



MECAME 2017

**3rd Mediterranean Conference on the Applications
of the Mössbauer Effect**

In the honour of Rivka Bauminger and Rolfe Herber

Jerusalem, Israel

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BOOK OF ABSTRACTS

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WELCOME TO MECAME 2017!

On behalf of the Organizing Committee, Program Committee and International Advisory Board, we wish to welcome you to the 3rd Mediterranean Conference on the Applications of the Mössbauer Effect, MECAME 2017, which is taking place at the Belgium House, Jerusalem, Israel, from May 5 till May 7, 2017. MECAME 2017 is being organized in the honor of Professors Rivka Erika Bauminger and Rolfe H. Herber, to celebrate their eminent scientific contributions to Mössbauer Spectroscopy (MS) and their 90th birthday.

R.E. Bauminger was a member of the original first Israeli MS group (headed by Professors Solly Cohen and Shimon Ofer) who started MS in 1959, shortly after the discovery of the Mössbauer Effect. In June 1, 1960 they sent a paper to Physical Review containing the discovery of ^{161}Dy MS (Phys. Rev. **120**, 406). Later Prof. Bauminger used MS to study magnetic properties of solids, charge fluctuations, mixed valencies, superconductivity, lattice dynamics, dynamics in proteins and iron in biological systems related to Medicine.

Professor Herber is also among the founders of MS beginning from his contribution to the Second International Conference on MS, Saclay, France, September 13-15, 1961, dealing with MS of iron containing organometallics. Professor Herber has published more than 300 scientific papers, numerous books and book chapters. He was also editor of several books. His major scientific contributions in Chemistry and Physics were in: MS of organometallics; inorganic solids and alloys; metal atom kinetics in molecular solids; vibrational anisotropy of metal atoms in molecular solids; chemical consequences of nuclear transformations; molecular architecture and macroscopic properties of solids.

Jerusalem is located in the Judean Mountains half way between the Mediterranean Sea and the Dead Sea. Jerusalem has a 3000 years history to display and considered the Holy City to Jews, Christians and Muslims. The old walled city and the New city have plenty to offer to the MECAME 2017 participants.

Mira Ristić, Israel Nowik and Israel Felner

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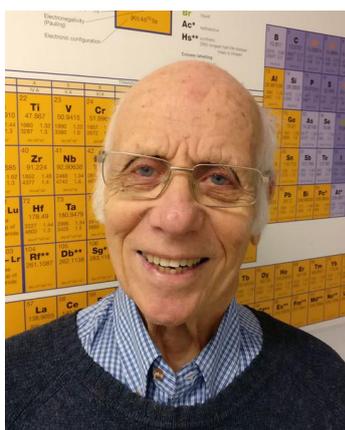
CONFERENCE SCOPE

Mediterranean Conference on the Applications of the Mössbauer Effect (MECAME 2017) is organized in the honor of Professors Rivka Bauminger and Rolfe Herber (Hebrew University, Jerusalem) for their 90 year anniversary. The objectives of MECAME 2017 are to promote the mutual understandings of the researchers, who are using Mössbauer Spectroscopy and related techniques in materials science, solid state chemistry and physics, coordination chemistry, environmental sciences, and earth and planetary sciences. This conference encourages at contributions dealing with biological and medical applications of Mössbauer Spectroscopy. Physical and chemical techniques related to Mössbauer Spectroscopy are also very welcome in the context of multi-analytical approaches in materials science and technology. Special emphasis will focus on progress in developments and methods using synchrotron radiation for NRS and SR Mössbauer.



Rivka (Erika) Bauminger was educated at the Hebrew University (HU), where she obtained her PhD degree in 1958. During 1961-1964 she was active at MIT as a Research Associate. At 1964 she was appointed as a Lecturer at the "Racah" Institute of Physics at the HU and became a full Professor in 1981. During 1990-1992 she served as the head of the "Racah" Institute of Physics. Very soon after the discovery of the Mössbauer effect Prof. Bauminger used this technique to study magnetic properties of solids, charge fluctuations, mixed valences, superconductivity, lattice dynamics, dynamics in proteins and iron in biological systems. She and associates were the first to discover and perform measurements using the ^{161}Dy isotope, as

well with many other rare earth and actinide isotopes. She published more than 250 scientific papers in peer reviewed journals and many review articles.



