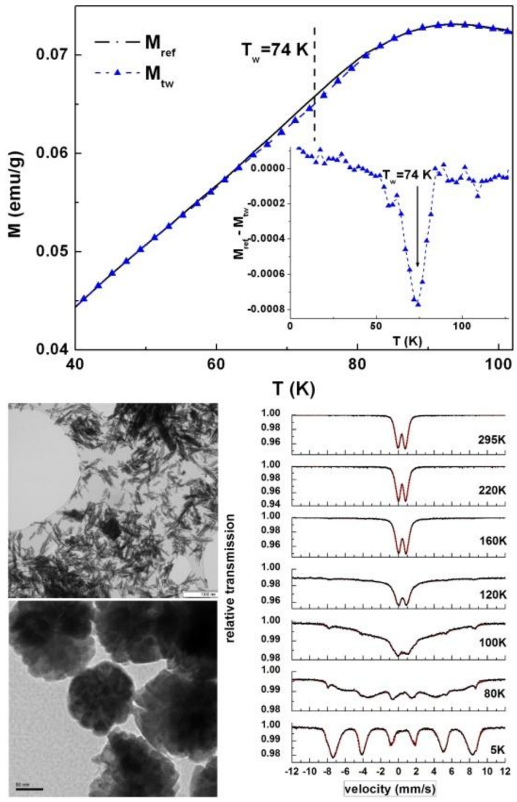

Fig.1 Zero Field Cooled memory effect at the waiting temperature Tw = 74 K (for waiting time tw = 3 h) in iron oxide nanorod system. Mössbauer spectra show magnetic relaxation of the sample in a wide temperature interval.

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Structural Disorder Phenomena in Nanostructured Oxides

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Because of their sensitivity to medium- and long-range structural order, diffraction techniques lose much of their resolving power in nanoscale & structurally disordered (amorphous) systems [1]. The important impact of the present work from the methodology point of view is an extensive employment of nuclear spectroscopic techniques – Mössbauer spectroscopy and multi-nuclear magnetic resonance (NMR). As these spectroscopic methods make observations on a local scale possible, valuable insight into the atomic and electronic structures (the short-range disorder effects) as well as into the dynamic and kinetic processes in nanostructured oxides is provided. By probing, in a quantitative way, the local environment of Mössbauer- and/or NMR-active nuclei in nanooxides, quantitative information on their (*i*) nonequilibrium cation distribution, (*ii*) canted spin arrangement, (*iii*) metastable nearest-neighbor atomic configuration, and (*iv*) deformation of the polyhedron geometry is obtained. Selected examples of the magnetic behavior of nanooxides are presented, which are discussed in terms of a competition between the effects of spin canting and site exchange of cations in the near-surface layers of nanoparticles [2].

Acknowledgment:
This work was supported by the DFG (SE 1407/4-1) and the VEGA (2/0097/14). The author is indebted to Professor Philipp Gütlich for encouraging and supporting interest in his work.

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Ferrites in Sustainable Energy and Environmental Remediation: Mössbauer Spectroscopy Characterization

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In recent years, ferrites, iron(III) oxide compounds, have been studied extensively because of their potential applications in high-density magneto-optic recording devices, gas sensors, color imaging, and semiconductor photocatalysis for water remediation [1]. In the past few years, we have studied the alkali and alkaline earth metal ferrites (*e.g.* $KFeO_2$, $CaFe_2O_4$, and $CaFe_2O_4$) and transition metal ferrites ($Ag_2Fe_2O_4$, $FeFe_2O_4$, and $CuFe_2O_4$) due to their involvement in synthesizing high-valent iron oxo compounds (e.g. ferrates, Na_2FeO_4 and K_2FeO_4) and in carrying out photocatalytic processes to oxidize pollutants under visible light [2]. In the presentation, synthesis of different kinds of ferrites will be first given, followed by their stability and characterization by surface analysis techniques and low-temperature and in-field ^{57}Fe Mössbauer spectroscopy. A heating of natural waste ferrihydrite and KNO_3 precursors forms $KFeO_2$, which on decomposition converted to monodisperse superparamagnetic maghemite (γ-Fe_2O_3) nanoparticles [3]. In the second part of the presentation, the applications of ferrites in generation of hydrogen and methane and in remediation of metals will be elucidated. Significantly, γ-Fe_2O_3 nanoparticles, produced from $KFeO_2$, can be efficient as magnetic sorbents for removing metal ions (*e.g.* arsenic and copper) in water. Interestingly, an addition of solid $KFeO_2$ into As(III) and Cu(II) ions containing water resulted in rapid coagulation of iron(III) hydroxides, which were efficient to remove As(III) and Cu(II) ions (Fig. 1). Furthermore, this efficiency was more than the sorption of Cu(II) ions onto the pre-formed maghemite nanoparticles (see Fig. 1) [3].

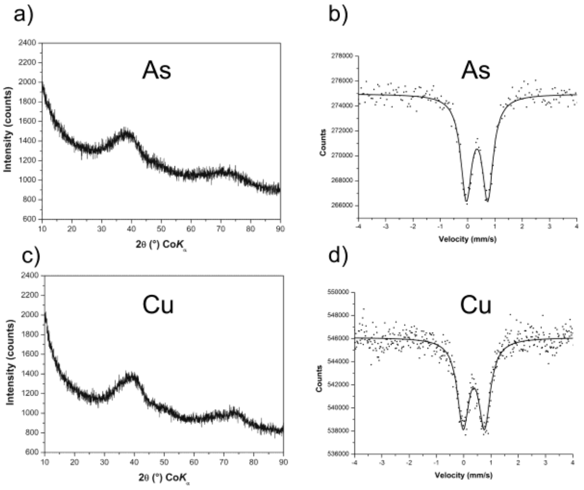

Fig. 1. XRD and Mössbauer spectroscopy characterization of samples obtained after the sorption experiments with As (a), (b), and/or Cu (c), (d).

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Application of Synchrotron Radiation Mössbauer Spectroscopy to Samarium Compounds

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Synchrotron radiation (SR) Mössbauer spectroscopy in principle enables us to carry out Mössbauer spectroscopy in all the known Mössbauer isotopes [1]. This means that Mössbauer spectroscopy can be carried out without preparation of any radioactive sources. Mössbauer spectroscopy using Sm isotopes were reported in several isotopes [2]. One of the popular isotopes is ^{149}Sm. Preparation of the radioactive source for ^{149}Sm Mössbauer spectroscopy required accelerators which can provide proton beams, because a (*p*, 2*n*) reaction is needed to make ^{149}Eu for ^{149}Sm Mössbauer source [3]. Meanwhile, many of works using ^{149}Sm nuclear resonant scattering were reported, which is one of the applications of ^{149}Sm Mössbauer effect using SR sources. This means it is easy to excite ^{149}Sm nuclei using synchrotron radiation.

Importance of valence degrees of freedom is one of the recent topics in solid state physics [4]. Much attention has been paid to the valence state in Sm intermetallic compounds for recent times on viewpoint of quantum criticality due to valence fluctuation. ^{149}Sm SR Mössbauer spectroscopy is a complementary technique to X-ray absorption spectroscopy near Sm absorption edges in determination of Sm valence states. We have carried out SR Mössbauer spectroscopy using ^{149}Sm nuclei in some samarium compounds. Thanks to employment of an electron yield method using avalanche photo diodes [5], we succeeded in observing ^{149}Sm SR Mössbauer spectra very rapidly [6]. We will present our recent development of SR Mössbauer spectroscopy using ^{149}Sm nuclei.

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Thermal and Optical Spin-State Switching of Surface-Adsorbed Iron Complexes

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In the last years we have explored various methods of depositing spin-switchable transition-metal complexes on surfaces. The complexes [Fe(bpz)$_2$(bipy)] and [Fe(bpz)$_2$(phen)] (bpz = dihydrobis(pyrazolyl)borate; Figure 1) could be deposited on various substrates from the gas phase, leading to the first high-quality films of Fe(II) complexes that exhibit both thermal spin crossover (SCO) and light induced spin state switching (LIESST) below a critical temperature TLIESST.[1]

Ultrathin (~7 nm) films of [Fe(bpz)$_2$(phen)] on Au(111) were further investigated using valence-band photoemission spectroscopy. The spin state of these molecules was determined as a function of temperature. Furthermore the influence of an external light source on the spin state was investigated at low temperatures. Light-induced (LIESST) as well as the vacuum UV-induced excited spin state trapping (VUVIESST) were observed at or below TLIESST. A dynamic population of the high-spin state was achieved at temperatures higher than TLIESST through irradiation with 532 nm light.[2]. By thermal evaporation also mono- and submonolayers of [Fe(bpz)$_2$(phen)] could be prepared. Through high-resolution STM applied at 5 K reversible electron-induced excited spin state trapping (ELIESST) was observed in single molecules of a double layer. Results of STS are compatible with DFT calculations which indicate a change of the HOMO-LUMO-gap from 2.1 eV in the low spin state to 0.4 eV in the high-spin state.[3]

An important prerequisite for spin-state switching of surface-deposited transition-metal complexes is the retention of the geometric structure. On Au(111) partial decomposition of the SCO complexes takes place[3]. On the other hand, the molecules stay intact on HOPG, where full thermal SCO and LIESST are observed for a submonolayer through NEXAFS.[5]

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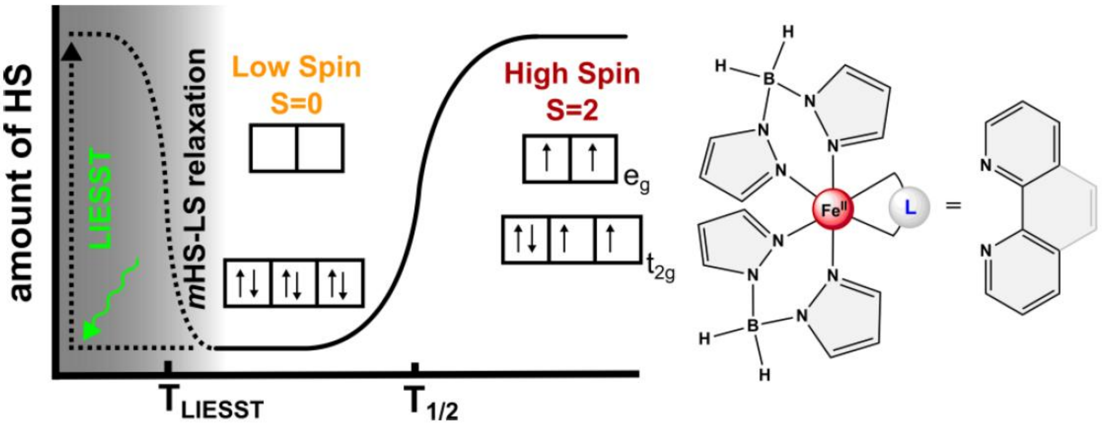

Fig. 1 Spin state switching in [Fe(bpz)$_2$(bipy)] and [Fe(bpz)$_2$(phen)].

Mössbauer Probed the Cationic Distribution of Spinel Oxides with Well Controlled Morphology as Electrocatalysts

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The morphologically and compositionally controlled synthesis of coordination polymers and spinel oxides are highly desirable for realizing new advanced nanomaterial functionalities. In this presentation, we report a novel and scalable strategy, containing a “copolymer-co-morphology” conception, to shape-controlled synthesis of various types of Prussian blue analogues (PBAs). Three series of PBAs $M_yFe_{1-y}[Co(CN)_6]_{0.67}$•$nH_2O$ (M_yFe_{1-y}-Co, M = Co, Mn and Zn) with well-controlled morphology have been successfully prepared through this strategy. Using Mn_yFe_{1-y}-Co PBAs as the model, by increasing the relative content of Mn, series of porous spinel $Mn_xFe_{1.8-x}Co_{1.2}O_4$ nano-dices with well-inherited morphology, similar crystallite size and high specific surface area could be obtained. ^{57}Fe Mössbauer spectroscopy provides an excellent tool for probing the cation distribution in the as-prepared spinel oxides, from which, a definite ratio of Fe^{III} at A and B-site of the spinel oxides was determined and the most possible cation distribution of the $Mn_xFe_{1.8-x}Co_{1.2}O_4$ nano-dices was estimated. When evaluated as electrocatalyst, the octahedral-site Mn^{III}/Mn^{IV} content was discovered to be directly correlated with the oxygen reduction/evolution reactions activity. We anticipate that our “copolymer-co-morphology” conception will be beneficial for morphologically controlled syntheses of other types of coordination polymers and double oxides. In addition, the series of $Mn_xFe_{1.8-x}Co_{1.2}O_4$ nano-dices may give us great opportunity for in-depth exploration of the relationship between the structure and catalytic performance of spinel oxides.

