



ICAME 2019

Tutorial Lecture

Investigation of Magnetic Structures with High-field Mössbauer Spectroscopy

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The application of external magnetic fields allows to broaden the knowledge which can be gained by Mössbauer spectroscopy enormously. In combination with magnetic measurements, detailed information about local magnetic and electronic structures can be obtained. In this tutorial I concentrate on investigation of magnetism of solids on different levels of complexity of magnetic structures. Starting with the influence of a magnetic field on the hyperfine interactions, examples of some simple magnetic structures (para-, ferro-, and antiferromagnetic) are discussed before coming to more complex ones with canted or inhomogeneous spin arrangement.

The measured hyperfine field is the vectorial sum of the internal field at the nucleus and an external field, caused by surrounding unsaturated orbitals or by an applied field. By solving the full Hamiltonian the value and direction of the internal field can be determined. It will be shown that care has to be taken, because the thus obtained internal field is only partially proportional to the magnetic moment, which usually is the physical property of interest. A clear separation is only possible, with the help of theoretical calculations.

If the external field is high enough, it allows to influence the dynamics of the spins. As an example, this will be shown for the case of a cluster glass. Although long range ordered, the magnetism of such compounds is highly inhomogeneous, with mixtures of ferro- and antiferromagnetic correlated spin clusters and uncorrelated spins, which behave as paramagnets. With the help of the external field local susceptibilities can be determined. Also moments of the paramagnetic spins and of the clusters are available. Further, the size of the clusters and their dynamics can be investigated. Key is the value of the external field, which deaccelerate the dynamics of the clusters into the time window of the Mössbauer effect, thus leading to relaxation spectra.

The focus of the tutorial is not only on the results of high-field investigations, but also on how to come to these results, by also discussing possible misinterpretations. This tutorial should convince that the investment in a high-field Mössbauer apparatus makes sense and should help to enter the field. An extended version of the tutorial will be published in [1].

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Mössbauer Spectrometry Applied to Fe-based Nanostructures

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^{57}Fe Mössbauer spectrometry is usually applied to powdered materials to probe the structural and chemical nature of Fe environments and the magnetic properties mainly related to Fe moments. It also contributes to investigate on the one hand the surface, interface and the grain boundaries in the case of nanoparticles, multilayers and nanostructured powders, respectively and on the other hand the hyperfine magnetic properties and their dynamics in correlation with superparamagnetic relaxation phenomena in the case of magnetic nanostructures.

The different types of nanostructures are presented to establish the main parameters which influence the physical properties and their modifications with respect to the overall microstructures. Next, we illustrate how zero-field and in-field ^{57}Fe Mössbauer spectrometry can be extremely relevant when this local probe technique is used to investigate local order and magnetic properties in different nanostructures, as nanocrystalline alloys, nanostructured powders, nanoparticles, hollow and functionalized nanoparticles and their assemblies. Through various examples, the purpose of this tutorial presentation is to draw attention to the description of the hyperfine structures (local structural disorder and magnetic dynamics), the interest of Mössbauer spectra series as a function of temperature and external magnetic field, the limitations, the complementarity with other techniques and computer modelling, and finally to correlate hyperfine data to the chemical nature and homogeneity of the samples.

Applied-field Mössbauer Investigations of Paramagnetic Iron Compounds

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A plethora of essential molecules in (bio)inorganic chemistry and technical applications depend on iron ions coordinated by distinct ligand groups. For instance, iron enzymes catalyze key steps in oxygen-dependent degradation of toxic molecules and the metabolism of organic substrates, in the bacterial metabolism supporting the global carbon cycle, and many other reactions [1,2]. Understanding of the processes on first-principal's level hinges on the possibility to probe electronic structures of catalytic iron centers. Experimentally this can be achieved by spectroscopic methods, of which spin-dependent techniques are most interesting because most iron oxidation states, ranging formally from Fe(0) to Fe(V), are paramagnetic and molecular spins can provide excellent insight into the iron valence electronic structure. In this regard, applied-field ⁵⁷Fe Mössbauer spectroscopy is a powerful technique, often in combination with electron-paramagnetic resonance spectroscopy or other magnetic measurements. It has the virtue that the ⁵⁷Fe nucleus is a local sensor that connects microscopic magnetic information with charge density (isomer shift) and charge asymmetry (quadrupole interaction), also intimately related with iron oxidation and spin states.

Paramagnetic Mössbauer spectra are different from solid-state magnetic spectra as they exhibit more features and depend more strongly on temperatures and applied fields [3]. Due to zero-field splitting (ZFS), the orbital ground states of iron split into diverse magnetic substates, each of which generates its own internal field at the ⁵⁷Fe nucleus and exhibits distinct magnetic subspectrum. We will introduce the spin-Hamiltonian (SH) formalism as a powerful technique for describing the magnetic properties and corresponding Mössbauer spectra. As the formalism is derived from ligand field theory, the involved parameters are accessible also from density functional theory and other modern quantum-chemical calculations for in-depth interpretations [4].

The characteristic signs of magnetic (an)isotropy resulting from ZFS will be demonstrated and used as the features for spectral assignments. The fundamental difference of integer and half-integer spin systems, exhibiting diverse field- and temperature response, will be discussed, as well as slow and fast spin relaxation. Field-dependent spectra with mixed magnetic and electric hyperfine interactions will be classified and fundamentally analyzed by using rather simple concepts like e.g. tabulated effective nuclear g values for magnetically perturbed quadrupole pattern in 1st order approximation. The different aspects of paramagnetic Mössbauer spectra will be demonstrated with examples from (bio)inorganic chemistry and hands-on SH simulations.

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Nuclear Resonance Scattering with High Energy Mössbauer Transitions

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Nuclear resonance scattering (NRS) became an important technique to study electronic, magnetic and dynamical properties of solids, especially under extreme conditions. This technique requires high-energy-resolution monochromatization of the X rays. Traditionally, such monochromatization is achieved using high-order reflections of perfect silicon crystals which provide an energy resolution of 1-10 meV [1]. Such monochromators are used for NRS with Mössbauer transitions below 30 keV, e.g. ^{57}Fe , ^{119}Sn , and ^{151}Eu . An extension of NRS to the energy region above 30 keV requires another concept of monochromatization.

In this talk two possible approaches of extension of NRS to the transition energies above 30 keV are presented. The monochromators based on low-order reflections of silicon crystals with the energy resolution of 30-150 meV was constructed at ID18, ESRF [2] and P01, PETRAIII [3] for the energies above 50 keV. These monochromators allows one to perform nuclear forward scattering with high-energy Mössbauer transitions, e.g. ^{61}Ni at 67.4 keV, and ^{73}Ge at 68.8 keV, and ^{193}Ir at 73.0 keV. Examples of the applications to study magnetic and dynamical properties with those isotopes will be shown in the talk.

Monochromatization which combines both high efficiency and meV energy resolution was achieved with a sapphire backscattering monochromator [4,5] which provides sub-meV energy resolution for 30-40 keV energy. Applications of these monochromators installed at ID18, ESRF and P01, PETRAIII to study phonon dynamics at different conditions including experiments under high-pressure low-temperature conditions will be presented in the talk.

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ICAME 2019

Keynote Lecture

Magnetic Transitions in Fe₂O₃ at High Pressures: Magnetism in the Earth's Mantle

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The Earth's crust-mantle boundary (Moho discontinuity) has been traditionally considered as a fundamental boundary between the magnetic crust and the nonmagnetic mantle. Nevertheless, this assumption has been questioned recently by geophysical studies and by the identification of magnetic remanence in mantle xenoliths^{1,2} which suggest deep magnetic sources. Owing to their high critical temperatures, iron oxides are the only potential sources of magnetic anomalies at mantle depths³. However, the lack of data on their magnetic properties at relevant pressure-temperature conditions hampers any conclusive result about the Curie depth, below which mantle temperature is too high to sustain any kind of long-range magnetic order. Here I report investigations of the magnetic transitions and critical temperatures in Fe₂O₃ polymorphs⁴ to 95 GPa and 1200 K by means of Synchrotron Mössbauer Source spectroscopy⁵ in laser-heated diamond anvil cells. The experiments were conducted at ID18 beamline of the ESRF. Our results demonstrate⁶ that hematite, α -Fe₂O₃, remains magnetic at the depth of the Earth's transition zones along cold or very cold subduction paths in the West Pacific region. The geophysical implications of these findings will be discussed.

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In-situ Mössbauer Spectroscopy on Mars – in Memoriam and Tribute to Göstar Klingelhöfer

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Dr. Göstar Klingelhöfer died suddenly and unexpectedly on January the 8th 2019. Among his many outstanding contributions to the fields of Mössbauer spectroscopy and planetary science is the development of the miniaturized Mössbauer spectrometer MIMOS II¹ and its successful application on the surface of Mars on board NASA's Mars Exploration Rovers (MERs). He was awarded the Eugen Sänger Medal in 2005, the Award of the International Board on the Application of the Mössbauer Effect in 2006, and the Helmholtz Award in 2007.

The MERs mission goals were to find signatures of past water activity at their landing sites, and to assess the past environmental conditions for their suitability for life. The iron hydroxide sulphate mineral jarosite identified with MIMOS II² provided in situ evidence for an ancient aqueous environment at Opportunity's landing site at Meridiani Planum³ during the Hesperian epoch, albeit at low pH conditions. The identification of iron carbonates at Spirit's landing site in Gusev crater provided evidence for extensive aqueous activity under near-neutral pH conditions during the Noachian epoch⁴, which preceded the Hesperian. Both environments would have been suitable for life. We hope that Dr. Klingelhöfer's legacy carries on with future in-situ applications of Mössbauer spectroscopy on Mars and other bodies in the solar system⁵. Besides these extraterrestrial applications the portable Mössbauer spectrometer MIMOS II has been used in several terrestrial applications, e.g. the investigation of archeological artifacts⁶, mineralogical transformation with time and depth⁷, in-situ identification of air pollution⁸, to name a few.

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Göstar Klingelhöfer Memorial Talk – My Way and the Future of MIMOS

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On the 8th of January 2019, Dr. Göstar Klingelhöfer died unexpectedly in his home in Germany. Among some of his outstanding achievements is, especially for the Mössbauer community, that he will always be remembered as the key player who managed to succeed to bring the Mössbauer effect successfully to space and perform the first extraterrestrial application on the surface of Earth's neighboring planet Mars [1,2].

His development of a miniaturized Mössbauer spectrometer (MIMOS) for space applications was awarded by the DLR Eugen-Sänger-medal (2005), by the IBAME award (2006), and the Helmholtz award (2007) for Metrology.

Dr. Klingelhöfer's endeavor started as Post-Doc in 1990 in Darmstadt at the Technical University Darmstadt under the guidance of Egbert Kankeleit.

After Kankeleit's retirement he continued his work at the Johannes Gutenberg University Mainz under the fruitful environment of Philipp Gütlich.

In 1990, a Russian request led to the development of MIMOS [3] for the Mars 94-96 mission. The mission failed but the MIMOS I worked. NASA had also plans in the mid 1990ies for the Mars and he became the Principal Investigator (PI) for MIMOS II on the ATHENA mission to Mars: Mars-Exploration-Rovers (MERs) 2003. The first extraterrestrial Mössbauer spectra was measured in January 2004 in the Gusev crater by the MER Rover Spirit. More highlights are presented by Schröder and Gütlich [see Abstract ICAME 2019].

In 2003 he was also PI of MIMOS II as payload on the Beagle 2 lander of the ESA Mars Express 2003 mission. Mars Express was a success but Beagle 2 failed. Other missions fail as well.

Göstar's and my life lines crossed in Mainz. I suggested an add on molecular sensor as upgrade for MIMOS II [4] and he made me a NASA MER member [1, 2]. Among my work on molecular magnetism are some highlights: the Strong Field-LIESST-[4, 5], the LiPTH-[4, 5], the HAXIESST-[4, 5], the SF-HAXIESST-[5], the SF-LITH-effect [5], beside sequential and concerted switching effects [5] and others MIMOS applications for TV and press.

We will discuss how Dr. Klingelhöfer's legacy carries on with future in-situ applications of Mössbauer spectroscopy (MIMOS I, MIMOS II (TRL9), MIMOS IIa (TRL5-6), ...) on the Moon, the Mars, some Asteroids and other bodies in the solar system with different space agencies (DLR, NASA, ESA, CNSA, JAXA, etc.).

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Study of Nuclear Structure in Mid-weight Mass Region of A=80-Quasi Particle Alignment and Magnetic Rotation*

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Nuclear structure at high spins in the mid-weight mass region of A=80 reveals many interesting features. Among them the quasi-particle alignment (QPA) and the magnetic rotation (MR) play important roles in nuclear structure in this mass region. The QPA and MR are all attributed to the proton and/or neutron alignments in origin. Magnetic moments or g-factors of intra-band high spin states are able to give exclusive information on QPA and MR. Motivation was made to study the QPA and MR through measuring g-factors of high spin states of ground rotational and magnetic rotational bands as functions of the nuclear spin and the proton and neutron numbers in A= 80 mass region.

Lifetimes of high spin states are very short, usually in the range of sub-ps or ps. Therefore, g-factor measurements of high spin states are very difficult due to the very small precession, the precession transfer and requesting very high magnetic field of several thousand Tesla. In the present work the transient magnetic field-Ion implantation integral perturbed angular distribution (TMF-IMPAD) method with 4 BGO Compton suppressed HPGe detectors at $\pm 60^\circ$ and $\pm 120^\circ$ respective to the beam direction was used to determine the g-factors of high spin states, which can produce the transient magnetic field of several thousand Tesla and measure the tiny precession of high spin states. To achieve the transient magnetic field the delicate three layer target assembly of a 0.4mg cm⁻² reaction target layer of ⁵⁸Ni or ⁶⁰Ni enriched to 99.8%, a ferromagnetic Fe layer of 1.575mg cm⁻² and a defect free Cu stopping layer of 12mg cm⁻² was adopted. The high spin states of the ground rotational band in ⁸²Sr, ⁸³Y, ⁸⁴Zr, ⁸⁵Nb, ⁸⁵Zr and ⁸⁶Zr and of the magnetic rotational band in ⁸⁵Zr and ⁸²Rb were populated by the fusion-evaporation reactions with the heavy ion beams from the HI-13 tandem accelerator at CIAE.

The experimental results show for the first time the dependence of quasi-particle alignments of ground rotational states on the spin and on the proton and neutron numbers. For the nuclides ⁸⁴Zr, ⁸⁵Zr and ⁸⁶Zr of Z=40 with different neutron numbers the proton alignment is followed by the neutron alignment in ⁸⁴Zr and ⁸⁵Zr, while the neutron alignment is followed by the proton alignment in ⁸⁶Zr. For the nuclides ⁸²Sr, ⁸³Y, ⁸⁴Zr and ⁸⁵Nb of N=44 with different proton numbers the proton aligns only in ⁸²Sr, the proton alignment occurs first and then is followed by the neutron alignment in ⁸³Y and ⁸⁴Zr and the neutron alignment is followed by the proton alignment in ⁸⁵Nb. The results illustrate that the phase transitions might take place at Z=40 and N=46 and at N=44 and Z=39 and 41. The proton and neutron alignments generate different patterns of g-factor vs. spin.

The g-factors of high spin states of the magnetic rotational band in ⁸⁵Zr and ⁸²Rb were measured systematically for the first time. The measured g-factors and deduced shears angles show the decrease of g-factors with the increasing of the spin along the band and demonstrate a step-by-step alignment of the valence protons and neutrons, providing direct and clear information on shears mechanism of magnetic rotation.

Theoretical calculations with different models were also carried out, which well reproduced the experimentally measured g factors.

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** The author presenting at the conference

Electrochemical Reactions of Tin Based Anode Materials in Alkali-ion Batteries

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Electrochemical energy storage is crucial for the development of renewable and intermittent energy sources, but is also widely used in many other applications as electric vehicles and portable electronic devices. Li-ion batteries are currently the dominant technology due to their high energy density and good cycle life, but new electrode materials are needed to improve performance. The main issues with this technology are the unevenly distribution of lithium across the Earth's crust and the increasing prices of this element and cobalt used for cathode. This could be a limitation for the large-scale development of Li-ion batteries, which explains the recent interest for Na-ion and K-ion batteries.

Graphite is the most widely used anode material for Li-ion batteries, but its specific capacity is limited to 372 mAh g⁻¹. This can be related to the intercalation process that only involves 1 Li per 6 C. High specific capacity cannot be obtained with such electrochemical insertion mechanisms that require stable host materials. Thus, other mechanisms involving the reaction of more Li per atom of the anode material must be considered. This is the case of alloying reactions as encountered for Sn that reversibly reacts with up to 4.4 Li, leading to the specific capacity of about 1 Ah g⁻¹. The electrochemical alloying reaction mechanisms are complex because of the formation of small and disordered particles and the possible existence of numerous stable and metastable phases. Thus, commonly used characterization tools such as XRD often fail, due to the absence of long range order. The present talk concerns the application of ¹¹⁹Sn Mössbauer spectroscopy that provides more relevant information. It is often difficult to distinguish the electrochemically formed Li-Sn phases from the only Mössbauer parameters [1] and complementary techniques, including first-principles calculations, will be considered to understand the mechanisms. Sn also reversibly reacts with Na and K, leading to the formation of Na-Sn and K-Sn phases, respectively, and the reactions can also be followed by Mössbauer spectroscopy [2].

However, alloying reactions suffer from large volume variations during charge- discharge cycles, leading to the loss of mechanical and electrical integrity and to instabilities of the surface electrolyte interphase (SEI), which prevents the use of βSn as anode material. Tin based compounds and composites were proposed to minimize these effects and the electrochemical mechanisms will be briefly discussed by considering operando Mössbauer measurements [3]. Finally, the electrochemical reactions of some compounds with Na and K will be reported. They show intriguing differences compared to Li that should be elucidated for future applications.

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ICAME 2019

Award Lecture

Four Decades of Nuclear Resonant Scattering in Synchrotron Era

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It's been almost 45 years since the idea of using a synchrotron source to excite the Mossbauer isotopes was proposed. Since then significant progress has been made in developing the methodology, instrumentation and data analysis. Application areas are extended into wide range of scientific disciplines. In this talk, I will review the key issues addressed by nuclear resonant scattering methods in geophysics and geochemistry such as velocity of sound of earth-bound minerals, iron valence and isotope fractionation in core-mantle boundary under high pressure. Similarly, determination of possible pathways related to the functions of iron-containing biological systems or catalysts will be discussed. The extension of the method to more than a dozen isotopes provides a wide ranging tool to study the interplay between magnetism and superconductivity in new quantum materials like pnictides. This presentation will review modern applications, and provide a prospective view.

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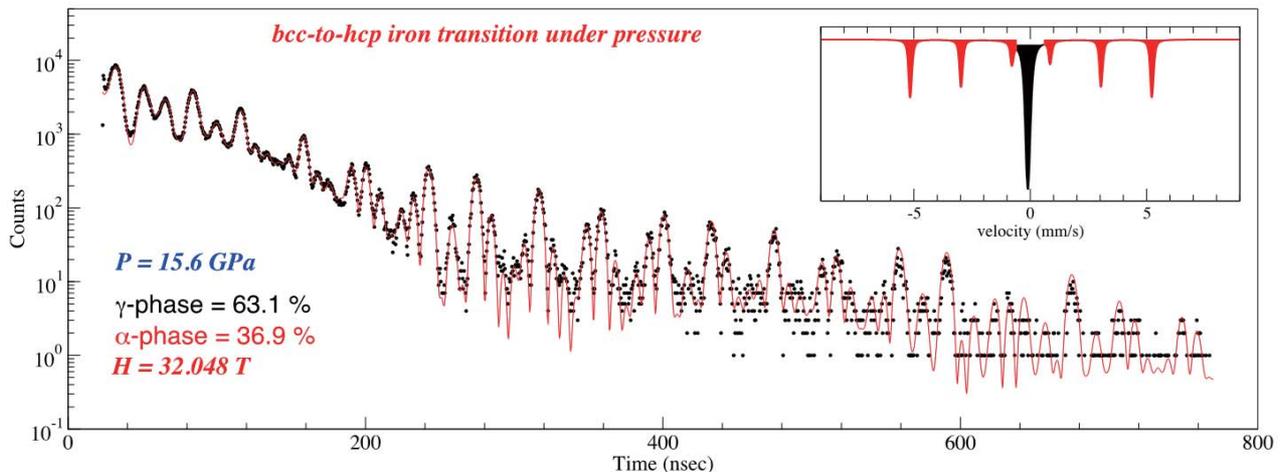


Figure A comparison of quality and precision of nuclear decay data of ^{57}Fe in a mixed phase sample of α -(bcc) and ϵ -(hcp) iron under pressure of 15.3 GPa at room temperature. The **insert** is the energy domain simulation of the fitting results, obtained by using a fitting program called CONUSS.

Dynamics Study Using Mössbauer Gamma Ray and Its Various Applications

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Mössbauer gamma rays from ^{57}Fe nuclei show the narrow energy width of 4.6 neV compared to its energy of 14.4 keV. The Mössbauer gamma rays can be used for probe beam of a unique quasi-elastic scattering experiment on “non-resonant sample”. The quasi-elastic gamma-ray scattering experiment reveals dynamics of the atoms, ions, and molecules which don't contain resonant nuclei. Therefore, the quasi-elastic scattering technique is broadly applicable to general samples. In addition, the technique is sensitive to the angstrom-scale motions in time scales between nano-seconds and micro-seconds, which are unmeasurable by any other techniques. These are unique advantages of the quasi-elastic gamma-ray scattering.

We consider the quasi-elastic gamma-ray scattering spectroscopic technique using time-domain interferometer based on synchrotron-radiation source. It has been shown that the technique reveals the microscopic dynamics in time domain much more effectively compared to the conventional radioactive-isotope-based technique often called as the Rayleigh scattering of Mössbauer radiation. [1] Recently, we developed advanced time-domain interferometer using multi-line Mössbauer gamma rays as the probe beam. [2] We show the new multi-line system is really useful system for studies on both basic science and industrial applications because of the high measurement efficiency of dynamics. We introduce the state-of-art spectroscopic technique for the quasi-elastic gamma-ray scattering.

In the presentation, we also show some application results obtained so far. First, we show our results on glass forming materials. By cooling glass formers, the time scale of the diffusion process rapidly increases toward the glass transition. The microscopic mechanism is far from full understanding. Our studies on typical glass formers revealed existence of local activated processes in addition to the diffusion process directly in microscopic viewpoint in supercooled state. [3] We found that the local activated process shows spatially restricted properties. We discuss the role of the local process to the nature of the glass transition mechanism. Then, we introduce results on soft-matter systems such as nematic, smectic, cholesteric, cholesteric blue phases of liquid crystals. As for smectic phase, where molecules show a nanometric layered structure, we revealed the molecular translational motion across the layer occurs in a time scale of 100 nano-second. We could directly observe the effect of the layer order on the microscopic molecular motions. The new microscopic insight is essentially important to understand the macroscopic diffusion coefficient in smectic phase.

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Sixty Years of Research Using Mössbauer Spectroscopy

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Mössbauer spectroscopy was introduced in the Hebrew University by S. G. Cohen, S. Ofer and E. R. Bauminger in 1959, and I became the first graduate student to join the research. The subjects of our research started with the nuclear properties of more than 15 candidate nuclides, continued with studies of general hyperfine interactions in magnetically ordered materials, and spin relaxation in paramagnetic materials¹. Additional subjects were: The properties of Np inter-metallic systems, the unique properties of the Eu³⁺ ion², transferred hyperfine magnetic fields in Rare Earth compounds, and multiple magnetic phase transitions in Mn compounds detected by the transferred field on an iron nonmagnetic probe³. Next were studies of valence fluctuation phenomena in Eu compounds⁴, theory and experiments of the dynamics of macro-molecules found in biological systems⁵, such as in human tissues, enabling the study of the human brain. We also undertook investigation of high T_c magneto-superconductors, vibrational dynamics in organometallic systems⁶, and lastly studies in which we try to test General Relativity using the Grenoble Synchrotron beam. My Hebrew University collaborators were S. G. Cohen, S. Ofer, E. R. Bauminger, I. Felner, R. H. Herber, J. Gal and Y. Friedman in Jerusalem. Off-campus my collaborators at Bell Telephone Laboratories were H. H. Wickman, G. K. Wertheim and R. L. Cohen. At Argonne National Laboratory, the collaboration was with B. D. Dunlap. The collaborators in Germany were G. M. Kalvius in München and G. Wortmann and G. Kaindl in Berlin.

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Unique Role of Operando Mössbauer Technique in Single-atom Catalysis

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The rapid development of single-atom catalysts (SACs) offers us new opportunities for capturing the reaction intermediates, identifying the active sites, and even monitoring the dynamic behaviors of both the geometric structure and electronic environment of the catalytic sites at atomic scale. However, due to lack of model SACs with definite coordination environment and the practical operando spectroscopic techniques with high atomic-resolution, up to now, little experimental evidence is available regarding the structural and dynamics of SACs during catalysis. On the other hand, nitrogen-coordinated single-Fe-atom on carbon (Fe-N-C) catalysts exhibit high oxygen reduction reaction (ORR) activity, which is indispensable for clean energy technologies such as fuel cells and metal-air batteries. However, conundrums over the nature of active sites and the reaction mechanism remain as major bottlenecks, restricting further developments of high-performance M-N-C single-atom catalysts.

Herein, we have explored the exact structure of active sites and provided electronic-level insight into the underlying ORR mechanism based on the newly designed model single-Fe-atom catalyst using *operando* X-ray absorption spectroscopies, as well as the newly developed *operando* ⁵⁷Fe Mössbauer technique. Combining with theoretical studies, the dynamic cycles of both the geometric structure and electronic configuration of reactive single-Fe-atom active center were evidenced via directly capturing the reactive intermediates under *in-situ* ORR conditions. We anticipate that our newly developed *operando* ⁵⁷Fe Mössbauer technique for the *in-situ* characterization on SACs shall pave ways for the further insight into the structural and dynamics of catalytic active centers during catalysis, which may provide proof-of-concept for single-atom heterogeneous catalysis as a conceptual bridge between homogeneous and heterogeneous catalysis.

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Invited Lecture

Lattice Dynamics of Rare-earth Silicide Nanostructures: Films, Islands, Wires

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The continuous downscaling of CMOS devices imposes severe material and processing challenges and demands a continuous search for new self-organized nanostructures integrated with the Si technology. Rare-earth silicides became especially attractive for future applications due to their metallic nature and low Schottky barrier heights [1-3]. Deposited on Si, depending on the amount of the material, temperature and surface orientation, some of the lanthanides self-organize in high aspect ratio nanowires, nanoislands and clusters [4]. Interconnects, contacts, and source/drain areas of the transistors are among the most critical components, which might be affected by size-induced phonon instabilities.

In order to perform a systematic study of the lattice dynamics modifications in these nanostructures, we have grown epitaxial EuSi₂ films and nanoislands [5,6] and DySi₂ films, nanoislands and nanowires [7] and investigated the Eu- and Dy- partial density of phonon states (DOS) by *in situ* nuclear inelastic scattering and first-principles calculations. We found that the phonon DOS of the nanoislands [8] and nanowires [9] strikingly deviate from that of the bulk and surface layers and it is strongly influenced by the atomic confinement at the nanostructure/substrate and nanostructure/nanostructure interfaces. These deviations result in remarkable modifications of the thermodynamic and elastic properties and open up new avenues for their manipulation.

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X-ray Quantum Optics with Mössbauer Nuclei

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Ideas from quantum optics play an important role in studying, controlling, and utilizing light-matter interactions in many regions of the electromagnetic spectrum. This raises the question, whether such concepts could also be utilized to improve or develop applications of Mössbauer nuclei [1]. In recent years, various effects known from the optical domain have already been experimentally demonstrated with nuclei. In this talk, I will introduce nuclear quantum optics, and address some of its challenges and future perspectives.

One of the key challenges is the lack of efficient strong x-ray control fields for nuclear quantum optics. I will show how the precisely controlled mechanical motion of a resonant target can be used to manipulate the effective index of refraction of a nuclear resonance, and thereby simulate the effect of such a strong control field in certain settings.

As a first application, I will address the problem that the spectra of short x-ray pulses delivered by state-of-the-art sources are orders of magnitude broader in energy than the narrow resonances. Thus, only a tiny fraction of the photons interact resonantly with the sample, while the vast majority of photons form an off-resonant background. I will demonstrate how mechanical motions allow one to shape the spectrum of a given x-ray pulse, such that the number of resonant photons in the pulse is significantly increased [2].

As a second application, I will discuss the generation of tunable phase-coherent x-ray double-pulse sequences resonant to nuclear transitions. Using a multi-dimensional spectroscopic measurement technique, I will demonstrate that these double-pulses can be used to coherently control the nuclear dynamics in a pump-probe setting. In a proof-of-principle experiment, we find clear signatures of basic light-matter interactions such as stimulated emission and absorption between the nuclei and the x-rays [3].

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Electron Structures and Nuclear Vibration Energy Spectra of Heme Carbene Derivatives

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Cytochrome P450, an important metabolic enzyme, involves in many biochemical reactions including reductive metabolism of halogenated compounds and ropylene epoxidation [1]. As one of the intermediates of those reactions, heme carbene has attracted extensive research interests. However the valence states [2] and electron configurations [3] of iron atoms of heme carbenes have been debated for many years.

In this work, a set of five and six coordinated iron porphyrin carbenes are isolated and characterized by single crystal X-ray, X-ray near edge absorption (XANES) and Mössbauer spectra [4-6]. The XANES studies suggested iron(II) oxidation state of the complexes, while the high field Mössbauer experiments determined $S = 0$ electronic configuration (Fig. 1, left) [4]. The Mössbauer spectra of six coordinated complexes suggest that the bonding of trans imidazole ligands only induced small decreases on ΔE_Q (~ 0.5 mm/s) compared to the [Fe(TFPP)(CPh₂)] precursor, which is consistent with the stronger π bonding ability of CPh₂ carbene (Fig. 1, middle) [5]. Moreover, synchrotron based Nuclear Resonance Vibrational Spectroscopy (NRVS) was applied to investigate the [Fe(TTP)(CCl₂)] single crystal. The combination of experimental and DFT studies (Fig. 1, right) further confirmed the strong-field property of the carbene ligand [6].

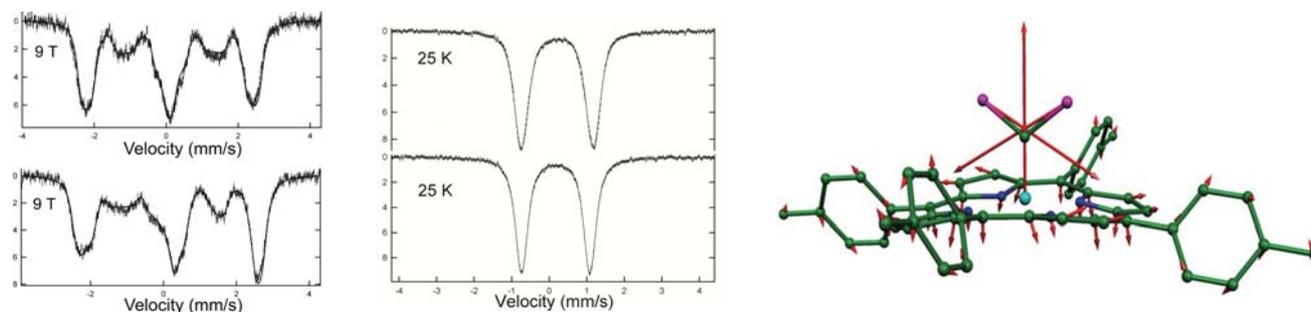


Figure 1. left: 4.2 K Mössbauer spectra of [Fe(TPP)(CCl₂)] (top) and [Fe(TFPP)(CPh₂)] (bottom) recorded under 9 T applied field; middle: Mössbauer spectra of [Fe(TFPP)(CPh₂)(1-EtIm)] (top) and [Fe(TFPP)(CPh₂)(1,2-Me₂Im)] (bottom) at 25 K; right: The predicted vibrational modes of [Fe(TTP)(CCl₂)] at 444 cm⁻¹.

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Structural, Optical and Photocatalytic Properties of Elongated Cu-, Co- and Sn-doped Goethite and Hematite Nanoparticles

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Iron(III) oxides are inexpensive, non-toxic and stable compounds which are extensively investigated for different applications. They can incorporate significant levels of various metal ions into the crystal structure, which can have a positive effect on different properties [1]. Due to significant absorption of solar radiation, iron(III) oxide nanoparticles and nanostructures are investigated for possible application as photocatalysts for decomposition of toxic compounds [2] and photoelectrodes for hydrogen production by water splitting [3]. Heterogeneous photo-Fenton reaction using iron oxide photocatalysts has emerged as a promising way for decomposition of toxic organic compounds by visible light [4]. Size and shape of iron oxide nanoparticles were shown to be very important for photocatalytic activity in heterogeneous photo-Fenton reaction [5,6]. However, the effect of doping on the photocatalytic activity of iron oxides has been much less investigated.

In the present work, the effects of Cu, Co and Sn ions doping on different properties (unit cell size, crystallite size, particle size and shape, hyperfine magnetic field, optical and visible light photocatalytic properties) of elongated goethite (α -FeOOH) and hematite (α -Fe₂O₃) nanoparticles were investigated. Elongated goethite nanoparticles doped with Cu, Co and Sn ions were synthesized by the coprecipitation of mixed Fe(NO₃)₃ and Cu(NO₃)₂, CoCl₂ or SnCl₄ aqueous solutions using a strong organic alkali tetramethylammonium hydroxide (TMAH). Elongated hematite nanoparticles (pure and doped) were produced by calcination of corresponding goethite nanoparticles. Incorporation of metal cations in the crystal structure of goethite and hematite was confirmed from the change in unit cell size (determined by XRPD) and from the reduction of hyperfine magnetic field (determined by Mössbauer spectroscopy). Also, a strong effect of doping on the nanoparticle size and shape was observed by FE-SEM. Diffuse reflectance UV-Vis-NIR spectroscopy showed a significant influence of doping on the position of goethite and hematite absorption edge. Optical band gaps in samples were estimated using Tauc plots. A significant reduction of direct and indirect optical band gaps in goethite and hematite nanoparticles by Cu, Co and Sn doping was observed. Visible light photocatalytic performances were examined by decomposition of rhodamine B dye in the presence of iron oxide photocatalyst and H₂O₂ under visible light illumination. Generally, hematite nanoparticles showed higher photocatalytic activities than goethite nanoparticles due to higher absorption of visible light. Photocatalytic activities of goethite nanoparticles were ranked as Cu-doped > Sn-doped > Co-doped > undoped, while photocatalytic activities of hematite nanoparticles were ranked as Cu-doped > Sn-doped > undoped > Co-doped. The high photocatalytic activity of elongated Cu-doped hematite nanoparticles can be explained by a combined effect of an enhanced separation and transfer of photogenerated charges (due to Cu doping) and their short distance from the particle surface (due to nanoneedle morphology).

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Manipulating Spin Transition to Achieve Switchable Multi-functions

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The spin transition of metal ions involves interconversion between electron configurations exhibiting considerably different functions and plays a substantial role in the chemical, physical, and biological fields. The photoinduced spin transition offers a promising approach to tune various physical properties with high spatial and temporal resolutions for producing smart multifunctional materials not only to explore their basic science but also to satisfy the demands of the next-generation photo-switchable molecule-based devices. Therefore, it is attracting considerable interest to utilize photoinduced spin transition to simultaneously tune multi-functions. However, two issues are challenging to achieve reversible and swift manipulation of functions: (1) the interconversion between different electron configurations of photoresponsive units should be reversibly switched via photoinduced spin transition; (2) effective coupling should be built between the photoresponsive and functional units to produce photo-switchable functions utilizing photoinduced spin transition. We will review our recent advances in the usage of spin transition of metal ions as actuators for tuning the magnetic, dielectric, fluorescence, and mechanical properties, wherein the role of a photo-switchable spin transition is highlighted. We mainly focus on the study of two spin transition categories, including spin-crossover (SCO) of one metal ion and metal-to-metal charge transfer (MMCT). Initially, we will describe a strategy for developing photoinduced reversible SCO and MMCT. The role of flexible intermolecular interactions in particular $\pi\cdots\pi$ interactions is discussed with respect to a photoinduced reversible MMCT. Then the SCO and MMCT units were assembled using metalocyanate building blocks to form a chain, wherein the spin states, anisotropy, and magnetic coupling interactions can be photoswitched to tune the single-chain magnet behavior. Besides magnetic properties, the photoinduced spin transition that is associated with the concomitant changing of charge distribution, bond lengths, and absorption spectra can be utilized to tune the multi-functions. Therefore, the transfer of an electron from a central cobalt site to one of the two iron sites in linear trinuclear Fe_2Co compounds resulted in the transformation of a centrosymmetric non-polar molecule into an asymmetric polar molecule, and the molecular electric dipole and dielectric properties can be reversibly switched. Moreover, the spin transition usually involved significant expansion or contraction of coordination sphere of metal ions due to the population/depopulation of the antibonding e_g orbitals. Therefore, colossal positive and negative thermal expansion behaviors were achieved in a layered compound by manipulating the spin transition process and the rotation of the functional units, thereby providing a strategy for synthesizing phototunable nanomotors. Photoinduced spin transition can also be used to modulate the fluorescence properties by controlling the energy transfer between the fluorescent ligands and the metal sites showing SCO.

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Mössbauer Investigation on Fused Iron Catalysts For α -olefin Synthesis Via Fischer-Tropsch Route

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Nowadays, Fischer-Tropsch synthesis (FTS) has been successfully applied in commercial production from coal or natural gas on a large scale. It would be economic feasible even in a small plant, if high value-added products, such as α -olefins, long chain alcohols etc could be yield via FTS. Iron catalyst occupies an indispensable status not only due to its low cost, but also for its high selectivity to olefins with low CH_4 productivity. Using a fused iron catalyst was a potential option for α -olefin production via FTS.

In present paper we focused on fused iron catalyst for Fischer-Tropsch synthesis for α -olefin. Three different fused iron catalysts (AAW, OT, IF) were made by different melting methods and various characterization technologies were used to study the bulk phase composition, and reduction and adsorption behaviors. The syngas conversion and CH_4 selectivity of AAW was very similar to a commercial fused Fe catalyst reported by Sasol, slightly better than OT, but much better than IF. The much inferior IF catalyst was attributed to contamination with Al (Si) from the container, as the melting pool leached the wall of the crucible severely. The introduction of Al (Si) resulted in the formation of an irreducible FeAl_2O_4 or/and Fe_2SiO_4 phase that resisted carburization, thus IF exhibited the lowest content of active carbide. The AAW catalyst, composed of mainly magnetite phase (Fe_3O_4) besides a trace amount of FeO , was reduced in steps and formed two active sites. Mössbauer spectroscopy result indicated that the spent AAW catalyst possessed the largest carbide content, which correlated well with its high activity and olefin selectivity.

Afterward, the reduction temperature was varied to obtain different Fe phase compositions for optimized fused-iron catalyst. These model catalysts were subject to the Fischer-Tropsch synthesis and phase evolution was monitored. XRD and Mössbauer spectroscopy were used to quantitatively determine the phase composition. They indicated that a high reduction temperature and high GHSV (gas hourly space velocity) favored the transformation from Fe_3O_4 to α -Fe, although a higher reduction temperature led to larger α -Fe crystallite sizes. Furthermore, α -Fe gradually transforms to an iron carbide (χ - Fe_5C_2) phase in a period of 12 h when exposed to syngas ($\text{CO} + \text{H}_2$). After a 500 h run in the FTS, the partial carbide regenerated into Fe_3O_4 again. Magnetite had negligible catalytic activity for the FTS, whereas iron carbide was active. Nonetheless, the activity was proportional to the surface area of iron carbide. Higher reduction temperatures guaranteed lower methane selectivity and a higher olefin to paraffin ratio.

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Structure determination of atomically dispersed Fe-N-C catalysts by Mössbauer spectroscopy

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Single-atom catalyst (SAC), with all the metal species dispersed as isolated single atoms, has now become a new frontier of heterogeneous catalysis.¹⁻³ Compared with nanoparticle catalysts, SACs offer the advantages of maximized metal atom efficiency, uniform and well-defined structure, and distinctive performances in a variety of selective transformations. In this contribution, I will start with a brief summary of the SAC development, and then introduce a special type of SACs, M-N-C (M represents transition metals like Co, Fe, Ni, etc.) catalysts with all the M species dispersed as isolated single atoms.⁴⁻⁶ The Fe-N-C SACs were prepared by a template-sacrificial approach with Fe(phen)_x (phen=1,10-phenanthroline) complex as the N/C source and nano-MgO as the template. After pyrolysis at 600-800 °C under N₂ atmosphere, the resultant material was further treated by acid leaching to remove the MgO template to obtain the Fe-N-C SACs. The Fe-N-C SACs exhibited high activity and excellent reusability for the selective oxidation of C-H bond. A wide scope of substrates including aromatic, heterocyclic, and aliphatic alkanes were smoothly oxidized at room temperature and the selectivity of corresponding products reached as high as 99%. By using subångström-resolution HAADF-STEM in combination with XPS, XAS, ESR and Mössbauer spectroscopy, we have provided solid evidence that Fe is exclusively dispersed as single atoms via forming FeN_x (x = 4, 5, and 6) and the relative concentration of each FeN_x species is critically dependent on the pyrolysis temperature. Among them, the medium-spin Fe(III)N₅ affords the highest TOF (6455 h⁻¹), which is at least one order of magnitude more active than the high-spin and low-spin Fe(III)N₆ structures and three times more active than the Fe(II)N₄ structure, although its relative concentration in the catalysts is much lower than the Fe(III)N₆ structures. This work has demonstrated that the Mössbauer spectroscopy is a powerful technique for determining the structure of Fe-N-C SACs.

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Learning from Precision Evaluation Studies and Learning about Hyperfine Interactions

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In this talk, I will discuss two separate topics that do relate to Mössbauer spectroscopy.

Within the electronic structure community, many computer codes are available to do density functional theory (DFT) calculations – say 20 or more. All codes perform the same basic tasks, plus some specialties specific for every individual code. They have been programmed independently over decades, and they have large user communities behind them. Do all of these codes make identical predictions? Does some have important bugs? In short, which one is the ‘best’? A few years ago, a team of 69 researchers set out to answer these questions [1].

The preceding paragraph describes a situation that is not unfamiliar to the Mössbauer community: there are many different codes available to fit/analyze Mössbauer spectra. They have grown over decades, they have their own user base, and the basic tasks they perform are the same for every code. Which one is the ‘best’, and how do you even define ‘best’?

I will tell you the story about how the electronic structure community succeeded to make a thorough assessment of the precision of its codes, in a positive way that pushed the community forward. And I will reflect with you on how such an approach could be applied to the fitting codes of the Mössbauer community.

A second topic deals with the question: how do we educate new generations of students/researchers about hyperfine interactions and the experimental methods based thereupon? In particular, how do we do this in a world in which few universities have the human resources to offer dedicated courses about these topics to students? I will introduce you to www.hyperfinecourse.org, a fully online course on hyperfine interactions and related methods, including Mössbauer spectroscopy. It can be used for self-paced individual study, or within a class context (flipped classroom / blended learning).

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Charge, Orbital and Spin Orderings in Perovskite-like Manganites: Probe Mössbauer Diagnostics

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We summarize the results of study of hyperfine interactions of ^{57}Fe probe atoms in two families of perovskite-like manganites: AMnO_3 ($A = \text{Bi, Tl}$) and $\text{AMn}_7\text{O}_{12}$ ($A = \text{Bi, Ca, Sr, Cd, Pb}$). Most of these compounds were obtained using the high pressure-high-temperature (HP-HT) synthesis for the first time [1-2]. ^{57}Fe probe Mössbauer spectroscopy was used for the investigation of the effect of the polar Bi^{3+} ions on the local symmetry and magnetic ordering of the Mn^{3+} ions in the ferromagnetic perovskite BiMnO_3 and double perovskite $\text{BiMn}_7\text{O}_{12}$. In these bismuth-containing oxides, a Bi^{3+} -induced polarization in combination with the Jahn-Teller (J-T) character of the Mn^{3+} cations lead to a significant distortion of the crystal lattice and the appearance of a whole cascade of temperature-induced structural and magnetic phase transitions. The ^{57}Fe spectra recorded in the paramagnetic temperature range ($T > T_C, T_N$) were discussed supposing Fe^{3+} probe ions to replace manganese in the $(\text{Mn}^{3+}\text{O}_6)$ polyhedra. The large quadrupole splitting observed below the temperature of structural phase transitions $C2/c \leftrightarrow C2/c$ (BiMnO_3) and $P1 \leftrightarrow I2/m \leftrightarrow I2/m(o) \leftrightarrow Im\bar{3}$ ($\text{BiMn}_7\text{O}_{12}$) can be explained by the strong J-T distortion and cooperative orbital ordering. The reduced, but finite quadrupole splitting above the orbital ordering temperature (T_{OO}), showed that J-T distortion remains after melting the orbital order. Theoretical calculations of the electric field gradient (EFG) tensor, which was performed for all of compositions, demonstrated that the major contribution to the EFG is well connected with dipole component, which is driven by high values of oxygen (α_O) and in particular cases of bismuth (α_{Bi}) polarizability. These contributions were discussed in terms of ions displacements from its centrosymmetrical positions (lattice contribution) and strains of its electronic shells (electronic contribution).

By means of ^{57}Fe probe Mössbauer spectroscopy we investigated double $\text{AMn}_7\text{O}_{12}$ ($A = \text{Ca, Sr, Cd, Pb}$) perovskites, where heterovalent ions Mn^{3+} and Mn^{4+} are located in octahedral oxygen surrounding with a different distortion degree versus their electronic structure. The detailed Mössbauer research in wide temperature range allowed to establish the features of $R\bar{3} \leftrightarrow Im\bar{3}$ phase transition due to charge ordering in Mn-sublattice as well as the appearance of structural modulation in these oxides associated with orbital ordering.

Mössbauer spectra recorded below magnetic ordering temperatures ($T < T_N$) demonstrates a broadened and generally asymmetrical Zeeman hyperfine structure which is characteristic for magnetic systems exhibiting noncollinear space modulated spin ordering. It was shown that hyperfine field B_{hf} at ^{57}Fe nuclei demonstrates a substantial anisotropy. Different mechanisms of these anisotropy including dipole and orbital contribution were discussed.

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Further Development of the Database of the Mössbauer Effect Data Center

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The idea and history of the Mössbauer spectroscopy database compiled and maintained by the Mössbauer Effect Data Center (MEDC) dates back to the 1960's when the structure and content of the database was shaped through the work and ideas of Muir et al. [1] and Stevens et al. [2]. Following 40 years of operation in Asheville, USA, MEDC moved to Dalian, China, in 2010 [3,4]. Data collection over several decades has resulted in a unique database that currently includes bibliographical details of above 60000 Mössbauer spectroscopy related publications, along with above 115000 associated data records, incorporating among others ca. 20000 explicitly given ⁵⁷Fe Mössbauer isomer shift and quadrupole splitting data pairs extracted from publications in conjunction with ca. 13700 different absorber materials. The scope of the database is being continuously extended by the Mössbauer Effect Data Center with newly added bibliographic and Mössbauer data. The database also forms the basis of the reference and data listing (and further associated) sections of the Mössbauer Effect Reference and Data Journal (MERDJ). An online version of the database is available via the WEB site of MEDC [5], which provides query access to database data on a subscription basis. In order to further enhance the added value the database contributes worldwide to the scientific research process with, recently a further development of the database was started. The way the database is stored and managed at MEDC has been renewed via the development of a new database management software, and the structure of different tables of the database has been extended by new fields such as, for example, the DOI link [6] of publications and the apparent magnetic field Mössbauer parameter published on the basis of spectra displaying magnetic splitting. The results achieved up to this point are going to be presented along with plans and upcoming steps of further development.

Acknowledgement

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Comprehensive Mössbauer- and X-Ray Spectroscopic Studies on Reengineered Molecular Switches

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Developing light-activated functional molecules has been a major goal in molecular engineering as such systems hold the promise for solutions to many technological problems ranging from IT to sustainable development. Although major advances have been realized in this field recently, achieving such economic and environment-friendly systems still seems far away. Transition metal complexes are among the most promising candidates because their properties can be tuned by varying the electronic and molecular structure of the ligands. Relevant efforts have been focused on engineering complexes of the abundant and harmless iron, particularly on the ubiquitous model systems with polypyridine ligands. The photophysics in these systems can be tuned from that of a molecular switch to that of a photosensitizer. The key to developing efficient functional molecules is to obtain a thorough understanding of the potential energy surfaces (PES) of the complexes, then to re-design the molecules to modify the relaxation pathway in a direction that is optimal for the required function. Controlled switching of the spin- or valence states of transition metal centers on a molecular level may give access to sub-picosecond time- and nanometer space regimes, surpassing existing technologies by orders of magnitude.[1]

Low spin divalent iron ions complexed with terpyridine ligands are very promising candidates for switchable molecular systems with properties necessary for applications: quick and efficient switching, long living excited states and room temperature functionality.[2-4] In order to unleash their potential, we apply theory inspired modifications on the coordinating ligands both with extending the terpyridine rings with electron donor or –acceptor side groups or with exchanging one of this tridentate ligands with characteristically different ones like cyanides while monitoring the changes with ^{57}Fe Mössbauer and hard X-ray spectroscopies.[5-7] This strategy enabled the swift tuning of the potential energy surfaces and thus the switching properties shown by the novel molecular complexes.

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⁵⁷Fe Mössbauer Spectroscopic Feature of Low-coordinate Iron Complexes with N-heterocyclic Carbene Ligation

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The knowledge on the formation, structure, spectroscopic feature and reactivity of low-coordinate transition-metal species lays the basis for modern organometallic chemistry. Low-coordinate iron species are among the reactive intermediates attracting great attention for their unique chemical and magnetic properties. This presentation will introduce our studies on low-coordinate iron complexes with N-heterocyclic carbene (NHC) ligation. NHCs are found excellent ancillary ligands to stabilize iron(V, IV, III, II, I, 0) complexes with their coordination numbers ranging from 4 to 2. The correlation of their structure features with their ⁵⁷Fe Mössbauer data of these complexes will be discussed.