Rolfe H. Herber was educated at UCLA, where he obtained his BSc degree in 1949. In 1952 he received his PhD at Oregon State University and was a post-doc at MIT from 1952 to 1955. From 1955 to 1959 he was appointed an Assistant Professor at the University of Illinois. At Rutgers University he was a Distinguished Professor of Chemistry from 1959 to 1994. From 1995 until the present he has been a Visiting Professor at The Hebrew University of Jerusalem. Professor Herber has published more than 300 scientific papers, numerous books, and book chapters. He has been the editor of several books. His major scientific contributions in Chemistry and Physics were in the following fields:

Mössbauer Spectroscopy of organometallics; inorganic solids and alloys; metal atom kinetics in molecular solids; vibrational anisotropy of metal atoms in molecular solids; chemical consequences of nuclear transformations; molecular architecture and macroscopic properties of solids.

ORGANIZATION AND SPONSORSHIP

MECAME 2017 is jointly organized by The Hebrew University of Jerusalem, Israel, and Ruđer Bošković Institute, Zagreb, Croatia.



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Erika Bauminger's magnetism supertransferred to superconductivity and biomedicine of nowadays

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In this lecture, in retrospect, I will briefly talk about the scientific fields of research of Prof. Rivka Bauminger, with an emphasis on similar or related areas, developed in parallel in my laboratory in Moscow, Russia. Mainly, it concerns some aspects of magnetism and superconductivity, and also includes some areas of biomedicine, which currently use magnetic nanoparticles and nanocomposites.

According to the list of publications of Prof. E.R. Bauminger (kindly provided to me by Prof. I. Nowik), she began her scientific career with a study of natural radioactivity in vanadium V^{50} (1952) and tantalum Ta^{180} (1956). Her first publication appeared in 1952, when she was 25 years old.

Her great activity in the field of Mössbauer spectroscopy began with the study of rare-earth elements. Soon after R. Mössbauer discovered his effect, Rivka observed the effect of nuclear resonance at dysprosium atoms Dy^{161} , situated in Dy_2O_3 and dysprosium iron garnet $Dy_3Fe_5O_{12}$, and this her pioneering work was published in 1960 [*Phys. Rev.* **120**, (1960) 406]. Then, the Mössbauer resonance was observed by Rivka's group in very many rare-earth elements, including Sm^{149} [1964], Tb^{159} [1966], Yb^{170} [1967], Sm^{152} [1967], Eu^{153} [1968], Gd^{154} [1968], Gd^{155} [1969], Pm^{149} [1970]. In addition, the Mössbauer effect was investigated at heavy isotopes of Ir^{193} [1967], Pu^{239} [1972] and Np^{237} [1973]. Most of these studies were related to the magnetic properties of oxides, alloys and compounds of the rare-earth elements. Exchange interactions, anisotropic hyperfine interactions, magnetic anisotropy, spin orientation and reorientation effects, mixed valences states of Eu, Goldanskii-Karyagin effect and so on were studied.

Since 1976, Erika has started to engage in and interest in the application of the Mossbauer effect for biological research. Her experience and knowledge in magnetism were transferred to biology. Her first paper ["*Iron in the whole bacterial cell*"] appeared in 1976, and since then, a lot of articles have been published in this field.

Subsequently, more than ten years (until 1987) she was fully involved in biomedicine, and she published about 50 works in this field. Manly, they were related to the Mössbauer studies of ferritin-like iron in red blood cells; iron in hemoglobin; iron storage proteins; cation exchange membranes;

dynamics and anisotropic diffusive motion of iron in protein, ferritin and myoglobin, in crystals of metmyoglobin and deoxymyoglobin. Mössbauer studies were also applied to malaria pigment in rat infected erythrocytes and in heart cell cultures; to magnetosome dynamics in magnetotactic bacteria; to iron uptake by teeth and bones, and so on.