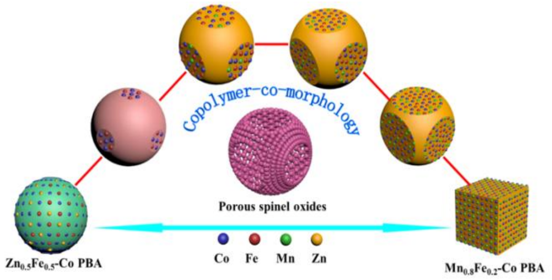

Fig. 1 “Copolymer-co-morphology” conception for shape-controlled synthesis of Prussian blue analogues and as-derived spinel oxides.

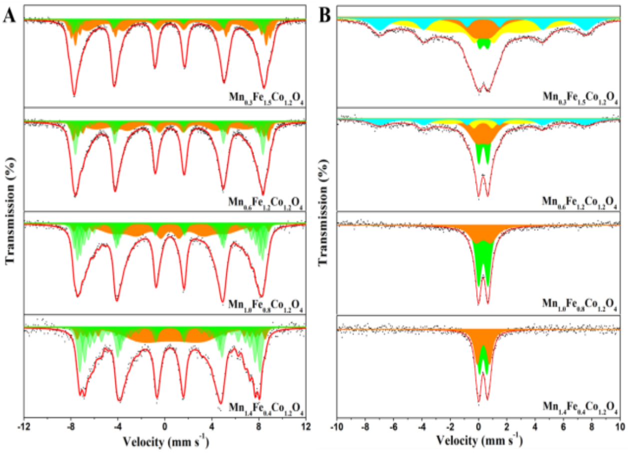

Fig. 2 Low and room temperature ^{57}Fe Mössbauer spectra of $Mn_xFe_{1.8-x}Co_{1.2}O_4$ nano-dices fitted follow the binomial distribution of the iron and non-iron cations.

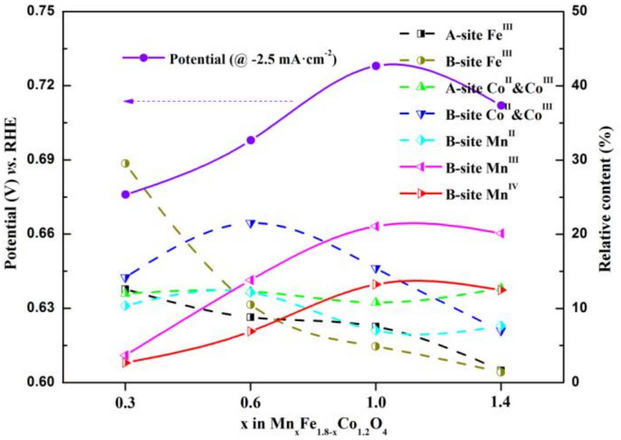

Fig. 3 Structure-function correlations between the oxygen reduction reaction activities and the relative contents of A-site or B-site cationic ions of $Mn_xFe_{1.8-x}Co_{1.2}O_4$ nano-dices.

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Nuclear Inelastic Scattering as a Tool for the Investigation of Spin Crossover Fe(II) Complexes

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Nuclear inelastic scattering (NIS) also called nuclear resonant vibrational spectroscopy (NRVS) is a synchrotron radiation based spectroscopy which is related to the Mössbauer effect. NIS uses a Mössbauer active nucleus (e.g. ^{57}Fe) as a nuclear probe in order to detect dynamic processes. The only selection rule of this technique is that it requires a non-zero projection of the displacement of the nuclear probe onto the direction of the synchrotron beam. NIS can be used to detect vibrations in the energy range from a few up to 1000 cm^{-1} and shows often much more vibrational features as compared to Raman and IR spectroscopy. A method that the can be applied parallel to NIS is nuclear forward scattering (NFS). These methods have been used nearly twenty years ago now and have become an important tool to characterise the Fe(II) spin crossover systems. In this talk I give a brief overview of the results obtained so far with particular focus on the combination of NIS results and DFT calculations as well as the application of NIS and NFS to single crystals and microstructured samples.

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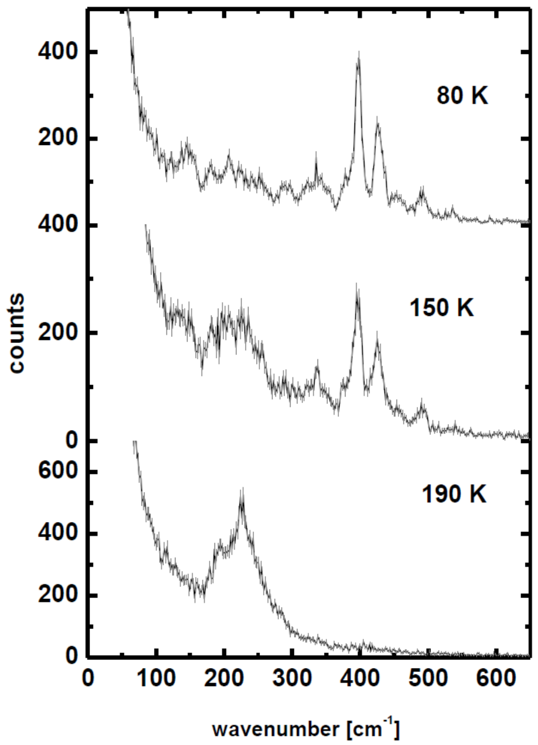

Fig. 1 Representative NIS spectra of spin crossover Fe(II) complex in low-spin (top) and high-spin (bottom) states and at transition temperature (middle)

Magnetism and Valence in the CsCl-Phases of EuO, EuS and EuSe at Extreme Pressures

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The magnetic properties and the valence state of initially divalent Eu-ions were probed in the Eu-chalcogenides EuO, EuS and EuSe in the CsCl-type (B2) high-pressure phases at pressures up to 120 GPa using ^{151}Eu nuclear forward scattering (NFS) of synchrotron radiation [1]. Together with previous data on EuTe [2], we present a magnetic phase diagram of EuX (X = O, S, Se, Te) in their B2-phases and compare it with the corresponding data in the NaCl-type B1-phases, studied most intensively with ^{151}Eu-Mössbauer effect and ^{151}Eu-NFS in the last decades [2–7]. Beside the magnetic ordering temperatures, important information is obtained on the Eu valence state and magnetic exchange mechanism from the observed isomer shifts and hyperfine fields, respectively. We observe for all EuX systems in the B2-phase ferromagnetic order, reaching T_C = 165 K for EuO at 75 GPa, followed by a decrease of T_C at higher pressures connected with the onset of mixed valence. EuS exhibits a steep increase of T_C with pressure, which saturates around 295 K at 120 GPa, connected with a mixed valence also saturating at v(IS) = ~2.5 at 120 GPa. For EuSe we observe an even steeper increase of T_C in the B2-phase starting from 110 K at 25 GPa and reaching T_C = 300 K at 77 GPa without any sign of saturation. These findings demonstrate that the strength of magnetic interactions, which is highest for EuO in the B1-phases, is now reversed in the B2-phases, being larger for the heavier chalcogen members. This behaviour is attributed to a strong ferromagnetic J_2 (Eu-X-Eu) exchange in the B2-phase, obviously enhanced by the covalency of the Eu-X bonds as well as by the different coordination and neighbour numbers, when compared to the B1-phase.

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Iron Films Deposited on Porous Alumina Substrates

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Properties of thin iron films are affected by the surface morphology of the films and the substrates [1]. In this study, the iron films were produced on porous alumina substrates, and the effects of pore size were investigated by Mössbauer spectroscopy. Porous alumina was produced by the anodic oxidation methods. An aluminum sheet (40 μm thick) and a carbon rod were employed as the electrodes. The anodization was conducted at 60 V for 60 min in a phosphoric acid solution (0.3 M) at various temperatures between 15 and 30 ºC, and the average diameters of pore were resulted in 160 to 250 nm. Arc deposition of iron was performed using the arc-plaza-gun (APG, ULVAC, ARL-300). The surface morphology was observed by scanning electron microscopy (SEM). Mössbauer spectra measured at room temperature of the iron films deposited onto the porous alumina are shown in the figure. The reduced thickness to α-Fe of the iron films was 150 nm. The Mössbauer spectrum of the iron film deposited on the porous alumina with 160 nm pores (Fig. a) was fitted into the combination of a sextet and a singlet, which were assigned to α-Fe and γ-Fe. The assignment was also confirmed by the XRD patterns. The iron film stacked on the flat surface of the substrate formed the α-Fe lattice, while the iron atoms penetrated into the nano-sized pores became γ-Fe. When the substrate had larger pore size (200 nm; Fig. b), the Mössbauer spectrum had a doublet and distributed hyperfine magnetic fields as well as α-Fe and γ-Fe. The doublet was assigned to iron oxide particles, and the distributed hyperfine magnetic fields attributed to large defects or rough surface of the α-Fe lattice because of the rough surface morphology of the porous alumina. The film produced on the porous alumina with the largest pore size (250 nm; Fig. c) did not have the component of γ-Fe. It was demonstrated that the surface morphology, especially pore size, changed the composition of iron films. γ-Fe was stabilized in the small pores.

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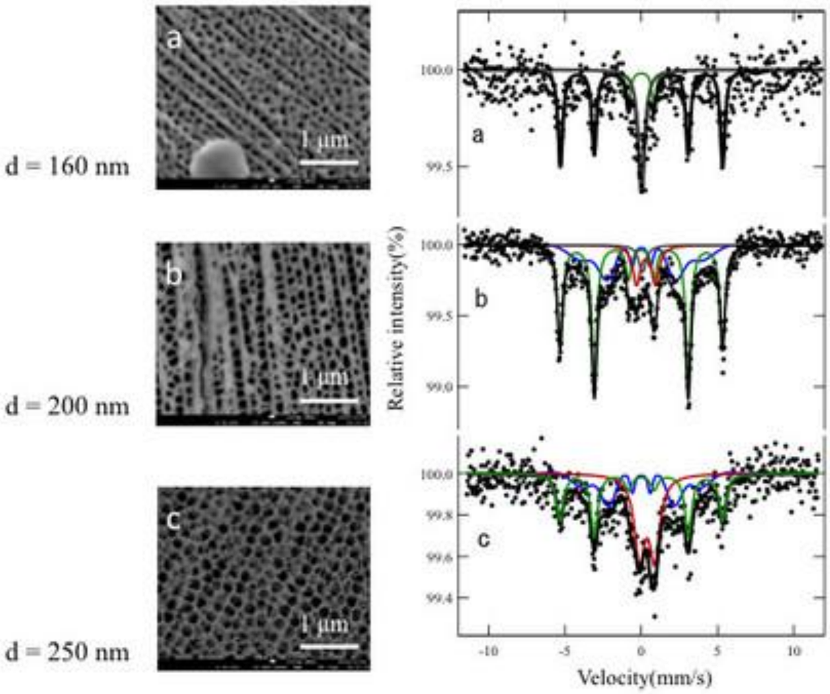

Fig. 1 SEM images (left) and Mössbauer spectra (right) of the iron films deposited on porous alumina. The average pore sizes were (a) 160 nm, (b) 200 nm, and (c) 250 nm.

ORAL PRESENTATIONS

Magnetic and Dynamic Properties of a σ-$Fe_{65.9}V_{34.1}$ Alloy

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Sigma (σ) phase $Fe_{65.9}V_{34.1}$ alloy was investigated by means of the Mössbauer spectroscopy. ^{57}Fe Mössbauer spectra were recorded in the temperature interval of 80-335 K. They were analyzed to get spectral parameters suitable for determining the Curie temperature, T_C, and the Debye temperature, θ_D. Concerning the former, the spectra were analyzed to get the hyperfine field distribution curves. By their integration, the average hyperfine field values, <B>, were calculated. Temperature dependence of <B> yielded T_C = 312 K. The Debye temperature was determined both from the temperature dependence of the average center shift, <CS>, as well as from the temperature dependence of the *f*-factor. The former gave θ_D = 403 K while the latter yielded θ_D = 374 K. The kinetic as well as the potential energies were revealed to grow linearly with temperature, and the rate of their increase was virtually the same i.e. the vibrations of Fe atoms are harmonic. The value of the force constant was determined.