Mössbauer Study of Iron-silicate Glass-ceramics Prepared from Domestic Waste Slag Exhibiting Visible-light Activated Photocatalytic Effect

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In this study, the relationship between visible-light activated catalytic effect and local structure of iron-silicate glass prepared from Japanese domestic waste slag was investigated by ICP-OES, XRD, UV-Vis and ⁵⁷Fe-Mössbauer spectroscopy. As a result of elemental analysis, a domestic waste slag (WS) collected at the Tamagawa combustion plant in Tokyo was composed of SiO₂ (23.3 in mass%), CaO (21.8), Al₂O₃ (16.7), Fe₂O₃ (11.5), Na₂O (6.6) and others (20.1) [1]. The XRD recorded for WS indicated the halo pattern of amorphous structure [1]. The RT-Mössbauer spectrum of WS was composed of two paramagnetic doublets: Doublet 1 with the isomer shift (IS) of 0.84 mm s⁻¹ and quadrupole splitting (QS) of 1.39 mm s⁻¹, and Doublet 2 with IS of 1.00 mm s⁻¹ and QS of 2.01 mm s⁻¹. Both doublets are due to distorted Fe^{II}O₄ [1]. In order to recycle WS as a visible-light activated photocatalytic material, the glass-ceramic with a composition of WS•10Na₂O•xFe₂O₃, WSNaFex with 'x' of 50 was heat-treated at 800 °C for 100 min. The Mössbauer spectrum measured at 80 K showed a magnetic sextet with IS of 0.41 mm s⁻¹ and an internal magnetic field (H_{int}) of 52.7 T, which is assigned to nanoparticles (NPs) of α -Fe₂O₃ in silica matrix [1]. The pseudo-first-order rate constant (k) of 2.65•10⁻³ min⁻¹ was estimated under the methylene blue decomposition test of heat-treated WSNaFex (x=50) under the visible light irradiation [1]. A higher k value of 9.75•10⁻³ min⁻¹ was recorded for heat treated R-WSNaFe30, WSNaFe30 prepared from chemical reagents without impurity elements. The low-temperature Mössbauer spectrum indicated the existence of NPs of α -Fe₂O₃ and other iron oxides such as CaFe₂O₄. More interestingly, a much larger k value of 28•10⁻³ min⁻¹ for the heat-treated R-WS was recently obtained under the irradiation of visible-light by adding 0.4 M H₂O₂ (that is the Photo-Fenton reaction). The RT-Mössbauer spectrum of R-WS showed one paramagnetic doublet with IS of 0.18 mm s⁻¹ and QS of 1.34 mm s⁻¹ due to distorted Fe^{III}O₄ tetrahedra. On the other hand, the smaller k value of 22•10⁻³ min⁻¹ and the larger IS 0.38 of mm s⁻¹ due to distorted Fe^{III}O₆ octahedra were estimated for the heat-treated WS. This result implies that the Photo-Fenton reaction is related to the covalency of the Fe-O chemical bond. It is concluded that α -Fe₂O₃ NPs and Fe^{III}O₄ tetrahedra included in the silica matrix is effective for the visible-light activated photocatalytic and Photo-Fenton reactions, respectively, and that the isolation of impurity elements from domestic slag results in the increase in catalytic effect caused by iron.

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Synthesis and Characterization of Akaganeites Formed in Presence of Cations and Their Use as Adsorbent of Contaminants in Water

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This presentation consists of three parts: firstly, we critically review the different controversial models used to fit Mössbauer spectra of pure akaganeite in the magnetic and paramagnetic regions and also in presence of external magnetic field. We argue that a reasonable model to be used is that which takes explicitly into account the existence of four non-equivalent iron sites related to the two monoclinic iron sites in the vicinity of occupied or unoccupied chloride sites [1]. We used this model to determine the room temperature recoilless f -fractions in akaganeite [2]. Secondly, we review the different studies performed by our group on the effects of cations such as Al^{3+} , Ti^{4+} , Cr^{3+} , Cu^{2+} , Mn^{2+} , Co^{2+} , As^{5+} , Sb^{3+} and Hg^{2+} , on the formation of akaganeite [3]. The results suggested that only a small part or none of the cations were incorporated into the crystalline structure. Additionally, Ti^{4+} , Sb^{3+} , As^{5+} and Hg^{2+} are cations that drastically affects the nucleation and growth of the akaganeites, promoting the formation of nanoparticles. By using the fitting model proposed in this work, we found that the hyperfine data at 77K suggested that the Fe 3d orbital population is mainly affected for those iron ions located in the vicinity of unoccupied chloride sites and also in the surface. Thirdly, we review the use of akaganeite as a possible adsorbent of metallic contaminants in water and present some preliminary results on the kinetics of absorption of some metals.

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Past, Present and Future of Mössbauer Spectrometer Designs

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The state of art in Mössbauer spectrometer design is presented on the base of the thirty years experience. The questions connected with Doppler modulation system, gamma-ray counters, detection conversion electrons and x-ray, data storage systems are mention.

Doppler modulation system included Doppler modulator (velocity transducer) and a control system (modulator driver) determinates the quality of an energy axis of a resonance spectrum. The most convenient and simple system used the linear Doppler effect was offered by R. Mössbauer and all modern spectrometers use this principle. The present progress of digital signal processing allows to change analog modulator drivers by digital control systems and consequently to have more stable parameters of spectrometer.

The choice of gamma-ray detector is primarily depended on the energy of Mössbauer transition. Proportional gas counters are used for gamma rays with low energy in the 1-30 keV range. As a gas admixture Ar, Kr, Xe with CO₂ and CH₄ are commonly applied. Scintillation detector most commonly NaI(Tl) are used for low and high energy gamma rays. Semiconductor detectors have superior energy resolution are not very frequently used in the low energy range. Special detectors named resonance detector have selective sensitivity to Mössbauer gamma rays and consequently they have unique resolution. New possibilities of modification of detector systems discovery with new modern scintillator as LaBr:Ce, YAP:Pr and SiPMT which can replace standard photomultipliers.

The data storage system registers the distribution of the number of events (gamma-quanta, x-ray quanta or electrons) transmitted through the sample or scattered by it as a function of their energy. The historically first method of spectra registration based on discretizing the velocity axis with fixed quantization step was used in spectrometers of the modulation type (modulation registration mode). The amplitude of output signal of the radiation detector is modulated according the real velocity of the motion between radiation source and sample, consequently multichannel amplitude analyzer is used for spectra accumulation. The second and most common method (time registration mode) uses sampling the time axis with fixed step of quantization for performance of a multichannel mode accumulation of Mössbauer spectra. The alternative method (time-modulation mode) of Mössbauer spectra registration with simultaneous sampling of the velocity signal and time scale was developed but it is not used across evident advantages. The progress in digital signal processing allows today to build the Mössbauer storage system used time-modulation mode without complication connected with past low level of electronic integration.



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Young Scientist Lecture

On a Hyperfine Interaction in ϵ -Fe

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In this study we discuss the advantages and disadvantages of conventional Mössbauer spectroscopy and synchrotron radiation based techniques, such as synchrotron Mössbauer spectroscopy or nuclear forward scattering of synchrotron radiation in order to identify a small splitting in the nuclear levels of ^{57}Fe .

We report the evidence of a long-sought finite hyperfine interaction in hexaferrum (ϵ -Fe) by introducing synchrotron radiation perturbed angular correlation spectroscopy at extreme conditions.

Our study indicates an energy splitting of about 3 neV in the nuclear levels of ^{57}Fe at 30(1) GPa and room temperature. Such a splitting is predominantly related to a quadrupole interaction, though the presence of modest magnetic interactions cannot be fully excluded.

This study paves the way for a systematic characterization of subtle electronic or spin state transitions at extreme conditions which are otherwise inaccessible.

Mössbauer Spectroscopy as a Useful Method for Distinguishing Between Real and False Meteorites

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Ordinary chondrites [1] represent the most frequent group of all meteorites (about 80% of all falls). The Mössbauer spectra of ordinary chondrites have characteristic features and may be used for recognition between real and false sample of a meteorite. The Mössbauer spectrum of non-weathered ordinary chondrites is composed of 4 phases: 2 doublets from olivines and pyroxenes (the minerals present on Earth) and 2 sextets from troilite and metallic phase (these 2 are created only in cosmic conditions) [2]. In the weathered ordinary chondrites additional subspectra from oxides and hydroxides of iron can be found [3], [4], [5]. Our laboratory received a sample, which according to the sender, could represent a part of Pultusk meteorite. The Pultusk meteorite fell in the form of meteorite rain on January 30, 1868 in Mazowia region, fifty kilometers from Warsaw (Poland) near Pultusk. The abundant decline of thousands of specimens weighing from a gram to several kilograms allowed for the gathering of hundreds of specimens. Parts of this meteorite are still found, but false samples also occur. In this paper we described how one can easily distinguish the original meteorite remnants from the fake ones. The Mössbauer spectrum of an unidentified sample of a meteorite was compared with the spectra of two meteorites: Pultusk and Grzempach. All Mössbauer spectra were obtained at room temperature. The fitting procedure was performed using the “Full Static Hamiltonian” analysis in the Recoil program. A feature that indicates that the tested fragment is not the original material from Pultusk is presence of the subspectra typical for strong weathering process. There are no mineral phases present in the material that are characteristic for meteorites (e.g. kamacite and troilite). For verification of our hypothesis, the samples were sent to the Mössbauer lab in Radom without information about their origin. The results of our experimental studies will be discussed.

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High-pressure Magnetic Phase of Eug_4

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Rare-earth Eu compounds represent an intriguing class of magnetic materials that provide a competing playground of Kondo physics, RKKY exchange interactions, and valence evolution. Here, we explore the evolution of antiferromagnetism under pressure via synchrotron-based Mossbauer spectroscopy. Contrary to previous electrical transport results, our observation provides direct evidence of a magnetic ground state at high pressure, continuous through a first order phase transition at 5 GPa and persisting to at least 13.6 GPa. We discuss this result in the framework of a potential interaction between evolution of the valence condition and an increase in the ordering temperature.

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Understanding the Unique Magnetic Properties of Planar [Fe(II)(Tpp)] – a Complex With Unquenched Orbital Momentum

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It was found that iron-porphyrins make very efficient and ultra-selective molecular catalysts for CO₂ reduction into CO. Understanding the mechanism of the reaction is the key to rationalize the high performance of the catalyst. In this regard, understanding the electronic structure of the archetypical catalyst [Fe(TPP)]ⁿ in all the charge states intervening in the reaction, n = 0, -1, and -2, is the first step to build up a knowledge of the reactivity of this particular catalyst (TPP = tetraphenyl porphyrin).

The electronic structure of [Fe(II)(TPP)] in particular has been extensively studied for several decades. While consensus has been reached on its intermediate spin state S = 1, the exact nature of its electronic structure remains controversial to this day, due to the near-degeneracy of its orbital states, leading to its extremely peculiar magnetic behaviour. The study aims to assign unambiguously the electronic structure of [Fe(TPP)], using a combination of SQUID and Mössbauer spectroscopy under variable fields and temperatures, supported by ab-initio CASSCF calculations. Specifically, an effective Hamiltonian acting on the space of the near-degenerated orbital states predicted by ab-initio calculations was designed in order to understand better the experimental data. The effective Hamiltonian was shown to parameterize properly the magnetization data as well as magnetic Mössbauer spectra. Unlike the phenomenological spin-Hamiltonian, it also provides a qualitative understanding of the relationship between the peculiar molecular and electronic structures of the system and its magnetic behaviour. Finally, the shortcomings of the Spin-Hamiltonian formalism in this peculiar case have been analysed by comparing it with the above-mentioned perfectly functional model.

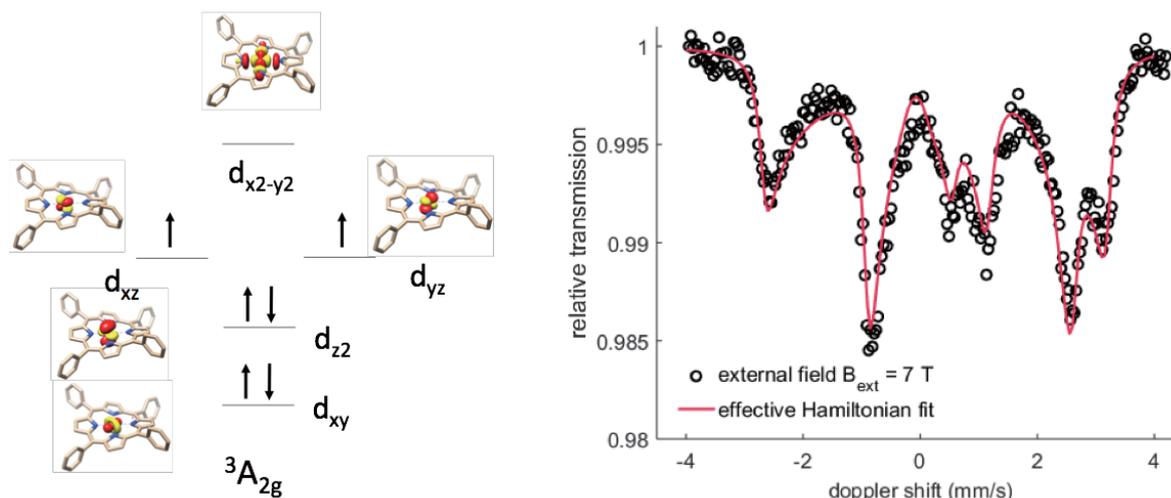


Figure 1. Electronic ground state of [Fe(TPP)] (left) and Mössbauer spectrum of [Fe(TPP)] at 1.7 Kelvins under an external magnetic field of 1 Tesla.

NRVS and NFS Study of an N₂-Reducing Molecular Iron-potassium Complex

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The production of ammonia from inert dinitrogen is essential for all forms of life. However, the detailed mechanism of N₂ triple bond activation by iron surfaces in the Haber-Bosch process has remained elusive.¹ Molecular iron-potassium complexes that catalyze N₂ reduction are of significant interest as they provide a direct means to assess the electronic-structural requirements of N–N bond cleavage within a simplified model system. Rodriguez et al. have reported a molecular iron complex which, when reacted with N₂ in the presence of a potassium-based reductant, generates a tetranuclear iron bis-nitride product in which the N₂ triple bond has been fully cleaved.² Structures of both the precursor and the product are known from x-ray crystallography. However, these two end points only demonstrate that the reaction happens and provide no insight into how the N–N triple bond is cleaved. An intermediate along the pathway to forming the bis-nitride product, the so-called “green intermediate,” has been characterized by Mössbauer spectroscopy, X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES); however, its exact nature has remained elusive. Attempts to characterize the green intermediate by traditional vibrational spectroscopies (including IR and resonance Raman) have thus far been unsuccessful.

In this study, a combination of Nuclear Resonance Vibrational Spectroscopy (NRVS) and Nuclear Forward Scattering (NFS) is used to try to understand how the N–N triple bond is cleaved by the iron complex. The “green intermediate” reaches maximum yields ~3 minutes after starting the reaction and decays fully to the bis-nitride product after 40 minutes. NRVS spectra were collected for the precursor and final product, as well as several intermediate points early in the reaction. NFS spectra obtained in parallel provided information about the amount of precursor and final product at each intermediate time point, which enabled deconvolution of the vibrational spectra and clear establishment of the NRVS features associated with the “green intermediate.” Furthermore, all spectra were collected with both ¹⁴N- and ¹⁵N-labelled N₂. This allowed us to clearly establish the spectral features associated with bound N₂. These results are correlated to our on-going DFT calculations of the NRVS spectra. The preliminary DFT calculations were validated by comparison to selected model compounds.

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Towards the Development of a Chromium Free High Temperature Water Gas Shift Catalyst

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The high temperature water gas shift reaction (1) plays a vital role in many industrial processes, including ammonia production and Fischer-Tropsch synthesis^[1]. The industrially used chromium/copper doped iron oxide (Fe₃O₄, magnetite) catalyst has changed little since its original discovery because of its high stability and low material costs. However, the use of chromium, which acts as a structural stabilizer, has recently come under debate because of the toxicity of its 6+ oxidation state, small amounts of which can exist in the fresh catalyst^[1]. The mechanism by which chromium stabilizes the structure is however still poorly understood. To underpin its exact role, a suite of chromium and chromium/copper doped iron oxide catalysts with different loadings were prepared, thoroughly characterised with Mössbauer spectroscopy, XRD, CO-TPR, TEM, and N₂-physisorption, and subsequently tested under industrially relevant water gas shift conditions in collaboration with Johnson Matthey. Mössbauer spectroscopy is the preferred technique to study the bulk structure of complex iron oxides like magnetite, providing unprecedented details on oxidation states, local geometry, and dopant incorporation^[2]. The Mössbauer spectra of used catalytic samples show that chromium is incorporated into the octahedral sites of magnetite, where isomer shift values show a decreasing trend from the bulk value of 0.67 mm s⁻¹ as the amount of chromium in the sample increases. Since this bulk value is an average of Fe²⁺ (~1.0 mm s⁻¹) and Fe³⁺ (~0.3 mm s⁻¹) oxide species, a decrease is a good indication of an overall more ferric like state indicating the removal of Fe²⁺ from the octahedral sites^[3]. Isomer shifts at the tetrahedral sites were unaffected by the presence of chromium showing the Fe²⁺ does not migrate there. Copper does not have a measurable effect on the bulk structure of the used catalyst samples in the Mössbauer spectra, indicating it could be present as copper nanoparticles as was recently suggested by Wachs et al.^[1] A thorough XPS analysis is currently underway to confirm this. Small amounts of α-Fe were also observed in all samples with no indication of chromium influencing the amount formed. *In-situ* Mössbauer spectroscopy and NAP-XPS studies are currently underway to provide detailed analysis of the bulk and surface of the catalyst under working conditions.



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ICAME 2019

Contributed Lecture

Hard X-ray Spectroscopy with "Newton's Prism"

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We demonstrate hard x-ray spectroscopy with greatly improved energy resolution without narrowing the spectral window by adapting principles of spectrographic imaging to the hard x-ray regime. Similar to classical Newton's prism [1], the hard x-ray spectrograph disperses different energies of x rays in space. Then, selecting each energy component with a slit ensures high energy resolution, whereas measuring x-ray spectra with all components of a broad spectral window, keeps the intensity. This new spectroscopic approach revealed anomalous atomic dynamics in alpha-iron, which will be discussed.

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Magnetic Properties and Lattice Dynamics in Type-I Clathrate Eu₈Ga₁₆Ge₃₀ through ¹⁵¹Eu Mössbauer Effect and Magnetic Circular Dichroism

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Cage-structured compounds such as clathrates have received much attention because the thermodynamic properties are associated with low-lying optical phonon modes of the guest atoms in the cage-structure. Among type-I clathrates, only Eu₈Ga₁₆Ge₃₀ contains rare-earth guest atoms and exhibits a ferromagnetic order at 36 K [1]. The Eu atoms occupy two over-sized cages, *2a* and *6d* crystallographic sites, which give rise to low-lying optical phonon modes. Since Eu atoms contain Mössbauer isotopes, magnetism and lattice dynamics were reported by ¹⁵¹Eu conventional Mössbauer spectroscopy and nuclear resonant inelastic scattering [2, 3]: ¹⁵¹Eu Mössbauer spectroscopy observed magnetic ordering through detecting a hyperfine field at ¹⁵¹Eu nuclei; ¹⁵¹Eu nuclear resonant inelastic scattering observed low-lying optical phonon modes at about 5 meV.

Recently, Onimaru and his coworkers succeeded in controlling the carrier density by changing the ratio of Ga and Ge atoms from the stoichiometric composition through annealing at adequate temperatures [4]. By substituting Ge for Si, moreover, the carrier density is increased and a chemical pressure is applied. In this work, we have investigated the effects of carrier doping and chemical pressure on the magnetism and lattice dynamics with Eu Mössbauer effect and Eu *L*-edge magnetic circular dichroism. We analyze how the annealing and substitution influence the Eu low-lying optical modes through ¹⁵¹Eu nuclear resonant inelastic scattering, and time window effects on the reported magnetic fluctuation of Eu₈Ga₁₆Ge₃₀ [3] through ¹⁵¹Eu Mössbauer spectroscopy and Eu *L*-edge magnetic circular dichroism with different time windows for detecting electronic states.

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Magnetic Field Tuning of Spin Dynamics in the Single-atom Magnet $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$

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$\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$ is as a candidate for novel functional magnetic materials in quantum computing or spintronic devices [1]. We present a systematic ^{57}Fe -Mössbauer study on highly diluted Fe centers in the hexagonal $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$ lattice as a function of temperature and magnetic field applied transverse and longitudinal with respect to the single ion anisotropy axis. Below 30 K the Fe centers exhibit a giant magnetic hyperfine field of 70 T parallel to the axis of strongest electric field gradient. This observation is consistent with a $\text{Fe}^1 d^7$ charge state with unquenched orbital moment and $J = 7/2$. Fluctuations of the magnetic hyperfine field are observed between 50K and 300K and described by the Blume two-level relaxation model. From the temperature dependence of the fluctuation rate a single thermal activation barrier of $E_A = 570$ K is deduced. Mössbauer spectroscopy studies with applied transverse magnetic fields up to 5T reveal a large increase of the fluctuation rate by two orders of magnitude. Longitudinal field studies show a splitting of the fluctuation rate into two distinct values with increasing field strength. The experimental observations are qualitatively reproduced by a single-ion spin Hamiltonian analysis. It demonstrates that for dominant magnetic quantum tunneling relaxation processes a weak axial single-ion anisotropy D of the order of a few Kelvin can cause a two orders of magnitude larger energy barrier for longitudinal spin fluctuations.

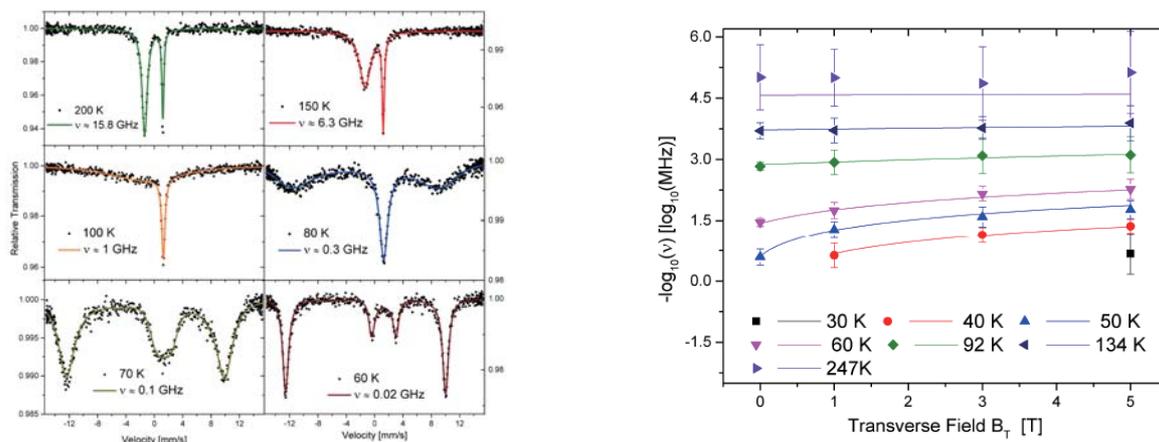


Figure Mössbauer spectroscopy on $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$ with $x=0.025$ (left), temperature and field dependence of the deduced spin fluctuation rate (right, lines represent a phenomen. fit)

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2D Spin-Crossover Complex $\text{Fe}(\text{4-methylpyrimidine})_2[\text{M}(\text{Cn})_2]_2$ ($\text{M} = \text{Ag}, \text{Au}$)Kosuke Kitase¹, Masashi Takahashi.^{1,2}, Takafumi Kitazawa.^{1,2}¹ - Department of Chemistry, Toho University, Chiba 274-8510, Japan² - Research Centre for Materials with Integrated Properties, Toho University, Chiba 274-8510, Japan

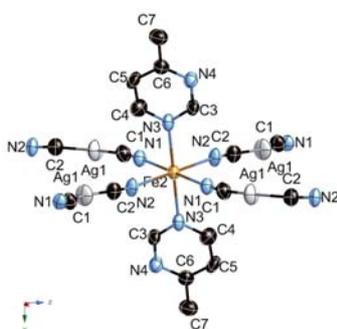
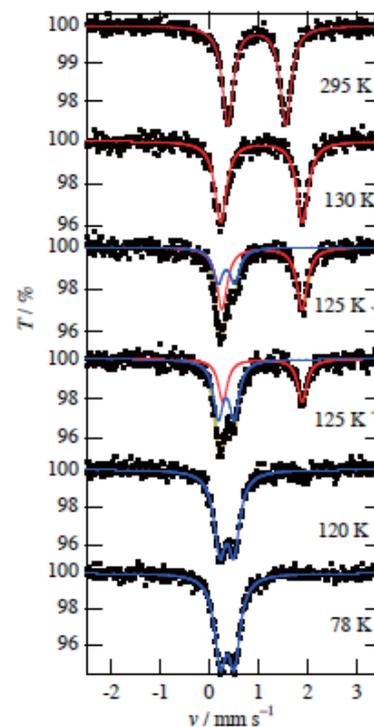
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The spin-crossover (SCO) phenomenon is a reversible spin switching in 3d metal ions between high-spin (HS) and low-spin (LS) states triggering by thermal, pressure, light, and guest molecule insertion. ⁵⁷Fe Mössbauer spectroscopy is a very powerful tool for iron(II) SCO materials because I.S. and Q.S. parameters are very sensitive to iron(II) spin states.^[1,2]

The Hofmann-type complex is coordination polymer with metal ion and cyanometalate. In this complex, the central metal ion is coordinated by cyanometalate in the equatorial plane and pyridine derivative ligands in the vertical axis.^[3,4] In this research We have synthesized two Hofmann-type novel complexes $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Ag}(\text{CN})_2]_2$ (**1Ag**) and $\text{Fe}(\text{4-methylpyrimidine})_2[\text{Au}(\text{CN})_2]_2$ (**1Au**).

The magnetic susceptibility measurements have indicated the one-step spin transition for **1Ag** and the two-step one for **1Au**. These results are supported by Mössbauer spectra (MS) and X-ray absorption spectra (XAS). A comparison of the crystal structures of **1Ag** and **1Au** shows a difference in the interlayer structure in spite of the structural similarity of intralayer structure between **1Ag** and **1Au**; while **1Ag** consists of the single layer structure without argentophilic Ag–Ag interactions, **1Au** has a double layer structure with aurophilic Au–Au interactions.

Figure 2 shows the temperature-dependent ⁵⁷Fe MS of **1Ag**. While only a doublet peak of HS state is observed at 295 K, a small doublet peak due to LS state is observed at 78 K. The LS–HS transition with a small hysteresis is observed between 120–130 K in MS. XAS of **1Au** indicates a peak shift of Fe K-edge but no shift for Au L3-edge, pointing out the origin of SCO to the Fe²⁺ site. No peak shift in Fe L-edge is observed as a result of the SOXIESST effect^[5].

Fig.1 ORTEP drawing of **1Ag**Fig.2 ⁵⁷Fe Mössbauer spectra of **1Ag**

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Development of Multiple Spin-transition Profiles within an Iron(III)-based Molecular System

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Concerted research endeavor on the magnetic properties of series of iron(III) salicyladimine complexes by Hendrickson *et al.*¹ several decades ago addressed a variety of spin-crossover curiosities, but produced only one complex, *viz* [Fe^{III}(3-OMe-salEen)₂]PF₆, that exhibited an abrupt hysteretic spin transition. Recently, two other analogues, namely [Fe^{III}(4-OMe-salEen)₂]NO₃² and [Fe^{III}(5-Br-salEen)₂]ClO₄³, displayed this rare magnetic behavior in this system. It is the paucity of iron(III) complexes with cooperative spin crossover that has spurred a revisit of the salicyladimine family of ferric complexes.

We have designed and generated a diverse range of iron(III)-salicylaldimine spin-crossover materials by modulating the ligand properties and varying the counter ions. The spin transitions have been established using pertinent physical techniques such as Mössbauer spectroscopy, ESR spectroscopy, magnetic susceptibility measurements and single-crystal X-ray analyses. Some of the newly fabricated materials display cooperative spin crossover consistent with the occurrence of noncovalent intermolecular forces in the crystal lattice. We have also explored the redox properties of these iron(III)-phenolate complexes.

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Water of Crystallization in Function of Iron(II)-Based Molecular Sensor

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There is currently a huge appeal for “chemosensors” based on spin crossover (SCO) materials for the sensitive and selective detection of gas- and vapor-phase analytes. SCO materials show an intrinsic nature wherein the metal center is very sensitive to subtle changes driven by guest intercalation, thus resulting in alterations of the optical outputs. In order to design chemosensors showing an olfactory-like response, we have been engaged in the develop of new Fe^{II} SCO materials through the synthesis and use of bis-azole molecular fragment (Htt) bearing 1, 2, 4-triazole and tetrazole^[1, 2]. Three mononuclear complexes: [Fe(tt)₂(H₂O)₄] (**1**), [Fe(tt)₂(H₂O)₄]•4H₂O (**2**)^[3] and [Fe(tt)₂(H₂O)₄]•5H₂O (**3**) were obtained by varying reaction conditions. The only difference between them is the number of solvent water molecule (Fig. 1), thus creates different sensing properties for methanol guest. **2** and **3** precisely detect methanol among an alcohol series. The sensing process is visually detectable, fatigue-resistant, highly selective, and reusable.^[4] However, the solvent free of **1** falls short in sensing ability. The sensing mechanism in **2** and **3** is attributed to molecular sieving effect from solvent water channel and subsequent spin-state change of iron centers, after a crystal-to-crystal transformation. Furthermore, **2** and **3** was developed as a simple colorimetric sensor that can differentiate a wide range of volatile analytes, which was then applied to the detection of toxic gases with the help of a hierarchical cluster analysis (HCA). ⁵⁷Fe Mössbauer spectroscopy was applied to investigate the driving spin state change of the analytes in this Fe-azole sensor material. This approach opens up perspectives for the further development of iron materials as potential optical sensor arrays through colorimetric techniques.

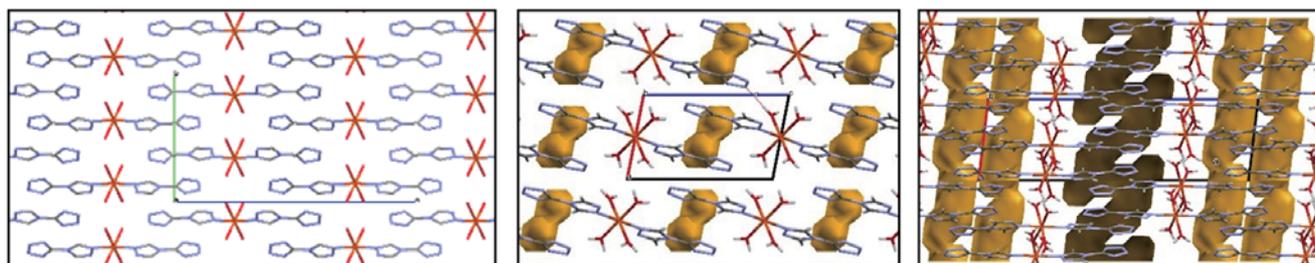


Fig. 1 Solvent accessible voids containing waters of crystallization in (a) [Fe(tt)₂(H₂O)₄], (b) [Fe(tt)₂(H₂O)₄]•4H₂O and (c) [Fe(tt)₂(H₂O)₄]•5H₂O, calculated using a 1.2 Å probe radius.

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Human Spleen and Liver: Application of Magnetization Measurements and Mössbauer Spectroscopy for Comparison of Healthy Donors and Patients with Hematological Malignancies

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Liver and spleen tissues contain the largest amount of ferritin, the iron storage protein, in the body. Ferritin molecule consists of the 24-subunit protein shell surrounding an 8 nm cavity for the iron core in the form of ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), its exact structure is remained unknown. Nevertheless, investigation of the iron cores in ferritin, especially in tissues, is of interest in order to understand the role of iron storage proteins in normal and pathological pathways. In spite of low iron content in spleen and liver tissues, in comparison with that in purified ferritin, we have studied spleen and liver tissues obtained from two healthy donors and from patients with hematological malignancies, by means of magnetization measurements and Mössbauer spectroscopy at various temperatures. The results obtained (see [1–4]) demonstrated some differences for normal and pathological spleen and liver tissues indicating variations in the iron content and in the iron core structure. In one case it was possible to relate the obtained results with physiopathology of disease. These investigations demonstrate the possibility to analyze ferritin in spleen and liver tissues with a small iron content using magnetization measurements and Mössbauer spectroscopy.

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Evaluation of Mössbauer Spectra Linearization Methods

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Mössbauer spectra linearity is a critical parameter to determine Mössbauer spectrometer accuracy. This talk will deal with various Mössbauer spectra linearizing methods. First method uses sine velocity waveform followed by linearization process [1]. Another method introduces additional modulation [2] based on the velocity error signal measured by laser vibrometer. Last evaluated method combines both of them and uses the velocity error signal measured by laser vibrometer as linearizing function. For purpose of linearization evaluation custom Mössbauer spectrometer based on [3] was constructed. Velocity driving system of the spectrometer is based on digital PID controller concept [4,5] deployed in FPGA chip of CompactRIO real-time hardware device.

The obtained data demonstrate that all evaluated methods increases the linearity of spectra in a wider frequency and amplitude range of a drive signal in comparison with those measured using a traditional measurement methods. Highest linearization effect has the method using sine velocity waveform, as generally harmonic movement is natural for used double loudspeaker type velocity transducers. Results show the possibility to use proposed linearization methods for higher velocity ranges using standard transducers and also shows potential to be applied in the simple control of transducers without PID regulation or in piezoelectric transducer applications.

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Mössbauer and EPR Studies of Iron Environments in Impact Assemblage of Zhamanshin Crater

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Impact-related rocks are the product of hypervelocity, high-temperature and high-pressure processes during a shock event, and their properties are the clues to reconstruct the conditions during the impact and a comprehensive study of iron-containing minerals in impactites helps to understand the redox conditions that took place during the collisions of cosmic bodies with the Earth. Zhamanshin impact crater (48°24'N 60°58'E) is located in Kazakhstan, 40 km southwest of the Yrghyz town. Zhamanshin structure dated at 0.9 ± 0.1 My (Florensky & Dabizha, 1980), has an internal diameter about 5-6 km and shows many features that make it a unique research object.

During May 2018 the crater site was sampled for detailed paleomagnetic research and adequate interpretation of these data requires investigation of iron oxidation state and its coordination numbers in a set of samples: (i) aerodynamically shaped small tektites (local name is irgizites); (ii) tagamites (local name is zhamanshinites); (iii) seuvites and (iv) impactites. Bulk chemical composition was studied using XRF (WDX) spectrometer and showing wide SiO₂ and FeO_{total} variation from 4.75 to 11 wt. % for iron and from 52 to 78 wt.% for silica. Seuvites show lower SiO₂ with higher FeO and the opposite is inherent for impactites. Glass material within all studied samples contains iron and presents highly heterogeneous structures with linear-shaped zone enriched in iron. Most of the samples contain hematite/magnetite inclusions and its amount highest in seuvites. Also, iron made some silicates and phosphates presented as a rare inclusion in the glassy matrix.

A room temperature Mossbauer spectra were obtained at IPGG RAS, Saint-Petersburg with ⁵⁷Co(Rh) source using SM-1201 spectrometer. All samples show iron both in ferric and ferrous state and iron oxidation states vary from 0.04 to 0.62. Mössbauer spectra of non-magnetic glasses have a characteristic form of asymmetrical, broad doublets and a few samples show iron in magnetic state presented in spectra by sextets with IS 0.30 mm/s, QS 0.2 – 0.4 mm/s and Heff about 50 T. Electron paramagnetic resonance studies were done using Bruker Elexsys E580 spectrometer. Room temperature EPR spectra indicate ferric iron presents in a form of iron-bearing inclusions and as a dissolve component in glasses. Using information about possible coordination numbers of ferric iron from EPR a better fitting model were chosen for Mössbauer spectra, which helps to evaluate tetrahedral/octahedral components ratio for studied samples.

The study was supported through the RFBR (grant 18-05-00626 A). The experiments were carried out using facilities of Resource Centers of St. Petersburg University.

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The Transformations of Iron-containing Phases in the Natural Environment Investigated by Mössbauer Spectroscopy

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The aim of this study is a complex characterization of soils from industrial areas. In the areas where endemic iron compounds are being enriched by industrial emissions, iron compounds transformation could be very complex and unpredictable.

Air pollutants are associated partially with industrial emissions. The products of these emissions are results of high temperature processes and are identified as particulate matter and technogenic magnetic particles. Their accumulation in the environment is concentrated mainly in the upper layer of the soil. The highest absorption occurs in the humus-organic soil layer and this process could vary depending on the geology of the studied area. The analysis of the mechanism determining transformation is carried out in the context of the temperature stability of iron-containing compounds as a result of physical and chemical transformations such as: oxidation, weathering, grinding, and as a function of the depth of accumulation. The obtained results in correlation with atmospheric conditions prevailing in a given area will allow to determine the parameters significantly affecting the final identified phases containing iron in the studied materials.

The main objective of this study was identification of iron (hydro)oxides occurring in soils being under deposition of industrial dusts for long time period. Topsoil samples collected in the vicinity of power station, metallurgical and coke plants were subjected to this investigation. After standard initial preparation, samples were divided into granulometric fractions ($\phi = 0.05-0.1$; $0.1-0.25$ and $0.25-0.5$ mm) which then underwent the magnetic separation using the isodynamic magnetic separator operated on different currents.

The factors which could affect the mechanisms of iron-containing phases will be investigated by magnetic, morphological and mineralogical analyses (e.g. Mössbauer Spectroscopy, bulk magnetic susceptibility, X-ray powder diffraction, scanning electron microscopy with energy dispersive spectroscopy).

The obtained results confirmed the occurrence of technogenic particles in soils of investigated area affected by industrial emissions. Results of magnetic and mineralogical analyses revealed various iron-phases in soil separates with a dominance of magnetite and maghemite. Correlation of obtained results with atmospheric conditions prevailing in a given area will allow to determine the parameters significantly affecting the final identified phases containing iron in the studied materials. To assess the temperature stability of iron compounds under specific conditions, conclusions will be used regarding significant factors affecting the change in the qualitative and quantitative composition of urban soils.

Mössbauer Spectroscopy of B20-type FeGe Thin Film Epitaxially Grown on Si(111)

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FeGe with a non-centrosymmetric B20-type structure is a chiral magnet with a period of 70 nm and a Curie temperature of 278 K¹. The magnetic vortex lattice so-called Skyrmion is formed by competition of the exchange, Dzyaloshinsky-Moriya interaction and the external magnetic field^{2,3}. Recently, two-dimensional skyrmion is discovered in an FeGe thin film⁴, which is expected to find application to the spintronics devices⁵. However, the difference of the magnetic property between thin films and the bulk of FeGe is not clarified yet. In this work, we prepared FeGe films epitaxial grown on Si(111) and measured the CEMS and the nuclear resonant scattering (NRS) with the synchrotron radiation.

Thin films of FeGe and ⁵⁷FeGe (95%-enriched) were grown on a clean Si(111) substrate by co-evaporation of Fe and Ge at a substrate temperature of 780 K under a vacuum of 1x10⁻⁸ Pa. The surface structure was characterized by reflection high energy electron diffraction, which confirmed [1-10] of FeGe(111) is parallel to [11-2] of the substrate in agreement with a previous work⁶. X-ray diffraction shows that the lattice constant of the FeGe film in the direction normal to the surface is 0.457 nm, which is compressed by 2% compared to 0.4679 nm of the bulk. The surface roughness of the film is estimated at 1.6 nm in the area of 2.5 μm by atomic force microscopy. The composition ratio of Fe and Ge is 1 and the mixing of Si in FeGe is not detected by X-ray photoelectron spectroscopy. The results of NRS and AC magnetic susceptibility with SQUID suggest that transition from a paramagnetic to chiral magnetic phase occurs at a temperature lower than 200 K. The CEMS spectrum at room temperature shows that the quadrupole splitting and isomer shift are 0.37 and 0.301 mm/s, respectively, which are different from the bulk values of 0.05 and +0.48 mm/s. Furthermore, the polar angle of the electric field gradient is estimated at 43.7°. We discuss the 2-D Skyrmion phase on the basis of the dependences of CEMS on the temperature and external magnetic field and the Hall effect.

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Valence States of Europium in Rare Earth Doped Lead Borate Glasses

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Rare earth doped lead borate glasses have luminescent properties which have applications as materials for radiation detection and scintillation. We have studied the valence state of europium in these materials using ^{121}Eu Mössbauer spectroscopy. For certain applications, either Eu^{2+} or Eu^{3+} may be preferable over the other. Our goal was to gain a better understanding of what variables control the amount of Eu^{2+} versus Eu^{3+} in these lead borate glasses, so that we can tailor these glasses for specific applications such as photostimulable X-ray storage phosphors or light emitting diodes. We expect that the ratio of Eu^{2+} to Eu^{3+} changes as a result of variations in the composition and crystallinity of the glass.

The Application of Mössbauer Spectroscopy in Catalytic Activation of Peroxymonosulfate on Ferrites

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The refractory organic pollutants have attracted much more attention in the field of wastewater treatment, which intrigued researchers to explore novel treatment techniques apart from the traditional advanced oxidation processes. Peroxymonosulfate (PMS), as a new chemical oxidant, have been studied widely during the last decade, based on the ability to produce strong oxidized sulfate radicals. Among all the heterogeneous catalysts for PMS activation, iron-based nanocomposites, specially ferrites, were important and attractive catalysts taking advantages of easy recovery, high efficiency, and good stability. However, further studies still needed to be explored on the structure variation and mechanisms in PMS catalytic activation to design more efficient catalysts, which promoted us to apply advanced Mössbauer spectroscopy in the characterization of iron-based catalysts. In our research, zinc ferrite was prepared through an extended soft chemical solution process, and applied in the activation of PMS for Orange II degradation under visible light, where synergistic effect among ferrite, PMS and visible light were proposed to significantly enhance the catalytic activity. [1] Furthermore, different kinds of cobalt-iron compounds (alloys, oxides, nitrides) were obtained under different calcination atmospheres (nitrogen, air, ammonia), which were verified by the Mössbauer spectra and XRD patterns. When applied in PMS activation, the obtained alloy catalyst showed the highest activity but experienced a certain oxidation after reaction according to the Mössbauer and XPS spectra. [2] Catalytic performances can be further improved via design of well-defined multi-shelled cobalt ferrite to take full advantage of active Co^{2+} , as well as decrease the particle aggregation. [3] Mössbauer spectra clearly suggested that B-site Co^{2+} was the main active site, since the lower amount of B-site Fe^{3+} , i.e. higher amount of B-site Co^{2+} showed higher activity in Orange II degradation. In addition, from the point view of active sites protection and effective utilization, yolk/shell cobalt ferrite/mesoporous silica (mSiO_2) catalyst was synthesized, which showed higher efficiency, better stability and recyclability than the conventional supported catalyst and naked cobalt ferrite without mSiO_2 [4]. The structure characterization of the fresh and used iron-based catalysts and the mechanism exploration in PMS-mediated organics degradation processes were realized by Mössbauer spectroscopy.

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Mössbauer Spectroscopy Study of M-type Hexaferrite ($\text{BaFe}_{12-x}\text{Ti}_x\text{O}_{19}$) Prepared by Sol-gel Method

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The M-type barium hexaferrite powders doped with Titanium (Ti) $\text{BaFe}_{12-x}\text{Ti}_x\text{O}_{19}$ with ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were prepared by sol-gel method. Proper amounts of high purity iron and barium nitrates ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$), and Titanium chloride (TiCl_3) were used as starting materials. Portions of the powders were pressed into disks and sintered at $1100\text{ }^\circ\text{C}$ for 4h. The sintered samples were characterized and their structural parameters were calculated using X-ray diffraction (XRD). The hyperfine interactions and its hyperfine parameters were investigated via Mössbauer spectroscopy (MS).

The X-ray diffraction (XRD) pattern for the undoped sample revealed a single phase of $\text{BaFe}_{12}\text{O}_{19}$, whereas the doped samples showed the formation of BaM hexaferrite phase in addition to hematite ($\alpha\text{-Fe}_2\text{O}_3$), Ilmenite (FeTiO_3) and Barium Titanium Oxide (BaTiO_3) as secondary phases. The Mössbauer spectra and its hyperfine parameters confirmed the phase formation detected by XRD patterns. The Mössbauer spectrum for the undoped sample ($x = 0.0$) shows pure BaM hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) with its five sextet components corresponding to the five iron sites ($4f_2, 2a, 4f_1, 12k$ and $2b$) of the BaM structure. The Mössbauer spectra for all doped samples show the presence of BaM hexaferrite as a major phase and other secondary phases ($\alpha\text{-Fe}_2\text{O}_3$ represented by sextet component with high hyperfine field and FeTiO_3 represented by quadrupole doublet) as impurities. The average particle size for the BaM phase were calculated using Scherrer formula. Structure parameters (a, c, V and ρ_x) and Mössbauer hyperfine parameters (B_{hf} and *Relative Intensity*) were illustrated as function of concentration x and their behavior was explained. The occupancy of Ti ions were also studied. Mössbauer spectroscopy revealed that the substitution of Fe^{3+} by Ti^{3+} ions occurred at the $4f_2$ and ($12k+12k_1$) sites at ($x = 0.2-0.6$) concentrations, while it occurred at the $2b$ and ($2a+4f_1$) sites at ($x = 0.8, 1.0$).

The Structure, Magnetic Properties and Cation Distribution of $\text{Co}_{1-x}\text{Ni}_x\text{FeO}_4$ Nanoparticles Synthesized by Sol-gel Method

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$\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.50, 0.75, 1.00$) nanoparticles were synthesized by sol-gel method. The effects of content and annealing temperature on the structure, magnetic properties and cation distribution were studied at room temperature by using X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, vibrating sample magnetometer, and Mössbauer spectroscopy. With increasing the Ni^{2+} content, the lattice constant and average crystallite size of $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ decreased. The coercivity and the saturation magnetization increased firstly and then decreased, showing the extremum value of 976.8 Oe and 59.7 emu/g at $x = 0.25$. With annealing temperature increased for 500 to 900 °C, the lattice constant and average crystallite size of $\text{Co}_{0.75}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4$ increased. The coercivity increased firstly and then decreased, showing a maximum of 1549 Oe at 600 °C. And the saturation magnetization increased with increasing annealing temperature. The Mössbauer spectra were fitted with two Zeeman sextets, indicating that all the samples were completely magnetically ordered and the cation distribution was discussed.

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Dynamics of Oscillations of Impurity Iron Ions in CaF_2 and SrF_2 Crystals

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Fluorite type crystals doped with iron grown on technology [1] Mössbaer spectra were obtained in the temperature range of 90-550 K. This study had two objectives:

- i) Determination of local Debye temperatures of impurity ions for different placement positions.
- ii) Determination of the dependence of the probability of recoilless absorption on the mass of the impurity and the mass of the atoms of the matrix.

The oscillation of a resonant atom depends on the phonon spectrum of the lattice. This relationship occurs through the probability of recoilless absorption. It is determined by the local Debye temperature for a given crystalline position with the given atom [2]. In connection with the foregoing, changes in the normalized areas of the spectra of different impurity ions from temperature were analyzed. The local Debye temperature for various crystallographic positions were found by the method of approximation of the curve of the change in the ratio of the normalized areas under the partial spectrum. The obtained data of local Debye temperatures are compared with the temperature change of the isomeric shift and broadening of the lines of partial spectra for replacement and interstitial iron ions [3]. As a result of the research, it was determined that the local Debye temperature for replacement iron ions in CaF_2 is two times higher than that of SrF_2 . While these matrices, the Debye temperature differ by 20% [4]. Perhaps we should take into account the difference in "Metal-Ligand" distances. Moreover, this fact confirms the temperature change of the isomeric shift. An increased value of the local Debye temperature was found for the interstitial two valence iron ions in the SrF_2 matrix as compared with the same ions in the substitution position. This is easily explained if one considers that the density of atoms is higher in the interstitial position in the first two coordination spheres [5].

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Mössbauer Spectroscopy of Metallic Iron Nanoparticles

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Metallic iron (also termed zero valent iron) nanoparticles are of particular research interest due to their high magnetic susceptibility and potential biomedical applications in hyperthermia treatment and magnetic resonance imaging. In this work, metallic iron nanoparticles were synthesized through a room temperature reduction reaction of FeCl_3 and NaBH_4 within a water/ethanol mixture. A Mössbauer spectroscopy study was performed at both room temperature and 6 K and revealed the synthesized nanoparticles were a 32%/68% combination of metallic iron and amorphous iron. After three days of air exposure, subsequent Mössbauer measurements showed the nanoparticles oxidized significantly. X-ray diffraction (XRD) results confirmed a mixture of metallic iron and amorphous iron. Transmission electron microscopy (TEM) showed that the nanoparticles were of spherical morphology with diameters ranging from 10-80 nm.

Effect of Etching on Spin Canting in Hydrothermally Synthesized Co-Ni Ferrite Particles

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Spin canting, an effect that leads to a different net magnetization in small particles because of a different orientation of the surface ions' spins, has been observed in a variety of spinels and it is still not absolutely clear whether spin canting in nanometer-sized particles occurs only at the surface but also in the inner core of these particles [1]. In this study, high-quality spinel cobalt-nickel ferrite nanoparticles were synthesized by undergoing a succession of synthesis routes comprised of chemical co-precipitation, hydrothermal treatment (HT), and etching in hydrochloric acid (ET) of concentration 2.0 mole/L. The particle sizes of both the HT and ET samples were approximately 40 nm. Both saturation magnetization and coercivity were found to increase remarkably because of etching. A Mössbauer spectroscopic study of these ferrite nanoparticles in external magnetic field of $B = 5$ T at room temperature was carried out. Both HT and ET samples showed a superparamagnetic (SP) component, although etching decreased its proportion. The degree of inversion in the HT sample was 0.55, while that for the ET sample was 0.7. Spin canting occurs in both A and B-sites in both HT and ET samples (Fig. 1). The A site and B site canting angles of the HT sample were respectively 19° and 23° , while canting angle of 11° was observed for both the A and B sites in the ET sample. The area of the spin-canting component is higher in the HT sample than in the ET sample. Magnetic frustration due to the reduced numbers of magnetic neighbors at the particle surface may be responsible for the spin canting. However, since the particle sizes are approximately the same and the canting does not disappear completely with the removal of the fine particles observed by transmission electron microscopy existing in the HT sample, this strongly suggests that the canting is not only a surface effect but also occurs around defects in the interior of the particles [2]. This was also investigated by considering the cation distribution of these particles.

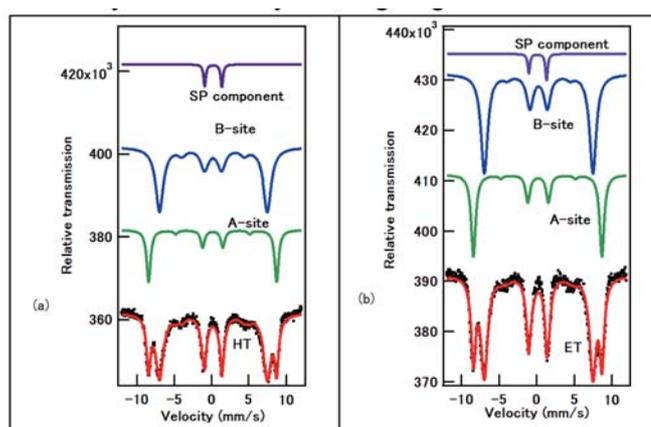


Fig. 1 High field (5 T) Mössbauer spectra of (a) HT and (b) ET Co-Ni ferrite nanoparticles.

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Effect of Co Addition and Internal Stress on the Nanoscale Magnetism in $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ Metamagnetic Alloy

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The effect of Co addition in the magnetostructural properties after combined thermomechanical treatments is studied in a Ni-Mn-Sn metamagnetic shape memory alloy, by X-ray diffraction, powder neutron diffraction, calorimetry, magnetometry and ^{119}Sn Mössbauer spectroscopy. The milling and the post-annealing processes do not produce any variation of transition temperatures and atomic order in the ternary alloy. However, the induced microstructural distortions affect greatly the martensitic transformation [1]. With Co addition, the saturation magnetization of $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ and $\text{Ni}_{45}\text{Mn}_{37}\text{Sn}_{13}\text{Co}_5$ samples decreases upon the presence of internal stress, this effect is accordingly reflected at atomic level. In the $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$, the effect of the annealing at nanoscale is barely observed. However, when Co is added, the hyperfine field is notoriously enhanced, and as a result, in the $\text{Ni}_{45}\text{Mn}_{37}\text{Sn}_{13}\text{Co}_5$ sample the annealing of the internal-stress-related singlet component becomes clearly observable. This result suggests that in contrast to the ternary alloy [2], in $\text{Ni}_{45}\text{Mn}_{37}\text{Sn}_{13}\text{Co}_5$ alloy, ^{119}Sn Mössbauer spectroscopy could be employed to track the evolution of the martensitic transformation as a function of the singlet component.