After the Nobel Prize of R. Mössbauer, another Nobel Prize awarded to J.G. Bednorz, K. A. Müller (1987) in the field of high-temperature superconductivity initiated a very active research of Erika in superconductivity. Since 1987, Rivka (in collaboration with I. Nowik, I. Felner and M. Kowitt,) investigated high T_c superconductors of the so-cold 1-2-3 family of copper-oxides $R_1Ba_2Cu_3O_7$ (with T_c of about 92 K). Iron impurity was introduced into the compounds $Y_1Ba_2Cu_{(3-x)}Fe_xO_{7-\delta}$, and the Mössbauer spectroscopy was applied to study correlations and competition between superconductivity and magnetism. Many interesting effects depending on iron concentration and oxygen stoichiometry were found, and about 25 papers in this field were published.

During the same period, Rivka Bauminger continued to deal with the problems of biology, and she published several Review Chapters, which include the follows: *Some Applications of the Mössbauer Effect in Biology* (1987); *Mössbauer Studies of Blood Diseases: Thalassemia and Malaria* (1990); *Conformational Motions of Iron-Containing Proteins* (1994); *Iron in Parkinson disease, blood diseases, malaria and ferritin* (1996); *Ferritin, the path of iron into the core, as seen by Mossbauer Spectroscopy* (2003); *Iron in neurodegeneration* (2013).

At present, another direction using the Mössbauer effect is actively developing in biomedical s research. This is connected with investigations of magnetic nanoparticles and nanocomposites of different type. Much attention is paid to the application of magnetic nanoparticles in biology and medicine and the focus is on targeted drug delivery, hyperthermia treatment, contrast materials in magnetic resonance imaging (MRT tomography), separation of biochemical products and gene manipulation and immunoassays. Incorporated in cancer tissue and exposed to high frequency magnetic field, nanoparticles warm up locally and destroy the cancer cells. Nanosized

magnetic particles are also promising for diagnosis due to their ability to distinguish individual molecules, which increases the sensibility of analysis. Furthermore, materials with magnetic nanostructures are can be useful for applications in high-density magnetic storage devices, magnetic heads, sensors; and also for use in microelectronics and spintronics.

In order to show the correlations of Rivka's studies in biology with research in my laboratory, I am going to present several examples in synthesis, structure, magnetic and electronic properties of nanocomposites based on transition metal chalcogenides and oxides designed for applications in nanotechnology, microelectronics and biomedicine. Complex nanodiagnostics, atomic structure and properties in sulfides, selenides and iron oxides, magnetic semiconductors, core@shell structures, magnetic nanowires in the pores of polymer track matrices, in the channels of carbon nanotubes, and in the shells of polymer microcapsules intended for target drug delivery now being investigated in my group.

As to the high T_c superconductors, my group also published many papers on magnetic and superconducting properties of the 1-2-3 cuprites $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ studied mainly by Mössbauer and neutron diffraction methods. In particular, we first published a paper about the coexistence of magnetism and superconductivity in these compounds [*Proof of the metallic nature of the chemical bond and coexistence of magnetism and superconductivity in the $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ system ($0 < x < 0.5$)*] by I.S. Lyubutin et al. JETP Lett., **47** (1988) 238]. A detailed review of our studies of the magnetic correlations in 1-2-3 superconductors induced by anion and cation doping was summarized and published in my Review [*Magnetic States Induced by Anion- and Cation Doping in the 1-2-3 HTSC Phases and their Correlations with Superconductivity*], I.S. Lyubutin, Crystallography Repots, v. 48, Suppl.1 (2003) pp. s103-125].

In the meantime, returning to history, the most existing phenomenon discovered more than 50 years ago (thanks to the Mössbauer effect) was the discovery of the magnetic hyperfine fields at nuclei of nonmagnetic tin (Sn-119) atoms [I.S. Lyubutin, K. P. Belov, JETP Lett. v. 1 (1965) p. 26]. It is established that in magnetic oxides of 3d-metals, the magnetic field can be supertransferred from Fe to Sn atoms by means of long exchange bonds Fe-O-Sn. This implies that superexchange interactions between magnetic M atoms can be implemented through a very long chemical chain involving

diamagnetic D atom M-O-D-O-M. A lot of very interesting papers in this field were published by both Rivka and my groups, and I wrote a Review Chapters of the book on this topic [I.S. Lyubutin, *The Technique of the Diamagnetic Nuclear Probe in Investigations of Magnetic Properties of Crystals* (Review). In the Book "Physical Crystallography" (ser. Problems of the Modern Crystallography), Nauka Pub., Moscow, 1992, 365 pages (p. 326-363)].