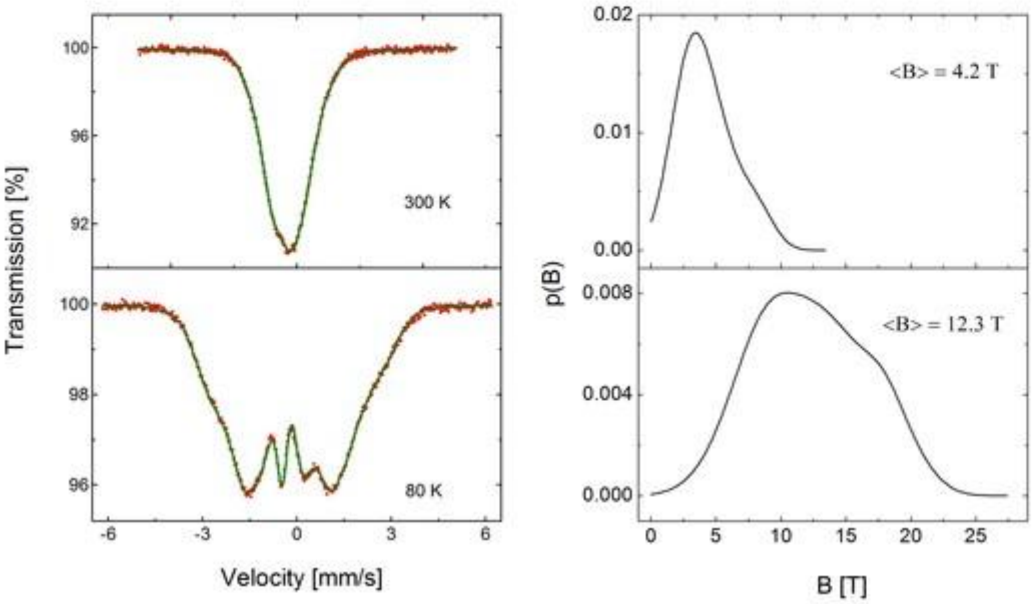

Fig. 1 (left) Examples of ^{57}Fe Mössbauer spectra measured on the σ-$Fe_{65.9}V_{34.1}$ alloy and (right) related hyperfine field distribution curves.

Structural Investigation and Hyperfine Interactions of $BaBi_xLa_xFe_{12-2x}O_{19}$ ($0.0 \leq x \leq 0.5$) Hexaferrites

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Barium hexaferrite, $BaFe_{12}O_{19}$, substituted by Bi^{3+} and La^{3+} ($BaBi_xLa_xFe_{12-2x}O_{19}$ where $0.0 \leq x \leq 0.5$) were prepared by solid state synthesis route. The effect of substituted Bi^{3+} and La^{3+} ions on the structure, morphology, magnetic and cation distributions of barium hexaferrite were investigated by X-ray powder diffractometry (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR) and Mössbauer spectroscopy. XRD powder patterns were refined by the Rietveld analysis method which confirmed the formation of single phase magneto-plumbite structure and the substitution of La^{3+} and Bi^{3+} ions into the lattice of barium ferrite. These results show that both La^{3+} and Bi^{3+} ions completely enter into barium hexaferrite lattice without disturbing the hexagonal ferrite structure. The EDX spectra confirmed the presence of all the constituents in expected elemental percentage. From ^{57}Fe Mössbauer spectroscopy data, the variation in line width, isomer shift, quadrupole splitting and hyperfine magnetic field values on Bi and La substitutions have been determined. Cation distribution in the presently investigated hexaferrite system was estimated using the relative area of Mössbauer spectroscopy.

Mössbauer Studies of Magnetic Nanoparticles for Biomedical Applications

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Magnetic nanoparticles (MNPs) have attracted great attention from many research fields. They have been found highly applicable and versatile in lithium ion batteries, supercapacitors, catalysis, labeling and sorting of cells, separation of biochemical products. Of particular interest is the use of MNPs for diagnostic magnetic resonance imaging, magnetic hyperthermia therapy and drug delivery.

In this paper we discuss some of the main features of MNPs. The review begins with an overview of magnetic property and single domain particles. The synthetic strategies developed for the generation of MNPs, with a focus on particle formation mechanism and recent modifications made on the synthesis of monodisperse samples of relatively large quantities are also discussed. Then, different methodologies for the protection and functionalization of the synthesized MNPs, together with the characterization techniques are explained. Finally, some of the recent biological applications of MNPs are reviewed, and some future trends and perspectives in these research areas will be outlined.

Studies of biocomposites was made by using different methods, but the main attention in this review was paid to Mossbauer spectroscopy (MS) because MS provides a unique information not available to other methods.

Improvement of bioactive properties and biocompatibility of created magnetic bioceramics due to using of matrix CHA which have excellent bio properties. It has been established that the introduction of a significant amount of the magnetic component does not significantly influence the phase composition of the bioactive CHA matrix at both structural and molecular levels and, hence, the initial high biocompatibility of CHA is retained. As a result, ceramic implants have been designed based on the carbonated hydroxyapatite (CHA) as the biologically active matrices. As magnetic components used modified hexagonal ferrite, spinel particles. Ferrite particles provided magnetic properties obtained bioceramics necessary for optimal magnetic therapy and thermal effects. The generation of heat in an alternating magnetic field created biocomposites meets magnetotherapy treatment.

Thus, the composite ceramics represents a new magnetic bioceramics that combine excellent biological activity of CHA and high magnetic characteristics of created magnetic particles of M-type hexagonal ferrite particles, Co-spinels.

Ferritin Nanoparticles in Biological Tissues

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Iron is an essential element for fundamental cell functions and a catalyst for chemical reactions. It can be found in human body mainly in the form of ferritin. Ferritin is a globular intracellular protein which serves as the major storage form of iron, since iron is the cell itself toxic. In addition, ferritin probably also facilitates iron transport to the place needs. This is because it is located in blood plasma, and is stored in the liver, spleen or bone marrow. Also primary iron storage protein is present in the cytoplasma of the cells and in small amounts also in the blood pool. It is one of the major proteins of iron metabolism [1]. Protein ferritin creates spherical formation with the size of 12 nm with the core of about 8 nm [2]. The iron accumulation originating from red blood cells in terms of their function predominantly occurs in the spleen and in the brain. It removes mainly particle-like material, old or damaged, own or foreign to the body. In case of excessive amount of iron in the spleen it is stored in cells in the form of hemosiderin [3] which is considered to be a proteolytic product of ferritin. In the current work, we focus on characterization of iron in biological tissues. We studied three types of samples prepared from human brain, human and horse spleen. Mössbauer spectrometry measurements were performed at room (~300 K) and liquid helium (4.2 K) temperature. A conventional constant acceleration spectrometer with ^{57}Co source in a rhodium matrix was used. The ferritin nanoparticles exhibit superparamagnetic behaviour due to their small dimensions at room temperature. The corresponding Mössbauer spectra show doublet-like patterns. Magnetic features of the investigated samples start to manifest themselves notably at low temperatures. Here, presence of magnetically split components was unveiled.

Acknowledgment:
This research was supported by projects MEYS No. LO1409 (CENAM) and VEGA 1/0836/15.

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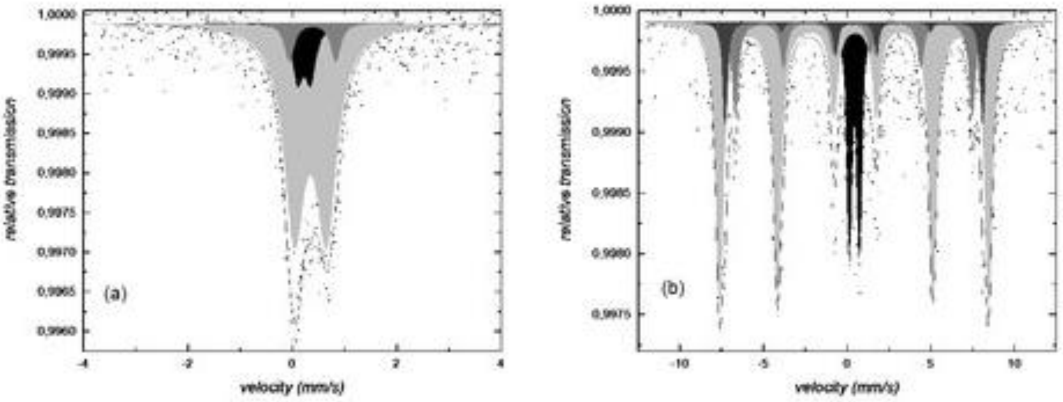

Fig. 1 Mössbauer spectra of brain tissue taken at 300 K (a) and at 5 K (b).

Mobility of Iron Ions in Porous Ferrisilicates

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Iron ions may be incorporated into two positions in porous ferrisilicates. They may occupy either framework-building tetrahedral (T) sites, or they may have only a secondary role by providing charge neutralization inside the pores (in extra-framework, EFW sites). Since iron may alter its oxidation state the siting may also be influenced by redox treatments. Ferric state is preferred in T sites thus they are less prone to respond to redox changes. In contrast, the $Fe^{3+} \Leftrightarrow Fe^{2+}$ conversions proceed more easily with EFW ions.

The applications of ferrisilicates are usually connected to their porous structure, hence the pores usually contain some other host molecules (water, organics, reactants, etc.). Thus a simple heating may result in redox changes on iron ions. Depending on the actual conditions, new iron containing species may form with altered compositions and charge, and they may be relocated. E.g. upon a simple evacuation neutral ferrous FeO may form from EFW ferric $Fe(OH)_2^+ \Rightarrow FeO + H_2O \uparrow + H^+$, then the formed neutral species may migrate. Another possibility is the T => EFW conversion. In catalytic processes dinuclear $Fe_T – O – Fe_{EFW}$ centres may also play role – they allow transfer of oxygen.

The distiction between T and EFW siting is rather strict for crystalline microporous structures. In the partly amorphous mesoporous structures this distinction is less sharp, the transormations proceed more easily. Various examples can be presented for the mentioned changes, one is shown in Fig. 1 recorded on a mesoporous MCM-41 ferrisilicate.

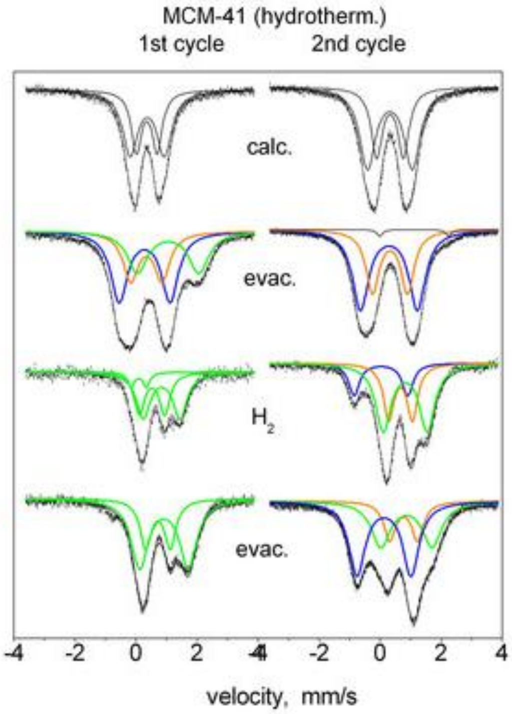

Fig. 1 Cycling of 350 °C treatments on mesoporous Fe-MCM-41 (calcination, evacuation, reduction calcination, blue: Fe^{3+} in T sites, brown: Fe^{3+} in EFW sites, green: Fe^{2+})

Observation of the Meissner Effect by the Mössbauer Effect in H_2S Superconductor at High Pressure

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High temperature superconductivity at high pressures has been predicted for numerous hydrides including H_2S [1]. Recent resistivity and magnetic susceptibility measurements indicated that a superconducting transition occurs in H_2S compressed to 150-190 GPa with a high onset temperature of 203 K [2]. However, measurements of the Meissner effect using SQUID or inductor methods at pressures above 130 GPa are difficult and experimental results do not allow a clear interpretation. For an unambiguous identification of the superconducting state a direct observation of the Meissner effect in an external magnetic field is desirable. Historically, the Meissner effect was defined as the expulsion of the external magnetic field from a superconducting sample as the sample enters the superconducting state with decreasing temperature.

We report on the direct observation of the expulsion of the magnetic field in H_2S compressed to 153 GPa [3]. A thin ^{119}Sn film placed into the H_2S sample volume was used as a sensor of the magnetic field inside the superconductor. The idea to use the Mössbauer isotope ^{119}Sn of nonmagnetic tin as a highly sensitive nuclear probe of the magnetic states in crystals was first suggested and developed in numerous works of the Moscow research group in the Institute of Crystallography RAS (see as an example Ref. 4). In the present study, the magnetic field at the ^{119}Sn sensor was monitored using nuclear resonance scattering of synchrotron radiation from the Mössbauer ^{119}Sn nuclei. Our results demonstrate (Fig. 1) that an external static magnetic field of about 0.7 Tesla is expelled from the volume of ^{119}Sn foil due to the shielding by the H_2S sample at temperatures up to 145 K, revealing a superconducting state of H_2S. The presence of the magnetic field at tin nuclei was identified by quantum beats in the time spectra of NRS. The resonant character of NRS ensures that we acquire data only from the ^{119}Sn sensor, with zero background from the sample environment.

Acknowledgements

Supports by Russian Scientific Foundation (# 14-02-00848) and Russian Foundation for Basic Research (# 14-02-00483a) are acknowledged.