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Separation of Electric Field Gradient and Hyperfine Magnetic Field Using Unpolarized Radiation in ^{57}Fe MS

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Problem of unambiguous determination of all components of the electric field gradient and hyperfine magnetic field in case of mixed hyperfine interaction was solved for the first time. Determination the hyperfine parameters from the Mössbauer spectrum has been widely discussed in the literature, and it is known that all parameters cannot be estimated from a spectrum of a texture-free sample [1]. Only three independent invariants and the hyperfine magnetic field [2,3] can be determined. Measurement of a single crystal with polarized radiation allows estimation of all parameters [3,4,5]; however, use of unpolarized radiation has not been fully discussed yet.

The intensity tensor components [4,5] allows construction of the velocity moments [2,6], quantities composed of absorption line positions and their amplitudes, accessible in the experiment. Combination of the first moments are proportional to the electric field gradient, while the second moment is proportional to the tensor product of the hyperfine magnetic field. Isomer shift is just the first moment of the texture-free absorber. Few measurements of single crystal absorber with different orientations of the wave vector of the radiation with respect to the absorber frame results in determination of all components of the hyperfine field tensors. Thus full separation of the electric quadrupolar and magnetic dipolar hyperfine interactions with unpolarized radiation is possible. Construction of dedicated holder allowing easy adjustment of the absorber. is presented.

Characteristic feature and advantage of the presented method is that one does not need to perform any orientation of the single-crystal absorber. Components the electric quadrupolar and magnetic dipolar hyperfine can be determined in arbitrary chosen reference frame of the absorber.

Application of the presented formalism is discussed for imaging of hyperfine interactions by use of intense synchrotron sources of nuclear resonant radiation.

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Curie Temperature Increase in ^{57}Mn Implanted $\text{Y}_3\text{Fe}_5\text{O}_{12}$

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Monocrystalline $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) is one of the potential spintronic candidate materials with capable spin wave propagation in few millimeters because of its high Curie temperature ($T_c = 560$ K, for bulk). In YIG, $[\text{Fe}_2]$ (Fe_3){ Y_3 } O_{12} , Fe is in the 3+ state at a ratio of 2:3 in the octahedral site (Oh.:16a) and the tetrahedral site (Th:24d). In this presentation, we report a local increase of T_c of YIG due to ^{57}Mn ion implantation. The ^{57}Mn ions generated by irradiating a UC_2 target with a 1.4 GeV proton beam at ISOLDE/CERN were selectively excited by laser ionization and accelerated to an energy of 50 keV before implantation into a YIG sample. ^{57}Fe emission Mössbauer spectra (eMS) were simultaneously acquired while implanting $^{57}\text{Mn}^+$ ($T_{1/2} = 1.5$ min, fluence = 2×10^8 Mn^+ /s, approx. 10^{-4} at.%). The eMS at RT, 434, 511, 605, 704, and 798 K were measured, of which four selected spectra are shown in Fig.1. The spectra were analyzed by least squares fitting with two sextets consisting of Pseudo-Voigt peaks. The sextets with large and small internal magnetic field, B_{hf} , are attributed to Fe^{3+} in the Oh and the Th sites, respectively, with a corresponding intensity ratio of 2:3. The B_{hf} of both sextets decrease with increase of temperature. The average B_{hf} analysed by the mean-field model via extrapolating the measured temperature range estimated the T_c to be 651 K, which is higher than in the bulk [1]. In the B_{hf} distribution, the low B_{hf} components are found to populate more at the Oh than at the Th, due to the distortion of local sites by the ion implantation. A doublet with large QS observed at high temperatures is assigned to paramagnetic Fe^{3+} in the Th, and a doublet with small QS to paramagnetic Fe^{3+} in the Oh. These results are considered to be due to the quick occupation of Fe^{3+} in the distorted Th and Oh by ion implantation.

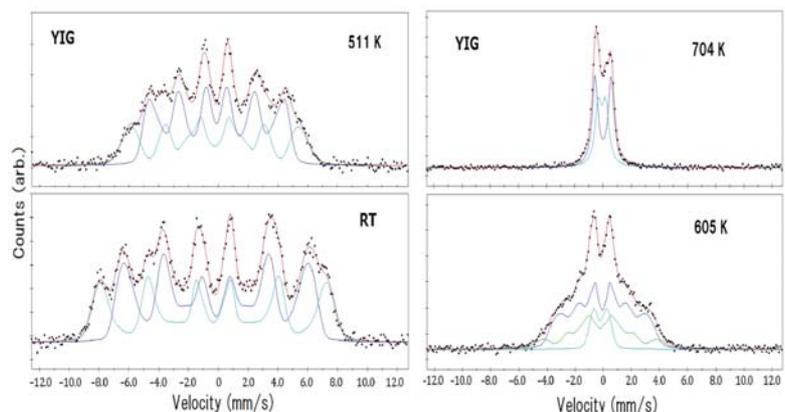


Fig. 1 ^{57}Fe eMS of YIG implanted with ^{57}Mn at RT, 511, 605 and 704 K.

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In-beam Mössbauer Spectra of ^{57}Mn Implanted into Solid Sulfur Hexafluoride

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In-beam Mössbauer spectroscopy using a short-lived nucleus ^{57}Mn is a useful tool to study a novel reaction in a solid material. We have previously reported the chemical state of the ^{57}Fe atom after β -decay of ^{57}Mn in a solid Ar [1]. Though sulfur hexafluoride SF_6 gas is generally inert and stable, it releases F atoms by the reaction of highly-energetic particles [2]. In this study, the reactions induced by implantation of ^{57}Mn into solid SF_6 are investigated.

The heavy iron synchrotron accelerator facility (HIMAC) at the National Institute of Radiological Science (NIRS) was utilized to perform the experiment. The ^{57}Mn nuclei were produced by a projectile fragmentation reaction of the primary beam of ^{58}Fe ions and a target of ^9Be . A parallel-plate avalanche counter (PPAC) was employed as a detector. A solid SF_6 sample was prepared by introducing the SF_6 gas through a flow controller onto a brass plate cooled down to 9 K using a vibration-isolated pulse-tube helium refrigerator. In-beam Mössbauer spectra of ^{57}Mn implanted into solid SF_6 were measured at 9 and 65 K.

The in-beam Mössbauer spectrum of ^{57}Mn implanted into the solid SF_6 at 9 K is shown in Fig. 1. The spectrum was fitted into a combination of a singlet (A) and a doublet (B). The species A ($\delta = -0.81(2)$ mm/s) and B ($\delta = -0.56(3)$ mm/s; $\Delta E_Q = 3.15(6)$ mm/s) were assigned to divalent iron fluoride FeF_2 and trivalent iron fluoride FeF_3 , respectively. The assignments were confirmed by the density functional calculations. The highly charged $^{57}\text{Mn}^{n+}$ ions implanted into the SF_6 induced the charge transfer process from SF_6 to $^{57}\text{Mn}^{n+}$. The $^{57}\text{Fe}^{m+}$ cations produced by the β -decay also oxidized surrounding SF_6 molecules. While the SF_6 molecule is stable in neutral, the ionized SF_6^+ cation easily decomposes releasing F atoms. These processes produced FeF_2 and FeF_3 trapped in the SF_6 matrix. The spectrum was also measured at 65 K, and new species FeF_4 was found as well as FeF_2 and FeF_3 .

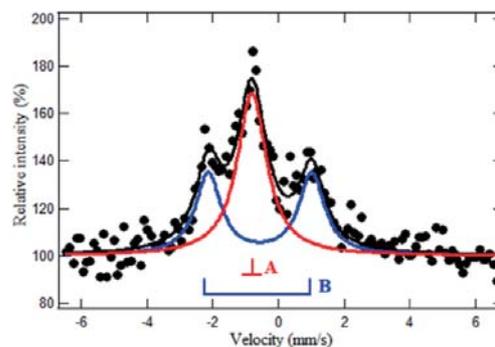


Figure 1. In-beam Mössbauer spectrum of ^{57}Mn implanted into the solid SF_6 at 9 K.

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Mössbauer Spectroscopy in Environmental Applications of Ferrates

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Iron in +6 oxidation state, called ferrate(VI) ($\text{Fe}^{\text{VI}}\text{O}_4^{2-}$, Fe^{VI}), is an emerging environmental-friendly material, which can play role in processes like oxygen generation from water, synthesis of organic molecules with selectivity, and treatment of water and wastewater, which are also sustainable (Fig. 1) [1,2].

Research on ferrate redox chemistry is in progress to comprehend electron-transfer and oxygen-transfer mechanisms to advance industrial cleaner (“greener”) technology for organic syntheses, energy storage, and oxidative transformation of pollutants [3,4]. The basic theme of the on-going research is to seek the involvement of high-valent iron intermediate species, i.e., ferrate(V) ($\text{Fe}^{\text{V}}\text{O}_4^{3-}$, Fe^{V}) and ferrate(IV) ($\text{Fe}^{\text{IV}}\text{O}_3^{2-}$, Fe^{IV}) in order to accelerate the oxidations carried out by Fe^{VI} . Fe^{V} and Fe^{IV} have much higher reactivity than that of Fe^{VI} and can enhance the activity of Fe^{VI} in combination of one- and two-electron reducing additives [5].

In the presentation, examples will be given to demonstrate the high oxidation capacity of Fe^{VI} by tuning its chemistry and efforts being made to identify the Fe^{V} and Fe^{IV} species in various reactions of environmental importance. Different ferrate species can be distinctly identified by Mössbauer spectroscopy (Fig. 2).

Examples will include the advances made in understanding the reaction using Mössbauer spectroscopy in conjunction with other experimental and theoretical techniques.

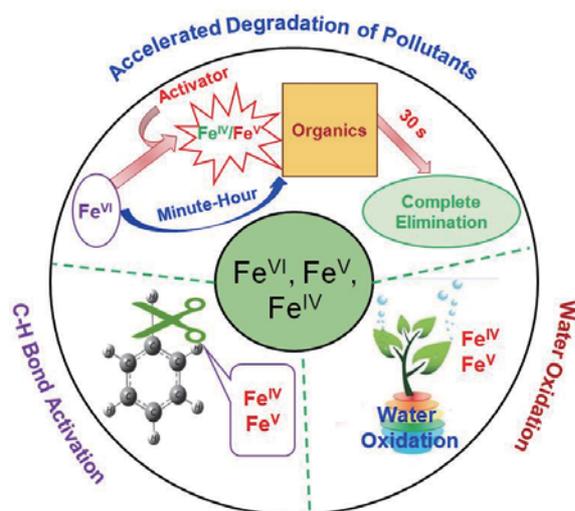


Fig. 1. Ferrate species, properties, and applications

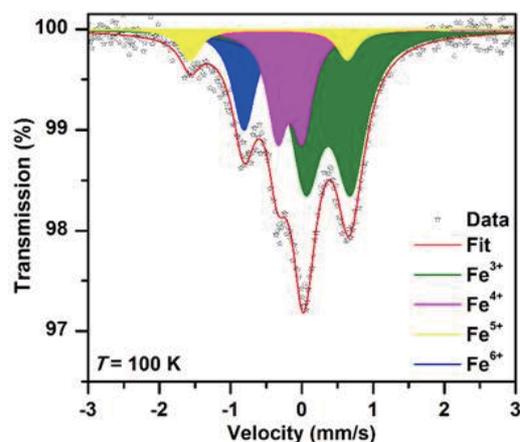


Fig. 2. Mössbauer spectra of Fe^{VI} , Fe^{V} , Fe^{IV} and Fe^{III} species formed together during disproportionation of ferrate(IV) in a water/ethanol environment. The sample was treated by rapid-freeze technique and spectrum measured at 100 K. (reproduced from [1] with the permission of the American Chemical Society)

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Structural Role of Iron in Nepheline-based Aluminosilicates for Nuclear Waste Applications

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Vitrified high level nuclear wastes (HLW) are susceptible to nepheline (nominally NaAlSiO₄) crystallization, which reduces the chemical durability of the final waste form and causes volume expansion which leads to cracking and hence increased surface area for leaching. Crystallization of such glasses is a function of the composition of starting glass-forming melt. Iron plays an important role in nuclear waste glasses, since it is present in a variety of concentrations which can variously affect processing as well as long-term corrosion behavior of such glasses. However, only a few studies have been conducted on HLW glasses with higher Fe concentrations. Moreover, the structural role of Fe in glasses is still not well understood because Fe can occur as both Fe²⁺ and Fe³⁺; can act as network modifier and/or network former; and can cluster when present at elevated concentrations. Therefore, a systematic study on the role of Fe in nuclear waste glasses for nepheline crystallization is necessary.

We have studied simplified HLW glass compositions along the NaAlSiO₄-NaFeSiO₄ join to assess the structural behavior of iron in nepheline-based aluminosilicates as a function of Fe-Al substitution, as it is known that Fe substitutes for Al sites in the nepheline structure. Glasses were prepared by a standard melt-quench method and then isothermally heat-treated to promote crystallization. Crystallization and thermal behavior of the prepared samples were investigated using X-ray diffraction (XRD) and differential scanning calorimetry (DSC), respectively. Back-scattered electron (BSE) images were obtained by scanning electron microscopy (SEM) to analyze the microstructure. Furthermore, coordination and redox state of iron for the glasses and crystals were determined using both Mössbauer spectroscopy and wet chemistry techniques.

The results show that Fe promotes the crystallization of nepheline over its high temperature polymorph (carnegieite) when substituted for Al in low additions. The glass transition temperature, T_g, and crystallization temperature, T_c, decrease with substituting Fe for Al, while staying within the range of 500 °C < T_g < 800 °C and 700 °C < T_c < 850 °C, respectively. BSE micrographs demonstrate that Fe oxides (i.e. hematite and magnetite) are present in cases even when their fractions are below the XRD detection limit. Fe redox determination measurements reveal that Fe²⁺/ΣFe is higher for the as-quenched glasses with lower Fe content at the expense of Al (Fe²⁺/ΣFe ~ 0.23±0.02 for Na(Al_{0.9}Fe_{0.1})SiO₄ glass). On the other hand, for high-Fe glasses, where there is not adequate Al in the structure to take the glass-forming role, iron tends to oxidize to Fe³⁺ and behave as a glass former, leading to lower Fe²⁺/ΣFe. Mössbauer spectra also indicate the presence of Fe magnetic oxides (i.e. magnetite, hematite, and maghemite) in heat-treated crystalline samples, which is consistent with the microstructural images.

In-field Mössbauer Spectroscopy Studies of Iron-based Multiferroic Delafossites

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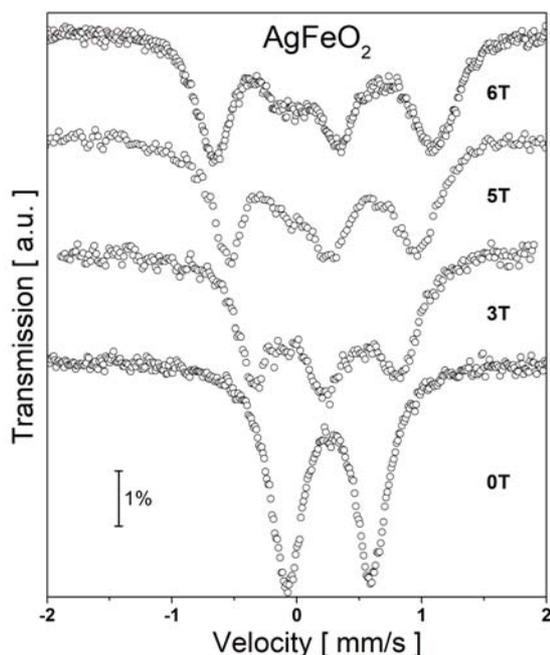
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Delafossites have characteristic layered structure, originally observed for the mineral CuFeO_2 discovered in Siberia in 1873. In iron-based delafossites, i.e., CuFeO_2 and AgFeO_2 , one layer consists of the close-packed monovalent Cu^+ or Ag^+ ions and the other one is formed by edge-shared Fe^{3+}O_6 octahedra with iron cations inside [1]. It was shown that delafossites can form two polytypic structures, depending on the orientation of planar layer stacking, i.e., the rhombohedral $3R$ type (space group $R\bar{3}m$) and the hexagonal $2H$ type (space group $P6_3/mmc$) [2]. Silver ferrite AgFeO_2 and copper ferrite CuFeO_2 belong to type-II multiferroic materials in which

magnetolectric coupling exists in the low temperature range. The ferroelectric polarization in this class of multiferroics is generated by an unusual magnetic structure, mainly by noncollinear spin configuration [3, 4].

A preparation of delafossites by wet-chemical methods provides material as a powder of nano-crystalline grain sizes. Room-temperature Mössbauer spectrum of CuFeO_2 or AgFeO_2 exhibits one asymmetric paramagnetic doublet with isomer shift value corresponding to high-spin Fe^{3+} ions in an octahedral oxygen environment. To get more information on magnetic properties of the nanosized delafossites we have conducted ^{57}Fe Mössbauer spectroscopy in external magnetic fields up to 6 T. We found a pronounced change in the hyperfine interactions parameters under the influence of the applied magnetic field (Fig. 1). The observed effect is tentatively ascribed to the coexistence of the $3R$ and $2H$ polytypes in our samples.



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Fig. 1 Room-temperature Mössbauer spectra of AgFeO_2 delafossite in magnetic fields of 0, 3, 5, and 6 T.

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Study on Paddy Soil in Fukushima Using Mössbauer Spectroscopy

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Contamination of radioactive cesium in rice has not become the subject of great consideration in Fukushima 8 years after the nuclear disaster at the Fukushima Daiichi Nuclear Power Plant (FDNPP). However, the mechanism of radioactive cesium uptake by plants is important, and the investigations have been continued since FDNPP accident. The effect of potassium on the absorption of radioactive cesium into rice plant has been revealed, however, there are some points which deviate from the correlation.¹ Contaminated rice was observed in the rice from the paddy field in Fukushima city, which is northwest, approximately 60 km far from FDNPP. The situation was investigated by Subcommittee Concerning Chemical Treatment, Japanese Society of Radiation Safety Management in 2013.² The transfer factor of radioactive cesium from soil to rice ear was different among four fields. It was shown that the grain size distribution in the soil influences the transfer factor.³ It was also suggested that the fallowing of fields affected the uptake of radioactive caesium into rice in other fields.⁴ The oxidative/reductive atmosphere in the field may affect the features of the soils and then the solubility of potassium and radioactive cesium in the field. In the present study we investigated the effect of oxidation state in the four paddy fields.

The samples were taken at Fukushima city, about 60 km northwest far from FDNPP in 2014 and 2018. The paddy fields are chiefly irrigated from a nearby pond and very slightly from the Abukuma River. The samples were taken from 4 paddy fields which are marked as A, B, C, and D. ⁵⁷Fe Mössbauer spectra were measured from April to July, 2015 and from April to May, 2019.

Figure 1 shows the typical ⁵⁷Fe Mössbauer spectra at the velocity scale of ± 14.2 mm s⁻¹. Divalent iron, trivalent iron, and hematite are shown. We also measured the spectra at the velocity scale of ± 4.4 mm s⁻¹ at room temperature to compare divalent and trivalent irons. We checked the relative area of divalent and trivalent irons. The relative area of divalent iron was slightly lower in field B compared with other fields. Such oxidative atmosphere may affect the features of the field and then reduce the elution of potassium affecting the absorption of radioactive cesium by plant.

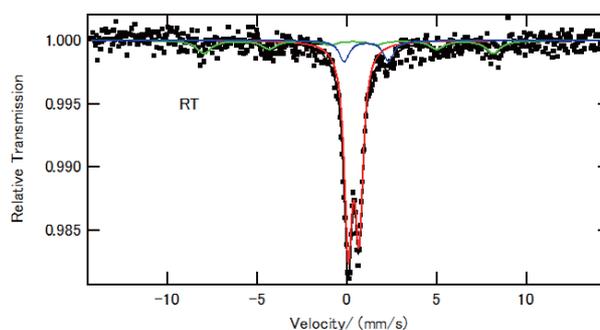


Fig. 1 Typical ⁵⁷Fe Mössbauer spectrum.

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Mössbauer Spectroscopy Explaining Specific Magneto-functionalities in Re-Fe Amorphous Thin Films

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Coupling of RE and Fe magnetic moments may lead to specific magnetic structures depending on the single ion anisotropy of the RE element and on the local atomic configurations around Fe.

The different cases of Fe-Gd and Fe-Dy thin films (with Dy strongly anisotropic as compared to the isotropic Gd) of various RE concentrations crossing the compensation point are considered. The systems are prepared by RF-magnetron sputtering being partially enriched in ⁵⁷Fe. The morpho-structural and compositional characterization was realized via Grazing Incidence X-Ray Diffraction, X-Ray Reflectometry, Transmission Electron Microscopy and Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy. Atomic local configurations and magnetic interactions were studied via Conversion Electron Mössbauer Spectroscopy and Superconducting Quantum Interference Device magnetometry. Magneto-optic and magneto-transport functionalities have been investigated by Magneto Optic Kerr Effect and Physical Properties Measurement facilities. Specific magneto-functionalities consisting in reversing the MOKE loops and the monotonous variation of the magneto-resistance curves when crossing the compensation concentration have been explained in direct connections to specific atomic configurations around Fe and different relaxations of the involved magnetic sub-lattices (of Fe and RE, respectively), as evidenced by Conversion Electron Mössbauer Spectroscopy. Careful ab-initio calculations via Density Functional Theory on series of compounds of different RE contents sustain the specific behaviour of the Fe magnetic moments and give support for the proposed mechanisms.

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Developing Electromagnetic Materials Using Mössbauer Effect

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Electromagnetic properties (permittivity and permeability) of magnetic materials are important for the performances of many electronic devices operating at high frequency [1]. For example, the electromagnetic noise suppression in the field of anti-electromagnetic interference (EMI) requires the materials having large magnetic losses or dielectric losses. There are two categories of magnetic materials for electromagnetic applications: ferromagnetic alloys and ferrimagnetic oxides. Both materials contain Fe elements with different working frequency scopes, which enable Mössbauer spectroscopy as a powerful tool to study the physical properties at the atomic level [2]. In this contribution, we will show two examples: Fe-based nanocrystalline alloys and spinel ferrites.

Firstly, we will show how both the Mössbauer spectra and the dynamic permeability spectra are related and vary with different volume fractions of ferromagnetic phases (e.g. Fig.1): Fe(Si) phase, Fe-based amorphous matrix phase and Fe-B phases under different annealing temperatures and time within the primary and secondary nanocrystalline temperature ranges. Our results show that Mössbauer spectra can tell us something new which cannot be learnt from other measurement techniques.

Secondly, Mössbauer effect is used to explain the variation of magnetization and dynamic permeability of Ni-Mn-Zn spinel ferrites due to the cation substitution and distribution between ‘tetrahedral’ interstitial site and ‘octahedral’ interstitial site, which are strongly affected by the sintering conditions [3]. According to the Snoek’s law, the dynamic permeability spectrum significantly depends on the saturation magnetization (M_s), magnetocrystalline anisotropy field (H_k). Both changes in M_s and H_k in our samples can be well explained using the Mössbauer effect.

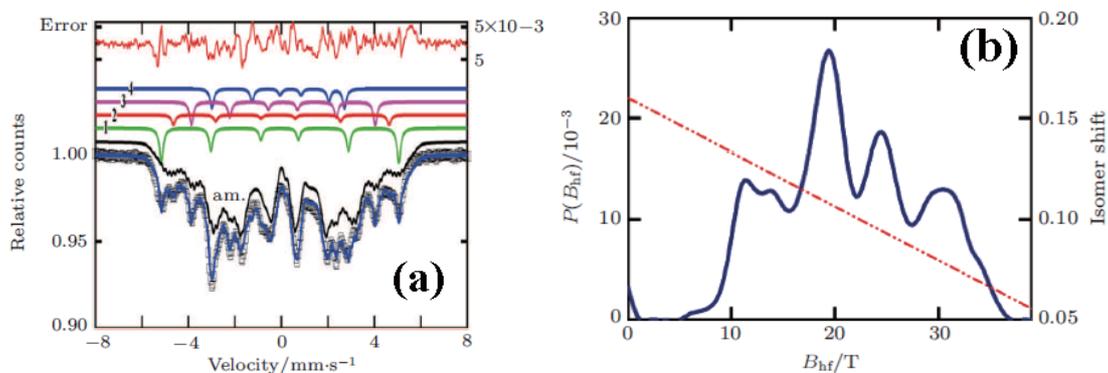


Fig.1 Mössbauer spectra of nanocomposites containing Fe(Si) nanocrystalline phase and Fe-based amorphous matrix phase.

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Iron Speciation by Mössbauer Spectroscopy and Its Implications in Various Studies on Petroleum Geosciences

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As the fourth most enriched element in the crust and being chemically active, iron is generally significant to the studies of Earth sciences. Mössbauer spectroscopy is one of the reliable and valuable techniques to measure iron species by far and implied in various fields such as petroleum geology and geochemistry, particularly in the research on oil and gas generation, migration, and accumulation, the properties of petroleum reservoir rocks, and even the net-path for oil and gas releasing etc. In the last decade, we performed field investigation and laboratory experiments on the oil and gas emission from the mud volcano systems in southern margin of the Junggar basin and outcrops of Jurassic sandstone with or without oil seepage in the Minhe basin in northwest of China, and also pyrolysis experiments for hydrocarbon generation with iron and/or iron-bearing components as catalyst under high pressure and temperature. All the study results are helpful and important for a better understanding of oil-gas-water-rocks interactions within mud volcanic systems, natural gas generation under critical conditions, physical properties and their variation of petroleum reservoir rocks. These research works with some publications indicated the suitable implication of Mössbauer spectroscopy in various studies on petroleum geosciences, which is significant for not only theoretical aspects but also for implications in petroleum industry.

Key words: iron speciation, Mössbauer spectroscopy, hydrocarbons generation, oil and gas seepage, reservoir rocks, mud volcano.

Magnetic Microstructures in Fe-Ni-C Alloy Studied by Nuclear Resonant Small-angle Scattering

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The Fe-Ni alloys are known to have typical invar properties, which shows minimal thermal expansion coefficient at room temperature at around 36 wt% of Ni. For general use of steel materials, trace amount of carbon or other metallic elements is added to promote hardness or toughness for various purposes by controlling the doping amount and the process of heat treatment. The properties of these controlled steel materials are related to the microstructures of precipitation of carbide and/or partial structural transformation such as Martensitic transformation. The Fe-Ni invar alloys can also be controlled by C doping to control not only the mechanical properties but also the invar properties. In the fcc Fe-Ni-C alloys, thermal expansion coefficient increases in the vicinity of the Curie temperature of about 180K, which is known as anti-invar property¹). To understand the mechanism of anti- invar property, it is important to understand not only the microstructures of structural or component inhomogeneity but also the microstructure of magnetic property. In fact, the Mössbauer and small-angle neutron scattering experiments of fcc Fe-Ni-C alloys suggested the evolution of magnetic order with changing temperature resulted in anti-invar properties²).

In this study, the nuclear resonant small-angle scattering is attempted to an anti-invar fcc Fe- Ni-C alloy in order to investigate the morphology of magnetic microstructures. The nuclear resonant small-angle scattering is advantageous in element-specific feature to detect only Fe element. Moreover, this method is able to detect microstructures in the electronic states or magnetic properties corresponding to Mössbauer parameters by measuring delayed emission from resonant nuclei discerned by timing technique^{3,4}). The angular profiles of the nuclear resonant small-angle scattering observed the evolution of the aggregation of the magnetic inhomogeneity in the size of a few tens of nm range as decreasing the temperature in the vicinity of the Curie temperature.

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Magnetic Properties of Nanoglasses

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Nanoglasses are metallic nanomaterials with nano-sized regions with a glassy structure. In these materials adjacent glassy nano-sized regions are joined together by interfaces. An enhanced free volume characterizes the atomic structure of these interfaces. The interfacial thickness is in order of a few interatomic spacing i. e. typically 1 nm or less. Nanoglasses are produced by evaporating glass-forming metallic materials in an inert gas atmosphere so that glassy droplets with a diameter of few (e.g. 2 or 3) nanometers are formed. These droplets are subsequently consolidated at pressure of up to 3 Gpa in ultra high vacuum. The resulting material is called a nanoglass. So far, nanoglasses have been prepared for a variety of chemical compositions (Fe-Si, Au-La, La-Si, Ni-Ti, Ti-P, NiPdP, Fe-Sc). The results of structural studies performed by WAXS, SAXS, Mössbauer spectroscopy, DSC, TEM (on the experimental side) and MD (on the theoretical side) show very interesting electronic and magnetic properties.

The aim of present investigation is to extend the knowledge and understanding of the magnetic properties of metallic nanoglasses, particularly the magnetic features of the interfacial regions. It will be demonstrated that the structural arrangement of atoms in the interfacial regions causes an unprecedented magnetic behaviour. The magnetic properties of Sc and Fe based nanoglass have been determined by Mössbauer and magnetisation study over the temperature range 4.2 K to 320 K and in magnetic fields of $0 \leq B_{ex} \leq 9$ T. The aim of the present study is the detection and physical interpretation of the unexpected magnetic behaviour exhibited by nanoglass.

Analysis of magnetisation data based on mean field theory has shown that nanoglass consist of magnetic clusters with extremely high magnetic internal magnetic fields. The Pauli paramagnetic state has now been observed in the interfacial regions. The occurrence of Pauli paramagnetism is the decisive feature that indicates that the atomistic structure as well as electronic arrangement of atoms at the interface regions of nanoglass is different from amorphous alloys free of interfaces. In other words, the atomic arrangement of the interface is a novel class of structure.

It will be shown that conduction electrons of nanoglass are tending to exhibit more wave character, which is in agreement with the wave-particle duality states. The consequence of the wave character on magnetic hyperfine field will be discussed in details.

Picosecond Dynamics of Optically Excited Solids by Time-resolved Nuclear Resonant Scattering

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Time-resolved pump-probe studies can provide insights into the dynamics and mechanism of light-driven phase transitions [1]. Nuclear inelastic scattering (NIS) is not bound by optical selection rules and provides the phonon density of states (pDOS) specific to Mössbauer-active nuclei, at the instant the resonant gamma photon is absorbed. Despite the suitability of NIS [2, 3], picosecond time-resolved optical pump-NIS probe (tr-NIS) studies are not yet reported. We developed a tr-NIS experimental setup (see figure 1) with a time resolution of 100 ps at the beamline P01, PETRA III, DESY, Hamburg. It has been used to investigate the dynamics following the excitation of a 3 μm thick Fe foil and a Fe (II) spin crossover (SCO) complexes by 250 fs laser pulses of wavelength 515 nm. In figure 2, the timing scheme deployed is depicted. The laser source was triggered in a way to obtain laser pulses only at every 4th synchrotron radiation (SR) pulse. By performing NIS using only the SR pulse accompanied by the laser pulses, we have access to the optically excited states. Upon laser excitation, in the case of the SCO complexes, we observe a sub-nanosecond spin-state transition. Aided by DFT calculations we identify the vibrational modes that help in the co-operative propagation of spin transition to regions of the SCO complex, which are not directly excited by the laser pulses. In addition, for iron we have obtained the time dependent variation of the thermodynamic parameters like e.g. the vibrational entropy and the mean force constant by evaluation of the time dependent pDOS.

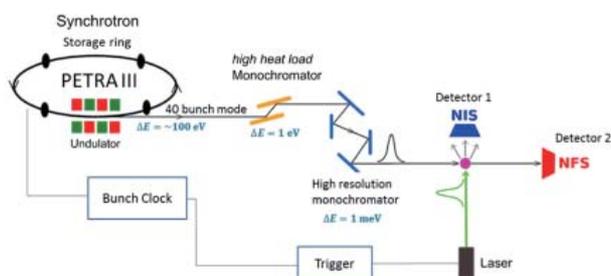


Figure 1. A schematic of the optical pump – NRS probe experiment

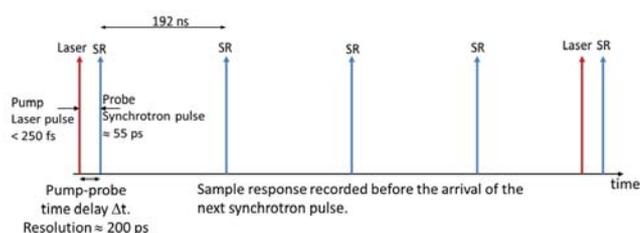


Figure 2. Timing scheme for simultaneous measurement of the excited and the ground state in the optical pump-NRS probe experiments

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Influence of Ligand Substitution on Magnetic Hyperfine Interaction in Dy₆-Based Single-Molecule Magnets/Toroics

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With the contemporary evolution of the research fields of spintronics, molecular electronics and quantum computing, single-molecule magnets (SMMs) arouse an immense amount of interest due to their intriguing magnetic and quantum properties combined on a nanoscale entity [1]. Lanthanide-based compounds and especially Dy-containing ones are among the best high-performance SMMs, characterized by long relaxation times of the magnetization reversal and high blocking temperatures [2]. For the currently required thorough characterization and understanding of these molecular materials, ¹⁶¹Dy time-domain Mössbauer spectroscopy, also known as Nuclear Forward Scattering, was recently shown by us to serve as an ideal method, yielding complementary information to conventionally applied magnetization measurement techniques [3].

Herein, we present the results of a ¹⁶¹Dy time-domain Mössbauer spectroscopy study carried out on polynuclear Dy₆-based wheel compounds showing special features of single-molecule toroics (SMTs). SMTs exhibit a toroidal arrangement of magnetic moments and can be manipulated by external electric and magnetic fields or by current [4]. We report the Dy magnetic hyperfine fields of the Dy₆-ring-system [Dy₆(teaH)₆(NO₃)₆]•8MeOH [5] and of its structurally almost isomorphous compound differing in a small ligand variation [Dy₆(Me-teaH)₆(NO₃)₆]•6MeCN [6].

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^{237}Np Mössbauer Spectroscopy Evolution for 4-Cyanopyridine Coordinated Neptunyl(II) Complex

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The molecular magnetism of Np(VI) coordination compounds is an attractive and valuable research area similar to that of Np(V) coordination complexes[1-3]. In the present work, 4-cyanopyridine coordinated neptunyl(II) complex was synthesized and measured by ^{237}Np Mössbauer spectroscopy. We now report ^{237}Np Mossbauer spectrum for $[\text{NpO}_2(\text{acac})_2(4\text{-cyano-py})]$ **I** (Fig.1) and the crystal structure of similar $[\text{UO}_2(\text{acac})_2(4\text{-cyano-py})]$ **II** (Fig.2). The neptunium(VI) ion in **I** is coordinated by six oxygen atoms and the one nitrogen atom of 4-cyanopyridine in the same way of the Uranium(VI) ion in **II**. ^{237}Np Mössbauer spectrum of the neptunyl(II) complex **I** has been measured at 10K, with observation for the 16 absorption lines due to the magnetic interactions (Fig.1). The isomer shift value obtained for **I** is $-39.4(5)$ mm/s, which falls in the range for the Np(VI) oxidation state. The relationship between the isomer shift and Np–O bond distance of the neptunyl group for oxygen coordination compounds is in good agreement with the crystal structure of **I**. The U–O distances of $[\text{UO}_2(\text{acac})_2(4\text{-cyano-py})]$ **II** are reasonable, being associated with the ^{237}Np Mössbauer parameters linked to the Np–O bond distances. Minor sites in the spectrum might coexist due to by-products.

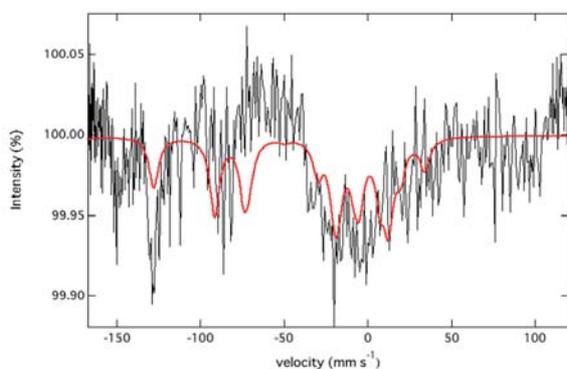


Fig. 1 ^{237}Np Mossbauer spectrum of **I**

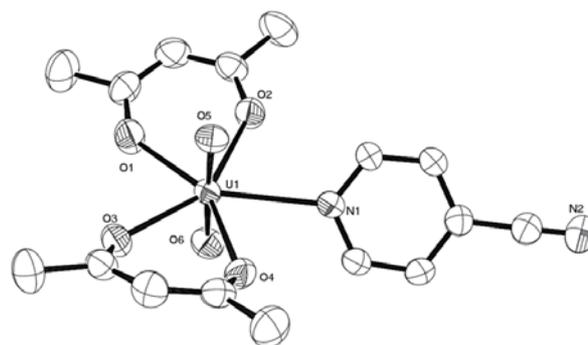


Fig. 2 Crystal Structure of **II**

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The Effect of Oxidant Species on Direct, Non-syngas, Conversion of Methane to Methanol Over FePO₄ Catalyst Material

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The effect of the phase transformation of FePO₄ catalyst material from the tridymite-like (tdm) FePO₄ to the α -domain (α -Fe₃(P₂O₇)₂) during the direct selective oxidation of methane to methanol was studied using oxidant species O₂, H₂O and N₂O. The main reaction products were CH₃OH, carbon dioxide and carbon monoxide, whereas formaldehyde was produced in rather minute amounts. Results showed that the single-step non-syngas activation of CH₄ to oxygenate(s) on a solid FePO₄ phase-specific catalyst was influenced by the nature of oxidizer used for the CH₄ turnover. Fresh and activated FePO₄ powder samples and their modified physicochemical surface and bulk properties, which affected the conversion and selectivity in the partial oxidation (POX) mechanism of CH₄, were investigated. Temperature-programmed re-oxidation (TPRO) profiles indicated that the type of moieties, utilised in the procedures, determined the re-oxidizing pathway of reduced multiphase FePO₄ system. Mössbauer spectroscopy measurements along with X-ray diffraction (XRD) examination of neat, hydrogenated and spent catalytic compounds, demonstrated a variation of the phosphate into a mixture of crystallites, which depended on operating process conditions (for example time-on-stream). The Mössbauer spectra revealed the change of the initial ferric orthophosphate, FePO₄ (tdm), to divalent metal form, iron(II) pyrophosphate (Fe₂P₂O₇); thereafter, reactivity was governed by the interaction (strength) with individual oxidizing agents. Fe³⁺ ↔ Fe²⁺ chemical redox cycle can play a key mechanistic role in tailored multistep design, while the advantage of iron-based heterogeneous catalysis primarily lies in being inexpensive and comprising non-critical raw resources. When compared to the other catalysts reported in literature, the FePO₄-tdm phase catalysts showed in this work exhibited a high activity towards methanol i.e. $12.3 \times 10^{-3} \mu\text{mol MeOH gcat h}^{-1}$ using N₂O as an oxidant. This catalyst also showed a high activity with O₂ as an oxidant ($5.3 \times 10^{-3} \mu\text{mol MeOH gcat h}^{-1}$). Further envisaged investigations will include continuous reactor unit engineering optimization.

Electric Explosion of Metallic Ribbons in Water

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Electric explosion of wires (EEW) is a known process: with a short, high current pulse a piece of wire is melted and evaporated in a few millisecond. The collapse of the instantaneous plasma bulb and the solidification of melted and the condensation of vaporized components is also fast in the liquid cooling medium afterwards [1]. Analogously, thin metallic ribbons can also be subjected to EEW. In the present study EEW of certain melt quenched iron containing ribbons is reported. Namely, crystalline $\text{Fe}_{50}\text{Co}_{50}$, amorphous $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_7\text{B}_3$ (Hipermet) and $\text{Fe}_{73.5}\text{Si}_{15.5}\text{B}_7\text{Nb}_3\text{Cu}_1$ (Finemet) were exposed to EEW. Characterization of the structure and crystallinity of the starting amorphous ribbons and the solidified metallic globuli formed in secondary EEW process provides mean to compare the speed of the two quenching processes, that of the primary cooling at the production of amorphous ribbon and that of during the secondary solidification in EEW. At the comparison further processes should also be taken into account at EEW, e.g. the composition of the metallic phase may change due to chemical interactions with the cooling liquid. Another phenomena, formation of metal-oxide core-shell structures is also common. Characterization of the original ribbons and the formed nanosized particles was performed with Mössbauer spectroscopy, X-ray diffractometry (XRD), scanning- and high resolution electron microscopy (TEM). For illustration 300 K Mössbauer spectra of Finemet alloy before and after EEW are shown in Fig. 1.

As the evaluation of spectra attests, the crystallinity dominates the spectrum after EEW, with sextets characterizing of iron sites surrounded with Si neighbours of various numbers. Further, a minor part of the spectrum can still be characterized with distribution of hyperfine fields. Thus, the cooling rate at the formation of primary amorphous ribbon was greater than at the secondary condensation in the case of the Finemet alloy. Further important details can also be obtained from interpretation of the XRD and TEM studies.

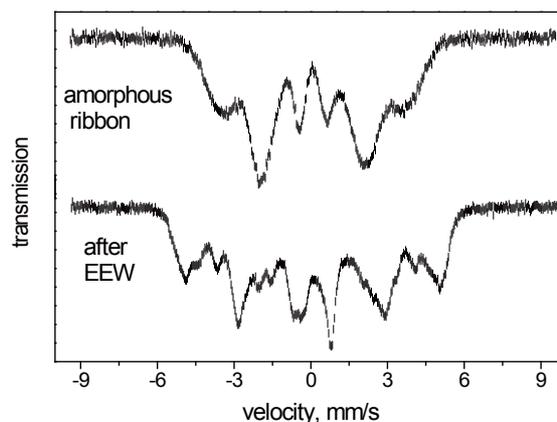


Figure 1. Mössbauer spectra of Finemet alloy prior (top) and after EEW (bottom)

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Poster

Mössbauer, Structural, Optical and Magnetic Studies on Ternary Nanohybrid $\text{Mn}_{0.4}\text{Co}_{0.6-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($X= 0, 0.2, 0.4, 0.6$) Spinel Ferrites

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The present work is focused on the effect of substitution of Co^{2+} and Cu^{2+} ions on the structural, morphological, magnetic and optical properties of nanocrystalline ternary doped ferrite nanoparticles (NPs) having formula $\text{Mn}_{0.4}\text{Co}_{0.6-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x= 0, 0.2, 0.4, 0.6$). The NPs were synthesized using sol-gel precursor methodology. Ferrite NPs characterized by XRD, FT-IR and Mossbauer spectroscopy. Alteration in surface morphology and surface area was studied using SEM-EDX, TEM and BET analyses. XRD patterns confirmed the formation of single phase ferrite NPs. The shift of this peak towards higher 2θ value on doping of Co^{2+} and Cu^{2+} ions in MnFe_2O_4 confirmed that dopant ions were successfully incorporated into spinel structure. Lowering in lattice constant was more on doping with Cu^{2+} ions as compared to Co^{2+} ions which was in accordance to their ionic radii. Variations in magnetic properties were assessed by VSM analysis. Doping of Cu^{2+} ions in MnFe_2O_4 NPs led to slight increase in magnetization, whereas doping with Co^{2+} ions appreciably increased the magnetization. The results were correlated with magnetic moment of metal ions. Maximum saturation magnetization value 64.98 emu/g was observed for ternary ferrite NPs having formula $\text{Mn}_{0.4}\text{Co}_{0.4}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$. Doping of MnFe_2O_4 with Co^{2+} and Cu^{2+} ions enhanced surface area. The change in Mossbauer parameters suggested the alteration in the environment of Fe^{3+} ions in presence of different divalent ions. presence of Co^{2+} ions in MnFe_2O_4 ferrite NPs caused distortion in tetrahedral and octahedral site as Co^{2+} ions prefer octahedral site and have larger size than Cu^{2+} ions which might be probable cause of distortion. Optical studies revealed lowering in band gap upto 2.03 eV on doping and minimum band gap was observed in $\text{Mn}_{0.4}\text{Co}_{0.4}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ NPs. The results confirmed the improved magnetic and optical properties of ternary doped ferrite NPs as compared to pristine counterparts.

⁵⁷Fe Mössbauer Spectrometry Elucidating Atomic Arrangements and Magnetic Properties of Al-substituted Fe₂MnGa Heusler Alloys

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Stoichiometric or non-stoichiometric Fe₂Mn-based Heusler alloys exhibit multiple crystalline structures and their complex magnetic properties are often attributed to different atomic arrangements [1]. Fe₂MnGa is a challenging system based on its half-metallic L2₁ state, which is expected to have a high spin polarization effect, but, on the other hand, due to its FCC-like state found in atomic ordered state. However, the total energy difference between the L1₂ (FCC-like) and L2₁ crystalline structure is only a few tens of meV [1], consequently a chemical pressure effect, caused maybe by atomic substitution, could lead to the desired FCC to L2₁ structural transition. From magnetic viewpoint, Fe₂MnGa, with L1₂ structure, presents T_C^{Mn} above 300 K, while the Fe sublattice (T_C^{Fe}) orders below about 300 K, and a non-collinear coupling occurs at low temperature [2]. Alternatively, Fe₂MnAl stabilizes in L2₁ structures, possesses two magnetic sublattices with T_C^{Fe} and T_C^{Mn} estimated at about 160 K and 50 K, respectively, and also the Fe and Mn sublattices couple non-collinearly at low temperature [3]. Based on these features, we have performed a systematic experimental study to investigate the structural transition from FCC to L2₁ phase and magnetic properties changes when Ga atoms are substituted by Al in Fe₂MnGa. X-ray diffraction data have suggested that the lattice parameter of cubic structure reduces with the increase of Al content, while magnetization and ⁵⁷Fe Mössbauer experiments have shown changes on magnetic and hyperfine properties of Fe atoms (isomer shift values scale with the lattice parameter when Al content increases, while the magnetic hyperfine field does not reduce linearly). A supercell L2₁ structure was used in the first principle calculations, based on Density Functional Theory, to explore changes of structural and magnetic properties of the Al-substituted Fe₂MnGa. Our results have clearly revealed the structural transition from FCC to L2₁ concomitantly with magnetic and hyperfine properties changes. More precisely, in case of Fe₂MnAl, two Fe-species were theoretically found in the L2₁ structure: Fe with non-zero magnetic moments and one set of Fe atoms with nearly nil moments. In-field and zero-field Mössbauer experiments, recorded at 15 and 50 K, also have suggested presence of two Fe components (1:2 ratio) with different magnetic moments. The magnetic moments of these two Fe-species are pointing antiparallel and at different directions relatively to the applied field of 8 T.

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Optimization of Preparation Conditions for Pure and Doped ε -Fe₂O₃ Nanoparticles by Sol-gel Process

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Iron(III) oxides are still capturing a significant attention due to their favorable physical, chemical and other properties. It is well known that iron(III) oxide shows a polymorphism with existence of four stable crystalline polymorphs, α -, β -, γ - and ε -Fe₂O₃, differing significantly in their crystal structure and hence physical features. Among them, ε -Fe₂O₃ is still considered as a rare iron(III) oxide phase that is hard to synthesize in a single-phase nature. Moreover, due to the thermodynamic reasons, it can be stable only in the nanosized form.¹ As ε -Fe₂O₃ shows a high coercivity at room temperature and coupled magnetoelectric features, it is widely regarded as a promising material for future generation of magnetic storage media and potential spintronic devices provided that it can be prepared in larger amounts with a definite level of purity and its properties can be fine tuned to meet the requirements of a given applications.²

In this contribution, we introduce a modified method to synthesize pure ε -Fe₂O₃ nanoparticles and ε -Fe₂O₃ nanoparticles doped by Sc, Ga and Ru atoms employing a sol-gel approach in combination with high temperature heat treatments.³ Various factors influencing the preparation and thus the purity of the prepared nanoparticles have been studied and assessed. The influence of increasing temperature of heat treatment on increasing amount of ε -Fe₂O₃ phase inside prepared samples was observed. For determination of structure and composition, X-ray powder diffraction, electron microscopy techniques, ⁵⁷Fe Mössbauer spectroscopy, and magnetization measurements were used. The values of coercive field were also determined for a series of synthesized ε -Fe₂O₃-based nanoparticles. From the results achieved, we identified optimized conditions for preparation of pure ε -Fe₂O₃ (over 93 wt. %) exhibiting large coercive field. Moreover, we properly understood the effect of doping on the alternation of magnetic features of ε -Fe₂O₃ and assessed its application potential.

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Mössbauer Study of Superconducting $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$

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Recently a new oxypnictide $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ with superconducting transition temperature of $T_c \approx 22$ K was synthesized [1]. The crystal structure of $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ can be viewed as an intergrowth of BaFe_2As_2 and $\text{BaTi}_2\text{As}_2\text{O}$ containing superconducting $[\text{Fe}_2\text{As}_2]$ layers and conducting $[\text{Ti}_2\text{O}]$ sheets.

We have synthesized polycrystalline samples of $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ via a solid-state reaction method [1] using high quality starting materials of Ba, Ti, Fe, As and TiO_2 . The properties of the sample were characterized using ^{57}Fe Mössbauer spectroscopy in transmission geometry. The spectra were measured with a maximum Doppler velocity of 2.55 mm/s at temperatures between 77 and 320 K.

The aim of this work was to study the properties of the Fe atoms. Mössbauer spectra of $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ exhibit a broadened singlet-like line, due to a small unresolved quadrupole splitting of ~ 0.3 mm/s. By fitting the second-order Doppler shift to the Debye model, a rather low Debye temperature of $\Theta_D \approx 350$ K is obtained. The isomer shift of Fe was ~ 0.4 mm/s relative to $\alpha\text{-Fe}$, which is compatible with e.g. intermediate spin divalent Fe. In fact, BaFe_2As_2 impurities present in some samples produced an identical spectral component as the target phase. The local surrounding of the Fe is very similar to that of $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ and chemically Fe should also be divalent in BaFe_2As_2 . At 77 K BaFe_2As_2 is magnetically split and readily separated from the main phase. To the best of our knowledge, there are no Mössbauer study reports on $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ in literature.

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Count Rate Variation in Nuclear Forward Scattering of Mixed-valent $R\text{BaFe}_2\text{O}_5$

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Double-cell perovskites $R\text{BaFe}_2\text{O}_5$ (R is a rare-earth metal) become antiferromagnets below $T_N \approx 430$ K. [1] Iron atoms of average oxidation state +2.5 are charge- and orbital ordered below Verwey-transition temperatures T_V between 220 and 290 K, depending on R . [2] This full order is preceded by a weak premonitory ordering at $T_p > T_V$. Above T_p , the Fe pairs facing each other across the pyramidal basal planes fully mix into $\text{Fe}^{2.5+}$ via their ordered d_{z^2} orbitals. [3] Between T_V and T_p , the orbital order is less apparent, and a weak, premonitory, checkerboard-like order of the two Fe charges emerges. [4]

Powder samples of $\text{GdBaFe}_2\text{O}_5$ and $\text{PrBaFe}_2\text{O}_5$ have been investigated by nuclear forward scattering (NFS) between 5 K and 317 K at the ID18 beamline of the European Synchrotron Radiation Facility in Grenoble. The three phases of charge-ordered, intermediate and valence-mixed state of each of the two perovskites have a distinct pattern of the NFS data. Hyperfine parameters obtained from fitting with the Motif software correspond to those obtained from energy-domain (ED) Mössbauer measurements. The results show that an external field of 4 T is able to push the charge-ordered $\text{GdBaFe}_2\text{O}_5$ sample partially into the intermediate state. An unexpected strong decrease in the count rate of the NFS signal occurs upon heating through T_V , followed by an equally sudden recovery of the count rate upon crossing T_p into the valence-mixed state. The decrease in the NFS count rate correlates with the slight broadening of the ED spectra observed in the intermediate state. Various mechanisms behind this count rate loss are discussed in our presentation.