Nowadays, high temperature superconductivity remains one of the main challenges of physics and chemistry of condensed state and it is in the focus of experimental and theoretical research. The main task is to find and explore new HTSC -based on hydride materials with record critical parameters. Theoretical calculations of the different groups by different methods are predicting in the hydride based materials very high values of T_c up to ~ 200 K and close to room temperature. The calculations also predict new HTSC compounds with unusual stoichiometry, which can be stable at high pressures, such as CaH_6 , LiH_8 , SiH_8 etc. However, the pressure range for these effects is very high (the megabar range), and experimental implementation of such studies are very difficult.

Recently, in our group a new approach to study superconductivity at high pressures was invent and realized experimentally [*Science*, **351**, (2016) 1303]. We proposed to detect a magnetic field inside superconducting H_2S at high pressures with the help of the Mössbauer isotope ^{119}Sn as a sensor of magnetic field. A thin film of tin with isotope ^{119}Sn was placed into the H_2S sample volume in a high-pressure diamond anvil cell (DAC). The magnetic field at the ^{119}Sn sensor was monitored using nuclear resonance scattering of synchrotron radiation (NRS) from the ^{119}Sn nuclei. Our results demonstrated that the H_2S sample shielded the ^{119}Sn sensor from an external static magnetic field of about 0.7 Tesla at temperatures in the range of 4.7 - 145 K, which proves the superconducting state of H_2S . Some details of this experiment will be presented in my report.

As follows from my review, Rivka's achievements of the past are now being supertransferred to new directions in research of biomedicine and superconductivity, stimulating their development.

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High-purity nuclear resonant polarimetry: applications and perspectives

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Recently, high purity polarimetry in the x-ray regime has been shown to be an extremely sensitive technique to detect tiny changes in the polarization state of x-rays caused by the interaction with an optically active medium [1]. The technique relies on the application of x-ray linear Bragg polarizers in a 90° crossed setting as shown in Fig. 1, which has been already successfully applied to nuclear resonant scattering from magnetic materials [2,3,4] and to enable experiments in nuclear quantum optics [5,6].

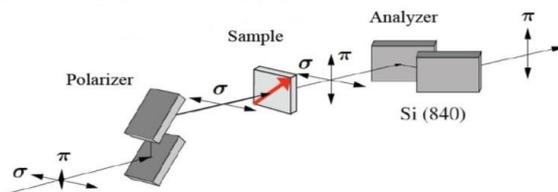


Fig. 1: Experimental Setup for nuclear forward scattering polarimetry experiments. The sample is located between two polarizing Si(840) channelcut crystals that are aligned in crossed setting to detect π -scattering.

Moreover, high-purity polarimetry can be employed to probe atomic charge anisotropies via x-ray linear birefringence (XLB) at the 14.4 keV nuclear resonance of ^{57}Fe . If the charge anisotropy in the system leads to an electric field gradient (EFG) at the ^{57}Fe nucleus, nuclear states with a finite electrical quadrupole moment are subject to an electric hyperfine interaction. As a result, the excited nuclear state of ^{57}Fe splits into two sublevels, shown in Fig. 2.

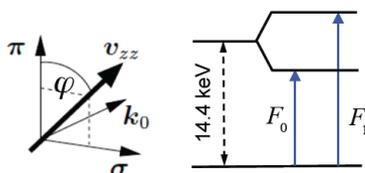


Fig. 2: Sketch of the nuclear forward scattering geometry for a linear polarization basis, and nuclear level scheme for the case of a pure electric hyperfine interaction