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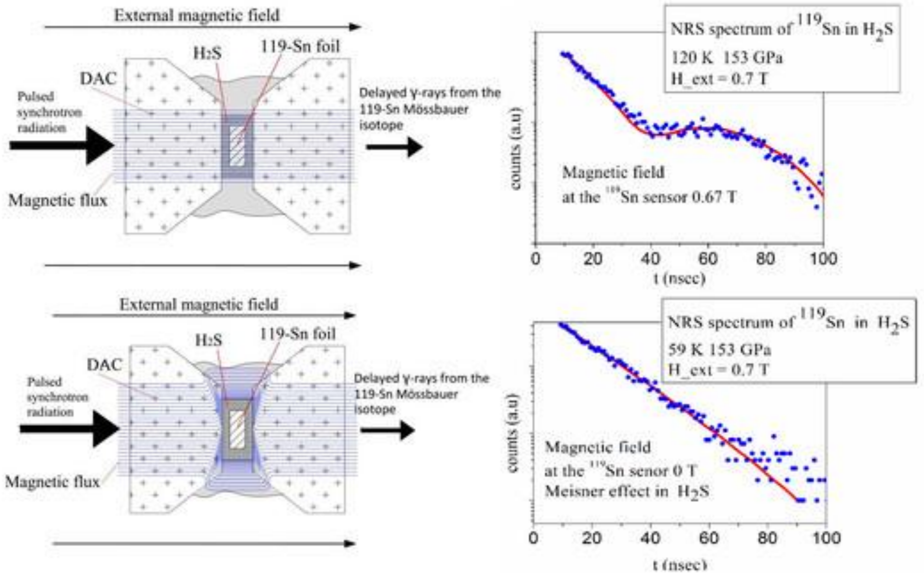

Fig. 1 The tin foil, surrounded by compressed H2S, is located in a diamond anvil cell at P = 153 GPa and an external magnetic field is applied. At T > Tc, the quantum beats in the NFS time spectra of 119-Sn indicate the magnetic splitting of tin nuclear levels. At T < Tc, the tin foil is screened from the external magnetic field by the superconducting H_2S, and no magnetic quantum beats are seen.

Mössbauer Spectroscopy of H, L and LL Ordinary Chondrites

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Ordinary chondrites are the most frequently found meteorites at the Earth. These meteorites consist of various iron-bearing phases such as olivine, pyroxene, troilite, metallic iron, chromite, etc. Ordinary chondrites were divided into three groups: H (high iron), L (low iron) and LL (low iron, low metal). Mössbauer spectroscopy is a useful tool for study iron-bearing phases in various meteorites, in particular, in ordinary chondrites. In the present work we consider the results of some H, L and LL ordinary chondrites investigation using Mössbauer spectroscopy with a high velocity resolution as well as optical and scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. Mössbauer spectra were fitted with spectral components related to corresponding iron-bearing phases. It was possible to reveal minor spectral components related to chromite, hercynite, ilmenite and paramagnetic taenite in the spectra of some meteorite samples. The estimated hyperfine parameters were used for comparison of H, L and LL ordinary chondrites and the same phases in different meteorites. The results obtained demonstrated variations in the phase composition in the studied ordinary chondrites as well as small variations in the hyperfine parameters of the same phases in different meteorites which could be related to small variations in the ^{57}Fe local microenvironment due to differences of ordinary chondrites formation.

Acknowledgements

This work was supported in part by the Ministry of Education and Science of the Russian Federation (Project No. 2085). Contribution to the study from A.A.M. was funded by the RFBR according to the research Project No. 16-32-00151 mol_a.

Substitution of Ga_2O_3 and GeO_2 for Fe_2O_3 in Conductive Barium Iron Vanadate Glass

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$15BaO\cdot 15Fe_2O_3\cdot 70V_2O_5$ glass showed an elevation of the conductivity (σ) from 1.0×10^{-7} to 4.0×10^{-2} Scm^{-1} (specific resistivity: 25 Ωcm) after the annealing at 460 °C for 30 min [1]. Increase in the σ was ascribed to the *structural relaxation* of the *3D*-network accompanying an increased probability of *small polaron hopping* from V^{IV} (or V^{III}) to V^{V}. Mössbauer study of heat-treated vanadate glass showed a decrease of quadrupole splitting (QS) of Fe^{III} from 0.67 to 0.60 (_0.02) mms^{-1}, which revealed a decreased distortion of FeO_4 and VO_4 units or *structural relaxation*. Heat treatment of $20BaO\cdot 10Fe_2O_3\cdot 70V_2O_5$ glass at 500 °C for 60 min resulted in an increase of σ from 2.8×10^{-6} to 4.3×10^{-2} Scm^{-1}. QS of this glass changed from 0.70 to 0.55 (_0.02) mms^{-1} after the annealing at 450 °C for 300 min [2]. Activation energy for the conduction (E_a) decreased from 0.38 to 0.13 (_0.01) eV by the annealing at 500 °C for 60 min [2], suggesting that E_a was involved with the energy gap between the donor level and the conduction band (CB) of the *n-type semiconductor model*.

Heat treatment of $20BaO\cdot 5ZnO\cdot 5Fe_2O_3\cdot 70V_2O_5$ glass at 450 °C for 30 min resulted in an elevation of σ from 2.5×10^{-6} to2.1×10^{-1} Scm^{-1} [3]. Mössbauer study of this glass showed a decrease of QS from 0.68 to 0.61 (_0.02) mms^{-1}. Similarly, $20BaO\cdot 5CuO\cdot 5Fe_2O_3\cdot 70V_2O_5$ glass showed a decrease of QS from 0.66 to 0.54 (_0.02) mms^{-1} in conjunction with the elevation of σ from 3.9×10^{-6} to 3.2×10^{-1} Scm^{-1} and a decrease of E_a from 0.16 to 0.10 (_0.01) eV [3]. It was concluded that “d-block elements” with an electron configuration of $3d^9$ or $3d^{10}$ in the outer-most orbital were preferable to the preparation of “highly conductive” vanadate glass [3].

Substitution of Ga_2O_3 and GeO_2 for Fe_2O_3 was investigated since Ga^{III} and Ge^{IV} atoms have the electron configuration of $3d^{10}$. *RT*-Mössbauer spectra of Ga_2O_3-substituted vanadate glass (Fig. 1) showed a decrease of QS from 0.69 to 0.52 (_0.02) mms^{-1}. After the annealing at 450 °C for 300 min, σ increased from 2.2×10^{-6} to 2.3×10^{-2} Scm^{-1}, which was one order of magnitude smaller than the σ’s of ZnO- or CuO-substituted glasses [3]. E_a of $20BaO\cdot 10Ga_2O_3\cdot 70V_2O_5$ glass decreased from 0.42 to 0.18 (_0.01) eV after the annealing at 450 °C for 120 min. The E_a of GeO_2-substituted glass also decreased from 0.42 to 0.20 (_0.01) eV, indicating that Ga^{III} and Ge^{IV} of “p-block elements” were less preferable to the preparation of “highly conductive” vanadate glass.

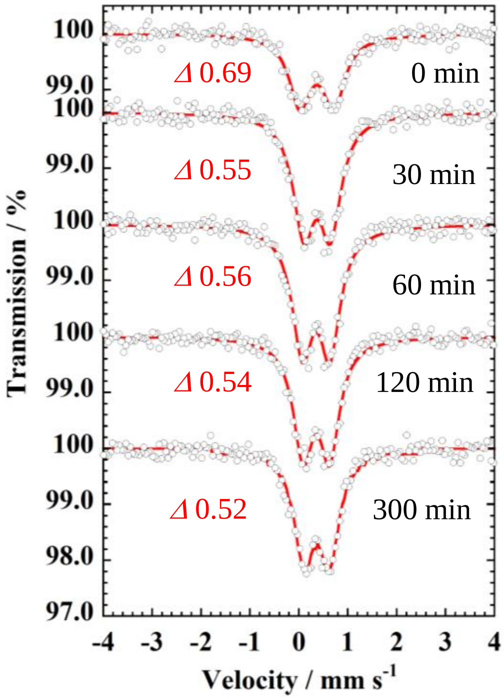

Fig. 1 *RT*-Mössbauer spectra of $20BaO\cdot 5Ga_2O_3\cdot 5Fe_2O_3\cdot 70V_2O_5$ glass measured after annealing at 450 °C.

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Electrical Conductivity and Local Structure of Aluminum-Containing Vanadate Glass

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Vanadate glass is known as a semiconductor having the electrical conductivity of 10^{-7}-10^{-5} Scm^{-1} caused by a step-by-step electron (polaron) hopping from V^{IV} or V^{III} to V^{V} [1]. $20BaO•10Fe_2O_3•70V_2O_5$ glass showed a remarkable increase in the conductivity from 10^{-6} to 10^{-1} Scm^{-1} after isothermal annealing at 500 °C [2]. Mössbauer study of the glass heat treated at 500 °C for 60 min showed a decrease of quadrupole splitting ($\varDelta$) of Fe^{III} from 0.70 to 0.55 mms^{-1}, which reflected the *structural relaxation* or *decreased distortion* of FeO_4 and VO_4 units constituting the 3D-network. Increase in the conductivity was ascribed to the *structural relaxation* in conjunction with an increased probability of small polaron hopping from V^{IV} or V^{III} to V^{V}. Nishida *et al*. revealed a marked decrease in the activation energy for the conduction (E_a) from 0.38 to 0.13 eV, and the substitution of CuO and ZnO for Fe_2O_3 resulted in higher conductivity than non-substituted vanadate glass [3]. It proved that smaller E_a and the electron configurations of $3d^9$ and $3d^{10}$ were preferable for the realization of higher conductivity.

In order to develop the conduction mechanism, $20BaO•xAl_2O_3•(10-x)Fe_2O_3•70V_2O_5$ glass (x = 0-10) was investigated. ^{57}Fe-Mössbauer spectrum of this glass (x = 5) measured before and after heat treatment at temperatures higher than glass transition temperature (T_g) or crystallization peak temperature (T_c) (Fig.1) showed a marked decrease of $\varDelta$ of Fe^{III} from 0.73 to 0.55 mms^{-1}, which reflected the *structural relaxation*. After the heat treatment at 450 °C for 100 min, the conductivity was increased from 1.4×10^{-6} to 4.7×10^{-3} S cm^{-1}, which was two-order of magnitude smaller than those of $20BaO•5ZnO•5Fe_2O_3•70V_2O_5$ (2.1×10^{-1} Scm^{-1}) and $20BaO•5CuO•5Fe_2O_3•70V_2O_5$ glasses (3.2×10^{-1} Scm^{-1}) heat treated at 450 °C [3]. After heat treatment at 500 °C for 100 min, a small decrease of E_a was observed from 0.23 to 0.18 eV. These results indicate that substitution of metal oxides of "p-block elements" for Fe_2O_3 is less effective for the realization of high conductivity, as recently observed in the case of Ga_2O_3- or GeO_2-containing vanadate glasses.

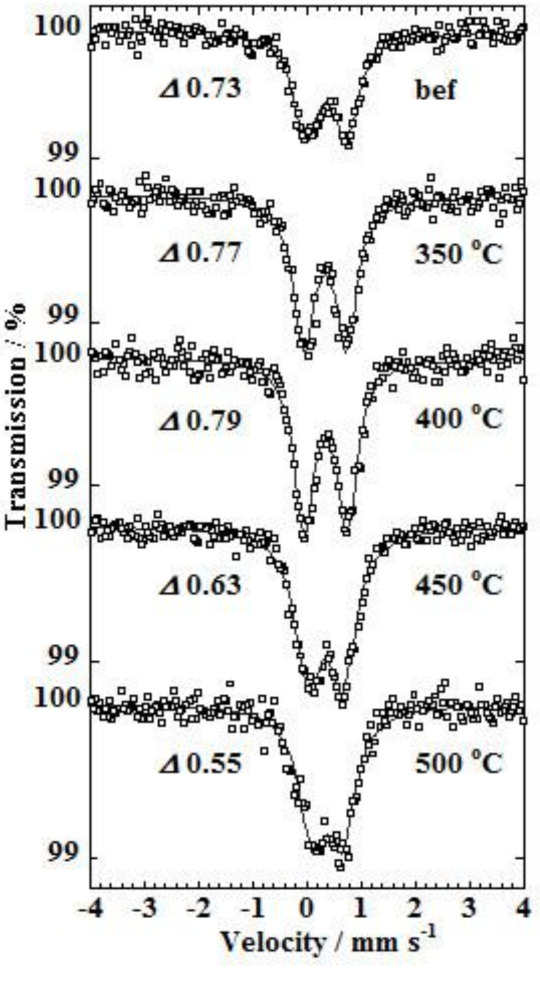

Fig. 1 ^{57}Fe Mössbauer spectra of $20BaO·5Al_2O_3·5Fe_2O_3·70V_2O_5$ glass recorded before and after heat treatment for 100 min.