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Modelling Quadrupole Coupling Constants in $\text{ErBa}_2\text{Fe}_3\text{O}_8$

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The crystal structure of the triple perovskite $\text{ErBa}_2\text{Fe}_3\text{O}_{8+w}$ [1] is related to the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor. Its tetragonal unit cell [1] contains trivalent iron in one octahedral and two square-pyramidal coordinations. A Mössbauer-spectroscopy study [2] of $\text{ErBa}_2\text{Fe}_3\text{O}_{8+w}$ revealed that the Fe^{3+} in the octahedral coordination has a surprisingly large quadrupole coupling constant of 4.3 mm/s, compared to ~ 0 mm/s for the square-pyramidal Fe^{3+} . Due to the spherical symmetry of high-spin Fe^{3+} , the quadrupole coupling constant is expected to depend mainly on contribution from the ligand coordination. However, at first sight, the ligand coordination does not seem to justify such a profound difference.

In this study, $\text{ErBa}_2\text{Fe}_3\text{O}_8$ characterized by synchrotron X-ray powder diffraction was studied by conventional ^{57}Fe Mössbauer spectroscopy in transmission geometry at temperatures between 77 K and 320 K. The quadrupole coupling constants have been modeled with point charges, dipolar contributions from the induced polarization [3] and orbital-overlap contributions [4]. Only a combined model with a significant dipolar contribution explains the large difference in quadrupole coupling constants. The two iron sites also exhibit a relatively large variation in Debye temperature.

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Iron Oxide-based Materials for Batteries and Contribution of Mössbauer Spectroscopy to Study Their Features

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Energy storage technologies, especially battery systems, play a key role in the global challenge for sustainable energy. Current lithium-ion batteries (LIBs) have surpassed previously competitive battery types due to their high energy and power capability. Nevertheless, developments in the field of electric vehicles and portable electronics encourage bring an intensive demands for further improvement in the field of energy storage.

The performance of rechargeable batteries depends on the thermodynamics and kinetics of electrochemical reactions in all the components (i.e., anode, cathode, electrolyte, and separator). Several strategies have been proposed for designing post-LIBs battery systems including the new types of materials for electrodes as silicon anodes, Li-metal anodes or metal oxygen systems, etc. [1]. In addition, the use of different types of transport ions (Mg^{2+} , Zn^{2+} , Ca^{2+} , and Al^{3+}) have been increasingly investigated [2]. Unfortunately, all these technologies suffer from low cyclability connected with degradation of a material or low carrier mobility due to a bigger size of transporting ions.

Iron oxides, such as α - Fe_2O_3 , γ - Fe_2O_3 , and Fe_3O_4 , show a potential to function as very promising anode materials for LIBs due to their high theoretical capacity ($\approx 1300 \text{ mAhg}^{-1}$), non-toxicity and low cost [3,4]. In this contribution, we review applications of ^{57}Fe Mössbauer spectroscopy for a complex understanding of processes of intercalation/deintercalation of Li-ions in the iron oxides matrices, which provides both structural and electronic information during the electrochemical cycling. Constructions of specific electrochemical cells are also highlighted [5], providing ^{57}Fe Mössbauer spectroscopy measurements in operando mode. Other techniques, such as X-ray powder diffraction and electron paramagnetic resonance, are also mentioned to complement Mössbauer spectroscopy data on structural and electronic changes during intercalation/deintercalation.

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Low-temperature Mössbauer Studies of AgFeO_2 and CuFeO_2 Delafossites

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Delafossites with ABO_2 structure are a relatively well-recognized group of materials. They have a unique pseudo-two-dimensional crystal structure, initially observed for the mineral CuFeO_2 , formed by two alternating layers. One consists of the close-packed monovalent Cu^+ or Ag^+ ions, and the latter comprises edge-shared FeO_6 octahedra. The delafossite structure can form two polytypes depending on the orientation of layers in stacking, i.e., the rhombohedral $3R$ type (space group $R\bar{3}m$) and the hexagonal $2H$ type (space group $P6_3/mmc$) [1]. Despite being analogous compounds, iron-based delafossites, i.e., AgFeO_2 and CuFeO_2 , exhibit completely different magnetic behavior below Néel temperatures. CuFeO_2 has multiferroic properties under an external magnetic field or after chemical substitution by nonmagnetic ions. Without an applied magnetic field copper ferrite possesses two magnetic transitions, at $T_{N1}=14\text{K}$ from the paramagnetic state to spin density wave phase and at $T_{N2}=11\text{K}$ to a collinear 4-sublattice antiferromagnetic phase. In the case, of AgFeO_2 changes in the magnetic ordering are dependent on polytype, they are seen at $T_{N1}=18\text{K}$ and $T_{N2}=11\text{K}$ for $2H$ and at $T_{N1}=15$ and $T_{N2}=9\text{K}$ for $3R$ polytype, respectively. However, the appearance of the cycloidal magnetic orderings for both polytypes below T_{N2} causes the emergence of the electric polarization without conditions required for CuFeO_2 [2]. Both materials are classified as II-type multiferroics [3].

In this work, we present the results of ^{57}Fe Mössbauer spectroscopy study of iron-based delafossites, i.e., AgFeO_2 and CuFeO_2 , prepared by the hydrothermal method. The spectra were measured in a wide range of temperatures, including the points of both magnetic phase transitions (at T_{N1} and T_{N2}), as well as at room temperature. Structural investigations carried by X-ray diffraction confirmed obtaining pure delafossite phases of AgFeO_2 and CuFeO_2 . According to Mössbauer measurements carried out at room temperature, both materials were in the paramagnetic state. Below T_{N1} for copper ferrite as well as the silver ferrite Zeeman sextets appeared. In the case of CuFeO_2 , spectra below T_{N2} were fitted with one component because of collinear magnetic ordering whereas spectra registered in the range $T_{N2} \leq T \leq T_{N1}$ required distribution of hyperfine magnetic fields. A completely different situation is observed in the case of AgFeO_2 . All patterns below T_{N1} are complicated and cannot be considered as the superposition of several Zeeman components. Hence, both regions of collinear and non-collinear ordering are characterized by a distribution of hyperfine magnetic field with a relatively strong correlation between B_{hf} and 2ε .

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Mössbauer Effect Studies of Zinc Ferrite Synthesized by Microwave Combustion Method

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Zinc ferrite nano-crystals were successfully synthesized from its stoichiometric metal nitrates and glycine mixtures, using a microwave assisted combustion method. The as prepared sample was subjected to high energy ball milling for different periods of time. Structural and magnetic properties have been investigated by XRD, FTIR, VSM and Mössbauer spectroscopy. Results revealed that the as-prepared sample is a monophase zinc ferrite possesses high crystallinity. A minor of α -Fe₂O₃ phase is detected after milling. The average crystallite size of the as prepared (AP) ZnFe₂O₄ powders is about 27 nm. This value decreased with milling time reach to around 9 nm after 330 min. FTIR spectra showed two absorption bands in the zinc ferrite structure related to octahedral and tetrahedral sites in the range of 400–600 cm⁻¹. The room temperature Mössbauer spectra of the samples are representing the coexistence of both ferrimagnetic ordering and superparamagnetic phases. The magnetic measurement at room temperature confirmed the ferrimagnetic behavior of the samples. The saturation magnetization value of the as prepared ZnFe₂O₄ is 47 emu/g was observed and its value decreases to 29 emu/g after 330 min of mill.

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Magnetic Hyperfine Interactions in the Mixed-valence Compound $\text{Fe}_3^{2+}\text{Fe}_4^{3+}(\text{PO}_4)_6$ from Mössbauer Experiments

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Iron phosphates demonstrate rich crystal chemistry and numerous practical applications. Many of these “mixed-valence” compounds, which contain iron ions in formal oxidation states of +2 and +3, are interesting because they can show intervalence charge transfer. These compounds have been extensively investigated due to interesting features in the crystal and electronic structure, despite that their magnetic properties have not been studied. The present work reports the results of the detailed Mössbauer study of the mixed-valence ferric-ferrous $\text{Fe}_7(\text{PO}_4)_6$ phosphate which exhibits two magnetic phase transitions at $T_{N1} = 45.5$ K and $T_{N2} = 16$ K marked by sharp singularities in both specific heat C_p and magnetization M . The $\text{Fe}_7(\text{PO}_4)_6$ compound was synthesized by a solid-state method from a stoichiometric mixture of FePO_4 and Fe by annealing at 1173 K for 130 h in evacuated sealed quartz tubes with several intermediate grindings. Hyperfine parameters of $\text{Fe}_7(\text{PO}_4)_6$ phosphate were examined using ^{57}Fe Mössbauer spectroscopy in a wide temperature range $4.2 \leq T \leq 300$ K. Four different iron sites were successfully detected: two for the high-spin Fe^{2+} and two for Fe^{3+} ions. Over the entire temperature range, Mössbauer data confirm the valence-localized nature of the distinct Fe^{2+} and Fe^{3+} sites (at least at time scales on the order of 10^{-8} s).

Mössbauer spectra below T_{N1} were analyzed by diagonalization of the full nuclear-interaction Hamiltonian. The substantial difference between the saturated hyperfine field (B_{hf}) values for the 5-fold (~ 5.0 T) and octahedrally (~ 10.1 T) coordinated ferrous sites was related to the symmetry of the local crystal field. It was shown that it is necessary to consider an additional electronic contribution to the EFG related with different electronic population of iron 3d-orbitals. From these observations, we have developed a crystal field model, which accounts for the set of observed quadrupolar and magnetic hyperfine parameters. This model shows that the Fe^{2+} ions have a well-isolated ground orbital singlet and a small single ion magnetic anisotropy. Using a crystal field calculation of the ferrous energy levels based on the point symmetry of the (Fe^{2+}O_5) and (Fe^{2+}O_6) sites, the contribution of the electron orbital current and that of the intra-atomic magnetic dipolar contribution in the B_{hf} field were estimated. The observed line broadening below the second phase transition at T_{N2} is approximated by the distribution of hyperfine fields $p(B_{\text{hf}})$ with a bimodal profile that is characteristic of spin-modulated magnetic systems [1, 2].

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Mössbauer Spectroscopic Evolution for Iron(II) Spin Crossover Hofmann-like Coordination Polymer Materials

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In the attractive research area of the valuable iron(II and/or III) spin crossover(SCO) systems, ⁵⁷Fe Mössbauer spectroscopy is a very powerful tool to allow very important information on developing switching materials because the ⁵⁷Fe Mössbauer parameters such as *IS* and *QS* are very sensitive for high and low spin states in the Hofmann-like SCO materials[1], as well as ²³⁷Np Mössbauer measurements being a very powerful tool for investigating the structures and chemical properties of Np coordination compounds due to hyperfine ²³⁷Np Mössbauer parameters having great sensitivities to the environment around the Np atoms[2]. As the hot atom chemistry, the nuclear-decay-induced excited spin state trapping (NIESST) for ⁵⁷Co-labelled Hofmann analogous complex ⁵⁷Co(py)₂Ni(CN)₄ was recorded using the emission Mössbauer spectroscopic study in nuclear probes for obtaining the local daughter site information [3]. We have recently demonstrated a soft X-ray–induced excited spin state trapping (SOXEISST) effect in the Hofmann-like SCO coordination polymers[4]. NIESST might be associated with SOXEISST in Hofmann-like SCO systems. We report ⁵⁷Fe Mössbauer spectra for a new Hofmann-like SCO compound based on [Pt(CN)₄]²⁻ using Ethyl Isonicotinate as shown in Figure 1.

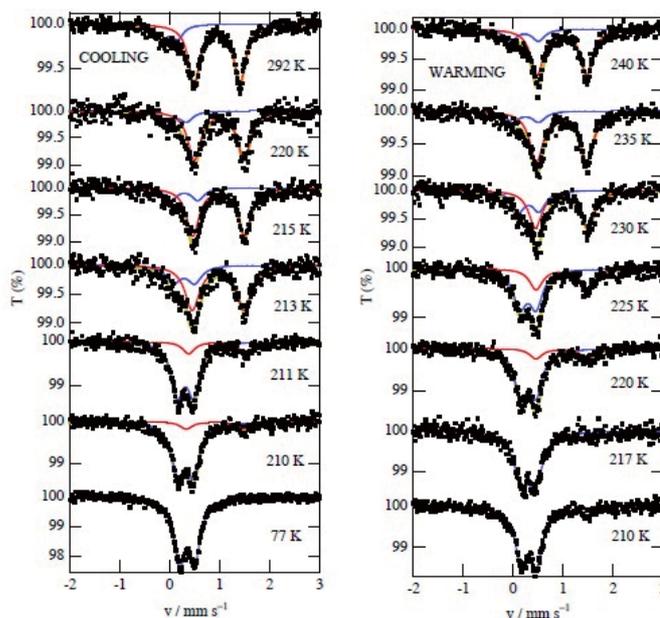


Fig. 1 ⁵⁷Fe Mössbauer spectra of SCO Fe(Ethyl Isonicotinate)₂[Pt(CN)₄]

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^{155}Gd Mössbauer Spectroscopy of the Intermetallic Compound GdNiAl**Hatem M. H. Saad¹, W.D. Hutchison¹, D.H. Ryan² and J.M. Cadogan¹***1 - School of Science, The University of New South Wales, Canberra, ACT 2600, Australia**2 - Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec, H3A 2T8, Canada***hatem.saad@student.adfa.edu.au**

The RNiAl compounds with R = Rare Earth (except Eu) crystallise in the hexagonal ZrNiAl-type structure with the $P\bar{6}2m$ (#189) space group [1] and the series exhibits frustrated magnetism, magnetocaloric behaviour and complex magnetic structures [2, 3]. Within this series, GdNiAl orders ferromagnetically around 60 K with further magnetic transitions at 30 K and 14 K being reported [4]. In addition, an abrupt change in the unit cell parameters at around 205 K upon cooling was reported for GdNiAl [4]. We collected X-ray and neutron powder diffraction patterns of GdNiAl; the Rietveld refinements of the XRD patterns revealed that the change at ~ 205 K is actually a transition between two different forms of the ZrNiAl-type structure; with these two forms coexisting over a temperature range from approximately 260 K down to 130 K. The Rietveld refinement of the neutron diffraction patterns revealed two different commensurate magnetic contributions: (1) A ferromagnetic component from ~ 60 K down to 32(2) K, and (2) a mixed Ferro/Antiferro-magnetic structure below 32(2) K. In the present work, GdNiAl is examined using ^{155}Gd Mössbauer spectroscopy. The hyperfine parameters of the ^{155}Gd Mössbauer spectra were obtained over the temperature range 50 K to 5 K by fitting using a least-squares diagonalisation of the full nuclear hyperfine Hamiltonian [5]. The temperature dependence of the Gd magnetic hyperfine field follows that expected for a Brillouin curve with $S = 7/2$, below ~ 60 K. The magnetic hyperfine field as $T \rightarrow 0$ is relatively small: $B_{hf}(0) = 16.9(3)$ T. In addition, the signs of the second-order CEF parameters derived across the RNiAl series from the electric field gradient of GdNiAl reproduce the preferred magnetic ordering directions of the R^{3+} moments that were reported for the RNiAl series on the basis of neutron diffraction and inelastic neutron scattering.

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The Influence of Annealing Temperature on the Magnetic Properties of BiFeO_3 Prepared by Sol-gel Method

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Recently, multiferroic materials have been the subject of intensive research because of their interesting physical properties as well as variety of potential applications. They may exhibit magnetoelectric coupling, which allows controlling of magnetisation by an external electric field, or induction of electric polarisation by applying an external magnetic field [1]. One of the most promising and most intensively studied multiferroic is BiFeO_3 . This is a rare example of a single-phase material in which ferroelectricity and antiferromagnetic ordering coexist at room temperature. BiFeO_3 has a rhombohedrally distorted perovskite structure and exhibits antiferromagnetic ordering up to the Néel temperature of $T_N \sim 643$ K due to superexchange interaction of Fe^{3+} ions. Simultaneously, it shows ferroelectric ordering with the Curie temperature of $T_C \sim 1103$ K [1]. The iron magnetic moments belonging to antiferromagnetic sublattices are slightly canted due to structural deformation of the perovskite cell resulting in a net ferromagnetic moment. However, a cycloidal spin structure in which the antiferromagnetic axis rotates through the crystal with long-range period of about 62 nm is superimposed on the antiferromagnetic ordering. This cycloidal spin structure leads to cancelation of macroscopic magnetization and inhibits observation of linear magnetoelectric coupling. Thus, many current scientific efforts tend to destroy the spin cycloid and to release the inherent magnetization in order to improve multiferroic properties of BiFeO_3 .

This work presents investigations of magnetic properties of BiFeO_3 prepared by sol-gel method and subjected to subsequent annealing at various temperatures. X-ray diffraction studies proved formation of rhombohedral BiFeO_3 . Scanning electron microscopy investigations enabled the observation of microstructure of the samples and the estimation of the mean grain size. The model assuming an angular distribution of hyperfine magnetic field and of quadrupole shift values was applied for Mössbauer spectra fitting [2]. Mössbauer investigations enabled the observation of gradual quenching of cycloidal spin order with decrease of mean grain size. Moreover, measurements of magnetization showed gradual appearance of hysteresis loop with decrease of annealing temperature revealing weak ferromagnetic behaviour of fine-grained BiFeO_3 .

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⁵⁷Fe CEMS Study on SnO₂ Films Doped with Dilute Metal Ions

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Oxide semiconductors doped with dilute magnetic ions have shown an interesting magnetic behavior at room temperature (RT). Diluted magnetism of SnO₂ doped with a several % Fe ions (including 1% ⁵⁷Fe) has been studied by Mössbauer spectrometry^{1),2)}. The ferromagnetism of SnO₂ powders codoped with dilute Co and Fe ions, Mn and Fe ions, Ni and Fe ions, V and Fe ions are enhanced compared with that of single ions doped SnO₂ powders. From previous studies³⁾, SnO₂ films codoped with double metal ions prepared by spray pyrolysis were characterized by ⁵⁷Fe conversion electron Mössbauer spectrometry (CEMS). CEMS spectra were taken at RT and low temperatures by a gas-filled proportional counter⁴⁾. In CEMS spectra for all samples, any magnetic sextets were not observed even if these SnO₂ films were measured at 20K by CEMS although the broad magnetic components were observed together with paramagnetic components in RT Mössbauer spectra of two metals codoped SnO₂ powders prepared by a sol-gel and thermal decomposition method. *Ab initio* calculations on supercell models of SnO₂ doped with Fe species have been also studied⁵⁾. These results showed that the configuration of substituted iron and oxygen vacancy is important for the magnetic behavior. In this study to confirm the phenomena, SnO₂ films codoped with Co and Fe ions, Ti and Fe ions, Cu and Fe ions were prepared on SnO₂ film/silica glass substrate heated at 400 °C by a spray pyrolysis. In RT CEMS spectra, two kinds of Fe³⁺ species were observed; one Fe³⁺ with $IS = 0.36-0.37$ mm/s and $QS = 0.69-0.75$ mm/s (D1) and another doublet with small IS and large QS (D2), which were affected by the other metal ions. At low temperatures, the paramagnetic doublets were more distinguished among these films. Further, low temperature CEMS spectra of Co and Fe codoped SnO₂ film showed a broad magnetic sextet.

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The Spin Fluctuations of ^{57}Fe Probe Nuclei in Two-dimensional Oxides



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We have studied the electronic state and the local surrounding of ^{57}Fe Mössbauer probe atoms within iron-doped two-dimensional systems $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$ and Ag_2NiO_2 containing nickel atoms in unusual formal oxidation states “+3”. The ^{57}Fe Mössbauer measurements have shown that in both structures iron is stabilized as Fe^{3+} in oxygen octahedral surrounding. According to calculations within the cluster configuration interaction method, the electronic state of nickel is dominated by the $d^7(\text{Ni})$ configurations corresponding to the ionic “ $\text{Ni}^{3+}\text{-O}^{2-}$ ” state. In the oxide $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$ with the K_2NiF_4 like structure and with a cationic 1/1 (Ni/Li) ordering, two sub-spectra were observed: the first, Fe(1), associated with Fe^{3+} substituted to the Li^+ sites due to the small local crystal field energy; and the second, Fe(2), corresponding to Fe^{3+} substituted to Ni^{3+} in the (NiO_6) sites. Drastic thermal evolution observed for the Fe(1) subspectrum has been interpreted by the spin-crossover between high spin 6A_1 ($S_{\text{Fe}} = 5/2$) and intermediate spin 4A_2 ($S_{\text{Fe}} = 3/2$) states. The experimental spectra measured in the entire range 77 - 300 K were described using the stochastic two-level model based on the assumption of the rapid electronic relaxation between two spin states related to the iron ions in the distorted $[\text{Fe}(1)\text{O}_6]$ centers. The relaxation frequencies and the activation energies of the corresponding spin fluctuations were estimated based on ^{57}Fe Mössbauer spectra. The results are discussed assuming a temperature-induced change in the electronic state of the $[\text{NiO}_4]^{5-}$ clusters in the layered perovskite $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$.

The observed in the $\text{Ag}_2\text{Ni}_{0.99}\text{Fe}_{0.01}\text{O}_2$ spectra ($T > T_N$) the line-area asymmetry has been interpreted by the texture effects, i.e., preferred orientation of platy crystalline in the plane of sample surface. It was shown that the structural phase transition at $T_S \approx 55$ K has a weak effect on the local structure of the ^{57}Fe probe atoms, while the development of the magnetic order at $T < T_N$ induces a continuous distribution of hyperfine magnetic fields H_{hf} at ^{57}Fe nuclei. This result is explained assuming that most of the Fe^{3+} spins behave as free spins with a weakened (frustrated) exchange interactions with its nearest magnetic environment, while small cluster spin glass behavior is observed for smaller part of iron probe atoms.

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⁵⁷Fe Probe Mössbauer Investigation of RCrO₃ (R = Sc, In, Tl, Bi) Perovskites

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Perovskite-type compounds with the general formula $R^{3+}B^{3+}O_3$, where $R^{3+} = Y$ and La-Lu and $B^{3+} = V, Cr, Mn, Fe, Co, Ni$ and $Ni_{0.5}Mn_{0.5}$, have been attracting a lot of attention for decades because of their interesting and important physical and chemical properties. In the extended family of $R^{3+}B^{3+}O_3$ perovskites we can find more peculiarities and interesting behaviors.

Perovskites with $R^{3+} = Tl$ have peculiarities because of the strong covalency of the Tl^{3+} -O bonds. Members with $R^{3+} = Bi$ show distinct structural and physical properties in comparison with $R^{3+} = Y$ and La-Lu because of the lone electron pair of Bi^{3+} and the covalency of the Bi^{3+} -O bonds. Sc- and In-containing chromites consist of “small” A-cation were for the first time investigated by Mössbauer spectroscopy in details. A partial cationic inverse was shown for these two compounds. Mössbauer spectra of $ACr_{0.95}^{57}Fe_{0.05}O_3$ ($A = Sc, In, Tl, Bi$) recorded at $T > T_N$ consist of quadrupole doublets with the isomer shift corresponding to the high spin Fe^{3+} ions. Spectra analysis exhibited several crystallographic sites for Fe^{3+} ions within $ACr_{0.95}^{57}Fe_{0.05}O_3$ ($A = Sc, In, Bi$) structures. The $BiCr_{0.95}^{57}Fe_{0.05}O_3$ spectra were satisfactory described as two unbroadened quadrupole doublets with approximately similar areas which are in agreement with the crystal structure of the compound. To explain the values of the quadrupole splitting of the doublets we calculated the EFG tensor using the crystal data for undoped $ACrO_3$ ($A = Sc, In, Tl, Bi$) chromites. Mössbauer spectra recorded at $T < T_N$ consist of hyperfine Zeeman structures reflecting combined electric and magnetic hyperfine interactions. The hyperfine magnetic saturation field $B_{hf}(0)$, superexchange integral $J_{Fe-O-Cr}$, and the values of the Néel temperature T_N were obtained from the temperature dependence of hyperfine parameters. A comparison of the magnetic ordering temperature values and the saturation hyperfine magnetic fields $B_{hf}(0)$ at ⁵⁷Fe in chromites $ACr_{0.95}^{57}Fe_{0.05}O_3$ ($A = Sc, In, Tl, Bi$) on $\cos^2\theta$ (where θ is Cr-O-Cr angle of superexchange interactions in perovskite-like chromites) revealed a dramatic changes in released values which are not coincide with rare-earth chromites. Possible explanation of such differences is discussed.

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Magnetic Properties of EuFe_2As_2 under Pressure Studied by Nuclear Forward Scattering of Synchrotron Radiation

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EuFe_2As_2 has been intensively studied in a member of the FeAs-based high-temperature superconductors. A commensurate stripe-type antiferromagnetic (sAFM) transition in Fe sublattice occurs at $T_0^{\text{Fe}} \sim 190$ K with a simultaneous structural change from a tetragonal $I4/mmm$ structure to an orthorhombic $Fmmm$ structure [1-4]. Furthermore, Eu^{2+} magnetic moments show a simple A-type antiferromagnetic order at $T_0^{\text{Eu}} = 19$ K [2-4]. The T_0^{Fe} is reduced by applied pressure or substitution and then bulk superconductivity appears at 2.5 GPa and low temperature, while the T_0^{Eu} gradually increases without any anomalies at 2.5 GPa [5-7].

We report on a nontrivial coupling between superconductivity and new antiferromagnetic order under pressure in EuFe_2As_2 by the ^{57}Fe and ^{151}Eu nuclear forward scattering and dc-magnetic susceptibility using single crystals [7]. We find a microscopic coexistence between the antiferromagnetic order in the Fe and Eu sublattices and superconductivity below $T_{\text{sc}} (=25$ K) at 2.7 GPa. The magnetic structure of the Fe sublattice changes from the sAFM one in the normal conducting state to the modified antiferromagnetic one (mAFM) in the superconducting state. In the mAFM state, the directions of the magnetic hyperfine fields H_{hf} at the Fe nuclei modulate along the c-axis and these H_{hf} values are identical. Furthermore, the mAFM state develops with the superconducting volume fraction below T_{sc} , indicating a strong interplay between the new antiferromagnetic order in the Fe sublattice and superconductivity. For the magnetism in the Eu sublattice, the A-type antiferromagnetic structure is maintained up to 5 GPa, although the magnetic order in the Fe sublattice is suppressed around 3 GPa. In this presentation, we also discuss the coupling between the itinerant Fe and the localized Eu^{2+} moments in EuFe_2As_2 under pressure.

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XRD, Mössbauer and Magnetic Study of $M_xCo_{1-x}Fe_2O_4$ (M = Zn Or Cd) Nanoparticles

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In the current work the $TM_xCo_{1-x}Fe_2O_4$ ($TM = Zn$ or Cd) nanosized compounds with average particle size of about 9 nm were synthesized and investigated by Mössbauer and magnetization measurements. The concentrations of Zn^{2+} or Cd^{2+} ions and crystallite size have significant effects on the magnetic properties. The ^{57}Fe Mössbauer spectral studies show ordered magnetic spin state for $x \leq 0.5$ and paramagnetic phase for $0.6 \leq x \leq 1.0$ compositions. This can be explained by the weakening of super exchange interactions between the ^{57}Fe nuclei at tetrahedral (A) and octahedral (B) sites due to the increasing contents of nonmagnetic Zn or Cd atoms. The Mössbauer spectra for Zn- and Cd-based compounds are closely related due to the similar electronic configuration of Zn^{2+} and Cd^{2+} ions. The magnetization data reveal the superparamagnetic nature of the compounds investigated. An increase in coercive fields from about zero at room temperature to ~ 3 kOe at 10 K due to spin freezing has been observed. The temperature dependence of magnetization show blocking temperatures higher than 300 K. The variations of the magnetic parameters such as saturation magnetization, coercive fields are discussed on the basis of Zn or Cd contents and crystallite size.

Mössbauer Study of Dilute Fe & Nb Co-doped SrTiO₃

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A diluted magnetic oxide semiconductor doped with magnetic ions is one of the candidate materials for spintronics application. The doping magnetic ions into wide band gap semiconductors such as SnO₂, TiO₂, and ZnO have been studied [1]. A homogeneous sample doped with magnetic Fe³⁺ and Nb⁵⁺ is expected to increase the magnetism and semiconductor. To clarify the relationship between its magnetization properties and the local chemical state of iron in SrTiO₃, Sr(Ti_{1-x-y}Fe_xNb_y)O₃ doped with Fe and Nb (x = 0.005, 0.01, 0.02, 0.04, 0.05, 0.08, 0.11, y = 0.05) were characterized by ⁵⁷Fe Mössbauer spectroscopy, XRD, and VSM. The samples were prepared by using a complex formation and thermal decomposition method. Sr, Ti, Fe and Nb standard solutions, citric acid, and ethylene glycol solutions were mixed in a nominal ratio, stirred at around 90 °C, and heated at 500 °C for 2 hours. After that, the samples were crushed and fired at 1000 °C for 4 hours. XRD showed that the crystal structure of SrTiO₃ is cubic (3.907 Å ≅ a ≅ 3.917 Å). All Fe and Nb ions are considered to be substituted in Ti site of the crystal since the impurity peaks were not detected. Some Mössbauer spectra of these samples are shown in Fig. 1. From the isomer shift, it is found that ⁵⁷Fe species in the sample exist as Fe³⁺ ions. These spectra consist of a paramagnetic peak and a magnetic relaxation peak. The 1%Fe+5%Nb doped sample showed the smallest lattice constant and the largest ferromagnetism among these samples. When 1% Fe+5%Nb doped sample was prepared by annealing at 1000 °C for 2 hours, a magnetic relaxation peak increased as a major component. It is considered that the dilute magnetism in this system is related with surface defects.

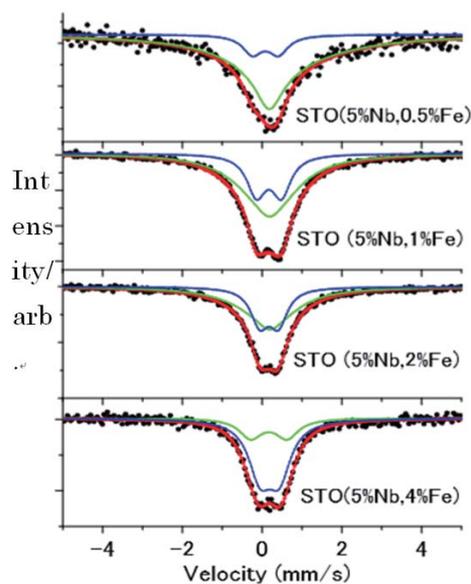


Fig. 1. ⁵⁷Fe Mössbauer spectra of Fe and Nb doped SrTiO₃ annealed at 1000 °C for 4 hrs.

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Theoretical and Experimental Investigation of Magnetic Properties of Fe-Al-Si Nanosystems

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The nanocrystalline state obtained through the Mechanical Alloying (MA) process in Fe-Al system is usually a complex one and exhibits interesting physical and magnetic properties [1-2]. In recent study of Fe based nanocomposites it has been found that further selection of third metallic/non metallic elements as matrix or as reinforce has open further opportunities to create novel magnetic materials superior than conventional iron alloys [1-2]. We report theoretical/experimental study of magnetic properties of $\text{Fe}_3\text{Al}_x\text{Si}_{(1-x)}$ ($x = 0.2-0.8$) nanosystems. Theoretically calculated (using SPRKKR code within full relativistic spin polarized mode) hyperfine fields (Fig. 2) of Fe-Al-Si systems reveals that the spins (@ two different sites of Fe) are perfectly collinear in direction of applied magnetic field and magnetic components of both the ferromagnetic sites coupled ferromagnetically which also reflects in theoretical calculations of bulk magnetization as it shows very high magnetic moments (Fig. 1). For experimental investigation of magnetic properties, $\text{Fe}_3\text{Al}_x\text{Si}_{(1-x)}$ nanosystems ($x = 0.2-0.8$) have been prepared by mechanical alloying (high-energy ball milling using a SPEX 8000M mixer/mill with tungsten carbide (WC) vials and balls (eight per vial, mass of the sample for ball to powder ratio(20:1, 5h). Room temperature bulk magnetization studies shows very high saturation magnetization ($\sim 178\text{emu/g}$) and soft ferromagnetic behavior in MA samples (Fig. 3). The Curie temperature of these MA samples is in the range of 700°C , combine with excellent bulk magnetization make them suitable candidate for high temperature applications.

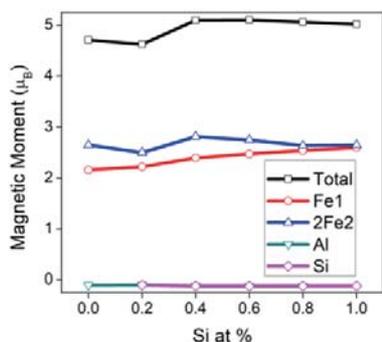


Figure 1. Theoretically calculated values of $\text{Fe}_3\text{Al}_x\text{Si}_{(1-x)}$ nanosystems

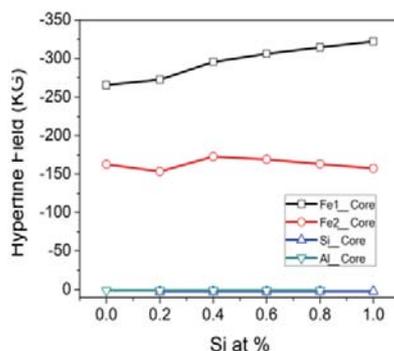


Figure 2. Theoretically calculated values of Hyperfine fields of $\text{Fe}_3\text{Al}_x\text{Si}_{(1-x)}$ nanosystems

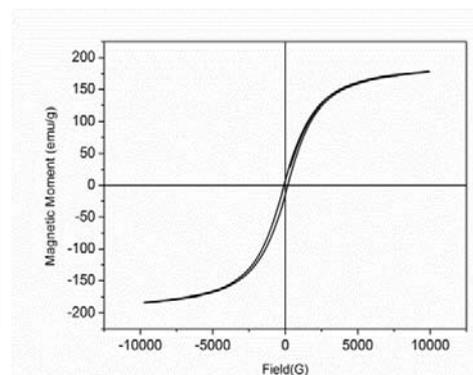


Figure 3. RT M-H of $\text{Fe}_3\text{Al}_{0.8}\text{Si}_{0.2}$ nanosystem

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From Spin- to Charge-modulations in $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ K. Komędera¹, A. Blachowski¹, J. Żukrowski², T. J. Sato³¹ - Mössbauer Spectroscopy Laboratory, Institute of Physics, Pedagogical University, Kraków, Poland² - Academic Center for Materials and Nanotechnology, AGH University of Science and Technology, Kraków, Poland³ - Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

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The $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ compounds represent ‘122’ iron-pnictide superconductors with superconductivity induced by isovalent chemical doping of the BaFe_2As_2 parent compound (e.g. the partial substitution of As by P) with simultaneous suppression of the spin-density wave SDW magnetic order. The samples with $x = 0$ (parent), $x = 0.10$ (under-doped), $x = 0.31, 0.33, 0.53$ (superconductors with $T_{sc} \approx 27$ K, 28 K, 14 K, respectively) and $x = 0.70, 0.77$ (over-doped) have been studied by the ^{57}Fe Mössbauer spectroscopy versus temperature. A development of the electronic charge modulation is observed within the temperature region of the superconductivity. It is seen as the oscillations of the spectral line-width versus temperature. Under assumption that above modulation is due to the isomer shift variation solely one gets 0.5 e_l/(Bohr radius)³ electron density oscillation on the iron nuclei across formation of the superconducting state. The similar effect was observed previously for others iron-based superconductors [1]. No charge modulation is observed for over-doped samples. The average spectral line-width is increased below 50 K for the optimally doped superconductors with $x \approx 0.3$ indicating traces of magnetic order due to the vicinity of the quantum critical point.

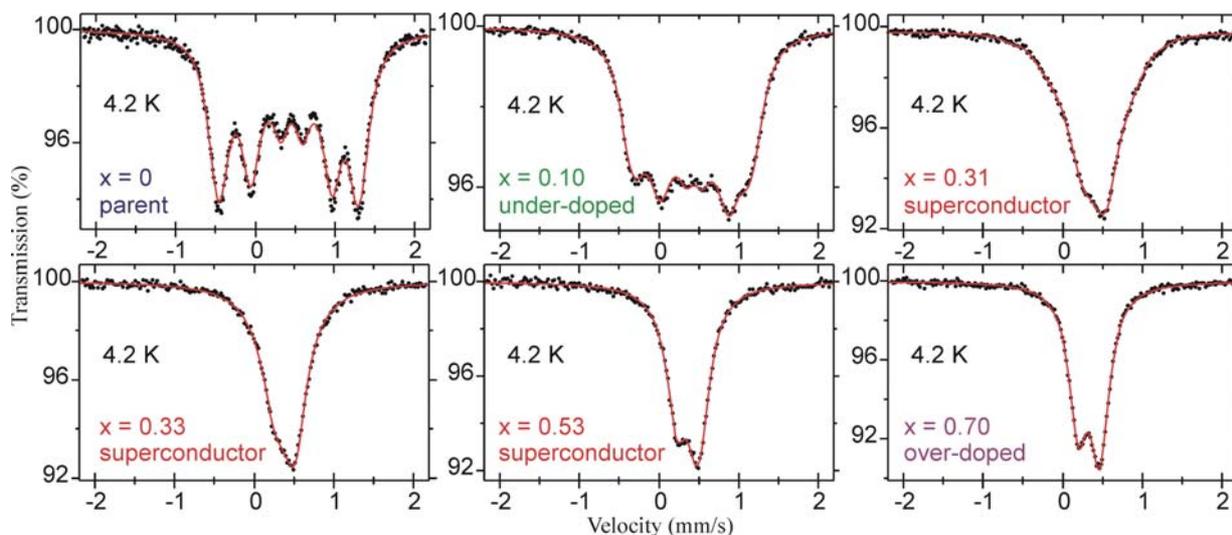


Fig. 1. ^{57}Fe Mössbauer spectra of $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ compounds at 4.2 K.

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Synchrotron Radiation-based ^{61}Ni Mössbauer Spectroscopy of Rare-earth Nickelates

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The perovskite rare-earth-element nickelates $R\text{NiO}_3$ (R : Pr, Nd, ..., Lu) display a first-order metal insulator (MI) transition with structural change and LaNiO_3 behaves as metallic state without a MI transition. In the insulating phase at low temperature, Ni atoms occupy two crystallographically nonequivalent sites with slightly different valences ($\text{Ni}^{3\pm\delta}$) while Ni atoms at metallic state occupy one site with Ni^{3+} . The transition temperature T_{MI} depends on the tolerance factor which is defined as function of the ratio of the relative R -O and Ni-O bond length¹⁾ and is turned by external pressure²⁾. The band gaps of these series are generated between Ni d -band and O p -band. In the insulating state at low temperature, $R\text{NiO}_3$ show antiferromagnetic transitions. However recent researches report that single crystal LaNiO_3 and pressure induced metallic EuNiO_3 display antiferromagnetic behavior at low temperature^{3,4)}. We have investigated the interplay between the magnetism of Ni ions of $R\text{NiO}_3$ (R : La, Eu, and Yb) and the conductivity using synchrotron radiation-based (SR-based) ^{61}Ni Mössbauer spectroscopy to clarify the correlation between electronic states of Ni ions and metallic or insulating phase.

These SR-based ^{61}Ni Mössbauer spectra observed at 2 K have a single line absorption feature. For the width of each spectrum, that of LaNiO_3 (metallic) is smaller than others (insulating, AFM). That reflects the difference of the magnetic moments at Ni sites.

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Spin Orientations of Iron Ions in Rare-earth Ferroborates $RFe_3(BO_3)_4$ ($R = Y, Nd, Sm, Gd, Ho$) at Low Temperatures

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Multiferroic materials have attracted a lot of attention in the last 10 years due to coexistence and interaction of ferroelectric and magnetic ordering [1–5]. One of the actively studied multiferroic systems is the rare-earth ferroborates $RFe_3(BO_3)_4$ ($R = Y, La-Lu$). They have two magnetic subsystems of iron and rare-earth ions demonstrate various complex spin dynamics at low temperatures depending on the type of R elements in composition.

In this work, the structural and spin states of iron ions in $RFe_3(BO_3)_4$ single crystals ($R = Y, Nd, Sm, Gd, Ho$) were studied using ^{57}Fe Mössbauer spectroscopy and single crystal X-ray diffraction. The dynamics of the orientation of the spins in the subsystems of rare-earth elements and iron in the low-temperature region of 4.2 - 40 K is studied and discussed.

Acknowledgements: This work was supported by the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS in part of «low-temperature XRD and Mössbauer measurements», Russian Foundation for Basic Research (Project No.17-02-00766a) in part of «analysis of the Mössbauer measurements data and EFG calculations» and performed using the equipment of the Shared Research Center of the Shubnikov Institute of Crystallography of FSRC "Crystallography and Photonics" RAS.

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Comparative Calculations of the Debye Temperature for Rare-earth Ferrobates $RFe_3(BO_3)_4$ According to X-ray Structural and Mössbauer Measurements

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Multiferroic materials have attracted a lot of attention in the last 10 years due to coexistence and interaction of ferroelectric and magnetic ordering [1–5]. One of the actively studied multiferroic systems is the rare-earth ferrobates $RFe_3(BO_3)_4$ ($R = Y, La-Lu$). They are interesting as model objects with two magnetic subsystems of iron and rare-earth ions and demonstrate the variety of properties and phase transitions depending on the type of R elements in the composition.

In this work, the comparative calculations of the Debye temperature according to X-ray structural and ^{57}Fe Mössbauer spectroscopy measurements for the $RFe_3(BO_3)_4$ single crystals ($R = Y, Nd, Sm, Gd, Ho$) were performed.

Acknowledgements: This work was supported by the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS in part of «low-temperature XRD and Mössbauer measurements», Russian Foundation for Basic Research (Project No.17-02-00766a) in part of «the Debye temperature calculations» and performed using the equipment of the Shared Research Center of the Shubnikov Institute of Crystallography of FSRC «Crystallography and Photonics» RAS.

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Interactions Between Germanium Atoms in Mechanically Synthesized Iron Based Fe-Ge Alloys Studied by ^{57}Fe Mössbauer Spectroscopy

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Mechanical alloying method was applied to prepare iron-based $\text{Fe}_{1-x}\text{Ge}_x$ solid solutions with x in the range $0.01 \leq x \leq 0.05$. The thermodynamic properties of the materials obtained in an planetary ball mill were investigated with the Mössbauer spectroscopy by measuring the room temperature spectra of ^{57}Fe for samples after an annealing process at 1270 K for 2 h followed by slow cooling to room temperature during 6 h. They were analysed in terms of parameters of their components related to unlike surroundings of the iron probes, determined by different numbers of Ge atoms existing in the neighbourhood of iron atoms [1]. Basing on the data we determined the binding energy E_b between two Ge atoms in studied alloys [2]. The latter was done using the extended Hryniewicz-Królas idea [3, 4]. It was found that the energy is positive or the Ge atoms in Fe matrix interact repulsively. In the next step the extrapolated value of E_b for $x = 0$, equal to 0.201(50) eV, was used for computation of the enthalpy of solution $H_{\text{Fe-Ge}}$ of germanium in iron [5]. According to findings of the $E_b(0)$ value is simply related to $H_{\text{Fe-Ge}} : H_{\text{Fe-Ge}} = -z \cdot E_b(0)/2$, where z is the coordination number of the α -Fe crystalline lattice, amounted to 8. The obtained value for $H_{\text{Fe-Ge}}$, equal to 0.80(20) eV/atom, was compared with corresponding one derived from calorimetric studies [6] and resulting from the semiempirical Miedema's model of alloys [7] as well as with that 0.88(19) eV/atom [8], derived from proper data for Fe-Ge solid solutions obtained by melting in an arc furnace.

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Mössbauer and Magnetic Studies on (La_{0.8}Ca_{0.2})_{1-x}Bi_xFeO₃ (x=0.0, 0.1 and 0.2) Perovskites

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The interest in perovskite oxide with formula ABO₃ increases due to their fascinating properties and also their applications in many areas (catalysis, solid electrodes and electrolytes of fuel cells and gas sensors) [1, 2]. It has been proved that the substitution of one or both A and B sites affect the properties of these perovskites [3]. (La_{0.8}Ca_{0.2})_{1-x}Bi_xFeO₃ (x = 0.0, 0.1 and 0.2) perovskites were prepared by the Sol-Gel method using a citric acid route, and then sintered at 800 °C (batch LCBFO-800) and 900 °C (batch LCBFO-900). X-ray diffraction patterns (XRD) showed that the compounds crystallize in an orthorhombic structure with a *Pnma* space group [4]. ⁵⁷Fe Mössbauer spectra of LCBFO-800 show 3 magnetic subspectra, two related to magnetite which is also observed by XRD, and the other one attributed to Fe³⁺ ions in a tetrahedral site. The lines are large, related to a certain extent of superparamagnetism, due to the small grain size of the particles of samples annealed at 800 °C. The spectra of LCBFO-900 compounds reveal two magnetic subspectra related to Fe³⁺ in octahedral sites. Furthermore, for both heat treatments, all spectra show a doublet that is more intense in the case of 900 °C sintering. Meanwhile, for all compounds, the M(H) curves indicate a superposition of ferromagnetic and antiferromagnetic contributions. The overall magnetism of the LCBFO-900 samples was found to be weaker than those annealed at 800 °C. The Curie temperature, determined both by M(T) and DSC curves, was found to be between 400 and 500 °C, in good agreement to almost all the ferrite perovskites [5]. It is concluded that the choice of sintering temperature affects the magnetic properties of the studied perovskites.

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Effect of Ni Substitution on Structural and Magnetic Properties of Nanocrystalline Cobalt Ferrite

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Composition series $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$, (NCFO), ($0.2 \leq x \leq 1.0$) were prepared by Sol-gel auto combustion method. The structure and sample stoichiometry of the as prepared NCFO were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques. Moreover, the influence of Ni substitution on the site occupancy in the NCFO series and on some magnetic properties have been examined by Mössbauer spectroscopy and vibrating sample magnetometer. The formation of phase-pure NiFe_2O_4 (NFO) was evident from the XRD patterns. The lattice constant obtained using MAUD program decreased from

8.368 Å to 8.334 Å for pure NFO. The crystallite size calculated was in the range of 29 - 43 nm. The average particle size was also measured using transmission electron microscopy (TEM) and it was found to be decreased from 85 nm at $x=0.2$ to 30 nm for pure NFO at $x=1$. Mössbauer spectra measured at 78 K showed two well-defined Zeeman sextets belonging to octahedral [B] and tetrahedral (A) sites, respectively. This result confirming the formation of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ spinel. The isomer shift (δ) values were assigned to Fe^{3+} ions distributed in both A and B sites. The quadrupole splitting (ΔE_Q) values were very small (almost zero) in the samples indicating that the local symmetry of the ferrites obtained is close to cubic. Hysteresis loops were measured at room temperature. A linear decrease in the saturation magnetization (M_s) and coercivity (H_c) with nickel concentrations were observed for NCFO nanoparticles. The abrupt decrease in blocking temperature was obviously observed for the samples with $x \geq 0.8$. The linear increase in Curie temperature (T_c) from 814 to 841 K was observed, when nickel concentration was increased from $x = 0.2$ to $x = 1.0$.

Structural and Magnetic Properties of Magnesium Ferrite Particles Synthesised by Combustion Method

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In this work, the MgFe_2O_4 particles were synthesised by a simple combustion method and followed by the high-temperature calcination. Here, we have used succinic acid as the fuel instead of using conventional urea/glycine. The prepared MgFe_2O_4 is characterised using X-ray diffraction, scanning electron microscopy, magnetization measurements and Mössbauer spectroscopy with a high-velocity resolution. The XRD pattern confirms the formation of highly crystalline cubic structured MgFe_2O_4 . The lattice constant is calculated using Rietveld refinement analysis, and the obtained value is $a = 8.378(1) \text{ \AA}$. As well as the structural formula of the synthesised MgFe_2O_4 can be written as $^{\text{IV}}[\text{Mg}_{0.1}\text{Fe}_{0.9}]^{\text{VI}}[\text{Mg}_{0.45}\text{Fe}_{0.55}]_2\text{O}_4$ with the inversion parameter of ~ 0.9 . The SEM analysis revealed the microstructure and morphological features of the MgFe_2O_4 , where the particles are agglomerated with sub-micron sized particles in size range between 100–200 nm. The FT-IR spectra confirm the presence of Fe–O and Mg–O functional groups. The VSM analysis confirms the soft ferromagnetic nature of MgFe_2O_4 with the high saturation magnetization moment ($M_s = 23.5 \text{ emu/g}$) and the coercivity ($H_c = 96.4 \text{ Oe}$). The room temperature Mössbauer spectrum of MgFe_2O_4 particles demonstrates typical asymmetric six-line pattern which was fitted using 16 magnetic sextets. The ^{57}Fe hyperfine parameters (hyperfine field H_{eff} and isomer shift δ) demonstrate that at least one minor magnetic sextet with $H_{\text{eff}} \sim 506 \text{ kOe}$ and $\delta = 0.473 \text{ mm/s}$ can be attributed to maghemite or hematite. Other magnetic sextets with δ smaller than $\sim 0.25 \text{ mm/s}$ and H_{eff} in the range $\sim 502\text{--}422 \text{ kOe}$ can be associated with the ^{57}Fe in tetrahedral (A) sites while magnetic sextets with larger values of δ and H_{eff} in the range $\sim 493\text{--}382 \text{ kOe}$ can be assigned to the ^{57}Fe in octahedral (B) sites in MgFe_2O_4 particles. If we consider the variations in the local microenvironments of ^{57}Fe in the A and B sites in inverse MgFe_2O_4 spinel similarly to those in normal NiFe_2O_4 spinel (see [1]) we can calculate that, within the coordination sphere of 3.5 \AA , all A sites have neighbouring both A and B sites while all B sites have neighbouring A sites only. Therefore, the distribution of Fe^{3+} and Mg^{2+} cations in both A and B sites may be a reason of the distribution of different local microenvironments around tetrahedral and octahedral positions in the inverse MgFe_2O_4 spinel and more than two magnetic sextets which can be expected for MgFe_2O_4 particles.

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Mössbauer and Magnetic Studies of $50\text{Fe}_2\text{O}_3$ - 50SiO_2 and $90\text{Fe}_2\text{O}_3$ - 10SiO_2 Ceramic Fibers Processed by Laser Floating Zone Method

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Iron containing silica fibers have found wide applications as high temperature materials, especially as reinforcements for high temperature ceramic matrix composites due to their high tensile strength, Young's modulus, excellent heat and oxidation resistance [1]. The Laser Floating Zone method (LFZ) is known to strongly impose non-equilibrium conditions promoting the formation of impurities in the ceramic fibers system [2].

The impact of pulling rate on the magnetic and structural properties of $50\text{Fe}_2\text{O}_3$ - 50SiO_2 and $90\text{Fe}_2\text{O}_3$ - 10SiO_2 ceramics prepared by LFZ was studied. The pulling rates were varied being: 25, 50, 100 and 200 mm/h. Hereafter the fibers are labelled as xLFZy where x is the iron oxide content in the composition and y stands for the pulling rate.

Various effects of the LFZ conditions on the phase composition, microstructural features and magnetic properties of as-grown fibers are analyzed and discussed. For the 90LFZ compounds some hematite is observed in the XRD spectra, which amount decreases with the increasing of pulling rate. All these observations are also supported by the obtained magnetic measurements. Moreover, it is not observed a change of crystallinity with decreasing pulling rate in the case of the 50LFZ compounds, but for 90LFZ samples the crystallinity increases with pulling rate decrease. ^{57}Fe Mössbauer measurements at room temperature show that in all samples the major component is magnetite, although some reaction with silica took place as it is found fayalite in a very small percentage.