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Local Structure and Magnetic Properties of Iron Phosphate Glass Prepared by Sol-Gel Method

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Phosphate glass is successfully applied to laser active material, optical material, cathode active material for LIB, *etc.* because it can incorporate substantial amount of rare earth metals [1]. It was reported that phosphate glass showed higher chemical durability when iron (Fe^{III}) coexisted [2,3]. Disadvantage for the practical use of phosphate glass lies in its higher melting temperature required for the sample preparation. In this study, a relationship was investigated between the local structure and magnetic properties of iron phosphate glass ($40Fe_2O_3{\cdot}60P_2O_5$, composition in mass%) prepared by sol-gel method. In a powder X-ray diffraction (XRD) study of the glass samples annealed for 2 h at 200, 300 and 400 °C, only a halo pattern was detected. After the isothermal annealing for 2 h at 500 and 600 °C, in contrast, a diffraction pattern due to α-Fe_2O_3 was detected. ^{57}Fe Mössbauer spectra showed only the absorption peak due to Fe^{III} before the annealing, while both Fe^{III} and Fe^{II} were observed after the annealing at 200, 300 and 400 °C (Fig. 1). Mössbauer spectra of $40Fe_2O_3{\cdot}60P_2O_5$ glass recorded before the annealing (Fig. 1) consisted of a doublet with isomer shift (IS) and quadrupole splitting (QS) of 0.31 and 0.56 mms^{-1}, respectively, reflecting the presence of $Fe^{III}O_4$ tetrahedra. Mössbauer spectrum of $40Fe_2O_3{\cdot}60P_2O_5$ glass annealed at 300 °C for 2 h consisted of two doublets; one with IS and QS of 1.11 and 2.39 mms^{-1}, respectively, ascribed to $Fe^{II}O_6$ octahedra and the other with IS and QS of 0.29 and 0.74 mms^{-1}, respectively, due to $Fe^{III}O_4$ tetrahedra. From the temperature dependency of the dc magnetic susceptibility, paramagnetic behavior was observed with an effective magnetic moment of 3.78 μ_B. A negative Curie-Weiss constant of -19.0 K was yielded, indicating an antiferromagnetic interaction occurring below 4 K.

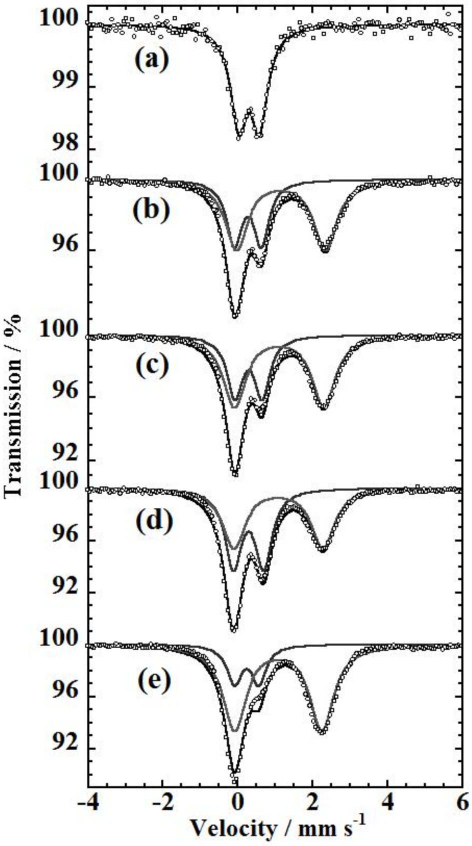

Fig. 1 ^{57}Fe Mössbauer spectra of $40Fe_2O_3{\cdot}60P_2O_5$ glass (a) before and after heat treatment for 2 h at (b) 200, (c) 300, (d) 400 and (e) 500 °C.

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POSTER PRESENTATIONS

Mössbauer Study of Iron Carbide Nanoparticles Produced by Laser Ablation in Alcohols

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Laser ablations of iron metal in alcohols were performed to produce iron carbide nanoparticles, and their Mössbauer spectra were measured. Productions of iron carbide nanoparticles [1,2] have been reported previously, but the reaction mechanism was not well understood. When increasing the number of particles floating in the solvent, further laser irradiation induces aggregation of the particles and photochemical reaction with the solvents. In order to reduce the effects of the laser irradiation on the product, we performed the laser ablation of iron metal in a circulating solvent, and filtering out the products during the laser ablation. The samples were measured by X-ray diffraction XRD, transmission Mössbauer spectroscopy, and transmission electron microscopy TEM.

The XRD pattern of the samples showed that the particles produced in methanol were the mixture of α-iron, γ-iron, and cementite, whereas the particles produced in ethanol were exclusively cementite. Mössbauer spectrum measured at room temperature of the sample produced in methanol (Fig. 1a) was fitted into a singlet, a doublet, and a broad absorption of the distributed hyperfine magnetic fields (DHMF), which were assigned to γ-iron, Fe/C amorphous, and small particles consisted of the mixture of iron carbide and α-iron, respectively. The spectrum of the particles produced in ethanol (Fig. 1b) showed the doublet of Fe/C amorphous and DHMF. The difference of the yields of metallic iron in two alcohols is attributed to the difference of the carbon supply of methanol and ethanol. TEM images of the particles showed that they have spherical shape but the size was not uniform, where the average particle size was 16 nm in both alcohols.

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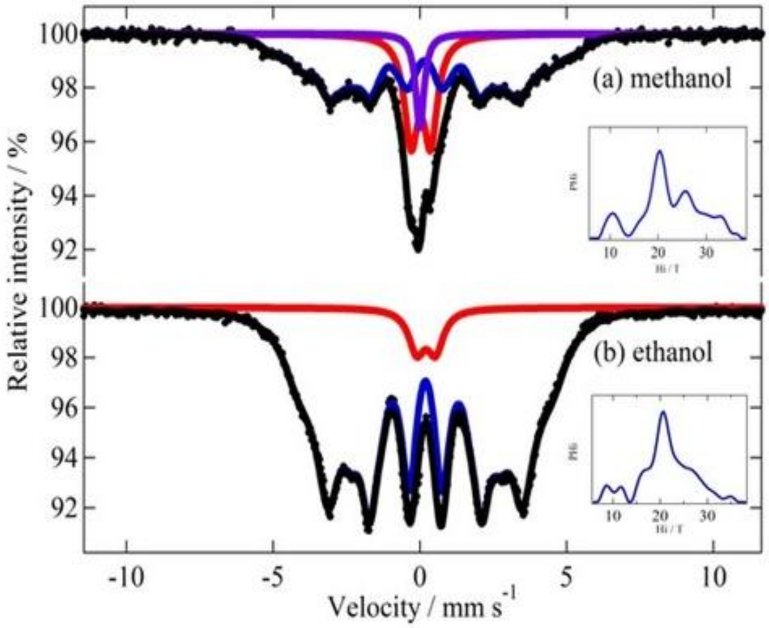

Fig. 1 Mössbauer spectra measured at room temperature of nanopaticles produced by laser ablation of iron metal in (a) methanol and (b) ethanol. The distributions of hyperfine magnetic fields are indicated on the right-hand.

Animal Model Study of Magnetic Nanoparticles Biodistribution by AC Susceptibility

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All materials intended for *in vivo* applications must pass number of specific tests, from biocompatibility and toxicity *in vitro* tests to biodistribution and pharmacokinetic *in vivo* studies on animals. Biodistribution results answer some very important questions: How long does injected material stay in blood circulation? What are the accumulation sites? How do external parameters, such as external magnetic field, influence behavior of your material? Various protocols for measuring biodistribution of different materials are commonly used. This paper presents one of alternative methods convenient for determination of biodistribution of magnetic nanoparticles [1,2]. The method is based on AC susceptibility measurements of animal tissues in question and uses the fact that paramagnetic and diamagnetic species naturally present in organism do not contribute to the imaginary part of susceptibility.

Acknowledgment:
This work has been supported by Ministry of Education, Science and Technological Development of the Republic of Serbia through the Project's Grant No. III45015.

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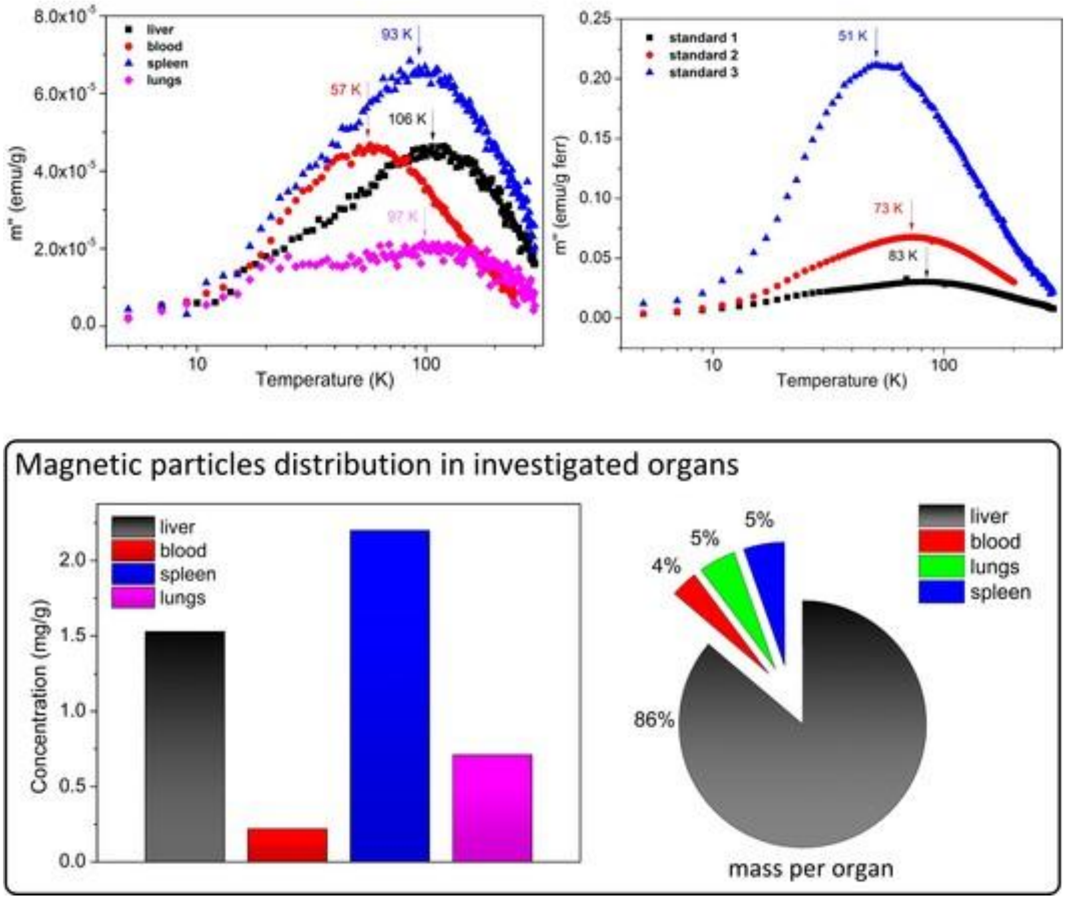

Fig. 1 Upper part: Imaginary part of magnetization of different tissues and standard samples. Lower part: Calculated mass and concentration of magnetic nanoparticles in tissues.

Mössbauer Analysis of the Mixed Olivines $LiFe_{0.9}Zn_{0.1}PO_4$

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The $LiFe_{0.9}Zn_{0.1}PO_4$ polycrystalline sample has been investigated by x-ray diffraction, vibrating sample magnetometer and Mössbauer spectroscopy. The crystal structure of the $LiFe_{0.9}Zn_{0.1}PO_4$ sample by using Rietveld refinement was determined to be orthorhombic (space group *P*nma) and the lattice constants are a_0 = 10.311, b_0 = 6.002, c_0 = 4.696 angstrom. The temperature dependence of zero-field cooled (ZFC) and field-cooled (FC) magnetization for $LiFe_{0.9}Zn_{0.1}PO_4$ under an applied field of 1000 Oe. The Néel temperature (T_N) of the sample is determined to be 48 K. The susceptibility curve of $LiFe_{0.9}Zn_{0.1}PO_4$ indicates that the sample antiferromagnetically ordered with decreasing T_N due to Zn substitution. Also, we observed that the change in slope below the spin reorientation temperature (T_S = 14 K). The Mössbauer spectra of $LiFe_{0.9}Zn_{0.1}PO_4$ were analyzed at various temperatures ranging from 4.2 to 295 K. The spectrum of sample was a fitted asymmetrical 8-line pattern which is considered by diagonalizing the 4x4 magnetic and quadrupole Hamiltonian matrix. The magnetic hyperfine field (H_{hf}) and electric quadrupole splitting (*delta* E_Q) values of the $LiFe_{0.9}Zn_{0.1}PO_4$ at 4.2 K were determined to be H_{hf} = 128.19 kOe, *delta* E_Q = 2.57 mm/s, the polar angle (theta) is 14 degree, the azimuthal angle (phi) = 0 degree, the asymmetric parameter (eta) = 0.9, the ratio of electric quadrupole interaction to magnetic dipole interaction R = 3.0. From these results, it can be explained that the change of Zn substitution can weaken superexchange interaction between the Fe ions.

Spin State Versatility in a Series of Fe_4 [2×2] Grid Complexes: Effects of Counteranions, Solvent and Intramolecular Cooperativity

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In the search of suitable molecules for miniaturized data storage and molecular electronics applications, [2 × 2] grid complexes composed of four metal ions and four compartmental ligand strands are discussed as promising candidates because such complexes can exhibit bi- or multistability based on a series of accessible redox or spin states. Spin-state switching exploits the so-called spin crossover (SCO) phenomenon, i.e., metal ions such as Fe^{II} (d^6) in octahedral ligand environment can undergo a transition from a high-spin (HS) to a low-spin (LS) state induced by an external stimulus. In this context, [2 × 2] grids have been proposed as attractive building blocks for potential application in molecular logic devices such as Quantum Cellular Automata (QCA), which encodes binary information (“0” and “1”) in elementary cells. If based on SCO transitions, QCA implementation requires a configuration with identical spin states at opposite corners of the grid (trans-[2HS-2LS]). Recently, we reported the new compartmental ligand 4-bromo-3,5-bis{6-(2,2′-bipyridyl)}pyrazole (HL^{Br}) and showed the formation of robust [2×2] grid complexes $[Fe^{II}_4L^{Br}_4]X_4$ with various counteranions ($X^- = PF_6^-$, ClO_4^-, BF_4^-, Br^-).[1] The grid $[Fe^{II}_4L^{Br}_4]^{4+}$ is stable in solution and according to Mössbauer spectroscopy features two high-spin (HS) and two low-spin (LS) ferrous ions in frozen MeCN. Six all-ferrous compounds $[Fe_4L^{Br}_4]X_4$ with different counteranions and different lattice solvent were structurally characterized by X-ray diffraction, and their magnetic properties were investigated by Mössbauer spectroscopy and SQUID magnetometry. Variations in spin state for the crystalline material range from the [4HS] via the [3HS-1LS] to the [2HS-2LS] forms, with some grids showing thermal spin crossover (SCO). The series of $[Fe^{II}_4L^{Br}_4]^{4+}$ compounds allowed to establish experimentally well-grounded correlations between structural distortion of the $\{FeN_6\}$ coordination polyhedra, quantified by using continuous shape measures, and the grid’s spin state pattern. These correlations evidenced pronounced cooperativity for the multi-step SCO transitions within the grid, imparted by the strain effects of the rigid bridging ligands, and a high stability of the di-mixed spin configuration *trans*-[2HS-2LS] that has identical sites at opposite corners of the grid. The results are in good agreement with recent quantum chemical calculations for such molecular [2×2] grid featuring strongly elastically coupled vertices.

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Lattice Dynamics, Phase Transitions and Spin Relaxation in $[Fe(C_5H_5)_2]PF_6$

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The organometallic compound Ferrocenium Hexafluorophosphate, $[Fe(C_5H_5)_2]PF_6$, has been studied by Mössbauer spectroscopy (MS), NMR, and X-ray diffraction by [1], mainly to determine the crystal structure at high temperatures (T). Here we present studies down to 95 K, Fig. 1. The spectral area under the resonance curve yields the recoil free fraction and thus the mean square of the vibration amplitude $<x^2>$, Fig. 2. For comparison the figure contains also the values obtained for Ferrocene $Fe(C_5H_5)_2$. For $[Fe(C_5H_5)_2]PF_6$ one observes a large discontinuity in slope at ≈ 210 K, indicative of a phase transition. The Mössbauer spectra which display a broad asymmetric absorption line at low T and a much narrower line at high T, were analyzed in terms of spin relaxation theory and yield accurately the hyperfine interaction parameters and the spin-spin and spin lattice relaxation rates in this paramagnetic compound, Fig. 3. The quadrupole interaction is small but certainly negative, ½eqQ = -0.12(2) mm/s, which causes the asymmetry in the spectra.

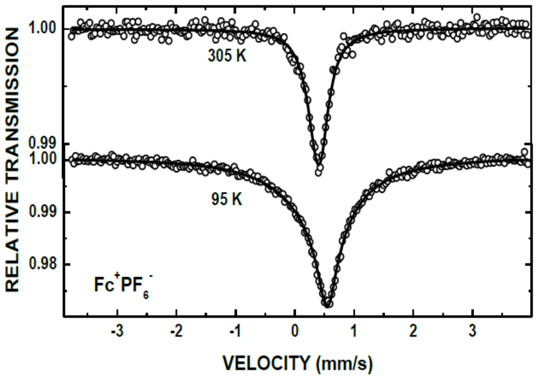

Fig. 1 The Mössbauer spectra of $[Fe(C_5H_5)_2]PF_6$ at lowest and highest temperature of measurement.

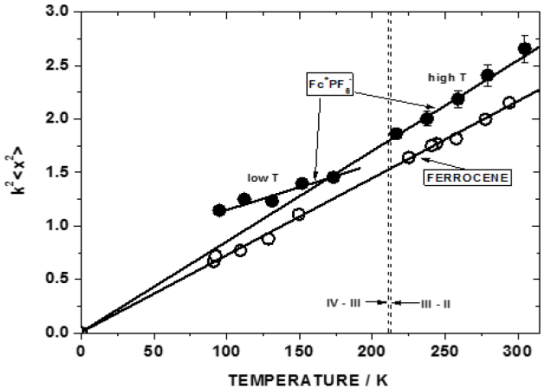

Fig. 2 The mean square of the vibration amplitude, times the square wave number of the γ ray, in $[Fe(C_5H_5)_2]PF_6$ and in $Fe(C_5H_5)_2$.

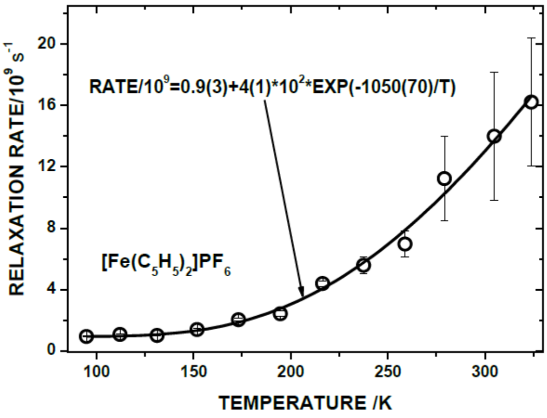

Fig. 3 The temperature dependence of the spin relaxation rate, the solid line represents the theoretical fit with spin-spin (at very low T) and the spin-lattice Orbach relaxation process at high T.

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Secondary Particles Precipitates in Be-Fe Alloys

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The mechanism of solid solution decomposition and growth of secondary particles precipitates (SPP) were investigated for the beryllium-iron system. The monocrystalline Be-Fe alloy (0.85 % Fe) and coarse-grained cast Be-Fe alloys (0.09-0.80 % Fe) were prepared from the beryllium of different purity. The samples for Mössbauer investigations were in the form of plates with a thickness of 2 to 10 mm. Mössbauer spectrometry was performed at room temperature with a conventional constant acceleration system with ^{57}Co (in Cr) source, with the resonant detector RSDU-2A (Ritverc) and with reference to the sodium nitroprusside spectrum. Mössbauer spectra of the monocrystalline samples were obtained after homogenization at 1100 ºC, and after isothermal annealing at 600 ºC for 2659 hours. And spectra of cast Be-Fe alloys samples were obtained after homogenization at 1100 ºC and annealing at 500-600 ºC for different durations. The spectra containing small intensity doublets and doublets with a small quadrupole splitting were fitted taking into account the spectra distortion resulting from the resonant detectors peculiarities. The changes of iron solid solution and the secondary phases fractions are analyzed as function of the annealing time. The kinetic of sold solution decomposition and the second particles precipitation growth are studied and analyzed taking into account recent results [1]. The following principal conclusions have been made in the study. The equation convolution of the three Lorentz lines increases the fitting quality of complex spectra containing small intensity doublets and doublets with a small quadrupole splitting. It was shown that the appearance and diffusion growing of the $FeBe_{11}$ nano-particles on the numerous dislocation crowds are the main events in the beryllium alloys. The phase distribution, the incubation period and the diffusion path was obtained. The correlation between the impurity concentration and Mössbauer spectra parameters of the phases was investigated. In the alloys with noticeable impurities, in addition to phase $FeBe_{11}$, a small quantity of phase with Mössbauer spectra parameters similar to those of compound $AlFeBe_4$ is appeared. The precipitates of phases at the grain boundary are detected only in the case of fine-grained materials, with great sum of grain boundaries. The precipitates on the nano-formation plates inside the grain can be both in fine-grained and coarse-grained, and monocrystalline materials of technical purity due to the specific dislocation structure that result in to small diffusion paths (some micrometers).

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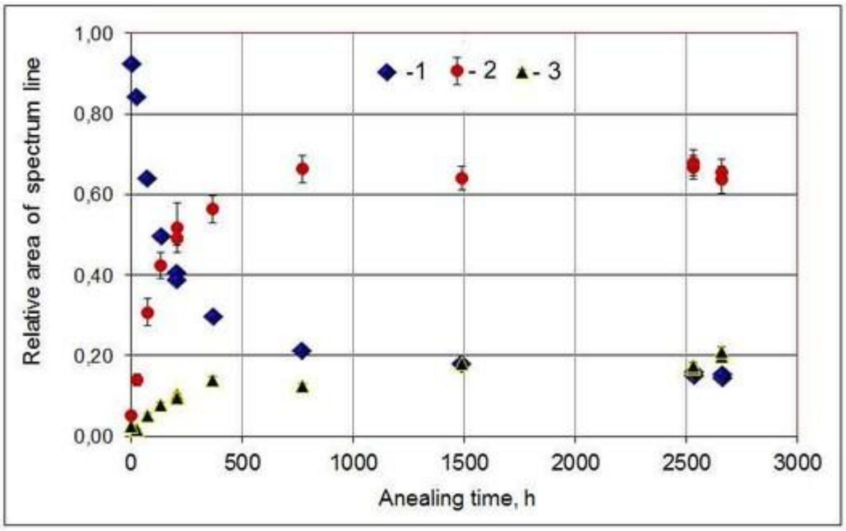

Fig. 1 Relative area of spectrum lines of the monocrystalline Be-Fe alloy after annealing: 1) the solid solution, 2) $AlFeBe_4$, 3) $FeBe_{11}$.

The Phase Transformations in Intermetallic Phases in Zirconium Alloys

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The development of nuclear power goes in direction of increasing of power station safety at simultaneous increasing of serves of channel tubes till 6-7 years and increasing in burning out of fuel till 60-70 MWt*days/kgU. The solution of this problem partially is connected with improvement of radiation and corrosion resistance of zirconium alloys. The knowledge of the state, the redistribution of atoms of alloying elements and phase transformation is necessary for understanding nature of the process in zirconium alloys and improvement their properties.

On the basis of experimental data the analysis of phase changes in intermetallic phases in alloys on the basis of zirconium (Zr – 1.03 at.% Fe; Zr – 0.51 at.% Fe; Zr – 0.51 at.% Fe – M (M = Nb, Sn,Ta) is carried out. The experimental techniques as Mössbauer spectroscopy on ^{57}Fe nuclei in backscattering geometry with the registration of the internal conversion electrons, X-ray analysis, X-ray diffraction and electron microscopy are used. As a result it is found the interrelation between process of growth of inclusions of intermetallic phases and segregation of these phases. The growth of particles derived by phase transformation, recrystallization and interrelated. In studded r case the phase separation of two types is detected, so iron is transferred from one phase to another at short diffusion paths. It was found that the kinetics of growth of inclusions is not controlled by bulk diffusion, and a lower value of the activation energy of migration of iron atoms can be bound with existence of enhanced diffusion paths and interphase borders. Using Mössbauer spectroscopy it was shown that the influence of the third element on the local environment of iron atoms in zirconium is associated with features of the crystallization process of double and triple alloys based on zirconium.

Precision of Iron the Solubility in Zirconium Alloys

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Zirconium alloys are used in nuclear reactors for the fuel cladding, spacers grids and other structural elements. Zirconium alloys are constantly being improved. Operation time of nuclear reactors and the amount of energy obtained from uranium depend on the lifetime of claddings. Nowadays the problem of increasing the service life of fuel cladding from 3 to 6-7 years and increasing the burning out of fuel till 60- 70 MWt* day / kg U have been resolving. For improvement of radiation and corrosion properties of zirconium alloys the chemical elements, such as iron, tin, chromium, nickel, copper, tungsten and others are added in a variety of alloys. The oxygen content in alloys influence on the properties too. Oxygen content ranges from 0.05 to 0.12 wt.%. The iron content varies from 0.1 (E110) and up to 0.7 wt.%. Zirconium alloy changes its properties even when adding small amounts of other elements. Therefore, knowledge of the state of the added elements is essential both scientific and practical point of view. Iron has Mossbauer isotope ^{57}Fe, and therefore its state can be study even at low concentrations by Mössbauer spectroscopy. To modify existing alloys and to create new alloys it is important to know how much iron is in solid solution and how the other elements affect on iron solubility in zirconium alloys. The solubility of iron in binary zirconium alloys was studded previously in the last century [1] and analyzed recently [2]. However, at that time the good computer programs were not used to fit the Mössbauer spectra therefore the obtained solubility values could not be accurately determined. In the present study we had précised the previously obtained values of the solubility of iron in the binary alloy. The précised value of iron solubility is 0.016±0.002 mas.%. at temperature of 600 °C. These data have compared with the data obtained for the alloys containing more iron for example 0.09 mas.% . The quenching of the binary alloy from beta-region temperature forms supersaturated solid solution. The annealing decomposes supersaturated solid solution into intermetallic compounds and solid solution. The figure shows the spectrum of the alloy Zr + 0.09 wt.% Fe, the parameters of which are shown in the table. It can be seen that the alloy has a complicated structure of the iron is in solid solution and various intermetallic compounds. Their relative concentrations are demonstrated in table. The concentrations are calculated with proposition that all phases have the same probability of resonant absorption.