The variation of magnetization as a function of pulling rate for 90LFZ showed that, the magnetic moment measured at 300 K has the highest value in 90LFZ100, while the maximum magnetization of 90LFZ ceramics was found for 90LFZ50 when the measurement is performed at 10 K. Inverse trend was observed in the case of fibers containing 50% of iron oxide; the maximum magnetization was found for samples 50LFZ50 and 50LFZ100 when the measurement was carried out at 300 and 10 K, respectively. In addition, generally the 90LFZ ceramics were more magnetic than the 50LFZ samples, as expected. The revealed behaviours can be described in terms of the temperature dependent interactions occurring between the magnetic clusters formed in the fibres.

From this study, we can suggest that Mössbauer measurements at different temperatures below 300 K are required to truly distinguish the magnetic interactions taking place within the clusters formed in the LFZ ceramics.

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Mössbauer Spectroscopy Study of the Cu Doped BaFe_2As_2 Iron -based Superconductor

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Abstract: Recent years of study about the Fe-based superconductors (FeSCs) indicates that the emergence of superconductivity is closely related to the ordered state such as antiferromagnetism and its fluctuation. Further investigation implies the existence of an electronic orbital ordered state, which is called the nematic phase, being adjacent to the region of antiferromagnetic phase transition. It makes a more intricate nature that distinct ordered states compete with each other in FeSCs and result in a complicated issue. Among FeSCs, the “122” series possesses the abundant physical properties, so we carried out the study of the representative BaFe_2As_2 by superseding Fe with Cu dopants in the aspects of the nematic phase, magnetic fluctuation, electronic correlation as well as the lattice dynamics. High quality of single crystal samples were synthesized by utilizing the FeAs self-flux method, the Cu doping levels of the compounds are 0.03 and 0.07 respectively in our research, and comparative analysis has been put into effect with different doping quantities involving the above mentioned physical characters. $\text{Ba}(\text{Fe}_{0.97}\text{Cu}_{0.03})_2\text{As}_2$ is at the boundary of nematic phase, antiferromagnetic phase and possible superconducting phase, while $\text{Ba}(\text{Fe}_{0.93}\text{Cu}_{0.07})_2\text{As}_2$ is at the boundary of paramagnetic phase and nematic phase. The consequence of Moessbauer Spectroscopy (MS) makes it clear that strong magnetic fluctuation occurs instead of long-range antiferromagnetic ordered state at low temperature, and the Curie-Weiss temperature of the fluctuation behavior approaches the quantum critical point (QCP). The nematic phase transition (NPT) of $\text{Ba}(\text{Fe}_{0.97}\text{Cu}_{0.03})_2\text{As}_2$ happens at around 75K, which is identical to the phase diagram. The occurrence of the nematic phase transition breaks the symmetry of the iron 3d orbitals, and the quadrupole splitting (QS) below 75K behaves a steep increasing which is mirrored in the MS data. This phenomenon also affects the inner-shell electrons that the isomer shift (IS) performs separately above and below 75K. We minutely analyzed the infection of the iron 3d orbitals caused by the nematic phase, fitted the QS data within the framework of this model and further provided an order parameter describing the NPT. By comparing the MS data of $\text{Ba}(\text{Fe}_{0.93}\text{Cu}_{0.07})_2\text{As}_2$ we discover that the increasing of the Cu doping level has the following effects: ① suppressing the magnetic fluctuation behavior in the sample and keeping the Curie-Weiss temperature away from the QCP, ② reducing the correlation effect among the electrons, ③ weakening the potential interaction in the lattice.

^{57}Fe Mössbauer Study of High-valent Fe Ions in Fe-substituted Li_2MnO_3 **Yasuhiro KOBAYASHI¹, Mitsuharu TABUCHI², Makoto SETO¹**¹ - Institute for Integrated Radiation and Nuclear Science, Kyoto University, Kumatori, Osaka 590-0494, Japan² - National Institute of Advanced Industrial Science and Technology (NAIST), Ikeda, Osaka 563-7577, Japan

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Fe substituted Li_2MnO_3 is known as a novel positive electrode material for high-capacity Li-ion battery¹⁾. In the study of this material, high-valent (4+ or over) Fe ions were observed²⁾. In previous study, most of such high-valent Fe ions had been observed in octahedral site of perovskite structure, for example SrFeO_3 ³⁾. However, Li_2MnO_3 has rock-salt related structure. To elucidate the origin of this high-valent Fe, we observed ^{57}Fe Mössbauer spectroscopy of $\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Mn}_{0.8})_{1-x}\text{O}_2$.

The 20% Fe-substituted Li_2MnO_3 ($\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Mn}_{0.8})_{1-x}\text{O}_2$) are prepared by coprecipitation-calcination method. For comparison, the samples were calcined at 750 °C in O_2 or N_2 atmospheres. The two samples are named as samples 750-O and 750-N, respectively. From the X-ray diffraction, the sample calcinated in O_2 include more substitute Fe atoms in Li site than the sample calcinated in N_2 . ^{57}Fe Mössbauer spectroscopy were done between 3 and 300 K. $\alpha\text{-Fe}$ was used for the velocity calibration.

Figure 1 shows ^{57}Fe Mössbauer spectra of 750-O and 750-N at 3K. The spectra were fitted by 3 magnetic components and 1 nonmagnetic component. We used pseudo-Voigt function for the magnetic components, which is due to assumption of Gaussian distribution of hyperfine magnetic field. Hyper fine fields of each magnetic components on 750-O are 45T, 22T and 12T, and isomer shifts are 0.45mm/s, -0.39mm/s and 0.07mm/s, respectively. First magnetic component is main component, which due to the normal Fe in $\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Mn}_{0.8})_{1-x}\text{O}_2$, and this component can be assigned as Fe^{3+} . Second and third magnetic components have slightly small isomer shift. These values can be assigned as Fe^{5+} and Fe^{4+} respectively. The ratio of these high-valent Fe ions in 750-N are less than 750-O, thus they are owing to the substitute Fe ions in Li site. And this Fe^{5+} component was detected in the spectra of only magnetic ordered state.

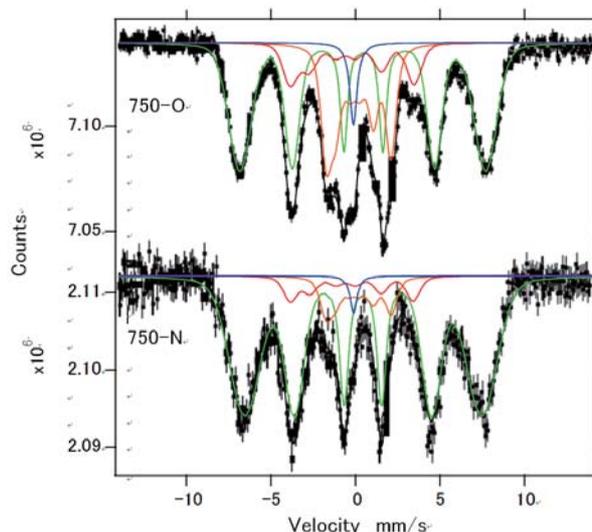


Fig. 1 ^{57}Fe Mössbauer spectra of $\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Mn}_{0.8})_{1-x}\text{O}_2$ at 3K.

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Synchrotron Mössbauer Spectroscopy in ^{151}Eu and ^{161}Dy under High Pressure

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Synchrotron Mössbauer spectroscopy (SMS) (aka. nuclear forward scattering) is a time-domain Mössbauer spectroscopy utilizing a synchrotron radiation source to excite the nuclei. The focused and intense synchrotron x-ray beam makes the technique compatible with complex sample environment such as high pressure and low temperature. In this talk I will discuss two case studies by ^{151}Eu in EuFe_2As_2 and ^{161}Dy in Dy metal to investigate the evolution of magnetism and valence under high pressure in diamond anvil cell.

EuFe_2As_2 exhibits complex phase diagram under pressure including magnetic orderings from both Eu and Fe sublattices and pressure-induced superconductivity at pressure of 2.5-3 GPa [1-7]. More recently, the magnetic ordering from Fe sublattice was found microscopically coexist with superconductivity under pressure from SMS experiments [8]. To investigate the evolution of magnetic and valence state of Eu sublattice, we have performed SMS experiment up to 37 GPa. The local magnetism in Eu sublattice persists up to 21.6 GPa with a drastic increase of magnetic ordering temperature and hyperfine magnetic field. At higher pressure the magnetic ordering of Eu is completely suppressed, possibly due to a significant increase of valence.

The magnetism in Dy has been investigated under high pressure up to 141 GPa using SMS. With increasing pressure Dy's magnetic ordering temperature changes drastically. At 10 K the hyperfine magnetic field of Dy remains almost constant with increasing pressure up to 141 GPa, showing the robustness of the local magnetism. At 120 GPa magnetic ordering temperature increases sharply to ~ 280 K and drops at higher pressure, in good agreement with the Doniach scenario proposed by previous electrical resistivity studies [9].

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Mössbauer and Magnetic Properties of Ni-Mg Nano-crystalline Ferrites Prepared by Microwave Combustion Method

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Single-phased Nano-series $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$), prepared by the microwave combustion method were investigated to determine their structural and magnetic properties using X-ray diffraction (XRD), Mössbauer spectroscopy (MS), and vibrating sample magnetometer (VSM). XRD pattern showed the cubic spinel structure with crystallite size variation within the range 20-45 nm. The different structural data obtained were discussed in the view of ionic radii of the entire ions and their distribution within the lattice. For instance, the obtained lattice constant showed an increase with increasing the Mg^{2+} contents which, is attributed to the large ionic radius of Mg^{2+} ions compared to Ni^{2+} . The Mössbauer measurements at 296 K and 78 K for all studied samples showed two well-resolved magnetic patterns corresponding to the tetrahedral A-site and octahedral B-site. The cation distribution among the two crystallographic sites driven from the Mössbauer measurements are consistently in good agreement with that obtained from the analysis of X-ray pattern. The magnetic hyperfine field of the B-site as well as of the A-site are clearly decreasing as the content of Mg^{2+} is increased which are expected since the Mg^{2+} ions with zero magnetic moment tend to replace Ni^{2+} ions with magnetic moment of $2.8\mu_B$ in the octahedral sites. This situation is quite supported by the increase of the lattice parameter. The saturation magnetization (M_s), coercivity and magnetic moment per formula unit μ_{exp} . are decreased with increasing Mg-concentration; a result which is in good agreement with the reduction of the magnetic hyperfine fields obtained from the Mössbauer measurements.

Structural and Mössbauer Studies of Iron-doped Manganite Perovskite

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The influence of Fe-doping on the structural and magnetic properties of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0.1 \leq x \leq 1.0$) was investigated. The samples were synthesized by auto-combustion Sol-Gel method. XRD refinement indicates that all samples are crystallized in orthorhombic single-phase perovskite with Pnma space group. The Scanning Electron Microscopy (SEM) micrographs showed aggregates of stacked grains of about ($0.2 \sim 5.0 \mu\text{m}$). Room-temperature (295 K) and liquid nitrogen (78 K) transmission Mössbauer spectra for all samples were carried out. The samples with ($0.1 \leq x \leq 0.5$) at 295 K and with ($0.1 \leq x \leq 0.3$) at 78 K consisted of pure paramagnetic doublet with almost similar isomer shift (δ) at 295 K. However, the samples spectra with $x \geq 0.6$ at 295 K and with $x=0.4$ at 78 K started to show the presence of a paramagnetic component superimposed on broadened magnetic sextets. This behaviour can be attributed to the presence of superparamagnetic domains in the samples which can be associated to the competition between double exchange (DE) interaction and super exchange interaction (SE) in perovskite lattice due to replacement of Mn^{2+} ions in B sites by Fe^{3+} ions. However at 78 K, all samples within the range ($0.5 \leq x \leq 1.0$) showed well resolved magnetic spectra.

Structural and Magnetic Studies of $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ Nanorods

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Single-phased, corundum-related, needle-shaped $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ nanorods (Figure. 1) (radius: 80-100, length: 200-300 nm) were prepared with the hydrothermal method and characterized with XRD, SEM, Mössbauer spectroscopy and magnetic measurements. The lattice constant ($a = 5.02 \text{ \AA}$) does not change for both samples with a small decrease in c (13.79 to 13.72) for the $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ [1].

The Mössbauer measurements taken (at 300 K, and 77 K) indicate the suppression of Morin transition for $\alpha\text{-Fe}_2\text{O}_3$ but it present in $\alpha\text{-Fe}_2\text{O}_3\text{@C}$. The hyperfine field of $\text{Fe}_2\text{O}_3\text{@C}$ was (51.1) which is very close to the bulk (51.5 T). However, for $\alpha\text{-Fe}_2\text{O}_3$ it was smaller (50.4) like which is comparable with what observed for this shape of particles with similar size. [2]

Magnetic study (at temperatures of 2-900 K and fields from 10-200 Oe) showed interesting magnetic behaviors like field dependent magnetization at same warming-cooling rates. Thermal hysteresis (15-30 K), and field dependence ($H = 10, 50, 100, 200 \text{ Oe}$) of the Morin temperature were also observed in warming-cooling cycles (Figure. 2(a)) due to the first order phase transition as a result of the relaxation of the magnetic moment of hematite particles in the weak-ferromagnetic phase. Some of These behaviors alters considerably when C is implanted into $\alpha\text{-Fe}_2\text{O}_3$ nanorods. Hysteresis loops (at fields -9 to 9 Tesla and at different temperatures between 2-400 K) (Figure. 2(b)) indicate field dependent magnetization of both samples. However, $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ has very small values of M compared to the one without carbon. This study add a value in explaining the suppression of Morin transition for nanosized particles and what is the effect of shape, size, and surface layer on the magnetic properties of $\alpha\text{-Fe}_2\text{O}_3$ nanorods.

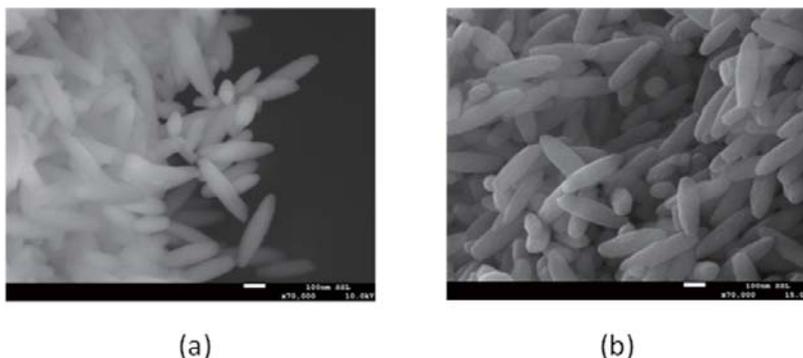


Figure 1. SEM images of as prepared (a) $\alpha\text{-Fe}_2\text{O}_3$ (b) $\alpha\text{-Fe}_2\text{O}_3\text{@C}$

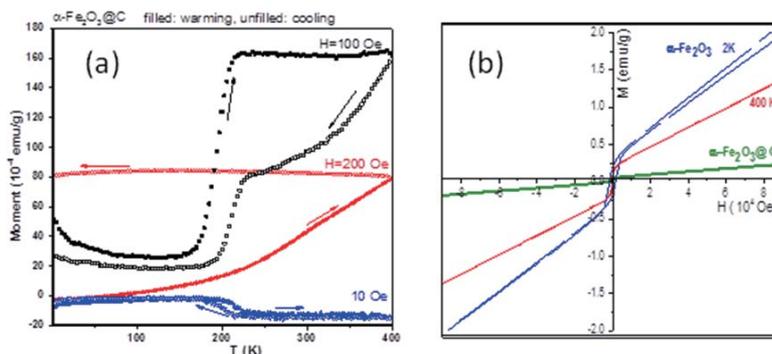


Figure 1. (a): change of magnetic moment (emu/g) with temperature (K) for $\alpha\text{-Fe}_2\text{O}_3\text{@C}$ (b): hysteresis loop for (Red and Blue: $\alpha\text{-Fe}_2\text{O}_3$ at indicated temperature and Green: $\alpha\text{-Fe}_2\text{O}_3\text{@C}$).

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Spin Crossover Hofmann-like Complex $\text{Fe}(\text{3-Cyano-4-Methylpyridine})_2[\text{Ag}(\text{CN})_2]_2$

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Various kinds of $\text{Fe}^{\text{II}}\text{-Ag}^{\text{I}}$ and $\text{Fe}^{\text{II}}\text{-Au}^{\text{I}}$ Hofmann-like spin crossover(SCO) complexes have been found recently.⁽¹⁻³⁾ We now have synthesized and characterized a novel Hofmann-like SCO coordination polymer complex $\text{Fe}(\text{3-cyano-4-methylpyridine})_2[\text{Ag}(\text{CN})_2]_2$ (**1**). **1** has been prepared using $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $\text{K}[\text{Ag}(\text{CN})_2]$ and 3-cyano-4-methylpyridine. The color of **1** is yellow at RT and red at 78 K due to the SCO behavior. The crystal structure of **1** is shown in Fig.1. The space group of **1** is *Pbca*. The octahedral $\text{Fe}(\text{II})$ ion is coordinated by two pyridine-like ligands and four $[\text{Ag}(\text{CN})_2]^-$ moieties. The temperature dependence of magnetic susceptibility of **1** is measured by using SQUID measurement, which indicate one step spin transition without hysteresis ($T_{1/2} = 180$ K). Fig.2 shows Mössbauer spectra of **1**. While a spectrum at RT consists of a single doublet of large quadrupole splitting due to the Fe^{II} high spin state. A spectrum at 78K consists of one doublet of small quadrupole splitting, indicating the Fe^{II} low spin state.

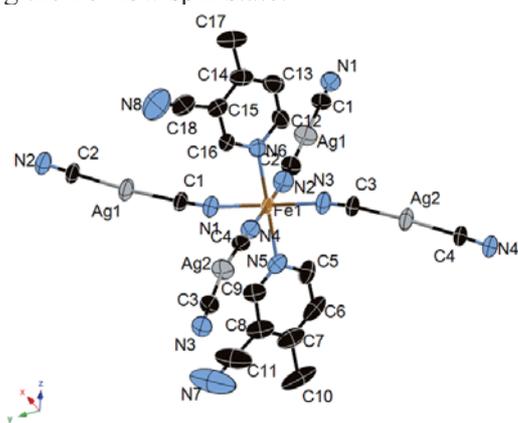


Fig. 1. Geometry around the iron(II) ion in **1**.

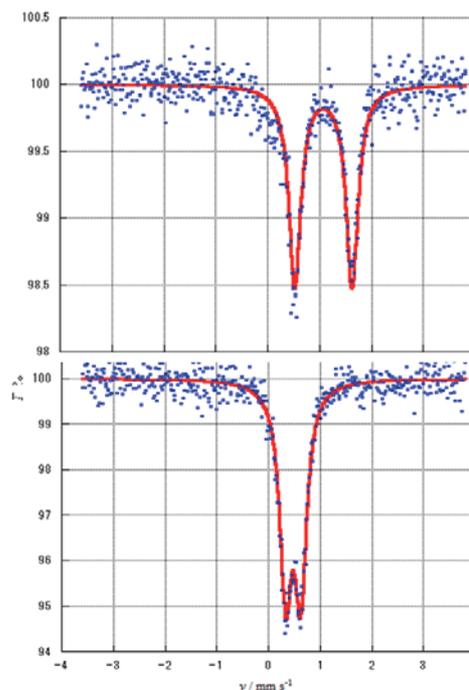


Fig. 1. Mössbauer spectra of **1** Upper :RT Lower:78K.

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ZnFe₂O₄ Nanoparticles with Different Crystallinity: A Comparative Study

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Zn-ferrite nanoparticles are widely studied on account of their intriguing electronic, magnetic and biology-related properties that make these materials promising candidates for being used in diverse applications such as hyperthermia therapy [1], MRI contrast agents [2], Li ion batteries [3], photocatalysis [4], as well as radar-absorbent [5], antimicrobial and anticancer materials [6]. While Zn²⁺ is known to have an affinity to be situated at the tetra-hedral site of the spinel, when prepared in the nanoparticle form considerable levels of inversion are usually found, with corresponding changes in the magnetic properties of the material [7]. In the present work we investigate and compare structural and magnetic properties of two different Zn-ferrite nanoparticle powder samples, prepared via coprecipitation process, displaying similar (~ 5 nm) particle size along with a considerable difference in crystallinity. Elemental composition of the samples is assessed by ICP-OES, whereas their structural and magnetic properties are explored through TEM, SAED, XRD, and FC/ZFC magnetization measurements, as well as electron magnetic resonance spectroscopy and ⁵⁷Fe Mössbauer spectroscopy measurements performed at various temperatures. Via comparison of the experimental results relations among structural and magnetic properties are going to be discussed.

Acknowledgements: This work was supported by the Hungarian National Research, Development and Innovation Office – NKFIH (K115784 and K115913). Kovács K.V. has been supported by the János Bolyai Postdoctoral Fellowship of HAS.

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Magnetic Behaviour of Amorphous $\text{Fe}_{90-x}\text{Co}_x\text{Sc}_{10}$ Alloys

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Amorphous $\text{Fe}_{90-x}\text{Co}_x\text{Sc}_{10}$ alloys, hereafter denoted as a- $\text{Fe}_{90-x}\text{Co}_x\text{Sc}_{10}$, have been produced by rapid quenching from the melt. The Curie temperature, T_C , was verified using mean field theory as well as Landau's theory of second-order phase transitions in zero and nonzero external fields. The atomic spacing dependence of T_C can be clarified by the empirical Bethe-Slater curve. The theoretical T_C of a- $\text{Co}_{85}\text{Fe}_5\text{Sc}_{10}$ is $T_C = 1150$ K, which is the highest T_C among amorphous alloys. The fluttering of the measured reduced magnetization, $M(T)/M(0)$, as a function of reduced temperature, T/T_C , is explained in the framework of Kober-Handrich model. According to this model is the exchange integral fluctuation, the main reason for the fluttering of $M(T)/M(0)$. In the case of a- $\text{Fe}_{90}\text{Sc}_{10}$, however, the exchange integral fluctuation is dominant only at zero external field, $B_{ex}=0$. At $B_{ex}=9$ T, however, the exchange integral fluctuation has no conspicuous effect on reduced magnetization. From the Mössbauer data it can be concluded that at $B_{ex}=9$ T, the frozen magnetic clusters control the behavior of reduced magnetization as function of T/T_C .

In opposite to ferromagnetic solids where the fluttering of $M(T)/M(0)$ is a characteristic indication of amorphous alloy, a- $\text{Co}_{85}\text{Fe}_5\text{Sc}_{10}$ does not exhibit any trace of the exchange integral fluctuation.

Mössbauer Spectroscopic Study on the Structure of $\text{Co}_{50}\text{Fe}_{50}/\text{Al}_2\text{O}_3$ Nanocomposites

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In this paper, $\text{Co}_{50}\text{Fe}_{50}/\text{Al}_2\text{O}_3$ nanocomposites with different Al_2O_3 contents were prepared by H_2 reduction of the precursor synthesized by sol-gel method. was used to prepare. The microscopic magnetic structure was studied by Mössbauer. The results show that the content of Al_2O_3 in the composite has an important effect on the grain structure and magnetic structure of CoFe alloy. When the content of Al_2O_3 increases from 0 wt% to 50 wt%, the Mössbauer spectra of each sample are composed of only one set of magnetic hyperfine sextet. For the sample with the Al_2O_3 content of 70 wt%, the Mössbauer spectra of the sample become two sets of peaks, one of which is magnetic hyperfine sextet and the other is quadrupole split doublet. Combined with the analysis results of XRD and TEM, it can be determined that the magnetic hyperfine sextet comes from the ferromagnetic CoFe grains, while the quadrupole split doublet comes from the superparamagnetic CoFe grains.

Keywords: $\text{Co}_{50}\text{Fe}_{50}/\text{Al}_2\text{O}_3$; composites; sol-gel method; Mössbauer.

Zero-field Splitting of Magnetically Isolated High-spin Fe²⁺ and Nephelauxetic Effect in Prussian Blue Analogues

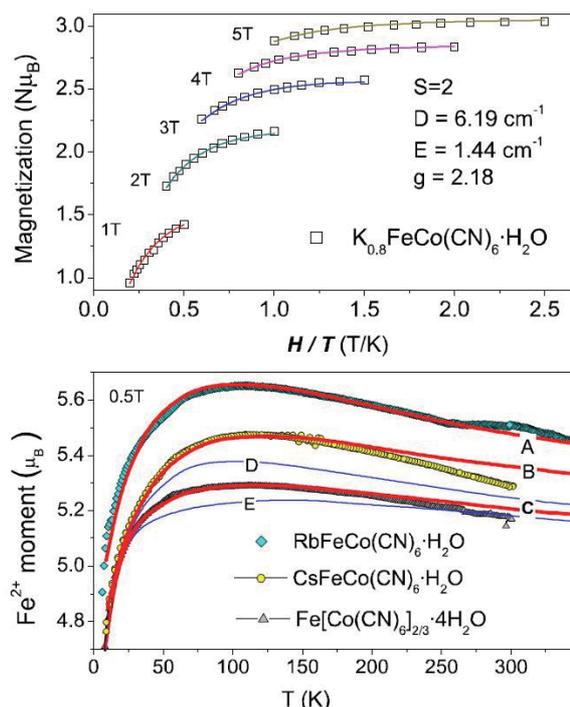
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In Fe-Co PBA the high-spin Fe²⁺ ions are perfectly magnetically isolated from each other. They are separated by the *nm*-range long links –NC—Co(III)—CN–, in which Co(III) is fully diamagnetic. In such a situation, the magnetic exchange between Fe²⁺ ions may come into play only at very low temperatures, below 2K. We have started our magnetic measurements from 2K and found no sign of exchange interactions. Thus, the low-temperature magnetic properties bear the clear information on zero-field splitting (ZFS) and spin-orbit coupling (SOC) in these purely paramagnetic materials. A variety of ligand configurations occurs in Prussian blue [1] and its analogues, as H₂O replaces easily the CN-linker, creating the network of extremely high porosity. The degree of randomness in the distribution of CN and H₂O ligands around Fe²⁺ is the degree of freedom that we can vary by choosing a preparation method (precipitation, ionic exchange, alkali-intercalation). Passing from axially symmetric to asymmetric configurations of ligands around Fe²⁺ we observe the changes in Fe Fenton catalytic activity, in corresponding Mössbauer spectral signatures (ΔE_Q), and in low-temperature parameters of ZFS and SOC. The SOC coupling constants are strongly reduced (see Figure caption) compared to the free-ion value $\lambda_0 = -100 \text{ cm}^{-1}$ owing to nephelauxetic (delocalization) effect, which consist of the radial orbital expansion owing to π -back-donation of the electron density from the ligand π -orbitals to the d-orbitals of Fe²⁺.

Figure 1. Top: low-temperature magnetization in various applied dc fields. The parameters *D* and *E* are indicative of frozen orbital motion of a mononuclear single-molecule magnet (MSMM). The positive *D* suggests an easy-plane MSMM. The orbital degeneracy is consistent with the large ΔE_Q in Mössbauer spectra. Bottom: The parameter of spin-orbital coupling λ of -63 and -70 cm^{-1} are determined in AFeCo(CN)₆ (A=Rb, Cs) via fitting the temperature dependencies of the Fe²⁺ magnetic moment. In the last PBA compound, the fitting curve (C) is the average of (D) and (E) with the weight factors given by the abundances of corresponding Mössbauer doublets.



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Structure and Magnetism of $L1_0$ Nanocomposite Fe-Mn-Pt Thin Films

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Among the rare-earth-free systems that are currently investigated in search for novel permanent magnet solutions for various applications, with special emphasis on the magnets required to operate in extreme conditions, the FePt binary system, where the tetragonal hard magnetic $L1_0$ phase can be formed by suitable microstructure processing via annealing, has been extensively studied. A variation of this system, the ternary FeMnPt system, has been also recently shown to exhibit good permanent magnet behavior due to the suitable formation of the $L1_0$ phase. In addition to be likely to form the $L1_0$ phase as its parent binary system, the ternary FeMnPt benefits from the reduced costs due to the reduced amount of Pt and may exhibit particular magnetic structure due to the influence of the antiferromagnetic Mn. In the present work, we have employed a mixed sputtering technique, based on the use of both elemental and compound target for developing $L1_0$ FeMnPt thin films with specific structural features, that triggers better magnetic performances in terms of coercivity and maximum energy products. The as-obtained films have been thermally annealed and characterized by means of transmission electron microscopy, X-ray diffraction, Mössbauer spectroscopy, magneto-optic Kerr effect (MOKE) and SQUID magnetometry. The aim is to correlate the Mn induced microstructural and lattice changes with the magnetic properties and to optimize the microstructure for an early formation of the ordered $L1_0$ phase and increased coercivity compared to the as-prepared, structurally disordered, face centred cubic initial state of the films. The structural characterization by means of high resolution electron microscopy and X-ray diffraction indicates the formation of highly ordered $L1_0$ phase regions in the samples annealed at 550 °C as revealed by long ordered (001) superlattice planes of the $L1_0$ structure. The high degree of ordering is confirmed by the large value of c/a ordering parameter (0.97). Evidence of existing several magnetic sublattices has been revealed by Mössbauer spectroscopy studies. Aside the evidence for the existence of very few, small regions of bcc Fe-rich areas, the annealed sample contains two magnetic sublattices, that are assigned to the $L1_0$ FePt and $L1_0$ FeMnPt phases, as proven by the hyperfine parameters of the Mössbauer sextets. Magnetic measurements confirms the Mössbauer spectroscopy studies. The hysteresis loops show strong coercive fields and also an inflection point that hints to the existence of two magnetic components with different coercive fields. These components are assigned to soft magnetic Fe-rich areas and to hard magnetic $L1_0$ phases. There are good premises for developing novel exchange spring nanocomposite magnets due to both strong coercivity and the co-existence of soft and hard magnetic phases.

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Metamagnetic Transition in FeRh Thin Film

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CsCl-type equiatomic Fe-Rh alloy exhibits a first-order transition from antiferromagnetic (AFM) order to ferromagnetic (FM) order around 350 K. In the FM state (Curie temperature is about 700K), the Fe and Rh atoms carry parallel magnetic moments of $\sim 2.2\mu_B$ and $\sim 0.7\mu_B$ [1]. The AFM-to-FM metamagnetic transition is triggered by a $\sim 1\%$ change in the unit cell volume, as a consequence of the coupling between magnetic and structural properties. In addition, strong changes in the electronic structure have been reported between both magnetic states, with an unusually low carrier density in the AFM phase [2, 3]. These two features suggest that FeRh is a good candidate for the electrical control of magnetism using ferroelectrics through piezoelectricity [4], creating novel multiferroic materials.

In this work we present the variation of hyperfine parameters in FeRh thin film deposited on BaTiO₃ (100) ferroelectric substrate in the temperature range between 25 °C and 165 °C. Nuclear resonant scattering at different grazing angles was used to determine the depth resolution of magnetic configuration in the FeRh layer. In room temperature the main magnetic component was found to be antiferromagnetically ordered (about 80%), which gradually turned into ferromagnetic with increasing temperature. During temperature reversal, different metamagnetic transition path was observed, resulting a hysteresis in hyperfine parameters.

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Spacing Control Interaction between Two Nuclear Ensembles at X-ray Regime

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For an individual atom, virtual photons emitted and reabsorbed by this given atom contribute to Lamb shift. In the presence of two (or more) atoms, virtual photons can be emitted by one atom and absorbed by the second one, leading to an exchange-type interaction [1]. This interaction will give rise to a split, and show a spacing-dependent signature [2]. In optical system, exchange interaction between atoms are of fundamental importance in quantum optics, quantum simulations, and quantum information processing [3]. In x-ray region, this kind of interaction between two nuclear ensembles has been used to achieve electromagnetically induced transparency (EIT) [4] and mimic Rabi oscillations [5].

In the situation of two atoms interacted with continuum of modes [2], exchange-type interaction has a typical feature that its strength shows periodic characteristic with $J \sim J_{\max} \sin(\varphi)$, where φ is the phase difference depended on the spacing between two atoms. So far, the spacing-dependent behavior is not studied for two nuclear ensembles in x-ray region. Here, a thin-film open-end planar cavity embedding two ensembles of resonant Mössbauer ^{57}Fe is designed. The present work proves that this kind of structure is a good candidate with continuum modes for x-ray cavity, and the periodic feature is also observed.

The calculated results are depicted at Fig. 1(b) and (c), obvious and negligible splittings are shown respectively. In the case of (b) for $k_z d \sim \pi$, the splitting is almost zero. And in the case of (c) for $k_z d \sim \pi/2$, the splitting takes its maximum $7.5 \gamma_0$ according to the reflectivity curves which is accessible to be obtained from the experiment. So the splitting takes its maximum when $\varphi = \pi/2$ or any odd multiple, and takes its minimum when $\varphi = \pi$ or any odd multiple, this phenomenon agrees well with the prediction that $J \sim J_{\max} \sin(\varphi)$.

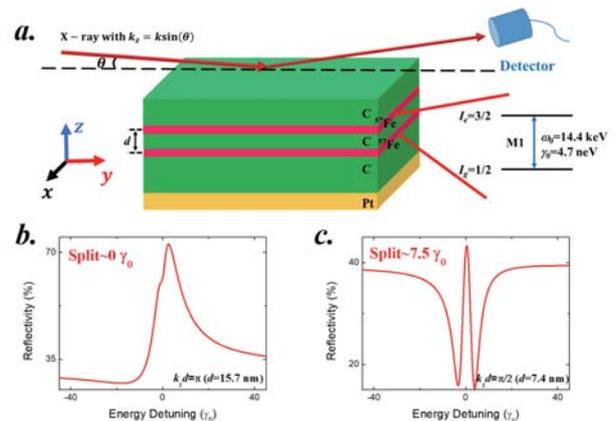


Figure 1. Thin film with embedded two layers of ^{57}Fe with spacing d and (a) the schematic of measurement. The thin film has only bottom Pt mirror layer in this configuration. (b) The numerical energy-resolved reflectivity curves in $d=15.7$ nm and (c) in the case of $d=7.4$ nm, both of (b) and (c) have convolved a Gauss function with $2 \gamma_0$ energy resolution.

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Preparation and Characterization of Spin Crossover Thin Solid Films

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Iron(II) spin crossover (SCO) complexes display a reversible transition from the low-spin state (LS, S=0) to a high-spin state (HS, S=2) by e.g. variation of temperature, pressure or by irradiation with light [1]. Therefore, these systems are promising candidates for information storage materials [2]. For practical device applications thin films of these properties are interesting. The SCO-compound [Fe(Htrz)₂(trz)](BF₄) (**1**) switches between the LS and the HS state with a 30 K wide thermal hysteresis loop above room temperature [3]. We have prepared thin films of **1** on a SiO₂ substrate by spin coating. The spin states of the films have been characterized by Mössbauer spectroscopy in reflection mode using a MIMOS II spectrometer. A low quadrupole splitting (LS state) at 300 K and a high quadrupole splitting (HS state) at 400 K were found for the film, as well as for bulk powder of **1**. This confirms a LS – HS transition above room temperature. Furthermore, synchrotron based nuclear resonance scattering measurements from 80 K to 400 K indicate that the hyperfine parameters are similar to those of the bulk powder of **1**. DFT calculations reproduce the calculated Fe-vibrational density of states of the bulk and the thin film sample of **1** and indicate a higher amount of HS Fe atoms being present in the film of **1** than in the bulk powder of **1**. These studies show that the SCO films prepared by spin coating have similar SCO properties as the bulk complex.

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Interface Sharpening in Miscible and Isotopic Multilayers: Role of Short-circuit Diffusion

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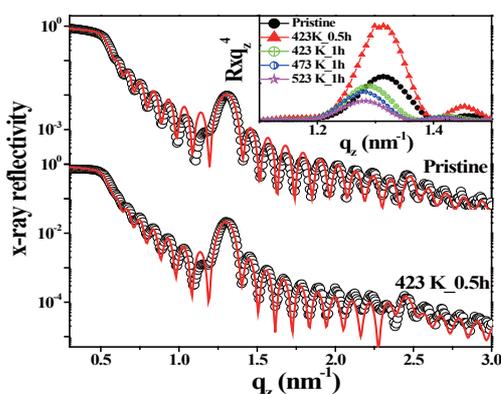
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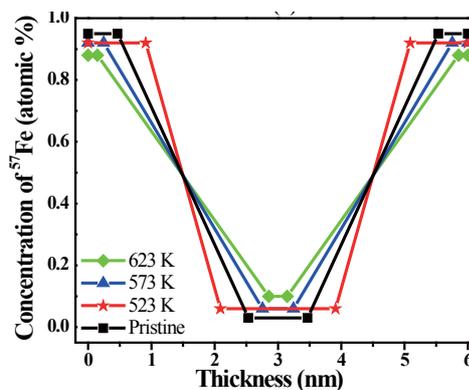
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Atomic diffusion at nanometer length scale may differ significantly from bulk diffusion, and may sometimes even exhibit counterintuitive behavior. In the present work, taking Cu/Ni as a model system, a general phenomenon is reported which results in sharpening of interfaces upon thermal annealing, even in miscible systems. Anomalous x-ray reflectivity from a Cu/Ni multilayer has been used to study the evolution of interfaces with thermal annealing. Annealing at 423 K results in sharpening of interfaces by about 38%. This is the temperature at which no asymmetry exists in the inter-diffusivities of Ni and Cu. Thus, the effect is very general in nature, and is different from the one reported in the literature, which requires a large asymmetry in the diffusivities of the two constituents [1, 2]. General nature of the effect is conclusively demonstrated using isotopic multilayers of ⁵⁷Fe/naturalFe, in which evolution of isotopic interfaces has been observed using nuclear resonance reflectivity. It is found that annealing at suitably low temperature (e.g. 523 K) results in sharpening of the isotopic interfaces. Since chemically it is a single Fe layer, any effect associated with concentration dependent diffusivity can be ruled out. The results can be understood in terms of fast diffusion along short-circuit paths like triple junctions, which results in an effective sharpening of the interfaces at relatively low temperatures.



X-ray reflectivity of Cu/Ni multilayer annealed at 423 K for 0.5 h. Inset compares the reflectivity at the Bragg peak of samples annealed at different temperatures.



Concentration profiles as obtained from the best fit of the nuclear resonance reflectivity data of the isotopic multilayer of ⁵⁷Fe/naturalFe, showing interface sharpening at 523 K.

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Phase Transformation Studies in Iron Oxide Nanoparticles Using Mössbauer Spectroscopy

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Iron oxide nanoparticles (NPs) with different phases possess immense application potential, mainly when crystallite sizes of their particles fall below 100 nm. These can be categorized into different forms according to their oxidation state. X-ray diffraction studies cannot clearly distinguish different phases of iron oxide. Mössbauer spectroscopy is an effective technique to study the different phases of iron oxide and the underlying transformation mechanism. In wustite (FeO), iron is present in the divalent state having Fm3m space group. Iron in trivalent state can have different phases such as α -Fe₂O₃ (hematite), β -Fe₂O₃, γ -Fe₂O₃ (maghemite) and ϵ -Fe₂O₃. Both β -Fe₂O₃ and ϵ -Fe₂O₃ are regarded as a rare iron oxide phases. They are thermally unstable and easily transformed into α -Fe₂O₃ upon thermal treatment. In Fe₃O₄, iron is in both divalent and trivalent state. It possesses inverse spinel structure having point group Fd3m. Long term exposure of bulk Fe₃O₄ to air atmosphere at room temperature leads to the mild oxidation into γ -Fe₂O₃ due to valence alteration of iron atoms. On annealing γ -Fe₂O₃ transforms into α -Fe₂O₃ via intermediate ϵ -Fe₂O₃ formation. On increasing the calcination temperature, γ and ϵ forms were not detected. With an increase in the heating time, β -Fe₂O₃ is also transformed into α -Fe₂O₃. This polymorphic change is confirmed by an increase of the sextet areas in the Mössbauer spectra. However in nanophase Fe₃O₄ is reported to be unstable and transforms to γ -Fe₂O₃. Mössbauer spectroscopy can help in exploring differences in nanophase and bulk Fe₃O₄ and predicting its stability.

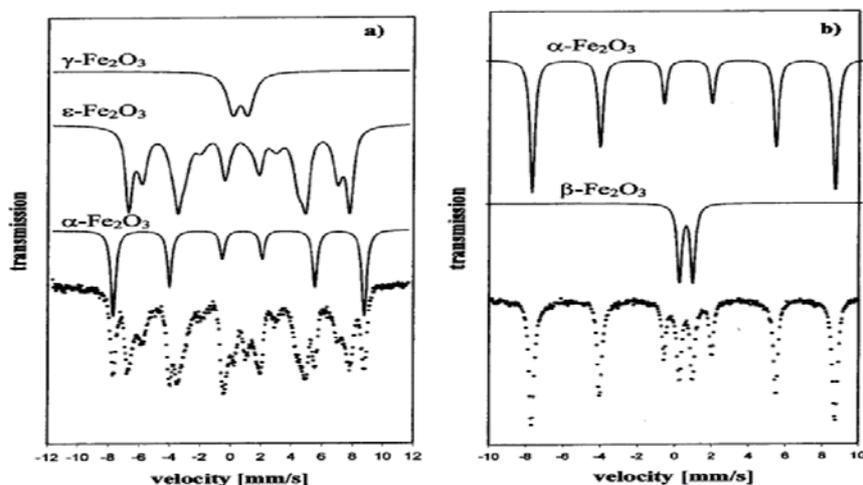


Figure RT Mössbauer spectra of iron oxides prepared by the thermal conversion of Fe₂(SO₄)₃ in air: (a) at 520 °C for 5h; (b) at 600 °C for 2 h (Adapted from Reference no. 1 with permission of American Chemical Society)

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Recent Advances in Mössbauer Spectroscopy of Ferrite Nanoparticles

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Ferrite nanoparticles (NPs) are in the limelight of current nanoscience because of enormous application potential. Excellent magnetic properties along with other functional properties, such as catalytic activity are some of the interesting aspects of the ferrite NPs. Mössbauer spectroscopy prove to be powerful tool in elucidation of structural and magnetic properties as a function of cationic size and substitution of one cation by another. The magnetic properties of the ferrites are related to relative strengths and types of intersublattice and intrasublattice interactions. Mössbauer spectroscopy can provide information on mechanically induced cation redistributions, superparamagnetic relaxation and changes of nearest-neighbor configurations. In most ferrites, the intersublattice and intrasublattice interactions compete with each other resulting in defects leading to different magnetic properties depending on the site occupancy. The study of combination of low-temperature, room-temperature and in-field Mössbauer techniques provides the structural information. The identification of different chemical and magnetic phases can be done by comparing hyperfine values, peak widths, relative peak areas and isomer shifts. The influence of the copper doping on the structure of Mn-modified ferrites had been examined using Mössbauer spectroscopy. With increasing Mn content, the Fe²⁺ ions present at Oh sites undergo substitution by Mn²⁺ ions due to which relative area of the Fe²⁺ ions decreases whereas the relative area of Fe³⁺ ions increases accordingly.

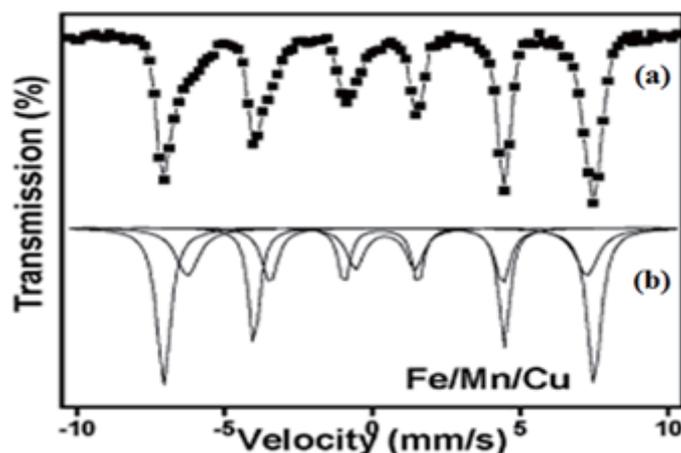


Figure Mössbauer spectra of activated Cu codoped modified ferrites at room temperature (Adapted from the reference 1 with the permission of American Chemical Society)

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Mössbauer Spectroscopy Study of Fe_xO_y @Carbon Core-shell Nanoparticles

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Magnetic nanoparticles have attracted great interest in a wide range of disciplines. However, pure (uncoated) magnetic nanoparticles tend to oxidize under the influence of the environment, which leads the deterioration in their properties, imposing restrictions on their use. Various ways have been invented to protect nanoparticles from environmental influences. One of them is the coating of nanoparticles with carbon shells, since carbon is an inexpensive, biocompatible and easily functional material. In particular, much attention was paid to the study of various carbon-coated magnetite nanostructures, since they are widely used in many fields, such as microwave absorption, biomedical applications, lithium-ion batteries, and absorption of some heavy metals.

The influence of synthesis temperature on the structural and magnetic properties of Fe_xO_y @carbon core-shell nanoparticles was investigated by X-ray diffraction, transmission electron microscopy (TEM), Raman and Mössbauer spectroscopy, as well as by magnetic measurements.

The Mössbauer spectra indicate that in the octahedral B-sites of magnetite there is an excess of $[\text{Fe}^{3+}]_B$ ions, which are located on the particle surface. These ions do not participate in the electron hopping $[\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}]_B$ above the Verwey transition. The wüstite phase appears and grows with a corresponding decrease in the fraction of $[\text{Fe}^{3+}]_B$ that does not undergo the electronic exchange. This proves that the wüstite phase is generated and formed on the surface of magnetite particles under the influence of carbon. The Mössbauer data allow one to monitor the dynamics of reduction of iron oxide from Fe_3O_4 to FeO under the influence of carbon.[1]

Acknowledgements: This work was supported by the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS in part of Raman spectroscopy measurements and by the Russian Science Foundation (Project No.14-12-00848-P) in part of Mössbauer spectroscopy measurements.

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Study of the Effect of Magnetic Nanoparticles Ordering in the Interlayer Space of Na⁺-montmorillonite on the Shape of Mössbauer Spectra

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Inorganic clays are natural ordered materials. Their fundamental units are multiple layers of stacked silicate platelets with average distance 10-15 Å and crystalline defects with ionically exchangeable divalent counter ion species. When intercalating clay, the distance between the platelets increases and the space between them is filled with solvent. The surface of the plates can interact with the solvent forming various hybrid materials.

Montmorillonite (MMT), one of layered aluminosilicate minerals, can provide a superior matrix to hybridize the magnetic nanoparticles (NP) because of its unique physicochemical properties such as tunable large interlayer space and cation exchange capacity [1]. Several types of metal oxide nanoparticles have been successfully introduced to the interlayer space via an intercalative route [2]. A number of recent studies show that such materials have unique magnetic properties that are not attainable in individual clay or iron oxide particles [1, 3]. Such properties are associated with a special magnetic order, which is formed as a result of the magnetic interparticle interaction of superparamagnetic particles embedded in a clay matrix, which makes it possible to successfully investigate NP-clay hybrid materials using relaxation Mössbauer spectroscopy. The

method is based on the nearness of the characteristic time of thermal fluctuations of the magnetic moment of superparamagnetic nanoparticles to the lifetime of the excited state of the Mossbauer nucleus.

We synthesized a hybrid material based on iron-oxide nanoparticles and Na⁺- montmorillonite. The synthesis was carried out using the precipitation of iron salts in aqueous solutions of clay with different concentrations. The effect of synthesis parameters on the magnetic properties of the obtained hybrid materials was analyzed. The magnetic behavior of the dipole- bounded ensembles of superparamagnetic nanoparticles in the obtained magnetically ordered materials was compared with magnetic behavior of powder particle samples.

Acknowledgements: The work was supported by the Russian Foundation for Basic Research under Grant 18-29-12081.

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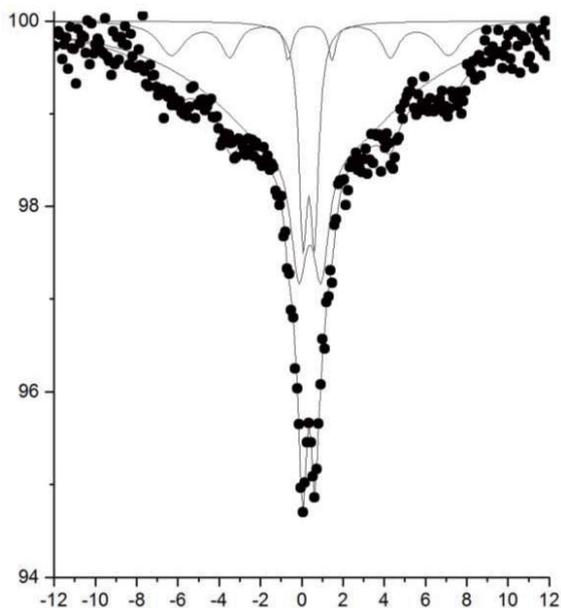


Figure ⁵⁷Fe Mössbauer spectra of superparamagnetic iron oxide nanoparticles, embedded in montmorillonite, at 300 K.

Structural, Magnetic and Electronic Properties of Biofunctionalized Iron Oxide Nanoparticles

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The unique combination of magnetic, optical and chemical properties of magnetic nanoparticles (NP) reveals broad prospects for practical applications in various areas [1]: genomic analysis, targeted drug delivery, hyperthermia, contrast agents for magnetic resonance imaging (MRI) [2,3]. For applications, it is important to consider not only the chemical composition, but also the size, morphology, crystal structure, methods of sample preparation.

In the present work, a detailed study of the structural, magnetic, and electronic properties of iron oxide nanoparticles functionalized by HSA protein (human serum albumin) by X-ray diffraction, transmission electron microscopy, Raman spectroscopy, ⁵⁷Fe NMR and Mössbauer spectroscopy were conducted. Iron oxide NPs reveal a spherical shape with the mean size of 5-6 nm (Fig. 1) and a cubic spinel crystal structure according to XRD. A phase composition was determined by Raman, Mossbauer and NMR spectroscopy. Superparamagnetic behavior and interactions between NPs were observed.

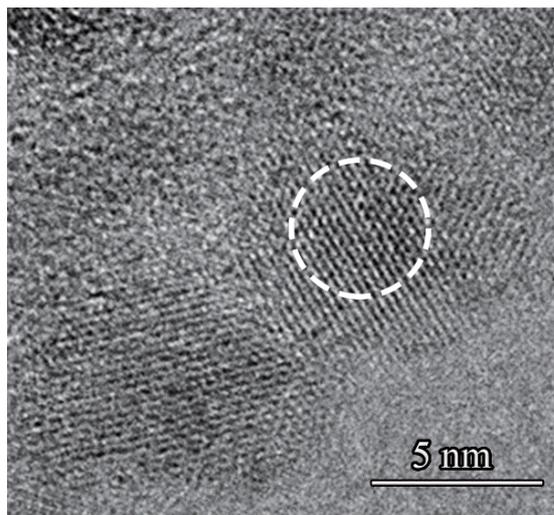


Fig. 1. TEM image of iron oxide nanoparticle

Acknowledgements: This work was supported by the Russian Science Foundation (Project No. 19-72-00095) in part of Mossbauer spectroscopy measurements and analysis, by the Ministry of Science and Higher Education within the State assignment FSRC “Crystallography and Photonics” RAS in part of the TEM measurements and data analysis.

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Structural and Magnetic Properties of the $\text{Fe}_{1-x}\text{Ni}_x$ Nanowires

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Today, much attention is attracted to the synthesis and properties of magnetic nanowires (NWs) [1] due to their possible applications for magnetic sensors, spintronic devices, hydrogen fuel cell electrodes, and biomedical technologies, including antitumor therapy.