[1] M. Stupel et al., Scr. Metall. 19 (1985) 739–740.
[2] V.P. Filippov et al., Hyperfine Interact. 217 (2013) 45–55.

Table 1. The parameters of the spectrum of alloy Zr + 0.09 mas.% Fe

δ (mm/s)	ΔE (mm/s)	S (relative units)	Mas.%	Compos
-0.43±0.03	1.56±0.08	11.58±3.67	0.010±0.003	Zr_3 Fe +O
-0.34±0.01	1.13±0.07	37.26±6.79	0.033±0.006	Zr_2 Fe +O
-0.31± 0.01	0.76±0.06	34.17±8.52	0.031±0.007	Zr_2 Fe
-0.07± 0.01	0.25±0.03	16.99±1.60	0.015±0.001	S.s. Fe

Magnetic, Mössbauer and Structural Monitoring of Spin State Switch in Iron(II)-Pyrazine Cyanoheterometallates

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Discovery of spin-crossover (SCO) behavior in the family of Fe(II)-based Hofmann clathrates has led to a drastic progress in the field of bistable molecular materials. To date this class of SCO complexes is represented by several dozens of individual compounds, and areas of their potential application steadily increase. Starting from Fe(II), square planar $M^{II}(CN)_4^{2-}$ (M^{II} = Ni, Pd, Pt) or linear $M^{II}(CN)_4^{2-}$ (M^{II} = Ag, Au) tetracyanometalates, and pyrazines Xpz (X = H, Cl, Me, I) as co-ligands we have obtained a series of new Hofmann clathrate like coordination frameworks. In a new 3D cyanoheterometallic framework $[Fe(pz)\{Au(CN)_2\}_2]$ a highly cooperative spin crossover is observed at 367 K and 349 K in heating and cooling modes respectively. Mössbauer spectroscopy reveals a complete transition between diamagnetic and paramagnetic states of the iron centers. The low spin (LS) to high spin (HS) transition induces a drastic structural distortion that incorporates large one-directional expansion (*ca.* 10.6 %) and contraction (*ca.* 9.6 %) of the lattice. Negative thermal expansion along *c*-axis below and above transition temperature is detected. In case of square-planar cyanometallates, depending on the nature of X and M, axial positions of Fe(II) are occupied by two 2X-pyrazines, or one 2X-pyrazine and one water molecule, or, alternatively, two distinct Fe^{II} positions with either two pyrazines or two water molecules are observed. Temperature behavior of magnetic susceptibility indicates that all compounds bearing FeN_6 units display cooperative spin transition, while Fe^{II} ions in N_5O or N_4O_2 surrounding are HS. Mössbauer spectroscopy is used to characterize the spin state of all HS, LS and intermediate phases (see abstract figure). Effects of a pyrazine substituent and M^{II} nature on the hyperfine parameters in both spin states are established.

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[2] M.C. Muñoz, J.A. Real, Coord. Chem. Rev. 255 (2011) 2068–2093.

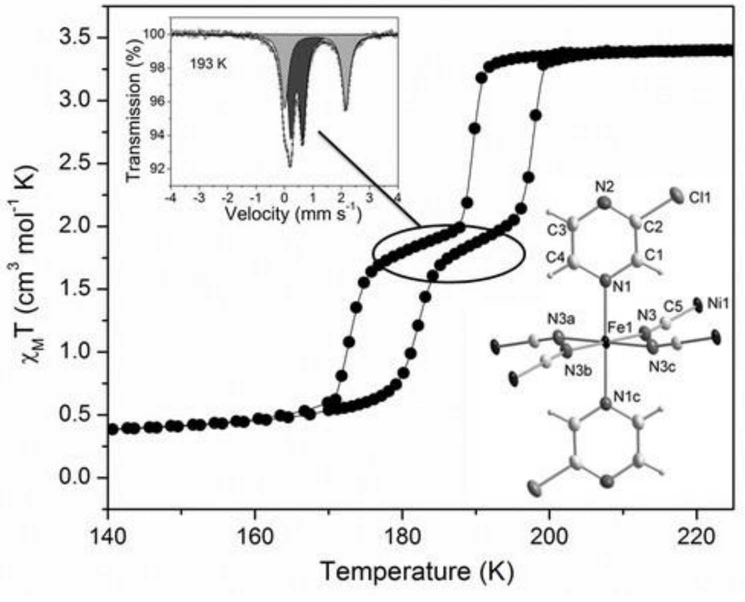

Fig. 1. Structural representation and spin transition curve of $[Fe(Clpz)_2Ni(CN)_4]$. Mössbauer spectrum of the intermediate phase is inserted.

Synthesis and Properties of Indium-Doped Iron Oxides

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Iron oxides are widespread compounds in nature and usually contain metal cations other than iron incorporated in their structure [1]. Also, doping of synthetic iron oxides with different metal cations can improve their properties (magnetic, electric, catalytic, photocatalytic, optical, gas sensing, etc) which can be essential for their applications in advanced technologies. In the present work properties of goethite (α-FeOOH) and hematite (α-Fe_2O_3) doped with non-magnetic In^{3+} ions were investigated. Indium-doped goethite samples were synthesized by a precipitation method at pH 12 using a strong organic alkali tetramethylammonium hydroxide (TMAH) for pH adjustment [2,3] Prepared samples were analysed using ^{57}Fe Mössbauer spectroscopy and other instrumental techniques. Maximum In-for-Fe substitution in goethite at about 8 mol% was estimated by the measurement of the unit cell expansion (XRD) and the reduction of the hyperfine magnetic field (Mössbauer spectroscopy) [3]. In-doped hematite samples were prepared by calcination of In-doped goethite samples at 500 °C [5]. An increase in size of hematite unit cell and a decrease in the hyperfine magnetic field suggest In-for-Fe substitution in the structure of hematite.

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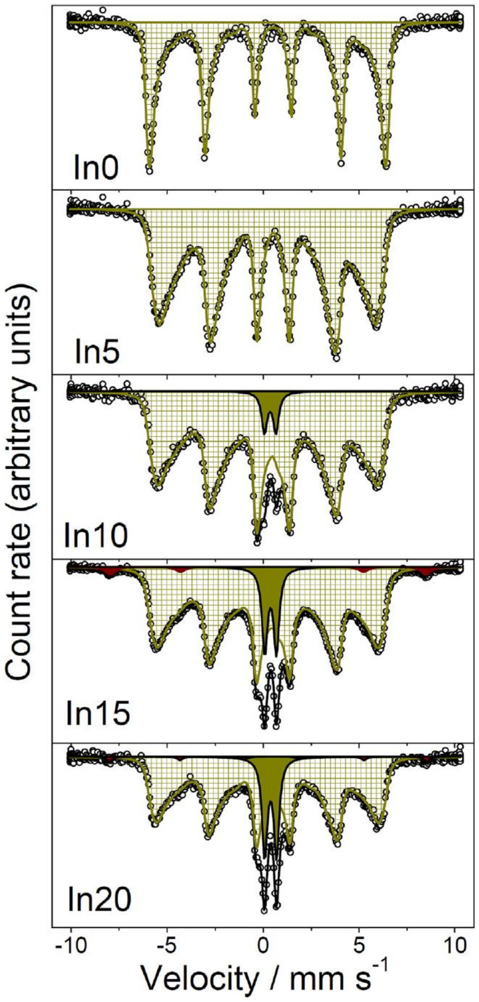

Fig. 1 ^{57}Fe Mössbauer spectra of In-doped goethite samples (with 0, 5, 10, 15 or 20 mol% In) recorded at 20 °C.

Mössbauer Study of pH Dependence of Iron Intercalation in Montmorillonite

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The intercalation of drugs into the interlayer space of clay minerals is one of the possible ways for drug delivery. The exchange of the interlayer cations of montmorillonite with the ions of rare earth elements is an effective approach to obtain catalysts, catalyst supports, sensors and adsorbents, too. In previous reports [1,2] ^{57}Fe Mössbauer spectroscopy has successfully been applied to show the incorporation of Fe ion into the interlayer space of montmorillonite via treatment with $FeCl_3$ in acetone. The aim of the present work was to prepare novel iron intercalated montmorillonite via treatment with $FeCl_3$ in acetone at different pH and to study the effect of pH on the incorporation of iron into the interlayers. For this study we applied ^{57}Fe Mössbauer spectroscopy that can give reliable information about the intercalation of iron via the appearance of magnetically split spectra, as a fingerprint of intercalated irons, at low temperatures. The 78 K ^{57}Fe Mössbauer spectra of montmorillonite samples reflected magnetically split spectrum part indicating the intercalation of iron into the interlayer of montmorillonite via the treatment with $FeCl_3$ + acetone between pH 2.7 and pH 4.14. It was found that the occurrence of intercalated iron in montmorillonite increases with the pH.

Acknowledgment:
The financial supports from the CAPES (No A127/2013) and OTKA (No K115913 and K115784) grants are acknowledged.

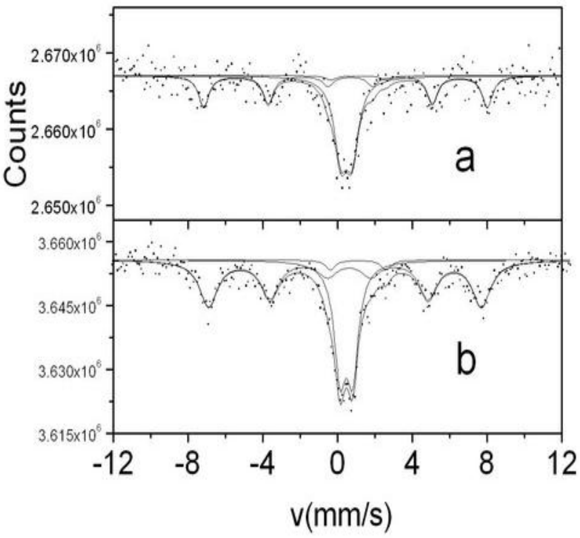

Fig. 1 78 K ^{57}Fe Mössbauer spectra of montmorillonite treated with $FeCl_3$ + acetone at pH 2.78 (a) and pH 2.90 (b).

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Mössbauer Study of M-type Ca-La Ferrite Single Crystals

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Magnetoplumbite-type (M-type) hexagonal ferrites, $M\mathrm{Fe}_{12}\mathrm{O}_{19}$ (M = Sr, Ba, etc.), are well known as base materials for commercial permanent magnets. Although $\mathrm{CaFe}_{12}\mathrm{O}_{19}$ is not stable in equilibrium, the M-type structure is stabilized by doping La to the *M* site. Co-doped (Ca-La)$\mathrm{Fe}_{12}\mathrm{O}_{19}$ is now known as a high-performance commercial permanent magnet [1], although the basic chemical and physical properties has not been established. To get information on the phase stability and microscopic chemical and magnetic structures of the Ca-La based M-type ferrite, we have grown single crystals of $(\mathrm{Ca}_{1-x}\mathrm{La}_x)\mathrm{Fe}_{12}\mathrm{O}_{19}$ ($0.4 < x < 0.6$) for the first time by a self-flux method and measured ^{57}Fe Mossbauer spectra at room temperature together with those of powdered samples. We discuss similarities and dissimilarities between familiar $\mathrm{SrFe}_{12}\mathrm{O}_{19}$ and (Ca-La)$\mathrm{Fe}_{12}\mathrm{O}_{19}$.

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One-Pot Production of Copper Ferrite Nanoparticles by Chemical Method

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Copper ferrite nanoparticles have potential for application in a wide variety of areas including catalyst [1] and electrochemical applications [2]. Although various methods have been reported for the synthesis of copper ferrite nanoparticles, these methods suffer from disadvantages such as the high temperature annealing process. In the present study, we examined the preparation of copper ferrite nanoparticles (below 5 nm in diameter) stabilized with gelatin under an ambient atmosphere at room temperature.

Copper ferrite nanoparticles were prepared by a modified hydrazine reduction system under ambient atmosphere at room temperature. Iron(II) chloride (7 mmol), copper(II) sulfate (3 mmol), sodium tartrate (10 mmol) and 400 mg of gelatin were dissolved in 50 mL of water. The pH of this solution was subsequently adjusted by the addition of sodium hydroxide. Then, hydrazine solution was added slowly dropwise while ultrasonicating the mixture.