In this work, we obtained arrays of $\text{Fe}_{1-x}\text{Ni}_x$ NWs by electrochemical deposition in the pores with diameters of 30 and 70 nm of polymer track membranes and studied their phase composition and magnetic properties. A generalized theoretical Stoner-Wohlfarth model [2,3] of the magnetic dynamics of nanocomposites was used to describe the magnetic properties and calculate the basic physical parameters of NWs. NWs demonstrate the formation of spontaneous magnetization during the synthesis process without the application of an external magnetic field and have ferromagnetic properties and high magnetic anisotropy substantially different from the bulk phases of the Ni-Fe solid solution. Quasi-one-dimensional magnetic ordering is observed in NWs with a diameter less than 60 nm.

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Metastable Iron Carbide Thin Films Produced by Pulsed Laser Deposition of Iron in the Methane

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Iron carbides have been extensively studied because of their various useful industrial applications. Hägg carbides (Fe_5C_2) and Eckstrom-Adcock carbides (Fe_7C_3) are known as metastable iron carbides. Although it has been reported that the metastable iron carbides were able to be synthesized in a form of nanoparticle [1], the particles consisted of a mixture of iron oxides and other iron carbides. Generally, it is hard to obtain pure metastable iron carbides. Pulsed Laser Deposition (PLD) is a very useful technique to produce films with controlled composition. This technique can produce iron carbide species unobtainable under normal conditions. We have previously reported iron carbide films produced by PLD of iron in the C_2H_2 atmosphere [2], where the mixture of iron carbides, Fe_3C , Fe_7C_3 , and paramagnetic amorphous Fe-C, were produced. In this study, we employed CH_4 as a reactive gas, because CH_4 is less reactive than C_2H_2 and the composition of C atoms can be easily controlled.

Pulsed laser light from a Nd:YAG laser (NewWave Research, Tempest 10; wavelength: 532 nm; pulse energy: 85 mJ; pulse duration: 5 ns; repetition rate: 10 Hz) was focused by a convex lens onto a ^{57}Fe metal block in the CH_4 atmosphere (0.5 - 40 Pa). Laser-evaporated Fe atoms were deposited on Al substrates. The substrate temperature was maintained at 573 K using a resistive heater. The samples were measured by transmission Mössbauer spectroscopy, and X-ray diffraction (XRD).

Various iron carbide films were produced varying the temperature of the Al substrates and the pressure of CH_4 atmosphere. When the substrate temperature was low (below 573 K), the films consisted of amorphous Fe-C or iron carbide with large defects. Thus, the substrate temperature was fixed at 573 K and the effects of the CH_4 pressure was investigated. The film produced in CH_4 atmosphere below 4.0 Pa consisted of a combination of Fe_5C_4 and $\alpha\text{-Fe}$; showing the three sets of sextets of Fe_5C_2 and one sextet of $\alpha\text{-Fe}$. The film produced at 4.0 Pa (thickness of 380 nm) was fitted into a combination of three sextets, which was assigned to pure Fe_5C_2 without any impurity. When the film was produced at 6.0 Pa (thickness of 380 nm), the film consisted of pure Fe_7C_3 ; the Mössbauer spectrum was fitted into a combination of five sextets of Fe_7C_3 without any other impurity. When the film was produced at 13 Pa of CH_4 , the Mössbauer spectrum showed a combination of Fe_7C_3 and an extra doublet; the doublet was assigned to paramagnetic amorphous Fe-C containing a large amount of C atoms. The film produced at the highest pressure of 40 Pa of CH_4 , only the double of amorphous Fe-C was observed. The above results indicated that the CH_4 pressures 4.0 Pa and 6.0 Pa were the best conditions to produce pure Fe_5C_2 and Fe_7C_3 , respectively. The XRD patterns of the films were also measured, and the results were in agreement with the results obtained by Mössbauer spectroscopy. The metastable iron carbide (Fe_5C_2 and Fe_7C_3) films without impurity might provide useful materials for the catalytic applications.

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Mössbauer Study of Nanocomposites MFe_2O_4 (M =Co and Mn)

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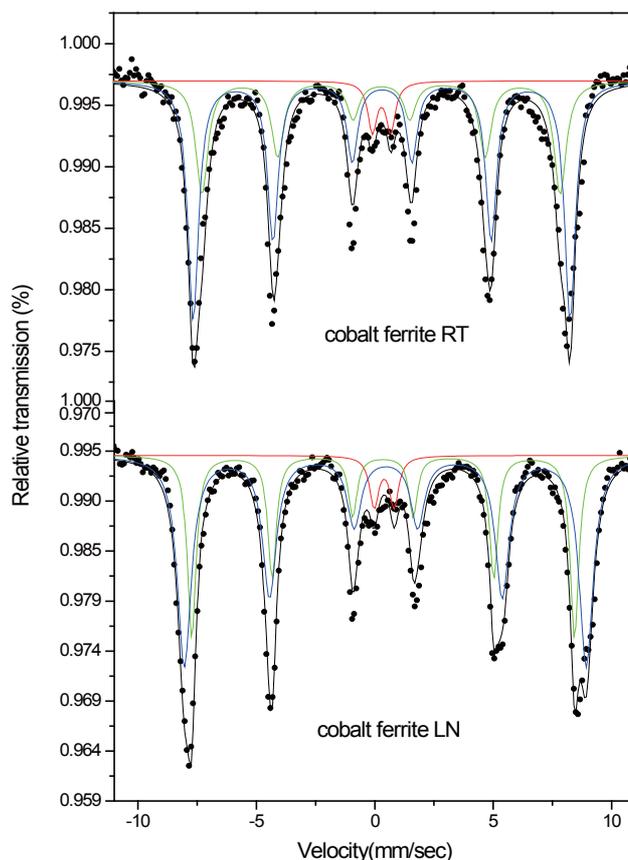
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The effect of particle size on the structural electrical and magnetic properties of MFe_2O_4 (M= Co and Mn) are investigated. The series were prepared using sol-gel method and studied using X-Ray diffraction, infrared (IF), Mossbauer (MS) spectroscopies, and vibrating mass spectrometer (VSM). XRD refinement reveals that each sample has single phase with the well-known spinel cubic structure. The X-ray analysis together with IR spectra confirmed that the synthesized powder is well crystallized. The crystalline size is in the range of 9nm - 15nm. The electrical properties showed semiconducting behavior. The magnetic properties of these compounds have been studied and showed ferrimagnetic ordering. The magnetic hysteresis loop is an indication to the degree of softness where the value of the measured coercivity H_C is 910 G. Mössbauer Measurements of the series are conducted at both 78 K and 295 K, and the performed data analysis are used to confirm the magnetic measurements findings, as well as the cations distribution between the tetrahedral and octahedral crystallographic sites.



Effect of Iron Oxide Nanoparticles Functionalization by Citrate Analyzed Using Mössbauer Spectroscopy

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Iron oxide nanoparticles (NPs) are developed for magnetic fluids for a long time. There are numerous studies by various techniques including Mössbauer spectroscopy of the effect of different NPs' preparations, size distribution, surface functionalization, coating, etc. In this study we consider the effect of the NPs surface functionalization. Iron oxide NPs were synthesized by co-precipitating Fe^{2+} (0.1 mol/L) and Fe^{3+} (0.2 mol/L) ions in hydrochloric acid (HCl) aqueous solution at room temperature. Ammonium hydroxide (1 mol/L) aqueous solution was added to the acidified metal ions solution to perform the NPs' precipitation. The resulting precipitate was boiled with iron nitrate ($\text{Fe}(\text{NO}_3)_3$) solution (0.5 mol/L) for 30 min. The resulting precipitate (sample FM) was thoroughly washed with acetone and dried for analyses. For surface functionalization with citrate, sample FM was dispersed in water and treated with excess of sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) aqueous solution under sonication for 10 min. The resulting sample (FMC) was thoroughly washed with distilled water for purification and dried for analyses. Samples FM and FMC comprise maghemite ($\gamma\text{-Fe}_2\text{O}_3$) NPs as the magnetically-ordered phase with average diameter of about 11 and 13 nm, respectively. Both samples were examined at room temperature using Mössbauer spectroscopy with a high velocity resolution as a method allowing to extract more spectral details than the conventional one. The Mössbauer spectra of FM and FMC measured in 4096 channels are shown in Fig. 1 and demonstrate visible differences. These spectra were fitted in different ways to explain the observed differences and results are compared with related data from the literature.

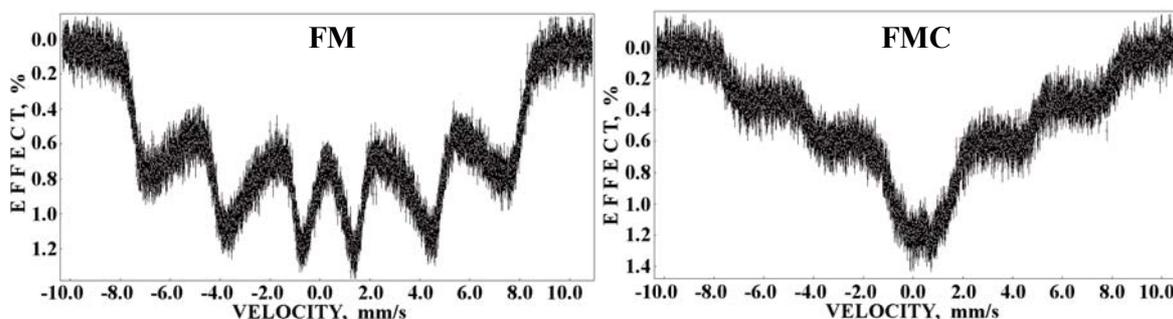


Fig. 1. Mössbauer spectra of nanoparticles without (FM) and with functionalization (FMC).

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Iron Nitride Thin Films Produced by ARC Deposition of Iron in the Nitrogen Atmosphere

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Various kinds of iron nitrides have been studied because of their important industrial applications. Generally, iron nitrides with high nitrogen contents are metastable and hardly obtainable as bulk solid forms. The metastable iron nitride is able to be stabilized in the form of a fine particle or a thin film. The arc-discharge of iron metal can generate an iron plasma even under an atmosphere with relatively high pressure, and thus, it provides convenient method to produce thin films consisting of iron compounds. In this study, we report production of the ϵ -Fe_{3,2}N and ζ -Fe₂N using an arc-plasma deposition of iron in the nitrogen atmosphere.

An ⁵⁷Fe-enriched metal was employed as an evaporation source. An iron plasma was generated using the arc-plasma-gun (ULVAC ARL-300; Discharge voltage 100 V; repetition rate 1 Hz; 10000 pulses), and the nitrogen gas was introduced to the space between the discharge electrodes controlling the flow rate (10 – 30 sccm). The iron nitrides were deposited onto Al substrates. The thickness of the films was 800 nm (α -Fe equivalent thickness), and the substrate temperature during deposition was maintained at a constant temperature (298 K or 573 K). The samples were measured by transmission Mössbauer spectroscopy, and X-ray diffraction (XRD).

First, the arc-deposition of Fe was performed under an atmosphere of N₂ while keeping the temperature of the Al substrate at 298 K. When the flow rates of N₂ were below 15 sccm, the films contained of α -Fe without any iron nitrides. When the N₂ flow rate was increased to 20 and 30 sccm, the Mössbauer spectra of the films showed distributed hyperfine magnetic fields, as well as a sextet of α -Fe. The distributed hyperfine magnetic fields having two maxima at ~12 T and ~25 T was assigned to ϵ -Fe_{3,2}N with a large amount of defects. The assignment was confirmed by the XRD pattern. Next, the arc-deposition was performed while heating the substrate at 573 K to promote crystal growth on the substrate; When the N₂ flow was kept at 15 sccm while deposition, the film was a mixture of ϵ -Fe_{3,2}N and ζ -Fe₂N. The films produced while keeping the N₂ flow rates at 20 sccm and 30 sccm were consisted of paramagnetic ζ -Fe₂N with a few lattice defects. It became obvious that ϵ -Fe_{3,2}N stabilized at a lower substrate temperature (298 K) while ζ -Fe₂N stabilized at a higher substrate temperature (573 K).

It was demonstrated that iron nitride films were successfully produced by arc-deposition of Fe under N₂ atmosphere. The composition of ϵ -Fe_{3,2}N and ζ -Fe₂N was able to be controlled by changing the N₂ flow rate and the temperature of Al substrate.

Hyperfine Interactions In ^{119}Sn Films Probed via Nuclear Resonance Scattering

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We present nuclear resonance scattering measurements probing the hyperfine interactions of β -Sn and its oxide, SnO_2 , prepared as thin films in confined structures. Thereby, we excite the Mössbauer isotope Sn, which is isotopically enriched in the tin layers, at its resonant energy of 23.88 keV with short synchrotron X-ray pulses. As the subsequent nuclear decay is a fingerprint of the nuclear energy level structure, the emitted photons are measured time- resolved. For certain geometries, e.g. thin film cavities, a direct measurement of the energy spectrum can be achieved with an additional Mössbauer drive. This method is well established for the Mössbauer isotope ^{57}Fe , e.g., to investigate electric field gradients [1], magnetic spin textures [2] or magnetization dynamics [3]. Moreover the direct measurement of energy spectra led to the research of hard X-ray quantum optics effects, e.g. the collective Lamb shift [4]. By applying the method to ^{119}Sn isotopes the research field can be further extended. Since β -Sn, as well as its oxides, is non-magnetic, Sn films can be used for probing magnetic environments [5] and for designing new thin film structures for the investigation of quantum optic effects. Experiments on thin Sn films, however, are rare since a drawback is their challenging preparation with the desired smoothness.

Here, we report the successful fabrication of β -Sn films. With that, we present our results measured at PETRA III on Sn films, embedded in different layered structures. We investigated the hyperfine interactions, when β -Sn is in contact with a magnetic layer (“permalloy”, Ni80Fe20) or non-magnetic layer (tantalum). Thereby, we found an enhancement of the Lamb-Mössbauer factor by a factor of 10 in ultra-thin films. By using the oxide form, SnO_2 , we looked at changes of the energy resonance line, when SnO_2 is placed inside of a thin film cavity structure. We achieved to measure the collective Lamb shift, even for 8 nm SnO_2 films. The results should be beneficial to future thin film experiments regarding tin as a probe for its magnetic environment and for nuclear quantum optics. The goal is to extend the application of nuclear resonance scattering to higher energy, higher sensitivity in magnetic heterostructures and pronounced nuclear quantum optics effects.

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Structural, Mössbauer and Magnetic Studies of Mechanothesized Nd-doped SrFeO_{3-δ} Nanocrystalline Particles

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We report on the mechanoynthesis, structural and magnetic characterization of 10 at% Nd-doped perovskite-related SrFeO_{3-δ} nanocrystalline particles (~80 nm) using XRD, Mössbauer spectroscopy and vibrating sample magnetometry (VSM). The material is formed starting from a stoichiometric mixture of α-Fe₂O₃, Nd₂O₃ and SrCO₃ at 800 °C which is *ca.* ~ 300 °C lower than those at which Nd-doped SrFeO_{3-δ} bulk modifications are conventionally prepared. Rietveld refinement of the XRD data and ⁵⁷Fe Mössbauer spectra have revealed the nanocrystalline particles to be composed of cubic Nd_{0.1}Sr_{0.9}FeO₃ and tetragonal Nd_{0.1}Sr_{0.9}FeO_{2.875} phases in the ratio of ~ 45 : 55. The Mössbauer results also show the Nd-doped SrFeO_{3-δ} nanoparticles to be superparamagnetic with blocking temperatures below 78K. A complex magnetic behavior, associated with the coexistence of the cubic and tetragonal phases, is detected for the nanoparticles wherein an antiferromagnetic-to-paramagnetic transition and an antiferromagnetic-to-weak ferromagnetic transition are detected at takes place at ~ 61 K and ~24 K, respectively. XPS measurements show a complex surface structure of the nanoparticles where traces of the initial reactants, *viz.* α-Fe₂O₃ and SrCO₃, were detected.

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Thermally Induced Transformations of Iron(III) Oxide Polymorphs in Various Atmospheres

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Ferric oxide belongs to the most important nanomaterials because of its benefits to fundamental research as well as its application potential spanning over a large variety of fields of human activities [1]. Additionally, iron (III) oxide exhibits polymorphism – a feature manifested by an existence of various structural forms differing in physical properties and thus with diverse potential applications of individual polymorphs [2]. Moreover, upon exposing to increased temperature/pressure, ferric oxide undergoes a polymorphic transformation, which can be of topotactic or non-topotactic nature. Therefore, these transformations provide a route to prepare different iron (III) oxide polymorphs with tailored physical properties tuned by a size, morphology and dimensionality [2]. Additionally, the course of a polymorphic transformation can be governed by atmosphere under which the transformation occurs while favouring emergence of rare and intermediate phases with interesting features. So far, phase transformations in oxidative atmospheres have been well studied in the literature [2]. On the other hand, less attention has been devoted to the transformations in reductive or inert atmospheres.

Herein, we present a study of thermally induced transformations of three different iron(III) oxide phases (i.e., α -Fe₂O₃, γ -Fe₂O₃, and amorphous Fe₂O₃) under reductive/inert atmospheres, i.e., the issue that has not been addressed in the literature yet [3]. The transformations were studied in situ by X-ray powder diffraction (XRD) technique in the temperature range from 25 to 900 °C. The transformation products were characterized by ⁵⁷Fe Mössbauer spectroscopy, XRD, and magnetization measurements. It was found out that some rare intermediate phases, such as Haag's carbide or magnetite of different stoichiometries, were formed during the reduction pathways. The presented experimental results open a journey to a more detailed knowledge on iron(III) oxide reduction paths. Identification of intermediate phases provides an option to further study them with respect to search for optimal conditions for their stabilization, to characterize their physicochemical properties and to assess their application potential.

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Synthesis and Characterization of Copper-nickel Ferrite Catalysts for Ethyl Acetate Oxidation

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Spinel ferrites can be denoted by the general formula $(Me_xFe_{1-x})_{tetra}[MeyFe_{2-y}]_{octa}O_4$, where Me is divalent metal ion occupying tetrahedral and octahedral sites in the unit cell. According to the location of divalent metal ion in crystalline lattice, ferrites can be classified as normal spinel, inverse spinel and partially inverse one. As it is known, different metal cations have preference to occupy differently coordinated positions. On the other side, the cation distribution in the spinel depends on the method of synthesis. In this way, the synthesis method has significant contribution in the control of the catalytic properties of these materials.

The aim of present work is to obtain C ferrite materials with different structural characteristics by variation of method of synthesis and to study their behaviour in catalytic VOCs removal.

Materials with nominal composition $Cu_{0.5}Ni_{0.5}Fe_2O_4$ was prepared by sol-gel auto-combustion technique using corresponding metal nitrates and citric acid as complexant/fuel agent. Different ratio between nitrates and citric acid was used to control combustion reaction. For comparison, $Cu_{0.5}Ni_{0.5}Fe_2O_4$ ferrite was synthesised by co-precipitation. Mössbauer spectroscopy at room and liquid nitrogen temperature was used for analysis of synthesised samples. Iron distribution in tetrahedral and octahedral position of spinel lattice was determined. Different degree of agglomeration of ferrite phase was estimated by superparamagnetic behaviour of samples. In addition, methods of X-Ray Diffraction, UV-Vis, FTIR, nitrogen physisorption, TPR with hydrogen were applied for structural characterization of the materials. Some quantity of secondary phases (metal alloys and hematite) was found in samples prepared by auto-combustion method. The catalytic activity of the samples in ethyl acetate oxidation strongly depended on the variations in the structural and texture characteristics of the samples. The sample synthesised at the lowest ratio of nitrates to citric acid is characterized with the smallest ferrite crystallite size, the higher surface and the best catalytic activity.

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Magnesium Doped Lithium Iron Orthosilicate Prepared by Solid-state Ball Milling

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$\text{Li}_2\text{FeSiO}_4$ has attracted great attention in the search of cathode materials for high-capacity lithium-ion battery for large-scale energy storage. It possesses high theoretical capacity (approximately $330 \text{ mAh}\cdot\text{g}^{-1}$), good thermal stability and cycling performance, nontoxicity, environmental friendliness and is of low cost. Unfortunately, $\text{Li}_2\text{FeSiO}_4$ suffers from low intrinsic electronic conductivity and slow lithium ion diffusion ability from slow Li^+ diffusion and low electronic conductivity. Several strategies have been proposed to overcome these obstacles to allow its use in practical applications, including creating conductive carbon coating on $\text{Li}_2\text{FeSiO}_4$ particle surface and doping with some transition metal cation in Fe and Si sites, including Mg^{2+} .

Mg-doped $\text{Li}_2\text{FeSiO}_4/\text{C}$ of monoclinic structure $P2_1/n$ have been synthesized by a citric acid assisted sol-gel method [1] and by using a hydrothermal method with Fe_2O_3 nanoparticle as Fe source [2]. This Mg-doped $\text{Li}_2\text{FeSiO}_4/\text{C}$ delivers high discharge capacity and its capacity retention is good. Mg-doping help to decrease the charge-transfer resistance and increase the Li^+ diffusion capability. By using a solid-state method, Huang et al. [3] prepared a $\text{Li}_{1.97}\text{Mg}_{0.03}\text{FeSiO}_4/\text{C}$ composite with orthorhombic structure indexed to the Pmn21 space group. Mg-doping in Li sites provided an enhanced electronic conductivity of $\text{Li}_2\text{FeSiO}_4$, resulting in the improved capability. Recently [4], a series of Mg-doped $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites were prepared through a solid-state reaction. The dominant crystal phase of all the samples is the monoclinic structure $P2_1/n$, but $\text{Li}_2\text{FeSiO}_4$ and metallic iron were detected as impurities. The results showed that $\text{Li}_2\text{Fe}_{0.98}\text{Mg}_{0.02}\text{SiO}_4/\text{C}$ has the higher specific capacity, better cycle stability and reversibility. An initial discharge specific capacity of $142.3 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1 C was observed. In this work, a 2 mol% Mg-doped $\text{Li}_2\text{FeSiO}_4/\text{C}$ composites was prepared via a solid-state ball-milling process, using citric acid as a source of carbon. The crystal structure of Mg-doped material was characterized by Mössbauer spectroscopy, XRD, FTIR-ATR, and XPS. Samples were also investigated by SEM, TEM, EDX, cyclic voltammetry, the charge-discharge test and electrochemical impedance spectra measurements. This work aims to provide understanding of structural changes upon Mg doping, the material purity and the effect on the electrochemical performance of $\text{Li}_2\text{FeSiO}_4/\text{C}$. Our results are in agreement with those of Li et al. [4].

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MS Characterization of the Neutron Irradiated JRQ Steels

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The RPV (reactor pressure vessel) is a crucial component of NPPs (Nuclear Power Plant), which defines basic safety and limits the whole lifetime and operation parameters of the nuclear facility. Any change of physical-mechanical parameters of RPV must be closely monitored due to its direct impact on the operation of NPPs. That is the reason why it is so important to put an accent on a high quality of RPV materials. The microstructure and consequently mechanical properties of RPV steels are affected during NPP operation by chemical processes, radiation damage and temperature variations. Especially for safety and operational reasons, it is essential to examine the microstructure of materials in order to know what influence are having all these effects to RPV steels under long-term stress and what design improvements it is possible to make for next generations of structural materials. Accumulated defects and changes of the mechanical properties of the RPV can reach a critical limit, where the NPP is not able to be operated any longer and must be shut down. An effective way to restore the plastic properties of the RPV and reduce the amount of defects in the crystal lattice is annealing.

In this paper, the specimens from JRQ (Japan Reference Quality) and JPA family of RPV steels, which correspond to the specification of ASTM A533B cl.1 steels were investigated. They were manufactured by Kawasaki Steel Corporation in Japan according to the order of the International Atomic Energy Agency (IAEA) and were used in various studies focused mainly on neutron embrittlement of various levels of irradiation and annealing conditions since the 1980s. The main difference of these steels is in Cu content, which is in both cases higher than the actual recommended level 0.008%. JRQ was proposed as a correlation monitor, which means a material with medium sensitivity to radiation damage (simulation of RPVs steels of older NPPs). JPA steel, designed as a special model alloy (Cu content of 0.29 wt% was chosen to represent steels with increased Cu content for research conducted on high-Cu RPV steels).

The irradiation of studied Japan model steels was performed in a prototype reactor VVER-210 in Rheinsberg (Germany) at a temperature of 255 ± 5 °C up to three different neutron fluencies for both materials ($\sim 10, 80, 140 \times 10^{18} \text{ cm}^{-2}$ ($E > 0.5 \text{ MeV}$)). The specimens of JRQ were subsequently annealed for 10 h at 6 different temperatures ranging from 350 to 475 °C in order to follow the recovery of the irradiated microstructure.

The changes in the microstructure irradiated/annealed steels by neutrons has been characterized by Mössbauer spectroscopy technique in scattering geometry and evaluated by NORMOS and CONFIT programs. Additionally, the gamma spectroscopy analyses were performed on neutron irradiated specimens.

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Mössbauer Spectroscopy Study of Y-type Hexaferrite ($\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$) Prepared by the Coprecipitation Method

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In this work we report the results of structural and Mössbauer spectroscopy studies for $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$ samples prepared by the Coprecipitation method in which the preparation conditions (pH, Precipitation Agent and the Agent Addition method) were changed in four procedures: Procedure A (pH=10, Precipitation Agent: NaOH + Na_2CO_3 , Adding method: dropwise), procedure B (pH=14, Precipitation Agent: NaOH + Na_2CO_3 , Adding method: one shot), procedure C (pH=8, Precipitation Agent: Na_2CO_3 , Adding method: one shot), procedure D (pH=14, Precipitation Agent: NaOH, Adding method: one shot).

The samples prepared by procedures A and B were sintered for 4 hours at different temperatures (700 °C-1100 °C), while those prepared by procedures C and D were sintered also for 4 h but at one temperature (1100 °C). The XRD patterns and room temperature Mössbauer spectra were recorded for the prepared samples.

By applying the Scherrer Equation, the average particle size for the Co_2Y phase was estimated wherever it appeared clearly in the XRD patterns for the samples.

The XRD patterns and the Mössbauer spectra for the samples prepared by procedure A showed no formation of Co_2Y type phase at 700°C, but spinel phases (CoFe_2O_4 and/or Fe_3O_4), BaCO_3 and BaM-type phase were formed. The Co_2Y phase is developed in the samples sintered at 800°C and 900°C with spinel species as impurities. However, single (pure) Co_2Y phase was formed at 1000 °C and 1100 °C.

The XRD patterns and the Mössbauer spectra for the samples prepared by procedure B showed different outcomes than those of procedure A: The sample sintered at 700 °C shows only spinel phases. The Co_2Y phase is developed at temperatures 800 °C and above with significant amounts of impurities. The impurities were Ba-spinel at 800 °C, (CoFe_2O_4 and/or Fe_3O_4) spinels at 900 °C and 1000 °C, and (CoFe_2O_4 and/or Fe_3O_4) spinels with traces of BaM-type phase at 1100 °C. Hence, no single (pure) Co_2Y phase was developed through procedure B.

The XRD pattern and the Mössbauer spectrum for the sample prepared by procedure C and sintered at 1100 °C showed no single (pure) Co_2Y phase but the formation of Co_2Y as a major phase, in addition to spinel species and BaM-type as minor phases. However, the sample prepared by procedure D and sintered at 1100 °C showed pure single Co_2Y phase, which was confirmed by both XRD patterns and the Mössbauer spectrum.

Role of CRM on Photocatalytic Behaviour of Reused Iron-based Metallic Glasses

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Fe-based metallic glasses have been extensively studied as new and advanced engineering materials for different applications due to their superior properties and potential. Wide variety of chemical compositions, possibilities for preparation of ternary and quaternary alloys, relatively low material cost and environmental friendly nature lead to great attention on their new applications in everyday life and industrial field. Recently metallic glasses have been also considered as good catalysts, including wastewater remediation where easy separation of catalytic material is also very important issue.

On the other hand sustainable industry and circular economy are being connected with reuse of fresh and spent materials. In case of purification catalytic processes of contaminated wastewaters Fe-based metallic glasses could be successfully applied. However, number of questions focused on the impact of crystallization processes, including nanocrystallization and cluster formation, change of physical and chemical properties on the catalytic properties should be determined. This will reveal further abilities of their exploitation and practical application, as well as will improve their catalytic performance.

The aim of the paper is to investigate the impact of partial crystallization of spent Fe-based metallic glasses on their photocatalytic behavior. In this regard four iron-based amorphous alloys containing critical raw materials (CRM) were investigated. Test reaction was photocatalytic degradation of Methyl orange (MO) azo dye. Metallic glasses with chemical composition $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$, $\text{Fe}_{78}\text{B}_{15}\text{Mo}_2\text{Si}_5$, $\text{Fe}_{67}\text{B}_{14}\text{Co}_{18}\text{Si}$, and $\text{Fe}_{40}\text{B}_{16}\text{Ni}_{40}\text{Mo}_4$ were prepared by melt spinning method, when nucleation and growth of crystalline phases are suppressed during cooling of liquid alloys. Samples were thermally treated in order to simulate spent materials at temperature of 823K for 30 min in Ar flow. These conditions are based on thermal *in situ* analysis of materials. Characterization of samples was done by Mössbauer spectroscopy at room and liquid nitrogen temperature, Conversion electron Mössbauer spectroscopy, X-Ray Photoelectron Spectroscopy, Thermal analysis, as well as RT and *in situ* high temperature X-Ray Diffraction analysis. Difference between the photo-catalytic properties of initial iron-based metallic glasses with homogeneous amorphous structure and thermally treated samples (their counterparts) was registered. This difference was explained by the presence of additives (Mo, Co and Ni), different degree of crystallization in studied materials and with formation of different oxide layers at the metal–water interface.

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Transformation of Zero-valent Nanoparticles under a Laser Beam Irradiation

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Nanomaterials can be characterized by various experimental techniques utilizing laser irradiation of samples (e.g. Raman spectroscopy, photoluminescence, dynamic light scattering, laser scanning microscopy, fluorescence correlation spectroscopy and others) [1]. It can happen that nanomaterials transform during the laser irradiation resulting to more or less changes of phase composition, particle size and/or their other properties. Therefore, techniques utilizing laser irradiation can become destructive and the changes of nanomaterial properties have to be taken into account [2].

In this study, we performed a series of experiments where zero valent iron nanoparticles (nZVI) were irradiated by a laser beam with given wavelength and power. Particularly, two lasers with the wavelengths of 527 nm (Nd:YLF laser) and 1064 nm (Nd:YAG laser) were employed. The power of the lasers was systematically raised up to 1.8 Watt. The duration of one laser pulse was 0.2 ms. The phase composition of the initial nZVI sample was determined by ⁵⁷Fe Mössbauer spectroscopy and X-ray powder diffraction. In addition to major Fe (0) (approx. 95 at% Fe) superparamagnetic ferric oxide (approx.. 5 at% Fe) as oxidized particle shell was identified. This nZVI sample was used as the initial for all the laser irradiation experiments.

Samples obtained after the laser irradiation were characterized by Mössbauer spectroscopy, X-ray powder diffraction, and transmission electron microscopy. FeO, Fe₃O₄, γ-Fe₂O₃, and α-Fe₂O₃ were identified as the transformation products after the laser irradiation. The relative contents of these phases in the samples depend on the experimental conditions. In the presented poster, an attention will be paid to evaluation and interpretation of Mössbauer spectra of the transformed samples. The results will be discussed with respect to used experimental conditions during the laser irradiation.

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Effect of Lithium on Structural and Magnetic Transitions of Barbosalite

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Effect of Li on the synthesis of Barbosalite [$\text{Li} : \text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$] have been investigated. Solvothermal method was adopted. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_3PO_4 , $\text{LiOH} \cdot \text{H}_2\text{O}$, and ethylene glycol (Sigma-Aldrich) were used with no further purification.

The samples are marked as Fe(II)-x and Fe(III)-x, where II and III represent the oxidation state of precursor Fe and x the weight of $\text{LiOH} \cdot \text{H}_2\text{O}$ in grams. Few planes in the XRD spectra were found to be merged at $\text{LiOH} \cdot \text{H}_2\text{O}$ concentration of 0.9 g. Additional peaks arises from $\text{LiOH} \cdot \text{H}_2\text{O} \geq 1.2$ g, which is assigned as LiFePO_4 . Magnetic properties of the particles were characterized by Mössbauer and squid magnetometer. Li intercalation in the Barbosalite affects the Fe^{3+} sites and the Fe^{2+} remains undistorted till 0.9 g. Higher Li content leads to structural transformation to LiFePO_4 . The change in the magnetism is a step ahead than the structural transition.

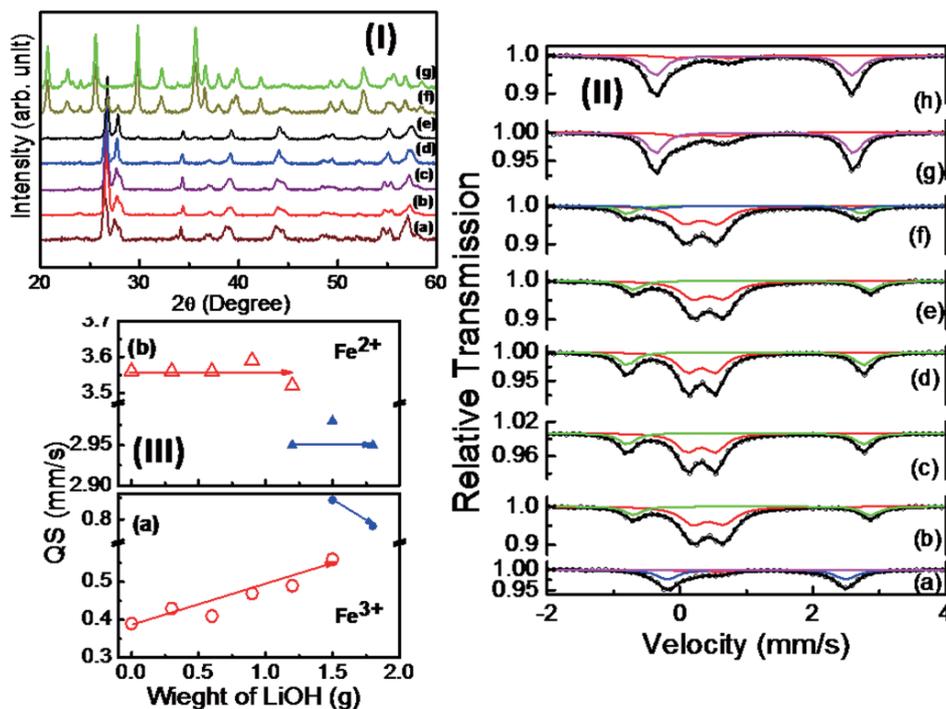


Figure 1. (I) XRD for (a) Fe(III)-0 ($\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$), (b) Fe(III)-0.3, (c) Fe(III)-0.6, (d) Fe(III)-0.9, (e) Fe(III)-1.2, (f) Fe(III)-1.5 ($\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2 + \text{LiFePO}_4$) and (g) Fe(III)-1.8 (LiFePO_4), (II) Room temperature (RT) Mössbauer spectra of Fe(II)-0 (a), Fe(III)-0 (b), Fe(III)-0.3 (c), Fe(III)-0.6 (d), Fe(III)-0.9 (e) Fe(III)-1.2 (f), Fe(III)-1.5 (g) and Fe(III)-1.8 (h), (III) Quadrupole splitting of the Fe^{2+} and Fe^{3+} in barbosalite.

Effect of H_3PO_4 in Nucleation of Triphylite

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LiFePO_4 were synthesized using solvothermal method. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2 gm), $\text{LiOH} \cdot \text{H}_2\text{O}$ (0.86 g) was dissolved in 15 ml ethylene glycol respectively. To the mixture of the solutions, x g of H_3PO_4 were introduced. After thorough mixing, the solution was transferred into a Teflon line autoclave at 185°C for 14 hr.

The XRD (Figure I) shows that, the diffraction pattern matched with the LiFePO_4 (JCPDF no. 81-1173). A close observation on the intensity reveals the variation in the peak intensity as the H_3PO_4 amount increases from 0.865 g to 2.04 g. The intensity of the plane (101) decreases as H_3PO_4 increases. The decrease in the peak deviates from the ideal LiFePO_4 reported. These indicate a preferential plane growth in LiFePO_4 . Mössbauer studies indicate the amount of Fe^{2+} having parameters of LiFePO_4 increases from 84 % to 89 % when H_3PO_4 increases from 0.865 g to 2.04 g. To verify the acidic effect on the nucleation of LiFePO_4 , H_2SO_4 was introduced during the preparation of solution. The presence of H_2SO_4 prevents the nucleation of LiFePO_4 .

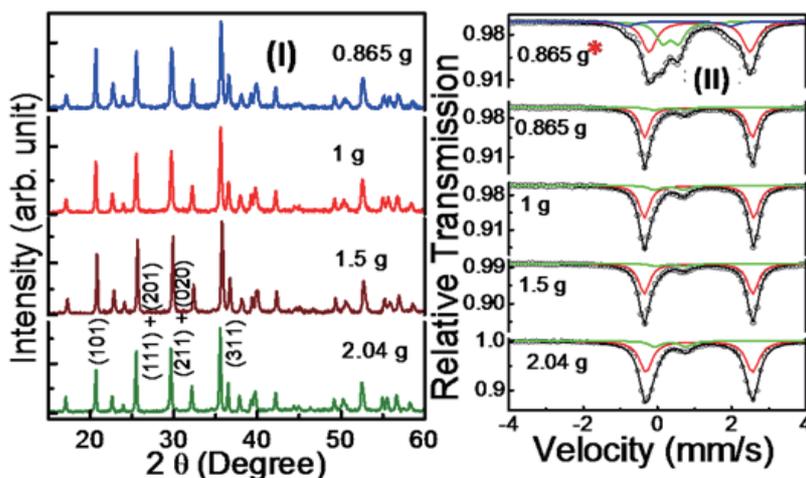


Figure 1 XRD (I); Mössbauer spectra (II) for the LiFePO_4 synthesized with varying H_3PO_4 . Mössbauer spectrum of the sample synthesized in the presence of H_2SO_4 (II*).

Changes of Phase Composition of Steels During Selective Laser Melting

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Selective laser melting (SLM), as one of additive manufacturing (AM) technologies, enables quick production of complex shaped three-dimensional (3D) specimens directly from metal powder [1]. In a layer-by-layer fashion, the SLM process creates bulk specimens by selectively melting and consolidating thin layers of powder using a laser beam, which scans over the surface. Various metal powders, including different steels, are used in this technology. Each steel powder is characterized by a concrete phase composition.

The influence of SLM process on phase composition final 3D specimen has been examined. Generally, the difference of phase composition between the original metal powder and final specimen can exist and consequently effects the utility properties of final specimen. There is a wide range of steels that are suitable to be processed by SLM. The maraging steel (CL50WS), an iron-nickel steel alloy, which is often used in applications where high fracture toughness and strength are required and the 316 L stainless steel (CL20ES), which is an iron-chromium steel alloy with high corrosion-resistance and high tensile strength have been investigated.

The influence of the SLM process on the phase composition, surface quality and hardness of the CL50WS and CL20ES steel specimens was examined using Mössbauer spectroscopy (MS), scanning electron microscopy (SEM), positron Doppler broadening spectroscopy (DBS) and micro hardness measurement. The difference between phase compositions of the initial CL50WS powder and final specimen displayed on martensitic to austenitic phase transformation was identified via MS [2]. This transformation proceeds during the SLM process. SEM presented imperfections of surface of final specimen. The spherical and irregular pores were observed as well as the particles of initial powder bonded on surface. The growth of vacancy defects in surface layer after consequent cutting was identified via DBS.

No difference between phase compositions of the initial CL20ES powder and final specimen was observed [3]. However the phase transformation of surface layer via cutting was identified by MS. The surface quality of the CL20ES specimen appeared to be better than this one of the CL50WS specimen. No spherical and irregular pores were identified by SEM, but the trails of SLM process on surface as crossing of weld metal layers were clearly seen.

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Sintering-resistant Au/ FeO_x-hydroxyapatite Nanocatalyst Achieved by Strong Metal-support Interaction

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Supported gold nanocatalysts have been treated as extraordinary effective catalysts because of their unique properties; however, their poor thermodynamic stability during the reaction remains to be resolved for the practical applications. Herein, we reported a sintering-resistant Au nanocatalysts by localizing the Au NPs in the interfacial regions between Fe₂O₃ and hydroxyapatite. Owing to the strong metal-support interaction, the Au NPs was not only partially encapsulated but also partially exposed. The resulting Au nanocatalysts are resistant to sintering and present excellent activity and durability after calcination at 600 °C.

HRTEM shows that HAP migrated onto the top surface of gold nanoparticles was observed, consistent with our previous discovery, indicating the pretty SMSI between gold and HAP. However, for Au/F-600 samples, no encapsulation of Au NPs was observed, suggesting that Fe₂O₃ couldn't stabilized Au NPs in oxidative atmospheres. And there was no large Au NPs in Au/FH-600 samples, which was different from that of Au/F-600 sample. It was worth noting that Au NPs were located in the interface between Fe₂O₃ and HAP, which was analogous to our previous report. And Au NPs were partially encapsulated by a thin layer, which should come from HAP. Line scan has also been examined to identify the composition of support approaching to Au NPs. The support in contact with the uncovered Au was composed of Fe and O while the other side in contact with covered Au was composed of Fe, Ca and O, indicating that the support was mainly Fe₂O₃ and a mixture of Fe₂O₃ and HAP, respectively. ⁵⁷Fe Mössbauer spectroscopy at 4.2K was also performed to identify the effect of calcination temperature on the crystal phase of FeO_x. The main phase of FeO_x in the Au/F-UC and Au/FH-UC was maghemite. After calcination at 600 °C, the maghemite turned to hematite totally in Au/F-600. While it was not in this case for Au/FH-600, in which the ratio of hematite only increased from 11.1% to 14.5%.

In conclusion, an ultrastable and highly active Au catalysts has been developed by tuning the SMSI between Au and supports. HRTEM proved that Au was primarily located at the interface between Fe₂O₃ and HAP, covered a thin layer which was from HAP. This unique structure enabled that catalyst have the high catalytic activity and excellent sintering-resistance and stability ability. Compared with commercial RR2Fe catalyst, Au/FH-600 catalyst was higher sintering-resistant and higher stable, demonstrating the importance of the strong metal-support interaction between Au and support, which provide a new synthetic way to develop ultrastable Gold catalysts with highly activity.

Key Words: Au Catalysts, Sintering-Resistant, Strong Metal-Support Interaction, Mössbauer Spectroscopy

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Structural and Optical Properties of Tin-doped Hematite (α -Fe₂O₃) Nanorods

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Due to their high stability, low toxicity, abundance and low cost, iron oxides are desirable materials for different applications. Hematite (α -Fe₂O₃) is an especially stable iron oxide compound and a semiconducting material ($E_g = 2.2$ eV) with strong absorption of UV and visible light with $\lambda < 600$ nm. Hematite can be regarded as suitable material for application as a photoelectrode for hydrogen production by water splitting using solar energy [2] or as a photocatalyst for decomposition of toxic compounds [3]. Photoelectrochemical and photocatalytic properties of hematite can be significantly improved by doping with various metal cations and/or by morphology modification [2,4].

A significant effect of tin doping on the photoactivity of hematite photoanodes for photoelectrochemical water splitting was reported in several recent publications [5-8]. This effect was explained by modification of optical, electronic and electrical properties of hematite by incorporation of Sn⁴⁺ ions as an n-type dopant. Also, a strong effect of nanoparticles morphology on the hematite photocatalytic activity has been reported. A higher activity of hematite nanorods compared to nanocubes or nanoplates was observed in decomposition of rhodamine B dye by heterogeneous photo Fenton reaction [4].

In the present work, structural and optical properties of hematite nanoparticles of elongated shape (nanorods) doped with tin were investigated. Sn-doped hematite nanorods were prepared by calcination of Sn-doped goethite nanorods obtained by precipitation in alkaline aqueous solution. Influence of Sn doping on the structural properties of hematite was studied using X-ray powder diffraction (XRPD), field emission scanning electron microscopy (FE-SEM) and Mössbauer spectroscopy. Incorporation of tin into the crystal structure of hematite was confirmed by measuring unit cell expansion by XRPD and hyperfine magnetic field reduction by Mössbauer spectroscopy. Also, the size and shape of hematite nanorods significantly changed by Sn doping. Optical properties were investigated using diffuse reflectance UV-Vis-NIR spectroscopy. A shift of absorption edge to higher wavelengths by Sn doping was observed in recorded spectra. A reduced direct and indirect optical band gap in Sn-doped hematite were estimated using Tauc plots.

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Preparation and Properties of Electrospun Cr-doped α -Fe₂O₃ Nanofibers

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Hematite (α -Fe₂O₃) is the most stable and the most common iron oxide phase [1]. Due to high stability in aqueous solutions, low toxicity, abundance and low cost, it has been extensively investigated for possible applications. Hematite strongly absorbs UV and visible light with energies above its band gap of 2.2 eV. For this reason, it has been investigated as a photoelectrode for photoelectrochemical water splitting [2] and as a photocatalyst for decomposition of organic pollutants [3]. The performance of hematite in these applications can be improved by using nanostructured hematite samples doped with different metal cations [2,3].

Electrospinning is an excellent method to produce nanostructured hematite fibers possessing a high specific surface area [4,5]. This property is essential in many applications (catalysts, photocatalysts, photoelectrodes, battery electrodes, supercapacitors, adsorbents, etc). Due to the same charge and similar effective ionic radius of Fe³⁺ and Cr³⁺ ions (64.5 and 61.5 pm, respectively), solid solutions α -(Fe_{1-x}Cr_x)₂O₃ can be prepared in the whole Fe-Cr concentration range ($0 \leq x \leq 1$) [6,7] with a gradual reduction of unit cell as Cr content increases. Optical spectra of Cr-doped hematite showed a reduction of the direct and indirect optical band gap to lower energies compared to pure hematite [7,8]. In these works the authors prepared Cr-doped hematite thin films using pulsed laser deposition [7] and oxygen plasma-assisted molecular beam epitaxy [8].

Aim of the present work was to prepare hematite nanofibers, Cr-doped hematite and eskolaite (α -Cr₂O₃) nanofibers using electrospinning method. Viscous solutions containing dissolved polyvinylpyrrolidone PVP ($M_w = 1\,300\,000$) and nitrate salts (Fe³⁺, Cr³⁺) in ethanol were electrospun, dried and calcined to obtain desired metal oxide nanofibers. Thus obtained fibers were characterized by several methods. XRD patterns showed the presence of corundum-type structure in all samples. Cr-for-Fe substitution in hematite nanofibers was confirmed by measuring unit cell reduction using XRD and hyperfine magnetic field reduction using ⁵⁷Fe Mössbauer spectroscopy. Field emission scanning electron microscopy (FE-SEM) showed the presence of 1D nanofibers in all prepared samples. Cr doping caused a shift of hematite absorption edge to higher wavelengths in UV-Vis-NIR spectra. A reduction of the direct and indirect optical band gap by Cr doping was estimated using Tauc plots. Visible light photocatalytic activities of the prepared samples were tested by decomposition of rhodamine B dye in the presence and H₂O₂ under visible light illumination. Hematite nanofibers showed a much better photocatalytic activity compared to Cr-doped hematite nanofibers and commercial hematite.

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Mössbauer Spectroscopic Observation of the High-spin Fe²⁺ Orbital Triplet in PBA

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The orbital-triplet (OT) states of the high-spin Fe²⁺ ion in inorganic and metal-organic substances are very rare. This rare case of the isotropic OT state was reported previously in Fe[Pd(CN)₆] and Fe[Pt(CN)₆] [1], however, it was not known in hexacyanometallates of the 3d series. The triply degenerate t_{2g} level is the energy-lowest one in a crystal field of cubic symmetry, but the triple degeneracy of the d_{xy}, d_{xz}, d_{yz} orbitals gets lost usually owing to spin-pairing energy, which splits the t_{2g} level, when the sixth electron of the d⁶ (Fe²⁺) ion supervenes to the symmetric semi-closed shell of the high-spin d⁵ configuration. The most obvious localization of the sixth electron on a single d-orbital (e.g., on d_{xy}) downshifts and sets aside the d_{xy} energy level, so that the d_{xy} orbital singlet state (OS) gets lowest in energy. In the Prussian Blue and its analogues (PBA), the degeneracy of the t_{2g} orbitals lifts off due to an effect of ligand replacement. Large quadrupole splitting (QS) of Fe²⁺ is an indication of the degenerate t_{2g} level. When a H₂O ligand replaces one (or a few) of six CN⁻ ligands, the octahedral coordination polyhedron Fe(CN)₅(H₂O) loses its cubic symmetry both in PB [2], and in PBA, and this event would allow the t_{2g} splitting for Fe²⁺. In fact, the Co(III) vacancies (denoted here □) and coordination water molecules enter the structure of Fe[Co(CN)₆]_{0.67}·[□(H₂O)₆]_{0.33}·2H₂O to allow the Fe²⁺ ions having the large QS values. The charge compensation can be achieved, in principle, without Co(III)-vacancies, but DFT calculation shows that the hypothetical PBA structures with Fe²⁺ having zero QS, such as cubic KFe[Co(CN)₆]·H₂O [3], are energetically unfavorable. However, it is an interesting and surprising feature of Fe²⁺ ion stabilized in the cubic structure of Prussian blues that its orbital degeneracy can be preserved for some part of the Fe²⁺ species, which looks in Mössbauer spectra as if we succeeded to drive a fraction of the sample to crystallize in the hypothetical phase of Keggins and Miles [3].

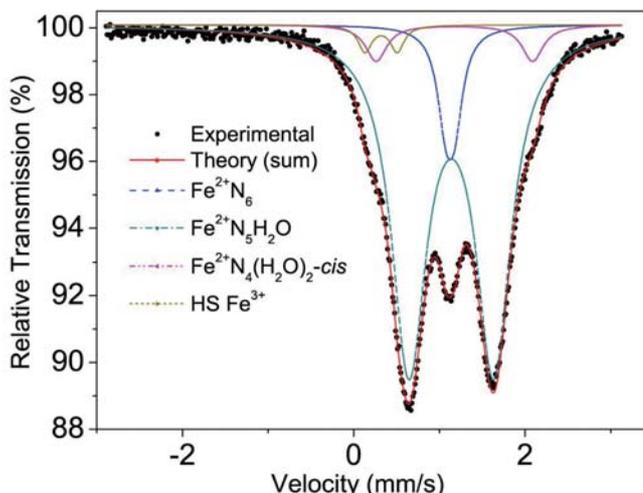


Figure 1. Mössbauer spectrum of RbFe[Co(CN)₆]·H₂O. The spectrum is fitted with four doublets: the main (84%) doublet is attributed to the orbital doublet (OD) state with IS of 1.13, QS of 1.01 and FWHM of 0.50 mm/s; the central singlet-like doublet (10%) is assigned to OT state with IS of 1.12, QS of 0.09 and FWHM of 0.26 mm/s.

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State Analysis of Fluorine-Doped SnO₂ (FTO) by ⁵⁷Fe Mössbauer Spectroscopy

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Spintronics materials that control electron spin in addition to electric charge by doping magnetic ions to an oxide semiconductor with a wide band gap are fascinating. Fluorine-doped tin oxide (FTO) with band gap $E_g = 4.4$ eV is used as more stable transparent electrode in solar cells than SnO₂ with $E_g = 3.62$ eV at room temperature. We have studied the crystal structure, chemical state and magnetic properties of tin oxides doped with Fe [1], and present here the results of FTO doped with Fe, prepared by a chemical method.

FTO samples with different doping amounts ($\text{Sn}_{1-x}\text{Fe}_x\text{O}_{2-y}\text{F}_{2y}$): $x = 0.01$ to 0.04 , $y = 0.10$ and 0.20) were prepared by mixing 0.1 M NH_3F , 0.2 M SnCl_4 , 0.01 M FeCl_3 and 0.01 M ^{57}Fe solutions, heating to dryness, grinding and calcinating. The obtained samples were analyzed by X-ray diffraction (XRD), sample vibration type magnetometer (VSM), and ^{57}Fe Mössbauer spectroscopy for estimating the crystalline distortion, magnetic properties, and chemical states, respectively.

XRD patterns of all Fe doped FTO samples showed a rutile crystal structure containing no precipitated iron oxide. VSM showed weak ferromagnetism for the strained samples. The Mössbauer spectra were decomposed into two doublets of Fe^{3+} (D1 and D2). The isomer shift (IS) and quadrupole splitting (QS) values of FTO changed due to the annealing temperature. The doublet with the small electric field gradient (D1) is assigned to Fe^{3+} in coordination site with small strain, and another doublet (D2) is to Fe^{3+} in large distortion site due to F^- ion and oxygen defect. These ratios change slightly depending on the doping rate of Fe^{3+} that substitutes the Sn atoms of FTO. Moreover, since the IS values tended to decrease as the temperature was increased, the Fe^{3+} bond is considered to be doped more strongly covalent than ionic as shown in Fig. 1. The defect structures of Fe doped FTO are discussed, using the oxygen defect model [2].

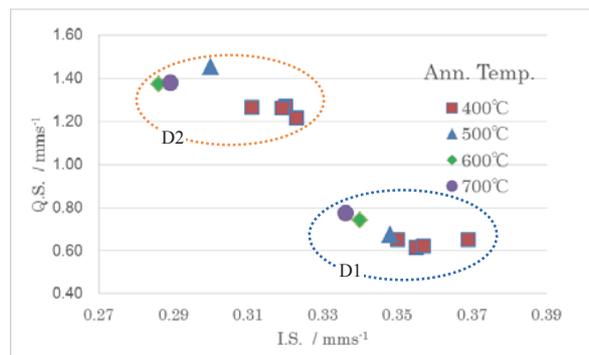


Fig. 1 Relationship between IS and QS of Fe doped FTO. D1: Blue circle, D2: Orange circle

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One-pot Synthesis and Characterization of Manganese-doped Maghemite

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Many researchers are focused to the investigation of the synthesis and properties of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) due to its possible applications in various fields. This magnetic material can be used as ferrofluid, catalyst or adsorbent as well as in biomedicine in diagnostic and cancer therapy. Generally it is known that doping of maghemite with various metal cations can pronounce some specific properties of this material.

In the present work we report a simple one-pot synthesis of maghemite as a single phase and also of Mn-doped maghemite. Starting chemicals were $\text{Mn}(\text{acac})_2$ and $\text{Fe}(\text{acac})_3$, where ac is acetylacetonate. A proper amount of $\text{Mn}(\text{acac})_2$ were added to $\text{Fe}(\text{acac})_3$ to obtain 0,1,3,5,10 and 20 mol% Mn into $\gamma\text{-Fe}_2\text{O}_3$. The corresponding mixtures $\text{Mn}(\text{acac})_2/\text{Fe}(\text{acac})_3$ were strongly mixed in achat mortar and heated at 300°C in laboratory furnace for a proper time. The prepared samples were characterized with XRD, ^{57}Fe Mössbauer, FT-IR and FE SEM. XRD patterns of reference and Mn-doped samples correspond to $\gamma\text{-Fe}_2\text{O}_3$ phase. Gradual doping of $\gamma\text{-Fe}_2\text{O}_3$ with Mn ions slightly shifted diffraction lines and crystallite sizes varied between 24 and 35 nm, as determined by the Scherrer method.

Mössbauer spectra recorded at RT and 80K showed decrease of HMF values with increase of Mn-doping. Fig. 1 shows Mössbauer spectra at RT of reference samples and those doped with 5 and 10 mol% (column 1) and Mössbauer spectra at 80K of the same samples (column 2). FE SEM images showed nanosize particles of good uniformity for all samples prepared at 300°C . Additional heating at 500°C produced phase transformation to reference $\alpha\text{-Fe}_2\text{O}_3$ phase as well as Mn-doped $\alpha\text{-Fe}_2\text{O}_3$ phase (SEM images - column 3, Mössbauer-column 4). This work showed that reproducible Mn-doped $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles can be produced by a simple one-pot synthesis thus avoiding additional solvents and surfactants.

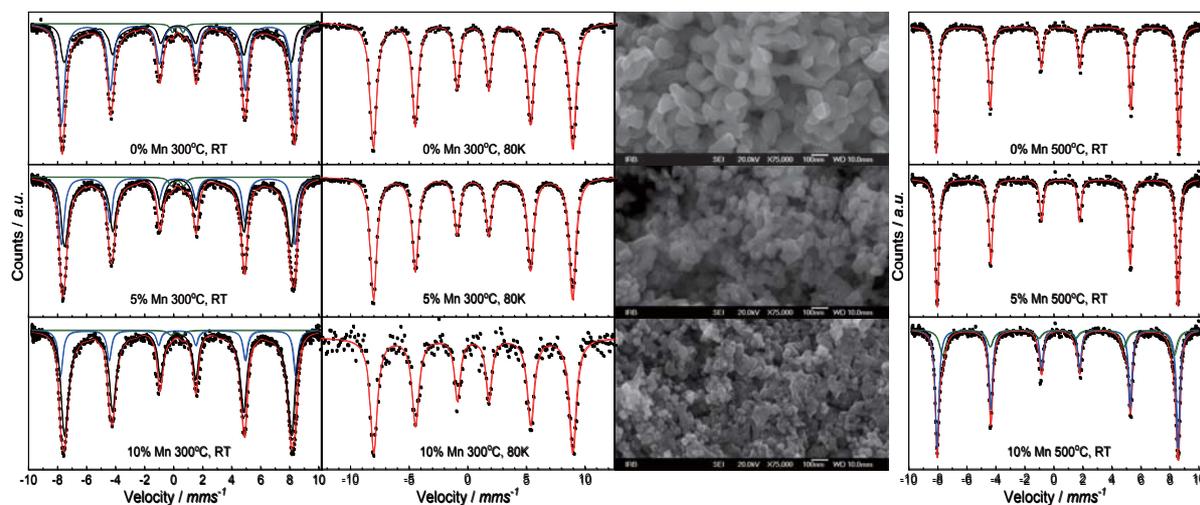


Fig. 1. Mössbauer spectra of the selected samples and corresponding FE SEM images

Ferrous Sulfates and Fumarates in Oral Supplements: ^{57}Fe Mössbauer and Raman Spectroscopic Studies

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Iron deficiency anemia is caused by insufficient iron in the human body [1,2]. A common way of treating this disease is through oral iron supplementation, and there are several types of iron-containing supplements on the market. We have used ^{57}Fe Mössbauer and Raman spectroscopies to the study of physico-chemical properties of six commercial iron compounds for oral supplementations [3,4]. The supplements are based on ferrous sulfates and on ferrous fumarates. The RT Mössbauer spectra of the samples were fitted with a dominant quadrupolar doublet that confirms the presence of the desired iron components, but for some samples, another weak doublet was required, that suggested the formation of little amounts of ferric impurities. We determined the amount of ferrous content in one supplement, taking into consideration the room-temperature relative recoilless f-fractions calculated for the other ferrous compounds [3]. 77 K Mössbauer spectra of the samples were fitted with two dominant quadrupolar doublets. The physical origins of the doublets were interpreted as due to the presence of several hydrated ferrous compounds [4]. Raman spectroscopy confirmed the presence of the hydrated phases.

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Characterization of *Mycobacterium Tuberculosis* Ferredoxin with Mössbauer Spectroscopy

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Due to the growing number of multiresistant strains of *Mycobacterium tuberculosis* (Mtb), tuberculosis threatens to become a serious health risk both in industrial and developing countries again [1, 2]. In bacteria a highly evolved cytochrome P450 mono-oxygenase (CYP) system is essential for the survival of the organism. Ensuring the viability and pathogenicity of Mtb, CYP-enzymes are targets for the development of new anti-tuberculosis drugs [2]. For their catalytic reactivity CYP-enzymes need electrons provided by ferredoxins (Fd) which act as electron transfer proteins. However, only few of the Fds involved in the CYP system of Mtb, have been characterized so far [2].

Here we present the first Mössbauer spectroscopic characterization of a Mtb ferredoxin (CNL73887.1). The Mössbauer spectrum taken at 77 K shows two components with a 1:2 ratio. Component 1 has $\delta_1 = 0.27 (\pm 0.02)$ mms^{-1} and $\Delta E_{Q1} = 0.53 (\pm 0.03)$ mms^{-1} and component 2 shows $\delta_2 = 0.44 (\pm 0.02)$ mms^{-1} and $\Delta E_{Q2} = 1.47 (\pm 0.03)$ mms^{-1} . These parameters are characteristic for a Fe^{3+} and two $\text{Fe}^{2.5+}$ ions present in a $[\text{3Fe-4S}]^0$ cluster. Analysis of the field dependent spectra by means of the spin Hamilton formalism assuming a total spin of $S = 2$ supports this finding. The experimental results are compared to a density functional theory calculation based on a crystal structure of *Rhodospseudomonas palustris* ferredoxin (pdb: 4ov1) [3].

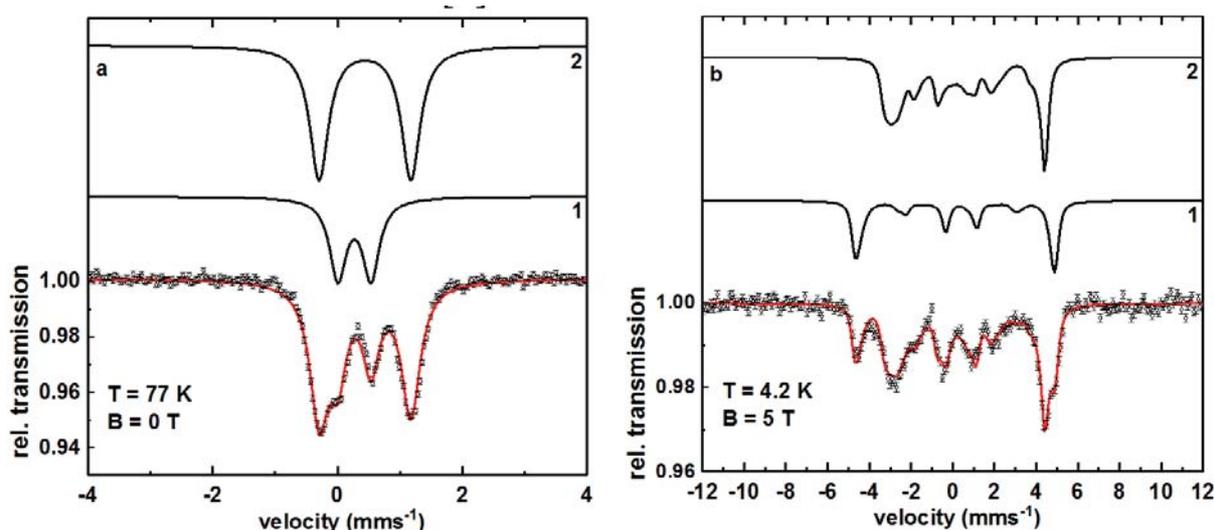


Fig.1 Mössbauer spectra taken at 77 K of *M. tuberculosis* Fd (a) and at $T = 4.2$ K with an external magnetic field of $B = 5$ T applied parallel to the γ -beam (b)

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Comparative Study of Nanosized Iron Core Features in Ferritin and Its Pharmaceutical Analogues by Transmission Electron Microscopy, Magnetization Measurements and Mössbauer Spectroscopy

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Ferritin is the most important iron storage protein in the body containing bioavailable iron in the nontoxic form. Therefore, its synthetic analogues were developed for treatment iron deficiency anemia and appeared to be very good pharmaceutical products. Ferritin consists of a protein sphere with 24 subunits which cover a cavity of 8 nm. This cavity carries the nanosized iron core in the form of ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) with inorganic phosphates. The size of the core in human ferritin usually is of 4–6 nm. Ferritin analogues consist of polysaccharide shell surrounding nanosized iron core in the form of akaganéite ($\beta\text{-FeOOH}$) mainly. We have studied a set of commercial iron-polymaltose complexes and human liver ferritin using transmission electron microscopy (TEM), magnetization measurements and Mössbauer spectroscopy. Magnetization and Mössbauer spectra measurements were done in the temperature range of 295–5 K. All studied samples demonstrated similar unusual Mössbauer line broadening with decreasing temperature in the range of 295–90 K, while both: the blocking temperatures and the slowing down of the magnetic relaxation, appeared to be at much lower temperatures [1]. These and other features of the iron cores in ferritin and its analogues, were considered as a result of the complex iron core structure, probably caused by variations in the regions/layers with more or less FeOOH close packing [2, 3]. TEM analysis confirmed this suggestion. Further investigations are on the way.

Acknowledgements: This work was supported by the Ministry of Science and Higher Education of the Russian Federation (the Project № 3.1959.2017/4.6) and by Act 211 of the Government of the Russian Federation, contract № 02.A03.21.0006.

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Synthesis of Nanoscale Magnetic Materials Based on Mesoporous Matrix of Mcm-41 Nanoparticles and Magnetite Iron for Targeted Drug Delivery

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Currently, great importance has the design of complicated nanocomposites as parts of the biomaterials suitable for targeted drug delivery. The efficiency of nanoparticles-assisted drug delivery for already known and developed chemicals to biological targets is low. Only 0.7% of the administered nanoparticles dose is found in the tumor. Such a low efficiency is an obstacle to use nano drugs in the area of clinical research.

In this paper we consider the possibility of synthesis of transport composites with an efficiency coefficient above 1%. For this reason, we developed the composite nanoparticles mesoporous silica/magnetite with a magnetic decapsulation system. We developed a new method of synthesis of nanoscale mesoporous mesostructured silica MCM-41 of the size less than 80 nm. The size is important for the absorption of particles by living cells (macrophages) and their transfer to the desired body area. The possibility is shown of heterocoagulation in mixed sol particles carrying the opposite charge – MCM-41 (SiO_2) and Fe_3O_4 . The magnetic properties of composites suggests that nanoparticles are superparamagnetic.

The selection of the medium for suspending the developed particles was also carried out. This allows to effectively introduce particles into the cell cytoplasm without cell death of macrophages. We have shown that nano-suspension retains its magnetic properties for a long time (up to 4 weeks of observation at room temperature). Cytotoxic studies have shown that the use of MCM-41/ (Fe_3O_4) nanoparticles did not cause cell death.

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Magnetic Spinel-ferrites Nanoparticles: Core-shell Magnetic Structure or Not

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A long time before the terms "nanoparticles" and "nanostructured materials" came into use in the 1980s. A few years after the discovery of the Mössbauer effect that the technique is extremely sensitive to some of the size-dependent properties of very small particles. In particular, the application of Mössbauer spectroscopy to studies in magnetic nanoparticles of superparamagnetic relaxation and magnetic structure became the subject of a large number of publications. The purpose of this work was to investigate the phase state, spin structure in the bulk and on the surface of MNPs of different MFe_2O_4 spinel ferrites and to find the technology for producing MFe_2O_4 MNPs optimized for biomedicine.

Ligand Field Analysis of Ruthenium Nitrosyl Complexes Using DFT Calculation Combined with ^{99}Ru Mössbauer Isomer Shift

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Ruthenium exists as ruthenium nitrosyls, $[\text{Ru}(\text{NO})]^{3+}$, in nitric acid solution and the composition is varied depending on concentrations of NO_3^- and OH^- ions.¹ The characterization of $[\text{RuNO}]$ species in nitric acid solution was a challenging task and has been required in the field of nuclear fuel reprocessing because a recent report suggested that the extracted $[\text{RuNO}]$ complex into organic phase obtained by solvent extraction maintains the first coordination sphere in the initial aqueous condition. As the first step to understand their chemical properties, we focus on several ruthenium nitrosyl complexes with fundamental ligands, namely, $[\text{Ru}(\text{NO})\text{L}_5]$ ($\text{L} = \text{Br}^-, \text{Cl}^-, \text{NH}_3, \text{CN}^-$; Figure 1), and discuss the metal-ligand coordination bonds by combining density functional theory (DFT) with the experimental data, especially ^{99}Ru Mössbauer isomer shift values (δ_{Ru}) reported by Greatrex et al.³

Scalar-relativistic DFT method, ZORA-BP86/SVP//DKH2-B3LYP/TZVP, was employed for $[\text{Ru}(\text{NO})\text{L}_5]$ complexes. We calculated the Mössbauer isomer shift by using linear regression analysis as previous study reported⁴ and showed in Table 1. This result indicated that the absolute values and the increased tendency from the complex with $\text{L} = \text{Br}^-$ to CN^- were consistent with those of experiment. Assuming that the complexes $[\text{Ru}(\text{NO})\text{L}_5]$ have octahedral symmetry, we also estimated the ligand field splitting values (Δ_o), which were calculated by using Ru d-orbital based MO analysis reported by Ishii and coworkers.⁵ This comparable correlation between δ_{Ru} and Δ_o values indicated that the stronger the ligand field becomes, the greater the back donation of Ru d-electrons to the ligands becomes. We will discuss the bonding nature of Ru d-orbital by using MO overlap population analysis.

Table 1 δ_{Ru} and Δ_o values for $[\text{Ru}(\text{NO})\text{L}_5]$ complexes

$[\text{Ru}(\text{NO})\text{L}_5]$	$\delta_{\text{Ru}} / \text{mm s}^{-1a}$		Δ_o / eV
	Calc.	Exp. ^b	Calc.
$\text{L}=\text{Br}^-$	-0.45(8)	-0.47(3)	4.8
$\text{L}=\text{Cl}^-$	-0.41(8)	-0.37(3)	5.1
$\text{L}=\text{NH}_3$	-0.20(8)	-0.20(3)	6.4
$\text{L}=\text{CN}^-$	0.14(8)	-0.12(3)	7.6

^aRelative values to Ru metal at 4.2 K. ^bReference 2.

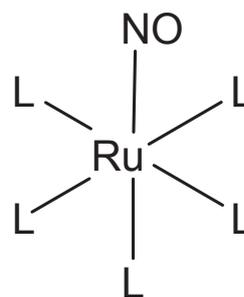


Figure 1 Structure of $[\text{Ru}(\text{NO})\text{L}_5]$.

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Nuclear Inelastic Scattering and Density Functional Study of a Fe(II) 2-dimensional Polynuclear Spin Crossover Complex

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The design of coordination polymers with switching and memory functions is an important subject for the search of new advanced materials for potential spintronic applications. Among these materials spin crossover (SCO) compounds are an important class [1]. The SCO effect depends critically on the vibrational properties of the material, which can be uniquely derived by nuclear inelastic scattering (NIS). [2] Here we report on first results of a NIS study of the 2-dimensional (2D) polynuclear SCO complex $\text{Fe}(\text{pyridine})_2[\text{Ni}(\text{CN})_4]$. [3] The vibronic properties of this complex were characterized by NIS of the sample in its high-spin (room temperature) and low-spin (167K) states. The results shown in Fig 1a reveal a complete change in vibrational pattern. In order to assign the vibrational modes the system was modelled with density functional theory (DFT) calculations. The infinite 2D sheet was calculated for a model containing 13 Fe and 12 Ni centres (see Fig 1b.). The calculations for the high-spin isomer were obtained using a model with the iron centres replaced with the Zn atoms. In this way vibrational bands in the partial density of phonon states (pDOS) were assigned to particular modes and the vibrational contributions to entropy were calculated for the low-spin and the high spin phase.

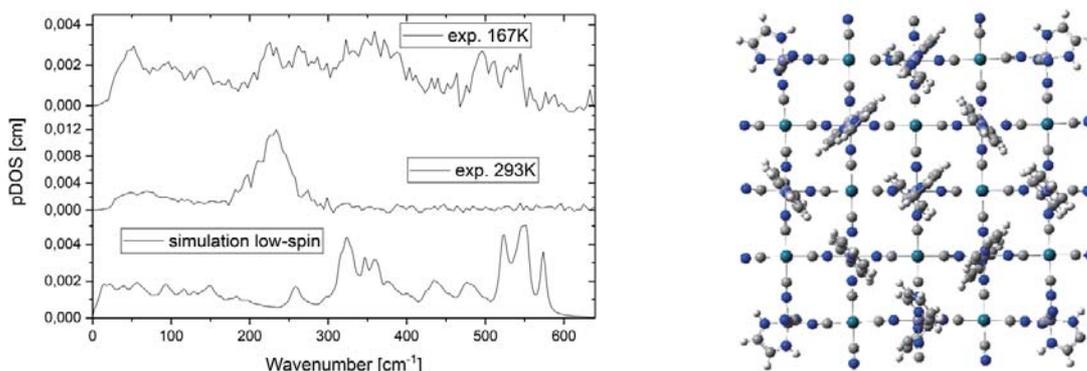


Figure 1. a) Experimental pDOS of the low-spin and high-spin isomers of $^{57}\text{Fe}(\text{pyridine})_2[\text{Ni}(\text{CN})_4]$ and the pDOS of the low-spin phase calculated with DFT b) Molecular representation of the system used for the DFT calculations.

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Mössbauer Study of PVC-plasticized Sensor Membranes

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PVC-plasticized membrane sensors are very popular analytical tool for quantification of various ions in aqueous media. While the thermodynamic theory behind the functioning of these sensors is quite well developed, there is a certain lack of instrumental studies of polymeric membrane ion sensors that would allow insights into their response mechanism at molecular level. Such studies are quite challenging due to the low content of species of interest in the membrane material and due to specific features of plasticized polymeric sensor membranes that do not allow using analytical methods requiring high vacuum. Mössbauer spectroscopy is a powerful tool for studying local chemical environment of the probe atom, however, the potential of Mössbauer spectroscopy for this particular application was not explored so far.

In this research we have studied the forms of iron existence in different PVC-plasticized membranes. Sensor membranes with octyl(phenyl)-*N,N*-di-isobutylcarbamoylmethyl-phosphine oxide (CMPO) ligand were studied. These membranes have shown the pronounced sensitivity towards Fe³⁺ ions in acidic media [1]. Three types of membranes were prepared: 1) dummy membrane containing poly(vinyl chloride) (PVC) and solvent-plasticizer *o*-nitrophenyl octyl ether (NPOE) only; 2) membrane with 10 mmol/kg of potassium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (TFPB) cation-exchanger; 3) membrane with 10 mmol/kg of TFPB and 50 mmol/kg of CMPO. In order to be able to observe Mössbauer effect we employed ⁵⁷Fe-enriched sample solutions to soak the membranes and performed the measurements at 80K to increase the recoil-free factor. Also it was necessary to employ the stack of three standard membranes (each ca. 0.5 mm thick) in order to increase the absolute amount of ⁵⁷Fe for reliable signal. Each spectrum was accumulated using 25 mCi ⁵⁷Co(Rh) source during 144 hours. Fitting of the Mössbauer spectra was done by superposition of Lorentz functions using the standard Levenberg-Marquardt algorithm. We have found that the chemical forms of iron vary in membranes having different compositions. We also have estimated the relative content of iron in various forms. These findings are the first attempt of Mössbauer spectroscopy application to study the polymeric chemical sensors.

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DFT Study of Hyperfine Interactions and Mössbauer Shifts in Halogen Complexes

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In this report, we present a DFT calculations based on the microwave spectroscopy, IR-, NMR-, ESCA-spectra, a nuclear quadrupole resonance and Mössbauer investigation of the donor-acceptor complexes formed from acceptors of 11, 13, 14, 15, 17 and 18 groups. On the other hand the aim of this work is to provide a rather simple interpretation of the observed main trends in the variations of Mossbauer chemical shift (δ) for usual and donor-acceptor complexes metal compounds based on a density functional theory calculation of the electron density at the nucleus [$\rho(0)$].

The geometries were first optimized at the DFT level by using the cam-B3LYP/DGDZVP within the GAUSSIAN'09 program. The use of all-electron basis set DGDZVP for all atoms is better with respect to accuracy and efficiency. These optimized geometries of the molecules have also been studied using the ADF program. We have used the OPTX exchange functional combined with PBE correlation functional with an uncontracted STO triple- ξ + polarization basis set using the frozen core approximation to treat the inner electrons. There are bases to consider, that the relativistic effects basic for such heavy atoms should be considered by the zero order regular approximation (ZORA) that is more reliable than the widely used Pauli formalism. These results have been used to calculate the geometrical parameters, nuclear quadrupole couplings, rotational constants, vibrational frequencies, NMR shifts and Mössbauer data [1].

The main observed trends in the variations of the Mössbauer isomer shift for ^{119}Sn , ^{121}Sb , ^{127}I , ^{131}Xe , ^{197}Au , ^{195}Pt , ^{187}Os , ^{57}Fe , ^{193}Ir compounds are interpreted in terms of the valence electronic populations, and are related to changes in the metal local environment. These series correspond to different ranges of experimental values for δ which have been correlated to the calculated values of $\rho(0)$ and the metal valence electron populations. Besides, linear correlations between Mossbauer and X-ray photoelectron spectroscopy shifts were obtained for some compounds.

On the other hand, the values of the valence electron charge density at the nucleus $\rho(0)$ have been evaluated from ZORA calculations for a number of metal compounds in order to check the accuracy of the theoretical approach. The linear correlations between the experimental values of δ and the calculated values of $\rho(0)$ are obtained.

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Characterization of Iron Ligand Vibrations in Two Dimeric Iron(II) High-spin Complexes by Nuclear Resonance Scattering

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The investigation of the vibrational properties of iron (II) high-spin complexes is of interest as they are of general importance for the iron-ligand bond strength which determines the catalytic performance of these complexes in homogenous catalysis^[1]. On our road to investigate such catalysts we have studied two different Fe(II) containing complexes. The dimeric structure $[\text{}^5\text{CpFeX}]_2$ consists of two iron cyclopentadienyl units (${}^5\text{Cp}$ = Pentaisopropylcyclopentadienyl, X = Br, OH⁻) bridged over two bromine or hydroxide ions.

The vibrational properties of these complexes were investigated using nuclear inelastic scattering (NIS). Fig. 1a and 2a show the experimentally determined partial density of states (pDOS) of iron-centered ligand vibrations of both complexes. In addition, we performed nuclear forward scattering (NFS) experiments on these complexes. The NFS data (not shown) displays quantum beat structures which are indicative for a ferrous high-spin state for all iron centers. To allocate the experimentally observed bands in the pDOS, theoretical calculations using density functional theory (DFT) have been performed based on structural data obtained by X-ray crystallography. The calculated pDOS shown in Fig. 1b and 2b reproduce the experimental data very well. In this way, we are able to assign almost each of the experimentally observed NIS bands to their corresponding molecular vibrational modes.

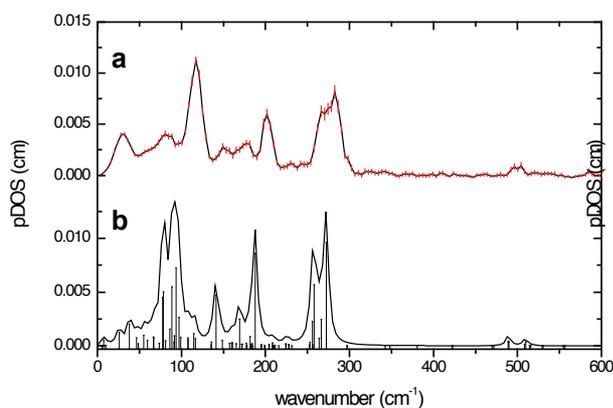


Fig. 1. Experimental pDOS of the Br-bridged Fe(II) complex (a) and DFT based simulation (b).

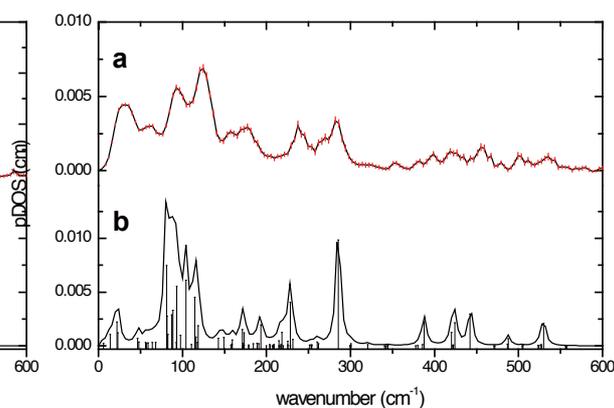


Fig. 2. Experimental pDOS of the OH-bridged Fe(II) complex (a) and DFT based simulations (b).

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Spin-crossover Phenomenon and Intermolecular Interaction for the Assembled Fe(II) Complexes Having Aromatic Rings

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Fe(II) octahedral assembled complexes can take two spin (high-spin and low-spin) states and spin-crossover (SCO) phenomenon appears between the two spin states by external stimuli, such as temperature, pressure, and light-illumination in intermediate ligand field. Fe(II) complexes bridged by 1,4-bis(4-pyridyl)benzene show SCO,¹ while the complexes bridged by 9,10-bis(4-pyridyl)anthracene do not show it.² The difference is thought to be due to the difference in intermolecular interaction. In the present study, iron (II) assembled complexes $[\text{Fe}(\text{NCX})_2(\text{L})_2]_n$ ($\text{X} = \text{S}, \text{Se}, \text{BH}_3$; $\text{L} =$ bridging ligand) were synthesized using m,n -bpna (= m,n -bis(4-pyridyl)naphthalene; $(m,n) = (1,4), (1,5), (2,7)$) (Fig. 1) to reveal the effect of intermolecular interaction on SCO.

SQUID and Mössbauer spectroscopy revealed that the SCO phenomenon depended on the bridging ligand and guest molecule for $[\text{Fe}(\text{NCX})_2(m,n\text{-bpna})_2]_n$. $[\text{Fe}(\text{NCX})_2(1,4\text{-bpna})_2]_n$ and $[\text{Fe}(\text{NCX})_2(1,5\text{-bpna})_2]_n$ showed SCO, while $[\text{Fe}(\text{NCX})_2(2,7\text{-bpna})_2]_n$ showed only high-spin state independent of temperature. $[\text{Fe}(\text{NCS})_2(1,5\text{-bpna})_2 \cdot (\text{toluene})]_n$ showed temperature-independent high-spin state, while the corresponding guest free complex showed SCO. The local structure was the parallel type of coordinated pyridines for $[\text{Fe}(\text{NCS})_2(1,5\text{-bpna})_2 \cdot (\text{toluene})]_n$. There was CH- π interaction between toluene and naphthalene in the bridging ligand. $[\text{Fe}(\text{NCS})_2(2,7\text{-bpna})_2]_n$ has racemic structure. The local structure was parallel type of coordinated pyridines and there was π - π stacking between lattices. The complex did not show SCO phenomenon. Because π - π stacking forced the unstable parallel structure and it was difficult for the complex to change the structure to become low-spin state with decreasing temperature. It was revealed from the present study that intermolecular interaction has the roll of the stabilization of one local structure to control the spin state in the Fe(II) assembled complexes.

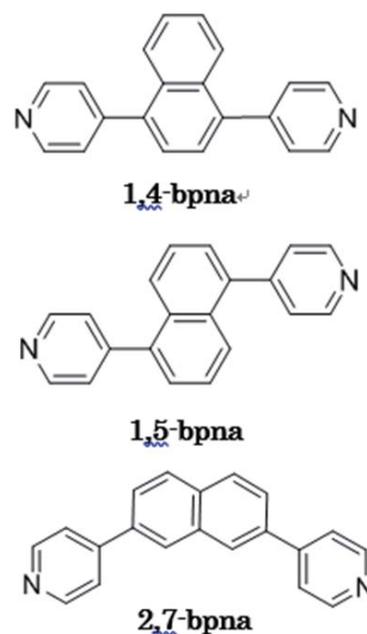


Fig. 1 Bridging ligand

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Mössbauer Study of Wide-hysteresis High-temperature Spin-crossover in Fe(1,2,3-triazolate)₂

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⁵⁷Fe Mössbauer spectroscopy was applied to study the spin-crossover (SCO) transition in the metal-organic framework (MOF) of the Fe(1,2,3-triazolate)₂. The spectra at room temperature and up to 280 °C have a shape of pseudo-single line with isomer shift typical for the low-spin (LS) divalent iron. The spectrum at 300 °C during heating shows partial spin transition with about half of iron transformed to the high-spin (HS) state. One can observe two sub-spectra related to Fe(II)-HS and they could be assigned to the Fe₁-HS and Fe₂-HS atoms according to the crystallographic properties of the Fe(1,2,3-triazolate)₂ with two inequivalent iron sites. The spectrum at 320 °C shows almost full SCO to the HS state. The isomer shifts for the Fe₁-HS and Fe₂-HS are almost the same which means that the electron charge densities are almost the same for both irons. On the other hand, the Fe₁-HS site has quadrupole splitting of about 1.5 mm/s due to large electric field gradient (EFG) typical for the HS divalent iron, but for the Fe₂-HS site there isn't quadrupole splitting thus there is null EFG. The lack of the EFG suggests that the Fe₂ site keeps the O_h symmetry in the HS state with lack of a static Jahn-Teller distortion. Another and more likely explanation of this phenomenon may be the dynamic Jahn-Teller distortion with the rapid inversions of the t_{2g} orbitals. The Mössbauer spectra during cooling show the HS iron down to 200 °C confirming the wide temperature hysteresis of the SCO. The spectrum at 160 °C shows the LS iron (with some traces of decomposition products) confirming reversibility of the SCO transition.

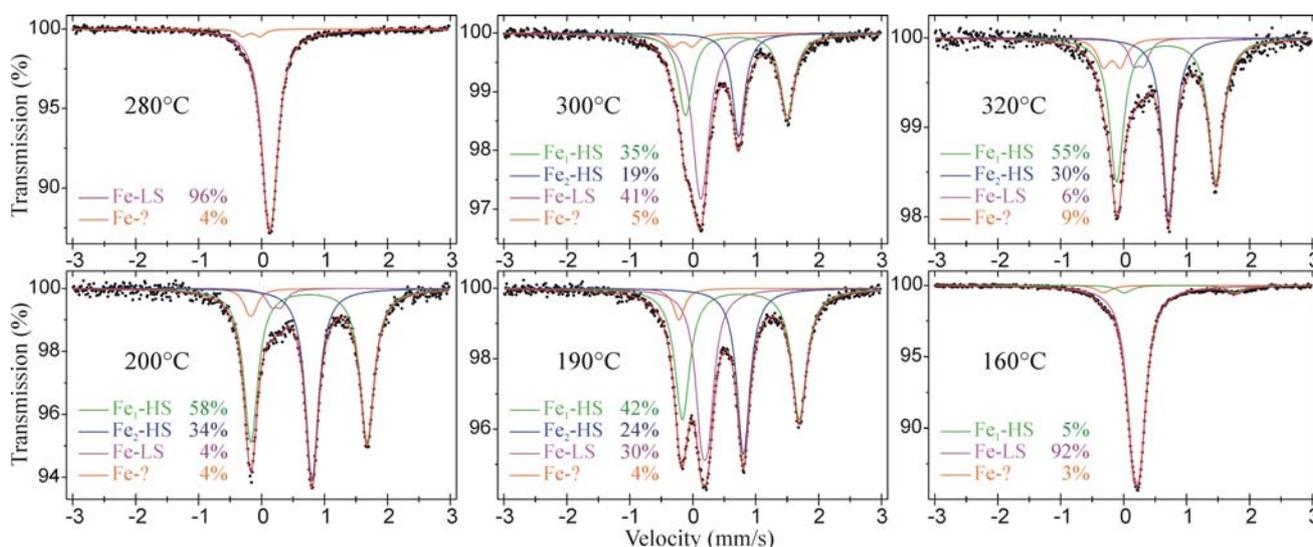


Fig. 1. ⁵⁷Fe Mössbauer spectra for the Fe(1,2,3-triazolate)₂ during heating (top row) and cooling (bottom row).

In-beam Mössbauer Spectra of ^{57}Fe Obtained after ^{57}Mn Implantation into Lithium Fluoride

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In-beam Mössbauer spectroscopy using a short-lived ^{57}Mn ($T_{1/2} = 1.45$ m) implantation is a powerful tool to study the characterization of localized ^{57}Fe atoms in solids [1]. Lithium fluoride is used widely as an optical material. It is important to investigate the occupied position and the chemical states of the dilute Fe atoms in LiF. Kowalski et al. reported that ^{57}Fe implanted on the surface of LiF was in Fe^{2+} and Fe^{3+} states being 20% and 80%, respectively, by CEMS [2]. In this study, the in-beam Mössbauer spectroscopy and DFT calculations were carried out to study the temperature-dependent site distributions of ^{57}Fe atoms arising from the β -decay of ^{57}Mn in LiF.

The detailed experimental procedures were described in our previous reports [3]. The in-beam Mössbauer spectra of LiF observed from 7 K to 873 K are shown in Fig. 1. It was considered that single absorption lines observed at high temperatures were corresponding to Fe atoms replacing at Li^+ sites. The assignments of the components were determined by the DFT calculations. The temperature dependent site distributions of ^{57}Fe atoms and time-resolved spectra by β - γ coincident measurement will be discussed.

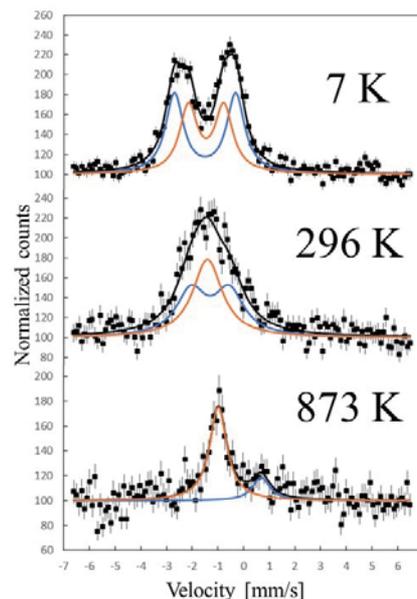


Fig. 1 In-beam Mössbauer spectra of ^{57}Fe after ^{57}Mn implantation into LiF between 7 K and 873 K.

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Mössbauer Spectroscopy, Magnetic and Photocatalytic Studies of Single-site Distorted Octahedral Iron(III) Oxide-titania Nanoparticles

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The development of new materials and latest technologies is mainly focused on the improvement of their performances; less concern is inscribed in the development of more ecofriendly and low-cost synthetic procedures.¹⁻⁴ A universal method for preparing distorted octahedral iron(III) oxide surface implanted on titania (FeO₆:TiO₂) nanoparticles (NPs) at first time, which are designed by a novel photochemical method. Different implanting level in FeO₆:TiO₂ NPs are prepared at dosage of visible light in terms of different irradiation times, in which visible light is mediated reduction of [Fe(bipy)₂Cl₂][FeCl₄] precursor complex on TiO₂ NPs surface. In combination with all the conventional techniques, the structure-activity relationships and photochemically formation of single-site FeO₆:TiO₂ NPs mainly explored by electron paramagnetic resonance, ⁵⁷Fe Mössbauer spectroscopy and X-ray absorption fine structure. Such materials have behaved as soft ferromagnetic character at room temperature. The NPs are soft ferromagnetic, having their hysteresis loops in the range -5 kOe < H < +5 kOe with the specific magnetizations of (2.70 to 23.10) × 10⁻³ emu g⁻¹ at room temperature. However, the magnetic property depends critically on oxygen vacancy, structural defects, chemical states of Fe and content. This strategy provides an alternative route to synthesize nanosized phase pure anatase x%FeO₆:TiO₂ NPs showing room temperature ferromagnetism. This work is expected to open up a general method for the synthesis of other transition-metal-surface implanted-metal oxide semiconductor with magnetic behavior.

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Co-Fe Prussian Blue Analogue for Efficient Fenton-like Catalysis: The Effect of High-spin Cobalt

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We report the Co-Fe Prussian blue analogue (Co-Fe PBA) as highly efficient Fenton-like catalyst for sulfate radical ($\text{SO}_4^{\bullet-}$) production to degrade Bisphenol A (BPA). Mössbauer spectroscopy in connection with the theoretical calculation show that the largely elongated $\text{SO}_4\text{-OH}$ bond length, strengthened adsorption and facilitated electron transfer for peroxymonosulfate (PMS) activation catalyzed by high-spin (HS) Co^{II} are the main factors for the excellent activity.

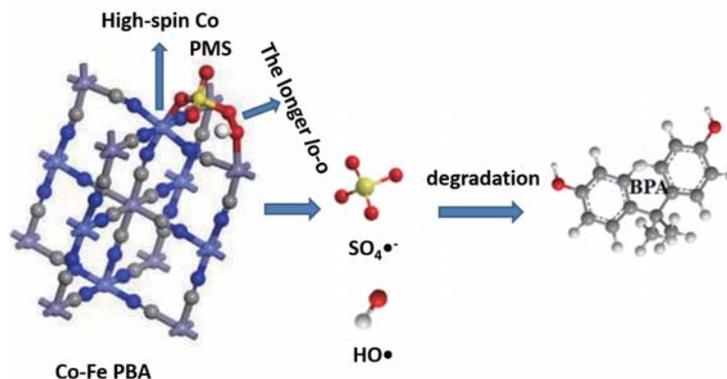


Fig. Proposed reaction scheme for the degradation of BPA by Co-Fe PBA

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Shape-Controlled Synthesis of Metal–organic Frameworks with Adjustable Fenton-like Catalytic Activity

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Controllable synthesis of metal-organic frameworks with well-defined morphology, composition, and size is of great importance toward understanding their structure-property relationship in various applications. Herein, we demonstrate a general strategy to modulate the relative growth rate of the secondary building units (SBUs) along different crystal facets for the synthesis of Fe-Co, Mn_{0.5}Fe_{0.5}-Co, and Mn-Co Prussian blue analogues (PBAs) with tunable morphologies. The same growth rate of SBUs along the {100}, {110}, and {111} surfaces at 0 °C results in the formation of spherical PBA particles, while the lowest growth rate of SBUs along the {100} surface resulting from the highest surface energy with increasing reaction temperature induces the formation of PBA cubes. Fenton reaction was used as the model reaction to probe the structure-catalytic activity relation for the as-synthesized catalysts. The cubic Fe-Co PBA was found to exhibit the best catalytic performance with reaction rate constant 6 times higher than that of the spherical counterpart. Via density functional theory calculations, the abundant enclosed {100} facets in cubic Fe-Co PBA were identified to have the highest surface energy and favor high Fenton reaction activity.

Keywords: secondary building units, shape-controlled, Prussian blue analogue, DFT calculation, Fenton reaction.

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57-Fe Mössbauer and Magnetic Studies of a New Diphosphate $Zn_5Fe_2(P_2O_7)_4$

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Phosphates exhibit many useful properties for industrial applications. However, according to the World Health Organization, the current processes in the phosphate industry generate significant amounts of solid waste containing dangerous substances that, beyond the authorized concentrations, are known to be very harmful for the environment and the health [1]. The need for novel phosphate-based materials and new production techniques that might reduce the environmental and health impact is therefore well recognized worldwide. Morocco is one of the major producers of phosphates worldwide, and the present work is in line with the national strategic plan for the valorization of phosphates [2].

Different types of phosphates have different magnetic properties, so that the study of their magnetism is desirable. In this study, we have focused on $[Zn^{II}_5Fe^{III}_2(P_2O_7)_4]$, a Zn^{2+} compound belonging to the pyrophosphate (diphosphate) family of compounds, for which the mixed-valence iron species $Fe^{II}_5Fe^{III}_2(P_2O_7)_4$ (or, in a simplified way, $Fe_7(P_2O_7)_4$) can be considered the parent species. The sample was prepared by a solid state reaction route at high temperature in air [3].

X-ray diffraction patterns revealed an orthorhombic structure with a $C222_1$ space group. The sample is thus isostructural with the parent $Fe_7(P_2O_7)_4$. Magnetometry measurements showed an antiferromagnetic-paramagnetic transition with $T_N = 15.4(1)$ K, smaller than that of $Fe_7(P_2O_7)_4$ which has $T_N = 25$ K [4].

^{57}Fe Mössbauer spectrometry showed that the substitution of Fe^{2+} ion sites was successful, but a small percentage (3.6%) of Fe^{2+} still remain. The room temperature (RT) spectrum is composed of a major Fe^{3+} doublet plus another Fe^{3+} doublet with a higher QS, probably due to the interaction of Fe ions with Zn. At 4.2 K a small Fe_{3+} doublet with a small QS is found together with a dominant sextet whose hyperfine parameters are close to the ones of $Fe_7(P_2O_7)_4$, but with a smaller hyperfine magnetic field of $B = 52.8$ T instead of $B = 54.6$ T for $Fe_7(P_2O_7)_4$ [4]. The doublet can be ascribed to a small impurity (about 7% of the total spectrum). The magnetic hyperfine splitting of the doublets found at RT to a sextet at 4.2 K is in agreement with the results obtained by magnetometry.

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Mössbauer Spectroscopic Investigation of Prussian Blue Analogues and Their Derivates Applied for Environmental Catalysis and Electrochemistry

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Nowadays, the scarcity of fresh water resources and the ever-growing environmental pollution have been attracting increased concern. The Fenton-like process has been widely investigated due to its high efficiency in removing persistent organic contaminants by in-situ production of $\text{SO}_4^{\bullet-}$ or HO^{\bullet} radicals. However, limited mechanism understanding hinders any significant advances in Fenton chemistry. In the past several years, our group has made a series of progress in investigating the mechanism of Fenton-like reaction, by using Mössbauer technique determine the coordination environment, spin state and oxidation state of iron ions. Herein, we systematically reviewed the application of Prussian blue analogues (PBAs) in the research fields such as shape-controlled synthesis of multi-metal nitrides (oxides), and their applications in catalytic activation H_2O_2 /PMS based Fenton-like reactions for the removal of organic pollutants. Mössbauer technique was applied to investigate the mechanism of the Fenton-like reaction, as well as the structure-function relationship between the catalysts and their activities.

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Analogies between the Biogeochemical Cycles of Iron and Nickel in Hydromorphic Soils; The Search of Ni^{II}-Ni^{III} DLH Minerals

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The biogeochemical cycle of iron in gleys of continental aquifers or maritime marshes, having shades from bluish-green to ochreous, is understood since the discovery of minerals *fougèrite F*, *trébeurdenite T* and *mössbauerite M*, that constitute the *fougèrite* group within the *hydrotalcite* supergroup (IMA 2012-049). All have a double layered hydroxide (DLH) structure with intercalated CO₃²⁻ anions. Since divalent and trivalent cations are from the same element, i.e. iron, the commonly named “carbonated green rust” GR(CO₃²⁻), which is an intermediate compound during the corrosion of steels, can oxidize *in situ* with a strong oxidizer such as H₂O₂ according to Fe^{II}_{6(1-x)}Fe^{III}_{6x}O₁₂H_{2(7-3x)}}CO₃•nH₂O where x is the ferric molar ratio $x = \{[\text{Fe}^{\text{III}}]/[\text{Fe}_{\text{total}}]\}$. Long-range order of Fe³⁺ ions in the brucite-like layers is obtained at $x = 1/4$ and $1/3$, but the mineral starts at $x = 1/3$ for *F*, then $2/3$ for *T* and 1 for *M*. Oxidation proceeds topotaxically and X ray diffraction (XRD) shows that lines of *F* are shifting towards higher angles and broaden, e.g. (00.3) line, as due to the deprotonation of OH⁻ ions into O²⁻. Mössbauer spectroscopy with a Co⁵⁷ source was used to follow the oxidation process and the existence of these minerals could not have been guessed without it. The same situation in the case of nickel, another transition element that is also di- or trivalent, is suspected. However, it would be a long-range order of cations with $x = \{[\text{Ni}^{\text{III}}]/[\text{Ni}_{\text{total}}]\}$. The reason is by analogy: *hydrotalcite* has an x value $\{[\text{Al}^{\text{III}}]/[\text{Mg}^{\text{II}}+\text{Al}^{\text{III}}]\}$ of $1/4$ as well as *pyroaurite* with $x = \{[\text{Fe}^{\text{III}}]/[\text{Mg}^{\text{II}}+\text{Fe}^{\text{III}}]\}$, but the most striking is Ni^{II}₆Al^{III}₂(OH)₁₆CO₃•nH₂O for *takovite* observed in many places over the world. If Ni^{II}₆Ni^{III}₂(OH)₁₆CO₃•nH₂O is prepared where $x = 1/4$ by coprecipitation the way all LDHs are, then by pouring enough hydrogen peroxide, a completely oxidized phase Ni^{III}₈O₆(OH)₁₀CO₃•nH₂O is synthesized. Even though lines are weak, one can check by XRD that the stacking is identical to that of the fully ferric equivalent *mössbauerite*, e.g. lines (00.3) and (01.2) are at the same positions. A program as that done for iron should use Ni⁶¹ Mössbauer spectroscopy to distinguish divalent from trivalent Ni cations but also various sites of Ni^{II} as seen for Fe^{II}. It involves a synchrotron to excite Ni⁶¹. Such experiments must validate the existence of four phases: (i) Ni^{II}₆Ni^{III}₂(OH)₁₆CO₃•nH₂O at $x = 1/4$, (ii) Ni^{II}₄Ni^{III}₄O₂(OH)₁₄CO₃•nH₂O at $x = 1/2$, (iii) Ni^{II}₂Ni^{III}₆O₄(OH)₁₂CO₃•nH₂O at $x = 3/4$ and (iv) Ni^{III}₈O₆(OH)₁₀CO₃•nH₂O at $x = 1$ leading to Ni^{II}_{8(1-x)}Ni^{III}_{8x}O₁₆H_{2(9-4x)}}CO₃•nH₂O. Moreover, a phase can be predicted, Ni^{II}₈H₂(OH)₁₆CO₃•nH₂O with only Ni²⁺ ions obtained by voltammetric cycling. Minerals, which are produced by bacterial reduction of Ni^{III}OOH minerals in waterflooded soils with anoxic conditions and organic matter intervene obviously in the biogeochemical cycle of Ni.

Study of Phase Composition and Morphology of the Fly Ash Type “C” Cenospheres

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Using the methods of Mössbauer spectroscopy on ^{57}Fe nuclei, scanning electron microscopy and X-ray diffraction, the studies of cenospheres extracted from fly ash “C” type were carried out. The Mössbauer spectra of the samples were recorded in transmission geometry on the spectrometer MS-1104Em at room temperature; the source of γ -quanta was ^{57}Co in the chromium matrix. The Mössbauer spectra were processed using the SpectrRelax software. The micrographs of the cenospheres were produced by the scanning electron microscope JEOL JSM-6610. The elemental composition was calculated to the oxides, the amount was reduced to 100%. The X-ray diffraction studies were performed on the diffractometer D8ADVANCE with the emitter $\text{CuK}\alpha$ in the Bragg-Brentano geometry.