The X-ray diffraction pattern of prepared samples exhibited the characteristic peaks of copper ferrite (JCPDS Card No. 34-0425) and metallic copper (JCPDS Card No. 4-0836). Transmission electron microscopic observation showed that the resulting nanoparticles were spherical and less than 5 nm in diameter. Mössbauer spectra of the copper ferrite nanoparticles were acquired at 293 and 19 K (Figure 1). The spectrum acquired at 293 K showed a doublet, which was attributed to the superparamagnetic behavior of small nanoparticles. The Mössbauer spectrum at 19 K of the same sample showed three sets of sextets, because the superparamagnetism of the specimen was no longer present at this low temperature. Two sets of sextets corresponded to the tetrahedral and octahedral sites of copper spinel structure [3], and another sextet with small hyperfine magnetic field corresponded to the surface or defects of the nanoparticles. Furthermore, we prepared the similar sample with increasing the ratio of copper salt. In the Mössbauer spectrum at 19 K of this sample, the component of the surface or defects increased and the sextet of octahedral sites decreased. These results indicated that the tetrahedral site is preferable for copper, and that metallic copper and the copper ferrite coexist in a single nanoparticle.

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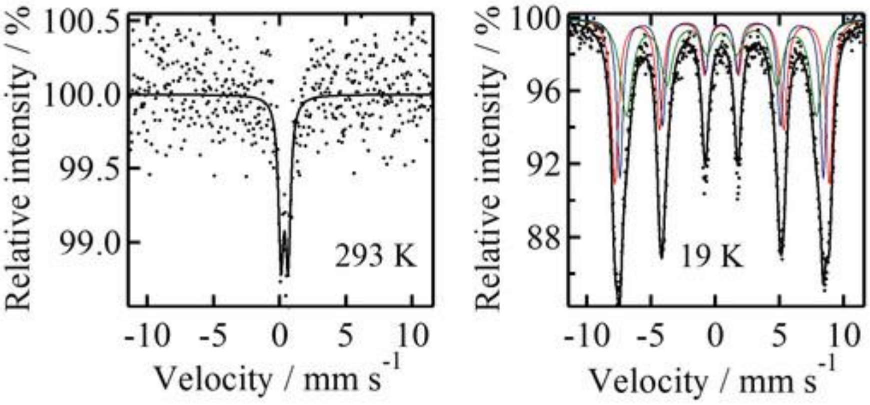

Fig. 1 Mössbauer spectra of copper ferrite nanoparticles obtained at 293 and 19 K.

The Precipitation of α-Fe_2O_3 Particles by Forced Hydrolysis of $FeCl_3$ Solutions in the Presence of Sodium Dodecyl Sulphate

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Hematite (α-Fe_2O_3) is the most stable iron oxide under ambient conditions. It has been widely investigated due to its potential for different applications in traditional and advanced technologies. For example, hematite particles can be used as pigments, adsorbents, fine abrasives, magnetic materials or sensors. Owing to their excellent semiconducting properties hematite particles have also found a potential for applications in photocatalysis for green energy production and environmental protection. The α-Fe_2O_3 particles can be synthesised by various experimental techniques, such as forced hydrolysis iron(III)-salt solution, sol-gel, hydrothermal/ solvothermal, thermal decomposition of iron-organic salts, etc. The properties of α-Fe_2O_3 particles are strongly influenced by their nano/microstructure. α-Fe_2O_3 particles of different nano/microstructure have been reported [1].

In the present work the effect of sodium dodecyl sulphate (SDS) on the precipitation kinetics and morphology of α-Fe_2O_3 particles formed by forced hydrolysis of $FeCl_3$ solutions was monitored. A direct phase transformation β-FeOOH → α-Fe_2O_3 *via* dissolution/recrystallization mechanism occurred in the absence of SDS. On the other hand, the addition of SDS into the precipitation system slowed the crystallization kinetics of α-Fe_2O_3. An intermediate, α-FeOOH phase precipitated which with a prolonged time of forced hydrolysis also transformed to α-Fe_2O_3.

Mössbauer spectroscopy showed that α-Fe_2O_3 particles precipitated in the presence of SDS possessed a lower degree of crystallinity, while FE SEM revealed that these particles are formed by aggregation of much smaller elongated primary α-Fe_2O_3 units (Fig. 1). The preferential adsorption of dodecyl sulphate groups on nuclei and crystallites of FeOOH and α-Fe_2O_3 phase during the forced hydrolysis of $FeCl_3$ solutions had a dominant role in the formation of elongated α-Fe_2O_3 particles.

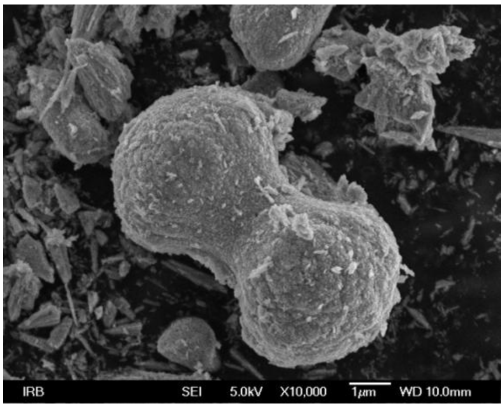

Fig. 1 FE SEM image of α-Fe_2O_3 particles precipitated in the presence of sodium dodecyl sulphate (SDS).

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^{57}Fe Mössbauer Spectroscopy Analysis of Fe-Bearing Phases in the Manufacture of TiO_2 Pigment

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TiO_2 white pigment [1] has found important applications in catalysis, printing inks, plastics, papers, solar cells and pharmaceuticals. In the manufacture of TiO_2 pigments two technologies are used. Ilmenite ore is used in the production of TiO_2 pigment by sulphate process, whereas rutile ore is used in the production of TiO_2 pigment by chloride process. In the present work the possibilities of Mössbauer spectroscopy in analysis of Fe-bearing phases which appear in the manufacture of TiO_2 pigment by sulphate process will be shown and discussed. XRD, FE-SEM/EDS and magnetometry were also used as supporting techniques.

Ilmenite ore from Australia used in the manufacture of TiO_2 pigment (*Cinkarna*, Celje, Slovenia) is analyzed. In this technology it is very important to know the Fe^{2+}/Fe^{3+} ratio in ilmenite ore [2,3]. Generally, ilmenite can be associated with other minerals, such as hematite, magnetite, rutile, fayalite, zircon, quartz and various aluminosilicates [1]. Mössbauer spectra of ilmenite ore were recorded from RT to liquid He temperature. The changes in the Mössbauer spectra, as well as corresponding magnetometric measurements were discussed.

In the manufacture of TiO_2 by sulphate process a significant amount of copperas ($FeSO_4 \cdot 7H_2O$) crystallizes as a by-product. In the technology mentioned copperas is calcined with the aim to produce H_2SO_4 acid which is returning to the process of ilmenite ore digestion. The RT Mössbauer spectrum of calcined copperas showed the superposition of one sextet corresponding to hematite and one central quadrupole doublet of small relative intensity. However, the Mössbauer spectrum of the magnetic fraction separated from calcined copperas with permanent magnet also showed the presence of substoichiometric magnetite ($Fe_{3-x}O_4$). Sulphur detected by EDS analysis of calcined copperas was a result of incomplete oxidation of copperas.

Copperas produced as a by-product undergoes oxidation at ambient conditions and this can be also monitored by Mössbauer spectroscopy. Copperas can be utilized in the manufacture of yellow pigment (α-FeOOH) with the aim to optimize the cost of TiO_2 pigment production.

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Iron Mössbauer Spectra Investigation of Nepheline Substrate Using for Preparing the Water Treatment Reagent

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The existence of the iron in drinking water could give a red color, a bad odor and healthy problems. The treatment of the water after sedimentation, flotation and membrane filtration need to remove of fine-grain particles of iron. For this process, the reagent was used with simultaneously coagulant and flocculant characteristics (features). The type of coagulant plays a significant role in the process of the water treatment. In this work the alumino-silicic coagulant-flocculant [1] was used. The reagent produced by synthesis of initial matter that is nepheline with sulfuric acid. The hypothetical formula of the reaction is $(Na,K)_2O \cdot Al_2O_3 \cdot 2SiO_2 + 4H_2SO_4 + aq \rightarrow (Na,K)_2SO_4Al_2(SO)_3 \cdot mH_2O + 2SiO_2 \cdot nH_2O$.

The initial nepheline (sample 1) contains different substances including iron. The product of the reaction of nepheline with sulfuric acid (sample 2) also contain iron as colloidal solution. Two samples were studied using Mössbauer spectroscopy in absorption mode. All of two samples were measured at the room temperature. There were found two magnetic components and two or three paramagnetic components in the sample 1 (Figure 1). The main area of subspectra of the iron (~60%) is in trivalent paramagnetic state (IS = 0.36±0.02 mm s^{-1}, QS = 0.46±0.02 mm s^{-1}). After synthesis of the reagent it was dried and a sediment was formed. The spectrum of this sediment is shown in the Figure 2. Figure 2 shows the room temperature Mössbauer spectrum of the polycrystalline reagent. Main area (~90%) of this spectrum is doublet with IS = 0.37±0.02 mm s^{-1}, QS = 1.01±0.02 mm s^{-1}. Comparison of spectra in the Figures 1 and 2 shows grate differences in their shape. The differences are discussed.

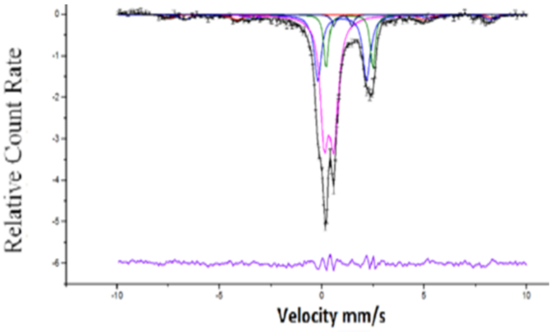

Fig. 1 Room temperature Mössbauer spectrum of nepheline minerals.

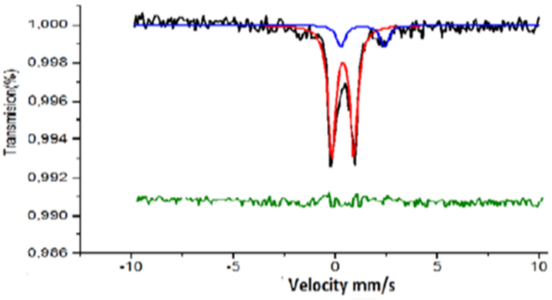

Fig. 2 Room temperature Mössbauer spectrum of dried reagent.

Acknowledgements:
The work was financially supported by the Ministry of education, agreement № 14.575.21.0086 dated 20 October 2014. Unique project identifier RFMEFI57514X0086.

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Spin Fluctuations in FeSe-Based Superconductors under Pressure

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Amongst different superconducting materials, iron pnictides and chalcogenides possess a promising family of high-T_c superconductors. Since a sudden drop of electrical resistivity below 8 K in FeSe was discovered [1], a lot of attempts to modify the composition and properties of the compound have been done. It is believed that the interlamellar distance in FeSe plays a crucial role in superconducting pairing. Introduction of alkali metals between FeSe layers as well as partial substitution of Se by Te lead to an increase in superconducting transition temperature [2]. However, the most elegant modification of FeSe has been done by the group of Clarke [3]. They have successfully intercalated tetragonal FeSe in liquid ammonia containing dissolved metallic lithium. Herein, we present a detailed Mössbauer spectroscopy study of this intercalate $Li_{0.6}(NH_3)_{0.8}(NH_2)_{0.2}Fe_2Se_2$ with T_c = 42 K (p = 1 bar) at ambient and under applied pressure. Its hyperfine parameters indicate a significant increase of d-electron density on ^{57}Fe atoms and electric field gradient comparing to non-intercalated FeSe. The observation suggests that T_c increases upon intercalation due to enhancement of charge carrier density at the Fermi level, which is mostly composed of 3d orbitals. Moreover, at low temperatures an appearance of the additional magnetic sextet in the spectra is observed. Parameters of the sextet reveal its dynamic nature down to 5 K assuming an emergence of rather magnetic fluctuations than static magnetic moments in the material. Relative intensity of the magnetic subspectrum remains around 25% up to 40 K, suddenly drops in the vicinity of T_c = 42 K and remains at the level of a few percent up to room temperature. Thus, intensity of magnetic fluctuations, which are known to mediate superconducting pairing, follows a superconducting transition curve derived from susceptibility measurements. We also present pressure dependent studies of $Li_{0.6}(NH_3)_{0.8}(NH_2)_{0.2}Fe_2Se_2$ superconductor up to 8 GPa. In contrast to FeSe, in this intercalate the pressure increase leads to gradual decreasing of onset transition temperature. Mössbauer spectra under pressure recorded using the Synchrotron Mössbauer Source at ESRF reveal suppression of magnetic fluctuations in the material as external pressure is increased. Thereby, we conclude about the important role of spin fluctuations in superconducting mechanism.

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INDEX OF AUTHORS