The cenospheres were extracted by magnetic and granulometric separation from fly ash, the precursor of which is pyrite. The cenospheres are the ensemble of spherical microcrystallites consisting of aluminosilicates with the admixtures of iron oxides. The size of the globules is less than $25\ \mu\text{m}$. Figure 1 shows the Mössbauer spectrum of the cenospheres. The spectrum has a complex phase composition and contains Fe_2O_3 ($6.0\pm 0.5\%$), Fe_3O_4 ($4.6\pm 0.2\%$), mullite Fe^{3+} ($77\pm 4\%$), Fe^{2+} ($7\pm 1\%$) and aluminosilicates in the paramagnetic state ($6\pm 3\%$). The X-ray diffraction analysis shows the reflexes of these phases. Figure 2 shows micrographs of the cenospheres. The chemical composition of the marked spheres is almost the same as average values: Al_2O_3 – 25.77 %, SiO_2 – 38.07 %, Fe_2O_3 – 4.87 %, Na_2O – 2.25 %, MgO – 4.8 %, P_2O_5 – 2.77 %, SO_3 – 0.56 %, K_2O – 0.26 %, CaO – 19.38 %, TiO_2 – 1.27 %.

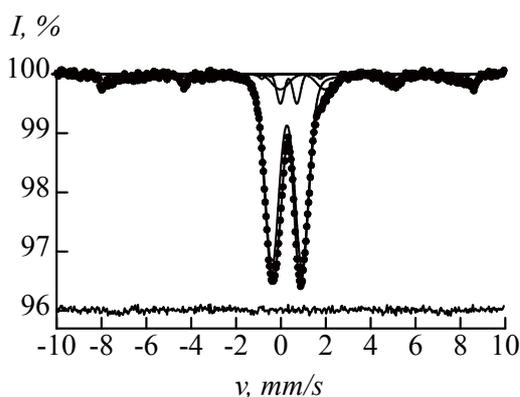


Figure 1 Mössbauer spectrum of cenospheres

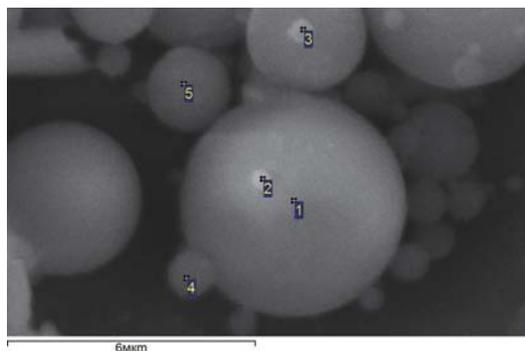


Figure 2 SEM image of cenospheres

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⁵⁷Fe Mössbauer Spectroscopy as a Powerful Tool to Understand Removal Mechanisms of Arsenites and Arsenates by Ferrate(VI) and Zerovalent Iron Nanoparticles

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Arsenic is a carcinogenic element to humans and usually enters the human body via drinking water. It is released into water sources in the form of both As(III) species (i.e., arsenites such as H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-}) and As(V) species (i.e., arsenates such as H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-}) by natural processes and anthropogenic activities. Arsenic poisoning are frequently reported to occur in various countries of the World, where the arsenic concentration in drinking water (50 – 3000 $\mu\text{g/L}$) significantly exceeds a level recommended by the World Health Organization (10 $\mu\text{g/L}$).

In this contribution, we present two strategies to treat arsenic-polluted water sources by zerovalent iron (ZVI) and ferrate(VI) nanoparticles, acting as reducing and oxidizing agents, respectively [1,2]. For both approaches, the reaction pathways were studied employing ⁵⁷Fe Mössbauer spectroscopy at low temperatures and under external magnetic fields. Moreover, the Mössbauer spectroscopy results were complemented by X-ray photoelectron spectroscopy. In the case of ZVI nanoparticles, it was shown that under anoxic conditions, the removal of As species proceeded with an enhanced efficiency, significantly dependent on absence/presence of the oxide shell. Two reaction pathways have been proposed through which As species are removed under anoxic conditions. More importantly, the reduced As species were found to be firmly locked on the surface of ZVI nanoparticles and covered by an iron(III) oxide shell, forming a compact superstructure that seems to prevent leaching of the sorbed As [1]. It was also demonstrated that if an iron(III) oxide shell forms on the surface of ZVI nanoparticles, it negatively affects the removal efficiency, significantly decreasing under anoxic conditions. In the case of ferrate(VI), an influence of inorganic ions and natural organic matter was studied on the removal of As species [2]. More specifically, the results showed three crucial effects of phosphates on arsenate removal mechanisms, including partial incorporation, competition between arsenates and phosphates sorption and complexation of iron(III) ions with phosphates ions, all affecting significantly the As removal efficiency.

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Mössbauer Spectroscopic Analysis and Adsorptive Studies on $\text{MFe}_2\text{O}_4@\text{NGO}$ (M=Mg/Ca) Nanocomposites for Sequestration of Ni(II) Ions

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Environmental pollution caused by heavy metal ions has become an issue of serious concern. Ni(II) ion is a typical contaminant that is crucial to the human health as well as ecosystem. Adsorption is considered as an effective approach for avoiding secondary pollution. In the present study, $\text{MgFe}_2\text{O}_4@\text{NGO}$ and $\text{CaFe}_2\text{O}_4@\text{NGO}$ nanocomposites (NCs) were synthesized by the ultrasonic treatment. The synthesized NCs were analysed by using different characterization tools. Mössbauer spectra of NCs were similar to the pristine NPs thus confirming the presence of ferrites in NCs. The doublets obtained in the spectra can be assigned to the superparamagnetic fraction in NCs. The isomer shift values are characteristics of Fe^{3+} state. These nanocomposites were evaluated for adsorption of Ni(II) ions. Effect of pH, adsorbent dose, initial metal ion concentration and temperature on the percentage removal of Ni(II) ions was studied. pH 6 was observed as an optimum pH for the study. $\text{MgFe}_2\text{O}_4@\text{NGO}$ displayed higher adsorption potential for Ni(II) ions as compared to $\text{CaFe}_2\text{O}_4@\text{NGO}$. Synergistic adsorption of Ni(II) ions and photocatalytic degradation of p-nitrophenol was also studied using synthesized NCs. $\text{MgFe}_2\text{O}_4@\text{NGO}$ NC displayed better adsorptive and photocatalytic potential as compared to $\text{CaFe}_2\text{O}_4@\text{NGO}$.

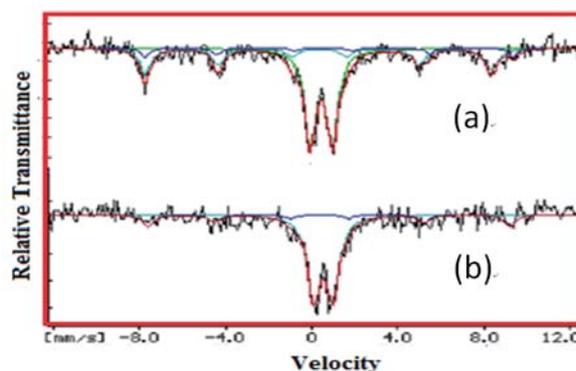


Fig. Mössbauer spectra of (a) $\text{MgFe}_2\text{O}_4@\text{NGO}$ and (b) $\text{CaFe}_2\text{O}_4@\text{NGO}$ nanocomposite at 300K.

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⁵⁷Fe Mössbauer Spectroscopy of Partially Radiation Damaged Allanites from Palawan, Philippines

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Minerals containing radioactive elements thorium and uranium, which were exposed to nuclear radiation over millions of years can serve as natural analogues to provide fundamental data for the confirmation of extra- and interpolated behavior of nuclear waste forms proposed for high-level waste disposal [1]. Prolonged irradiation, due to alpha-decay of Th and U contained in the mineral, can cause metamictization or degradation of the minerals crystal structure and may affect its physical integrity and stability [2-5]. A better understanding on the hyperfine parameters including valence states of natural analogue, due to alpha-irradiation effects in the mineral can provide useful information for studying long-term alpha-particle damage accumulation. Allanite, with a general chemical formula, $(Ca,REE)_2(Fe^{2+},Fe^{2+})(Al,Fe^{3+})_2O[Si_2O_7][SiO_4](OH)$ (where REE stands for rare-earth elements, Th and U), found in San Vicente, Palawan, was the natural analogue investigated in this study using transmission ⁵⁷Fe Mössbauer spectroscopy and correlated with the mineral's absorbed alpha-dose. The Mössbauer results show an increase in Fe²⁺ doublet intensity and line widths with increasing absorbed alpha-dose.

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Mineralogy of Reactive Iron Species and Nanoparticles in the Environment

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The biogeochemical iron cycle exerts control on the global carbon cycle¹. Much of this interaction takes place via reactive iron species, which generally occur in the form of colloids and nanoparticles. At the same time, engineered iron nanoparticles gain ever wider importance; from printing to remediation of contaminated groundwater to medical applications. Yet, once released into the environment, their fate is unclear. In both cases, determining the mineralogy of these particles is critical to understand the underlying processes but challenging to achieve with standard methods.

In soils and sediments, chemical sequential extraction protocols are often used as a proxy method to obtain mineralogical information. We show, however, that there are often large discrepancies between extracted iron and targeted minerals when individual extraction steps are checked with Mössbauer spectroscopy. We suggest that the efficiency of sequential extraction steps should be verified with Mössbauer spectroscopy or another suitable method if mineralogical information, not operational iron pools, is required.

While soils and sediments generally yield enough material to obtain iron mineralogy with a standard Mössbauer experiment^{2,3} in dilute systems such as ocean water the difficulty is in obtaining enough material for a Mössbauer measurement. We have developed a new method of filtering, concentrating and presenting nanoparticles to the ⁵⁷Fe Synchrotron Mössbauer Source (SMS)⁴, where the highly focused beam enable the analysis of microscopic samples volumes⁵. We present first result from the application of this new method to nanoparticles and colloids filtered from peatland draining river waters in Scotland.

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North West Africa Stony Meteorite: A Case Study

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New results on the study of a North West Africa stony meteorite found in the 1990s [1] gave a new enlightening on its identification. Grouped already in achondrites meteorites, the fact that Sulfur was found in its elemental composition, changed our attempt of classification.

Physical and chemical characterizations were further conducted on the NWA meteorite study, including ⁵⁷Fe Mössbauer spectrometry. The Fe-bearing phases will be discussed within the light of new elemental results.

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Comparative Study of Stony And Stony-iron Meteorites Using X-ray Diffraction, Magnetization Measurements and Mössbauer Spectroscopy

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Stony and stony-iron meteorites consist of several similar iron-bearing crystals such as olivine (Fe, Mg)₂SiO₄, orthopyroxene (Fe, Mg)SiO₃, clinopyroxene (Fe, Ca, Mg)SiO₃, troilite FeS, chromite FeCr₂O₄, hercynite FeAl₂O₄, etc. These meteorites were classified as non-differentiated (for example, ordinary chondrites) and differentiated (for example, achondrites and pallasites). These two groups have different thermal history and evolution in space. Therefore, it is interesting to compare structural and physical parameters of the same iron-bearing crystals, undergoing different extreme factors in different meteorites. For this reason, we carried out a comparative study of some examples of (i) ordinary chondrites, (ii) one achondrite and (iii) one pallasite, by means of: X-ray diffraction (XRD), magnetization measurements and Mössbauer spectroscopy. The phase composition of meteorites fragments was determined using XRD and Mössbauer spectroscopy. The unit cell parameters and Fe²⁺ occupancies of the M1 and M2 sites in silicate phases were deduced from the XRD data. Magnetization measurements showed magnetic phase transitions for chromite and, in some cases, for hercynite. Using the relative areas of the Mössbauer spectral components related to the ⁵⁷Fe in the M1 and M2 sites in silicate phases, these Fe²⁺ sites occupancies were obtained and appeared to be in agreement with similar results calculated from the XRD data. Using results of both techniques, the temperature of equilibrium cation distribution (T_{eq}) in olivine and orthopyroxene (the distribution of Fe²⁺ and Mg²⁺ between the M1 and M2 sites) was calculated for all studied meteorites and agreed mainly [1–3]. T_{eq} is related to the meteorites' thermal history and evolution in space. Some differences in the ⁵⁷Fe hyperfine parameters, saturation magnetization moments, phase composition and T_{eq} were obtained for studied meteorites.

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Iron Sites in Radiation-damaged Allanite-(Ce): The Effects of Thermally Induced Oxidation and Structural Reorganization

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Allanite-(Ce) is a cerium-rich variety of the REE-mineral allanite with the ideal composition ${}^{A1}\text{Ca}{}^{A2}\text{Ce}{}^{M1,M2}\text{Al}_2{}^{M3}\text{Fe}^{2+}[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$. It is part of the epidote-group (1) and has a monoclinic ($P2_1/m$) structure with three different octahedral positions (M1, M2 & M3) that form edge-sharing chains linked by SiO_4 tetrahedra and Si_2O_7 groups. On the A1 position rare earth elements (mainly Ce) are incorporated as well as actinides, e.g. thorium. Through the alpha-decay of the unstable nucleus the long-range order becomes destroyed. Fe^{2+} as well as Fe^{3+} can occupy the M1 as well as the M3 position (2). Th containing allanite is an interesting natural material, as actinide containing minerals in general have found to be suitable model substances to study the long-term effects of nuclear radiation on ceramics (3). Step-wise thermal annealing in air up to 1000 K leads to structural reorganization that improves the mechanical properties (hardness and elastic modulus). Further, iron oxidation ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$) coupled with H^+ -loss could be detected via ${}^{57}\text{Fe}$ Mössbauer spectroscopy and mass spectrometry. Mössbauer spectroscopic measurements on three different samples during step-wise annealing not only show an increase in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, but also a shift in the Fe concentration from one position to another. This is believed to be due to the decreasing quantity of amorphous fraction in the mineral due to thermal annealing. It is proposed that the destroyed long-range order leads to the formation of a new “site”, with differing hyperfine parameters of the Fe nucleus, that vanishes during thermally induced structural reorganization. Additionally, in the sample showing the fastest structural reorganization not all Fe^{2+} was oxidized, possibly due to a higher resistance to the oxidation process of iron atoms located in crystalline regions.

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Investigation of Particulate Matter in Urban Areas for Air Quality Monitoring

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The investigation on particulate matter (PM) in atmospheric aerosol of a densely populated urban area (city of Sofia) combines lidar monitoring with on-the-spot sampling at sites with high concentration of dust products as determined by a lidar probing. The latter was performed by lidar system at operational distances exceeding 25 km and the probing line wavelength equal to 510.5 nm. Samples were taken using a Hygitest 106 (Maimex), a high-efficiency portable device for sampling and PM concentration determination. Comparative analysis of PM seasonal variations was done using elemental analysis, Mössbauer spectroscopy at room and liquid nitrogen temperature, X-Ray Diffraction analysis as well as Electron Microscopy (Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy).

Scanning electron microscopy images showed the PM aerodynamic diameters to vary from tens of nanometers to a more than 10 micrometers. The elemental composition and particle size distribution of PM was also obtained. The main target of our investigation was the smallest fraction of PM due to its significant negative effect to human health and environment.

The physicochemical analysis of PM samples lead to conclusions about chemical composition of studied airborne PM, the quantity, crystallinity degree and dispersion of compounds. The obtained data showed high heterogeneity and complex character of studied particulate matter. Powder XRD revealed the presence of X-ray amorphous phases and phases with low crystallinity degree and small particle size in all registered patterns. The main crystallite phases registered are silicate, aluminosilicate, carbonate, silicate hydroxide and sulfate phases. More detailed information about iron-bearing compounds was obtained using Mössbauer spectroscopy, as the Fe was registered as one of the dominated elements in studied PM according to elemental analysis. This allows us to make important conclusions about PM phase composition and particles size. The majority of Fe-bearing compounds are superparamagnetic (SPM) phases with nanometric size both oxides and hydroxides, together with aluminosilicate glasses, sulfates, carbonates and coals, clay minerals, etc. As a result of analyses are drawn important conclusions in regard to suggest the common characterization procedure analyse the emissions from different sources. Preparation of such methodology will enable further activities in order to reduce the atmospheric PM pollution.

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⁵⁷Fe Mössbauer Spectroscopy Investigations of Iron Phase Composition in Natural Origin Clay Minerals

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Clay minerals found applications in pharmacy, cosmetology and environmental engineering. This group of minerals has extensive properties such as: chemical inertness, good bio-compatibility, high specific surfaces area, large pore volumes, and mechanical stability. Kaolin group minerals include kaolinite and halloysite, which are built from identical 1:1 layers but they are stacked in different ways. Halloysite has chemical composition with the higher water content than kaolinite. The chemical composition of halloysite is subject to slight changes due to the presence of impurities (Fe oxides).

In this work, the effect of chemical treatment modification of halloysite mineral and mechanical grinding on kaolin mineral will be studied. The Clay minerals sample were collected at a Polish strip mine “Dunino”.

The obtained results indicate that the chemical treatment combined with the magnetic separation, applied to the refining of the raw halloysite, gave promising results and showed the presence of the following phases: light silicate fraction consisting mainly of halloysite; heavy iron oxides - rejection from magnetic separation an intermediate product consisting mainly of aluminosilicate and iron chlorides resulting from the treatment of HCl. The polygraphic magnetic separation in the weak magnetic field used in the study allowed the separation of heavy magnetic minerals (i.e. Fe₃O₄), which were difficult to remove by other methods. The main product, i.e. purified aluminosilicate, in which the predominant mineral is halloysite, can be purified in other processes for use in polymer composites, in the production of ceramics or in high-quality sorbent.

The effects of several-hour mechanical grinding of kaolinite were studied by X-ray, scanning electron microscopy and Mössbauer spectroscopy. It has been found that there are two types of structural change in the process of dry grinding of kaolinite. One is the production of a non-crystalline substance attended by the disordering of the crystalline part, and the other is the reaggregation process. The process of the reduction in the particle size and the process of the production of the non-crystalline substance are connected to the process of the reaggregation. In a certain stage of the dry grinding, the reaggregates are spherical particles which have a zeolitic structure. As the grinding further progresses, the structure of the crystalline part in this radial particle becomes disordered due to the mechanical stress, and it changes into an amorphous substance at last. Consequently, the effect of dry grinding of kaolin mineral depends on the structural perfectness of aluminosilicate layers of the kaolin mineral, that is, the internal crystallinity of the kaolin mineral.

Accurate Determination of Fe^{2+} and Fe^{3+} Contents in Minerals by Mössbauer Spectroscopy

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Iron-containing minerals are essential materials of terrestrial planets, the moon and asteroids. Accurate determination of Fe^{2+} and Fe^{3+} contents is crucial to fully characterize a rock forming mineral, and $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio is an important factor for magma crystallization models. Mössbauer spectroscopy is one of the techniques used in the determination of $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio, and in obtaining Fe-site occupancies in minerals. Here, I will review Mössbauer spectroscopy of Fe-containing minerals and evaluate aspects of $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ and Fe-site occupancies determination, with focus on the silicate minerals, pyroxene, amphibole and mica. The major issues of obtaining accurate Fe^{2+} and Fe^{3+} contents from Mössbauer spectroscopy, e.g. thickness effects, preferred orientation (texture effects) and spectral fitting procedures, are addressed and spectra of selected minerals of terrestrial and extraterrestrial origin are presented and discussed.

Characterization of a Newly Fallen Nigerian Meteorite

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X-ray diffraction (XRD), Fields Emission Scanning Electron Microscope (FE-SEM) with EDS and Mössbauer Spectroscopy (MS), were applied to investigate a newly fallen solid piece of debris on April 19, 2018 named Ipapo from south western part of Nigeria (Lat: N 08° 14' 25.7" and Long: E 003° 33' 47.0").

X-ray diffraction matching results together with the FE-SEM analysis confirm the presence of the four kinds of iron-bearing minerals namely olivine, pyroxene, kamacite (Fe-Ni alloys) and troilite (FeS). The Mössbauer spectra recorded at 295 K and 78 K consists of two strong paramagnetic doublets emanating from olivine of quadrupole splitting 2.9 mm/s and pyroxene of quadrupole splitting 2.1 mm/s which are superimposed on two magnetic subspectra attributed to kamacite and troilite phases. From the Mössbauer subspectra absorption area, the ratio of the olivine absorption area to pyroxene absorption area indicates that the meteorite can be classified as an L-ordinary chondrite. The mole fraction of the Fe end-member of olivine (fayalite) and the orthopyroxene (ferrosilite) obtained from the EDS data will be used to identify the petrological type of the meteorite.

A Study on Evaluation of Redox Condition of Tokyo Bay Using Chemical States of Sedimentary Iron as an Indicator by Means of Mössbauer Spectroscopy

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Hypoxia is a big problem particularly in inner bay such as Tokyo Bay in Japan. To understand and solve the problem, it is important to know when or where hypoxia occurred. However, the data of water quality in Tokyo Bay are absolutely lacking. Then, we attempted to assume the historical redox condition of seawater by analyzing chemical states of iron in sediment cores. We sampled sediment cores off the coast of Yokohama (flat seafloor **Y1** and **Y2**), and Makuhari (flat seafloor **M1**, and dredged trench **M2**) through 2016-2017 (**Fig.1**). Yokohama is located near the center, Makuhari is inner part of Tokyo Bay.

These sediment cores were sliced every 2 cm and analyzed for the chemical states of iron by using Mössbauer spectroscopy. To detect sextet, we measured in velocity range of -10 to 10 mm s^{-1} . We also measured in velocity range of -3.33 to 3.33 mm s^{-1} , in order to obtain sufficient resolution to separate two doublet which are caused by pyrite (I.S. = 0.307 mm s^{-1} , Q.S. = 0.610 mm s^{-1} at 293 K¹⁾) and paramagnetic high spin Fe^{3+} .

As a result of the analysis, in most layers of Y1 and Y2 cores, and in few layers of M1 and M2 cores, sextet which is attributed to hematite or various iron (hydr)oxides was observed. This indicates that seawater in Yokohama may be more oxic than that in Makuhari. This is consistent with monitoring data of dissolved oxygen content in seawater.

However, pyrite was observed in most samples regardless of the sampling point. This indicates that anoxic conditions can occur even at relatively high dissolved oxygen sites in Tokyo Bay. In addition, the simultaneous detection of pyrite and iron oxide from one sample suggested that the chemical state of iron could be preserved after deposition and thus could be an indicator of past redox condition of seawater.

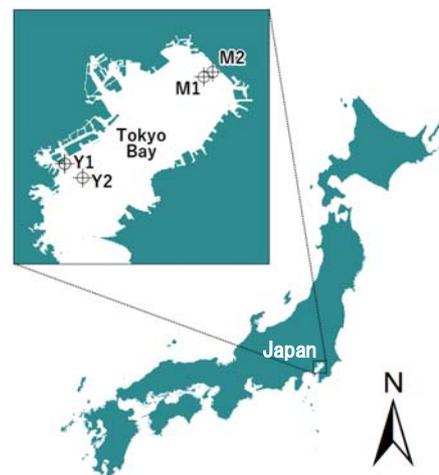


Fig. 1 Sampling point

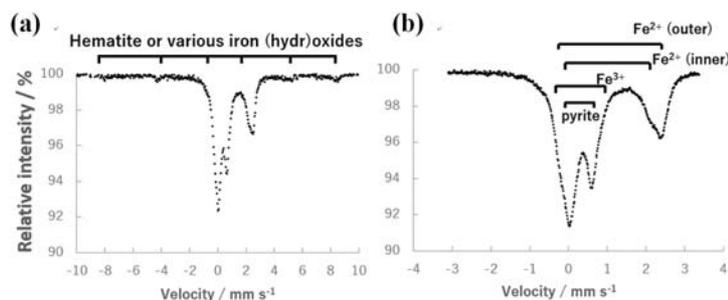


Fig. 1 Mössbauer spectra of surface sediment of Y2 Velocity range is (a) -10 to 10 mm s^{-1} (b) -3.33 to 3.33 mm s^{-1}

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Iron Species in Serpentinized Peridotite from Darbut Ophiolite, NW China

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Serpentinization is a hydration and redox reaction that may transform mantle-forming minerals including olivine and pyroxenes into hydrous phyllosilicates (e.g. serpentine and/or brucite), iron oxides, and also hydrogen. Six rock samples with various degrees of serpentinization were collected from the Darbut fault zone and analyzed for iron species using Mössbauer Spectrometer (MS). The identified iron species was dominated by paramagnetic ferrous (para-Fe²⁺), paramagnetic ferric (para-Fe³⁺), and magnetite (Fe₃O₄). The relative contents of ferric iron (Fe³⁺) were increased from 18% in sample DB-01 to a range of 45% - 54% in the samples DB-02 through DB-05 including para-Fe³⁺ and mag-Fe³⁺, respectively, and the highest content of Fe³⁺ was 70% in the sample DB-06. Sample DB-01 had a lower concentration of Fe³⁺ compared to all other samples, showing a weak oxidation, whereas sample DB-06 had a higher concentration of Fe³⁺, indicating a stronger oxidation. The analytical results also indicated the total amount of iron (tot-Fe) and relative content of ferric iron (Fe³⁺/ΣFe) were closely related to the formation of magnetite and serpentine in the serpentinized peridotites, being positively increased with the elevation of serpentinization degrees and H₂ yields.

Key words: serpentinized peridotite, iron species, mössbauer spectra, redox

Phonon and Mössbauer Spectra Changes in Fe²⁺/Fe³⁺ Mixed-valence Prussian Blue Analogues under Oxidation

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In photocatalytic reactions, the mixed valence Fe²⁺/Fe³⁺ is responsible for maintaining and regenerating the catalytic activity of iron-based catalysts. During the operation of the catalyst, oxidation and reduction of Fe centers initially occur at different rates, but subsequently these rates equalize, as the average valence of iron approaches the equilibrium value. At the initial stage of the reaction, the catalyst changes its composition, and the catalytic activity decreases mainly due to changes in the mean valence, but not due to possible contamination of the surface by the reaction byproducts or degradation associated with surface poisoning. When the composition of the catalyst reaches an equilibrium composition, the mixed-valence compound becomes functional as a “true catalyst”, the phase composition of which remains further unchanged. Both vibrational frequencies and Mössbauer spectroscopy parameters (such as isomer shift or electron density) correlate with a decrease in catalyst turnover frequency (TOF), as its mixed-valence state evolves from freshly prepared to an equilibrium state, which in equilibrium is characterized by the TOF value of the “true catalyst”[1].

In this work, we investigated the catalyst, the composition of which varies between ferric hexacyanocobaltate and ferrous hexacyanocobaltate. For the sake of increasing the efficiency of nuclear inelastic scattering (NIS) spectroscopy the ⁵⁷Fe-enriched samples were prepared in a series of solid solutions of the Prussian Blue Analogs ⁵⁷Fe[Co(CN)₆]₂•2H₂O, and ⁵⁷Fe₃[Co(CN)₆]₂•12H₂O, which are two end-members of the mixed-valence series. Synchrotron radiation was monochromatized ($\Delta E \sim 1$ meV) to excite the 14.4 keV Mössbauer transition in both Fe³⁺ and Fe²⁺ species embedded in simple octahedral (6N⁻) and composite (5N⁻/H₂O, 4N⁻/2H₂O, etc.) environments, respectively. Phonon densities of states (DOS) derived from the NIS spectra showed the energies of the Fe²⁺-N and Fe³⁺-N vibrations at 26 meV and 34 meV, respectively. In addition, the oxidation-related hardening was observed for the lowest-energy (8 to 9 meV) mode associated with rotations of rigid octahedral units FeN_{6-m}O_m (m=0, 1, etc.), where O denotes the oxygen atoms belonging to water molecules. Shifts in the highest C-N vibration frequencies, far beyond the range of the present experiment, with the density-functional theory were estimated as well. This work was supported by Chinese Academy of Sciences Visiting Professorships for Senior International Scientists (2011T1G15) and National Natural Science Foundation of China (21476232).

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Lattice Dynamics of Iron Atoms in Spinel Structure

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Greigite and magnetite are important magnetic materials with inverse spinel structure, where Fe^{3+} ions occupy tetrahedral sub-lattice (A-site) and both Fe^{2+} and Fe^{3+} ions occupy octahedral sub-lattice (B-site). Despite the similarity of lattice structure between the two materials, they exhibit completely different magnetic properties. In the present work, comparison in lattice dynamics between the two materials was performed by ^{57}Fe Mossbauer spectroscopy. Dynamics of iron atoms in tetrahedral and octahedral lattices were studied. Estimation of Debye temperature θ_D from the temperature dependent central shift (CS) value gives the values: $805 \pm 10\text{K}$ and $760 \pm 10\text{K}$ for A- and B-sites, respectively. The discrepancy of the two θ_D values reveals different lattice vibration between A- and B-sites. The Lamb-Mossbauer factor ratio f_B/f_A is found to be 0.98 at room temperature. The different low-temperature behaviors of hyperfine magnetic field for the two sites were observed. Lattice dynamics of iron atoms in greigite and magnetite were investigated.

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Spectral Data Smoothing with PLS Regression

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Instrumental data processing quite often requires the important preliminary step of signal smoothing in order to get rid of excessive noise. Various smoothing methods were suggested through the last decades each having their own benefits and drawbacks. In general, there are three main concepts that can be employed for construction of smoothing methods: 1) averaging in a certain spectral window (like e.g. Savitzky-Golay filter); 2) frequency domain representation (Fourier filter); 3) signal approximation with appropriate mathematical function (e.g. ALS procedure by Paul Eilers). This report describes a novel approach to the signal smoothing. The overall idea behind this type of filtering is in sorting the signals according to the variance they hold. This can be implemented through signal reconstruction with the help of partial least squares (PLS) regression – a basic tool of chemometrics. The presentation will show that PLS smoothing allows for significant signal-to-noise ratio improvement in Mössbauer spectra without serious distortion of line parameters (width, position, amplitude). Moreover, the PLS smoothing allows for spectral resolution improvement. The examples from Mössbauer spectrometry illustrate the process of filtering parameters selection and show that the suggested procedure can be successfully applied for spectral preprocessing both in quantitative and qualitative analysis. The basis line employed for PLS decomposition can be of any complexity (e.g. triplet), thus the smoother performance can be adapted to the wide variety of real world applications.

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Mössbauer Spectroscopy at High Pressures: State of the Art

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High pressure intensely changes all properties of materials. Pressure-induced magnetic, structural and electronic transitions predicted in strongly correlated electronic systems by many theories, now can be observed experimentally. This becomes to be enabling by the development of the high-pressure diamond-anvil-cell technique and, in particular, due to the synchrotron radiation (SR) facilities, which nowadays develop well along with other extreme environments such as temperature and applied magnetic fields. Mössbauer spectroscopy is in fact the only method by which it is possible to obtain information on the magnetic state of a material when operating at high and ultrahigh pressures. In the high pressures experiments, a sample is located in a diamond anvil cell (DAC) where the working volume is very small. The characteristic size of the sample is about 20-50 μm in plane and about 5-15 μm in thickness. This size is too small to accumulate sufficient statistics in a standard Mössbauer experiment in the laboratory.

For the high pressure measurements we need a highly focused and intense SR beam to record the Mössbauer spectra from the very small samples in DAC. There are two synchrotron Mössbauer methods – the Nuclear resonance forward scattering (NFS), in which spectra are recorded in the time domain mode, and the Synchrotron Mössbauer source (SMS) technique. In the SMS method, synchrotron radiation is used instead of radioactive ^{57}Co source in traditional transmission Mössbauer spectroscopy (TMS) which is commonly used in the laboratory. The SMS spectra are recorded in energy representation (as well as the TMS spectra). This "new" method has only recently been developed in the world and applied in real experiments, especially in ESRF (the beamline ID18) and in Japan (SpringS8), and is mainly used to study samples of very small size and at high pressures. The spectra processing and analysis which is well developed for the energetic TMS spectroscopy can be applied to the SMS spectra, but it is not well developed for the NFS method.

The most interesting pressure-effects observed in many crystals were associated with transitions from the magnetic to the nonmagnetic state (magnetic collapse), which were implemented by the spin crossover in $3d$ ions transiting from the high-spin (HS) to the low-spin (LS) state. The spin HS-LS crossover is accompanied by the structural phase transitions and some crystals transform from the dielectric to the semiconducting or metallic state. For Mott-Hubbard insulators, these effects can be explained by the suppression of strong $d-d$ electronic correlations. In addition to materials science, the high-pressure magnetic properties of iron and minerals are extremely important for the geophysics of the Earth and planetary science. The HS-LS transition can dramatically alter the physical and chemical properties of the minerals most common in the lower mantle of the Earth. These effects, observed experimentally along with the predicted metallic state arising under these P - T conditions, open up a new concept in the advancement of geophysical science.

In this lecture, we are going to sum up the new magnetic and electronic effects initiated by pressure and observed experimentally. Inevitable correlations of the magnetic state with the crystal structure, electronic and transport properties will be discussed.

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Mössbauer Spectra of Ferromagnets in Alternating Magnetic Fields

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The radio-frequency (rf) magnetic field generates in ferromagnets both the magneto-strictive vibrations and periodic reversals of their magnetization. As a consequence, the Mössbauer absorption spectrum attributes a fringe structure, collapsing to single or double line at high rf frequencies. Assuming strictly periodic reversals of the magnetization and the related magnetic field at the nucleus ^{57}Fe , we built general theory of the Mössbauer absorption [1,2], which well correlates with the experiments of Pfeiffer [3]. Moreover, we considered the situation, when a constant magnetic field is superimposed along the rf one. In this way we reported [2] the effect of quasi-Zeeman splitting for the quasi-energetic nuclear levels, providing splitting of the central absorption line as well as sidebands. These calculations well agree with our observations [4].

Furthermore, we analyzed transient behavior of the time-dependent absorption cross section [1]. It was shown that it suffers attenuating oscillations after reversal of the field, having even negative value in some time intervals. Besides, a dynamical scattering theory has been presented [5] for such transient effects. The magnetization reversal was shown to cause strong flash of the transmitted radiation intensity to be followed by its oscillations, which attenuate during a time of the order of the nuclear lifetime. The corresponding numerical calculations well agree with the experimental observations of Smirnov and Shvyd'ko [6]. We also found that these beats of the radiation intensity are accompanied by suppression of inelastic channels and reactions for the nuclei, located near the face surface of the crystal. On the contrary for deeply lying nuclei there will be an enhancement of the reaction yield.

In addition, we studied both theoretically and experimentally [7] peculiarities of the Mössbauer forward scattering spectra of the weak ferromagnet FeBO_3 exposed to the rf field, by taking into account both the periodical reversals of the magnetic field at the nuclei and their coherent vibrations. It was shown that these spectra consist of equidistant lines spaced by double frequency of the applied rf field in contrast to their absorption spectra.

Our calculations are generalized, taking into account the stochastic nature of the reversals, i.e. by introducing a reversal probability, periodically dependent on time, and by solving the corresponding master equations. This allowed us to analyze dependence of the above phenomena on the strength of the rf field and temperature.

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Mössbauer Microreactor for In Situ Observations

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In this work we present a new microreactor system for in situ Mössbauer measurements [1]. The reaction chamber provides a sealed environment that can be heated up to 450 °C and pressurized with various inert or reducing gases up to 10 bars. The uniquely designed chamber keeps the radiation source-detector distance at minimum and is compatible with both transmission and emission arrangement [2,3]. The installation and exchange of the samples can be easily done via the dismantlable window. Detailed study on the suitable gamma radiation transparent material is included as well. The microreactor chamber is supplied with a digital control system and PID regulator. Virtual instrumentation methods [4] are used for both measurement and temperature/pressure management of the device. The capabilities of the presented system were tested by carrying out a series of thermal transformation experiments, i.e., the thermal decomposition of ferrous oxalate in an inert atmosphere. In future, we believe that the presented system could provide new insight into several scientific fields, such as metallurgy, solid-state reactions and catalysis [5].

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Conversion Electron Mössbauer Spectrometer Operating at Low and High Temperatures with a YAG:Ce Scintillator

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We present preliminary results obtained during research on a new Conversion Electron Mössbauer Spectrometer build to operate at low and high temperatures.

The used detector, a photomultiplier tube with a YAG:Ce scintillator, is sensitive to both X-rays and (conversion) electrons. Electrons and X-rays have different average depths from which they come out of the sample. Detected electrons are much more likely to come from close to the surface, whereas X-rays can come from greater depths in the sample. The focus of this research lies mainly on the detection of electrons, as it wants to create a tool to study the surface area of samples. X-rays can therefore consider noise.

By applying an electric field over the sample and detector, electrons were accelerated towards the detector making more electrons being detected and giving them higher energies. X-rays on the other hand were not influenced by the application of the electric field. The electrons became therefore distinguishable from X-rays and the background.

The preliminary results were obtained at room temperature with a $^{57}\text{Fe}_2\text{O}_3$ sample. The intensity of the electric field E during measurements was 0 and 1500 V/cm. The spectrum was recorded for two different discrimination windows 15-35 and 35-65 relative units, respectively. Results are demonstrated in Table where the resonance effects are represented by the spectrum area.

The obtained results indicate that application of an electric field serves to better distinguish the contribution of the conversion electrons (0 - 7.3 keV) from the contribution of the backscattering X-rays (6.3 keV).

Table: Comparison of the spectrum area for different condition.

	Window 15-35		Window 35-65	
	$E = 0 \text{ V/cm}$	$E = 1500 \text{ V/cm}$	$E = 0 \text{ V/cm}$	$E = 1500 \text{ V/cm}$
ATM 10^5 Pa	7,7	8,3	0	0
VAC 10^{-4} Pa	12,5	19,6	3,8	8,0

Time Domain Mössbauer Spectroscopy: Ultra-Resolution Far Beyond the Line Width Γ

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The quantum beats (QB) Mössbauer spectroscopy (MS) excited by SR-pulse is a brand-new spectral method which is different from the conventional MS. In the efficiency and the resolution, it is superior to the CMS. The high efficiency of the spectrum is due to using the meV bandwidth of pulsed SR in data collection of the QB, which is equivalent to the "white beam" directly stimulating all the transition energy levels of the Mössbauer nucleus in the sample. It can significantly improve the utilization efficiency of photons. This feature is generally acknowledged. However, the QB spectroscopy can obtain a higher energy resolution that is not limited by the nuclear line width of Γ . This characteristic is not sufficient acknowledged that the resolution of the QB spectrum is beyond the limitation of Γ .

There are two reasons why the resolution of the QB spectroscopy can break through the limitation of Γ : one is that the QB spectroscopy is to observe the spectral information in the conjugate space of energy, which can directly avoid the restriction of Γ (indirectly restricted by the deexcitation time); the other reason is the nuclear resonant forward scattering QB spectrum is an interferometric fringes. It reflects the dynamical interference between the HFS energy level of the resonant nuclei. These fringes, like a vernier scale, where the primary and secondary rulers are compared, can bring a better resolution which is smaller than the scale division.

In our discussion, we take the Mössbauer nuclei ^{57}Fe as an example. After obtaining the QB spectra lines with higher resolution from the experiment, the traditional ^{57}Fe HFS model cannot explain them, which means traditional ^{57}Fe HFS model is not complete enough, and more sophisticated HFS needs to be considered.

The quantum number of the hyperfine structure in the atom is $F^{[1]}$. From the symmetry point of view, it is speculated that quantum number $F=I+J$ needs to be taken into account in the completely hyperfine structure of a nuclear system, which considers the synthesis state of the total angular momentum quantum number J of the outer electrons in the nucleus and the total nuclear spin of I . F quantum number produces a more complex energy level of HFS. When we consider the HFS of F in ^{57}Fe nucleus, the number of energy level transitions rises from 6 to 72, which is basically distributed within the Γ width ($\sim 5\text{ neV}$). To confirm our conjecture, we analyze the QM spectrum of hematite powder and discuss the correspondence between each spectral line and the HFS structure.

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Synchrotron-radiation-based Mössbauer Absorption Spectroscopy of ^{99}Ru

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Synchrotron-radiation (SR)-based Mössbauer absorption spectroscopy is a method for Mössbauer spectroscopy using various nuclides as its probe and we can obtain the absorption-type energy-domain Mössbauer spectra by this method.^{1,2)} Recent improvement by the detection of internal conversion electrons³⁾ extends its applicability and Mössbauer spectroscopy of ^{40}K , ^{61}Ni , ^{73}Ge , ^{119}Sn , ^{125}Te , ^{127}I , ^{149}Sm , ^{151}Eu , ^{174}Yb and ^{189}Os was performed until now.⁴⁾ Among those nuclides, the nuclear resonant energy of ^{174}Yb , 76.5 keV, is the highest, but the third generation SR facility covers the X-rays with somewhat higher energy, typically below 100 keV. However, SR-based Mössbauer absorption spectroscopy of nuclides whose nuclear resonance is around such high energy is usually difficult, because the recoilless fraction decreases, as is similar in conventional Mössbauer spectroscopy using RI, and the intensity of SR decreases in such high energy range.

In this viewpoint, the nuclear resonant energy of ^{99}Ru is 89.6 keV and thus ^{99}Ru is one of the nuclides near the limit on nuclear resonant energy. ^{99}Ru conventional Mössbauer spectroscopy using RI has been measured since 1966 with ^{99}Rh sources, which is synthesized by proton irradiation and shows nuclear decay half-life of 16 days.⁵⁾ Relatively many experiments were performed using RI because the ideal energy width of Mössbauer spectra $2\Gamma = 0.15$ mm/s is sufficient to observe the isomer shift; for example, the difference of isomer shift between Ru^{2+} and Ru^{3+} is typically 0.2 mm/s.⁶⁾ Furthermore, the nuclear resonant forward scattering of synchrotron radiation by ^{99}Ru was successfully observed in ESRF recently.⁶⁾ Here, we report the trial for the SR-based Mössbauer absorption spectroscopy of ^{99}Ru . The experiment was performed in SPring-8 and a Mössbauer spectrum of Ru nanoparticles without ^{99}Ru enrichment were obtained, showing the isomer shift of -0.02 ± 0.05 mm/s.

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A Novel Mössbauer Spectrometer Using Fast Shutters

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A new approach is described for performing Mössbauer spectroscopy (MS) at a synchrotron using fast shutters. Combining with micro-focusing and a suitable pulsed time-structure, a fast shutter offers a means to mechanically separate the many fast-scattering processes from the slow scattering of low-energy nuclear resonances.¹ Furthermore, using two fast shutters allows one to measure without relocating the sample both the time spectra of nuclear forward scattering as well as the familiar energy absorption spectra if combined with a single-line reference material. A test instrument involving a pair of fast shutters has recently been developed at the Advanced Photon Source to investigate the performance and possibilities of this approach using current technology. This development offers both another method for performing MS and a means to reject unwanted X-ray pulses. The latter benefitting other X-ray techniques requiring either long dark times between pulses or low pulse-repetition rates. The advantages and limitations using this approach as well as initial measurements will be presented.

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Recent Trends in Nuclear Resonant Scattering at P01 PETRA III

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The Nuclear Resonant Scattering (NRS) station at the Dynamics Beamline P01 at DESY in Hamburg is in user operation since almost 8 years now [1]. We present the status of the beamline including recent research highlights and new sample environments. In particular a cryo-magnet system allowing for sample temperatures down to 2K and magnetic field up to 2 Tesla in arbitrary direction and up to 6 Tesla in beam direction is presented and first tests on a planned Synchrotron based Mössbauer Source are discussed. The features of the envisaged upgrade of the PETRA III synchrotron to a Multi-Bend-Achromat machine PETRA IV and the related new opportunities for Nuclear Resonant Scattering will be presented as well.

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Non-linearity Correction of the Velocity Scale of a Mössbauer Spectrum

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Calibration of the velocity scale of a Mössbauer spectrum is the first step when starting measurements of unknown samples. The spectrum of an α -Fe foil fixes 6 or 12 velocities on the channel scale for single-branch (saw tooth) or mirror (triangular and sinusoidal) mode, respectively. In case of good linearity of the transducer, the set-point velocity value can be assigned to each channel or, more precisely, to the beginning and the end of each channel. Some kind of correction becomes necessary if there is a significant non-linearity between the set-point and actual values of the velocity, a situation occurring in most Mössbauer spectrometers. Neglecting this correction results in an incorrect velocity assignment to a channel which, during spectrum evaluation, distorts the χ^2 surface and, therefore, the step-down algorithms for fitting. We present an approach to the evaluation of calibration spectra by which the non-linearity of the spectrometer can be determined and used for correction of the velocity scale in further experiments.

In terms of this approach, the calibration of the velocity scale of a Mössbauer spectrum using a standard absorber is approximated by a non-linear velocity-to-channel function which is extracted not only from the position of the absorption lines but also from the full shape of the spectrum. In case of triangular or sinusoidal mode, the full (i.e., unfolded) spectrum is evaluated. The non-linear correction by a Fourier expansion up to 18 coefficients allows for fitting calibration spectra of α -iron of an effect-to-noise ratio of $\approx 10^3$ with χ^2 -values of unity within the standard deviation of χ^2 . The fit of the spectrum [1, 2] taken on an 0.995 % purity α -Fe foil at room temperature and properly accounting for resonant self-absorption in the source [3], finite absorber thickness and magnetic texture of the absorber, did not identify any broadening of the α -Fe lines beyond the natural linewidth, however, a satellite hyperfine field of 30.62 T ascribed to Mn impurities [4] was found besides the main component of 33.05 T. No satellite field was observed when a 0.9999 % purity α -Fe foil was used for calibration. The method was also successfully tested for $^{57}\text{Co}(\alpha\text{-Fe})$ source vs. α -Fe absorber in which case 15 or 30 velocities are fixed for single-branch or mirror mode, respectively. The described procedure provides an efficient check of the linearity of the drive unit and its dependence on conditions like load, frequency, maximum velocity or temperature so that, by this way, the ageing of the transducer can be monitored.

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Incoherent Nuclear Resonant Scattering from a Standing Spin Wave

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trajectory at ferromagnetic resonance in a magnetic thin film [1]. We introduce a method to study the spatial profiles of standing spin waves in ferromagnetic microstructures. The method relies on nuclear resonant scattering of ^{57}Fe using a microfocused beam of synchrotron radiation, the transverse coherence length of which is smaller than the length scale of lateral variations in the magnetization dynamics. In this study, the spatial profile of standing spin wave in a 2 μm permalloy ($\text{Ni}_{80}\text{Fe}_{20}$) stripe is mapped using NRS. To use NRS to map the standing spin wave in the stripe, the ^{57}Fe nuclei in the stripe are excited by a 14.4 keV synchrotron pulse. Specifically, a 100 ps synchrotron pulse excites the Zeeman split energetically very narrow nuclear levels. Detection of the temporal decay of the ensemble of nuclei yields information on the hyperfine fields acting on the nuclei and the magnetization state of the system. Magnetization dynamics are associated with a reduction in the hyperfine field at the nucleus [1]. The temporal response of the ^{57}Fe nuclei in the permalloy stripe as well as the fit produced by the incoherent scattering model are shown in Fig. 1a. Using this experimental method, the nuclear resonant scattering signal due to a confined spin wave is determined on the basis of an incoherent superposition model of coherent scattering from regions within the transverse coherence length [2]. From the fits of the nuclear resonant scattering time spectra, the precessional amplitude of the magnetization across the stripe predicted by an analytical model is reconstructed (Fig. 1b). Our results pave the way for studying non-homogeneous dynamic spin configurations in microstructured magnetic systems using nuclear resonant scattering of synchrotron radiation.

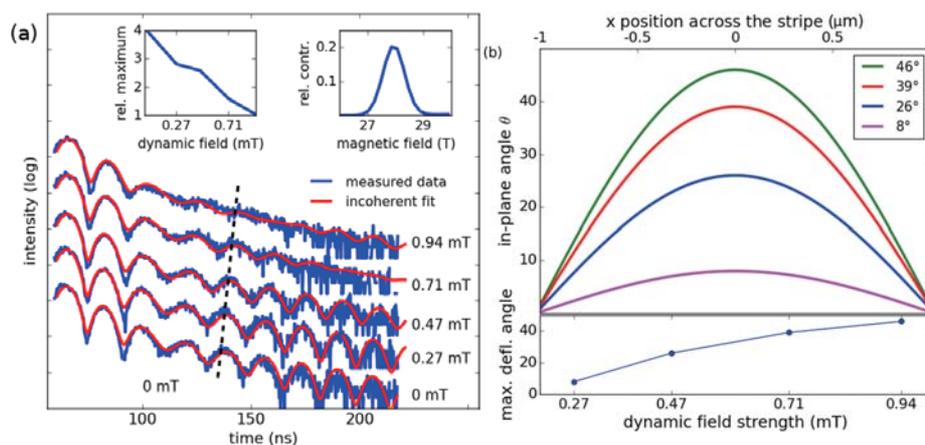


Fig. 1 (a) NRS time spectra taken from the standing spin wave excited at its resonance frequency of 2.65 GHz for different dynamic magnetic field strength. (b) In-plane deflection angle as a position dependent function across the stripe.

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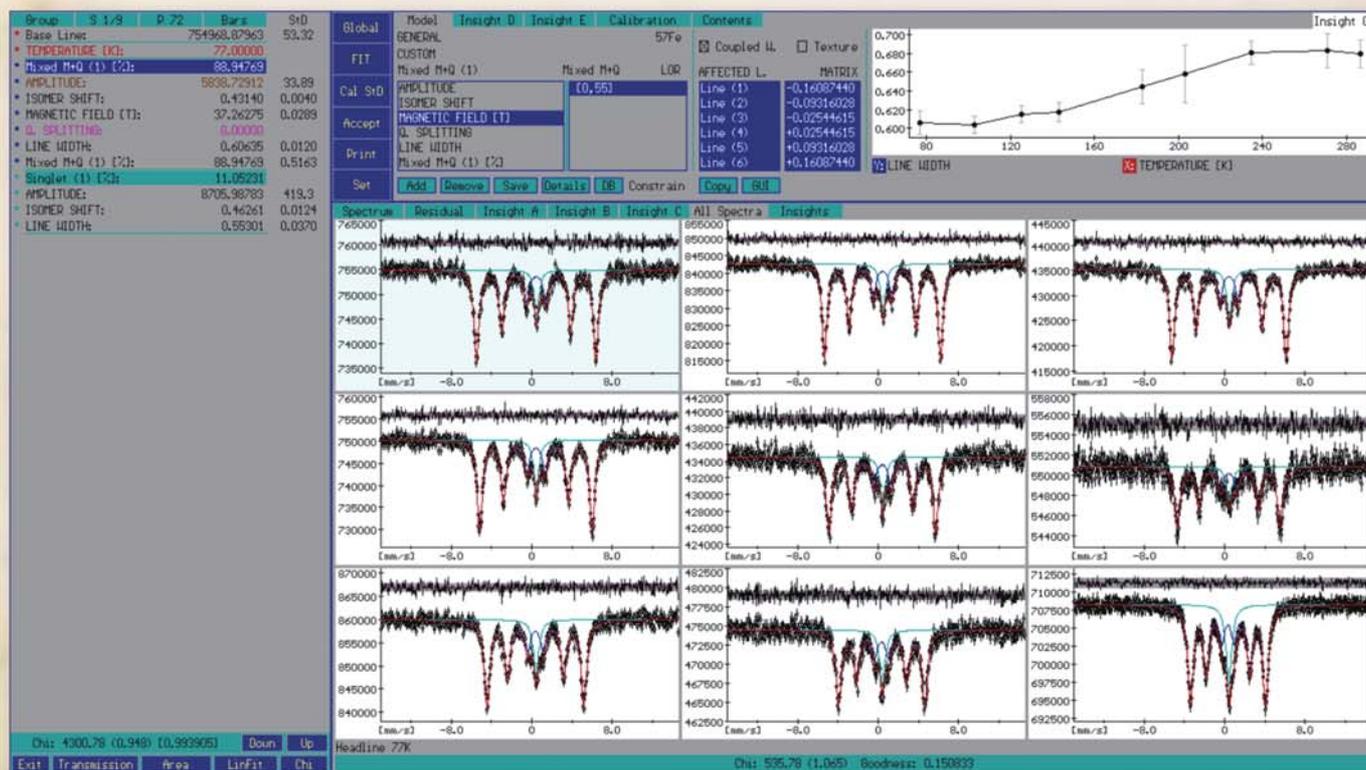
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