This leads to a pronounced optical activity in the vicinity of the nuclear resonance. In this case the nuclear forward scattering amplitude is given by [7]:

$$f_{\text{res}} = \frac{3}{8\pi} \begin{pmatrix} F_1 + (\hat{\sigma} \cdot \hat{v}_{zz})^2 [F_0 - F_1] & (\hat{\sigma} \cdot \hat{v}_{zz})(\hat{\pi} \cdot \hat{v}_{zz}) [F_0 - F_1] \\ (\hat{\sigma} \cdot \hat{v}_{zz})(\hat{\pi} \cdot \hat{v}_{zz}) [F_0 - F_1] & F_1 + (\hat{\pi} \cdot \hat{v}_{zz})^2 [F_0 - F_1] \end{pmatrix}$$

where v_{zz} is the main axis of the electric field gradient, σ and π are the linear polarization basis vectors and F_0 , F_1 describe Lorentzian functions that represent the resonant transitions between the nuclear ground state and the two levels of the excited nuclear state with $\Delta m = 0$ and $\Delta m = \pm 1$, respectively. Thus, if the main axis of the EFG is not parallel or perpendicular to the incident linear σ polarization, the off-diagonal elements of the matrix are non-zero and the polarization state of the transmitted radiation turns out to be elliptical. Consequently, probing the π -component of the transmitted radiation in a setup with two crossed polarizers provides a sensitive measure of the orientation of the EFG relative to the plane of linear polarization of the incident light.

In this talk we will give a review of the field of nuclear resonant polarimetry. Specific examples range from probing the reorientation of electrical field gradients upon a high-spin/low-spin transition in a metal-organic complex to recent experiments in the field of nuclear quantum optics.

- [1] B. Marx et al. Phys. Rev. Lett. 110 (2013) 154801
- [2] T. Toellner et al., Appl. Phys. Lett. 67 (1995) 1993
- [3] D. P. Siddons et al., Nucl. Instrum. Meth. B 103 (1995) 371
- [4] E. Alp, W. Sturhahn, T. Toellner, Hyp. Int. 125 (2000) 45
- [5] K. P. Heeg et al., Phys. Rev. Lett. 111 (2013) 073601
- [6] J. Haber et al., Nature Phot. 10 (2016) 445
- [7] R. Röhlberger, Springer Tracts in Modern Physics, Vol. 208 (Springer, Heidelberg 2005)

Fundamental studies of spin crossover phenomena in iron(II) compounds

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A brief introduction into basics of complex chemistry and concepts of ligand field theory will be followed by the principle and the occurrence of thermally induced spin crossover (SCO), one of the most fascinating dynamic electronic structure phenomena in coordination compounds. The thermal condition and the driving force for the occurrence of SCO in iron(II) compounds as well as the physical methods used for the characterization of SCO behavior will be described. The spin state switching behavior is expressed in terms of the function $\gamma_{\text{HS}}(T)$, the fraction of high spin (HS) molecules as function of temperature. This function may adopt various forms depending on the strength of cooperative elastic interactions between the spin state changing molecules in solid material. Experiments will be discussed which proof the existence of such cooperative interactions and influences on the SCO behavior, such as metal dilution in mixed crystals, isotopic substitution and exchange of crystal solvent molecules in the lattice affecting the hydrogen network, and application of pressure. The cooperative interactions are of mechanical nature and can be interpreted on the grounds of elasticity theory. Results of crystal structure determination are very helpful in understanding the mechanisms of SCO in solids.

Mössbauer spectroscopy has proven to be a powerful technique to elucidate the spin state behavior in oligo- and multinuclear iron(II) compounds. Selected examples will be discussed.

Special focus will be devoted to “light-induced excited spin state trapping”, the so-called LIESST effect. The mechanisms of the light-induced low spin to high spin conversion and for the radiationless thermal relaxation of the trapped metastable state will be explained with a Jablonski diagram. It could be demonstrated that the LIESST phenomenon can also be afforded by energy release from the nuclear EC decay of ^{57}Co in a ^{57}Co -labelled iron(II)- or cobalt(II) coordination compound used as Mössbauer source versus a single-line ^{57}Fe compound as absorber. This experiment is known as Mössbauer Emission Spectroscopy (MES). The nuclear decay with energy release is considered the “molecular light source”, which leads in much the same way to trapped metastable ligand field states. Examples of resulting Mössbauer emission spectra showing the resonance lines of “nuclear decay induced excited spin state trapping” (NIESST) will be discussed. The relaxation mechanism of NIESST is closely related to that of LIESST.

The lecture will conclude with brief a glance at current efforts and future perspectives in SCO research.

- [1] P. Gütllich, H.A. Goodwin (eds.), “Spin Crossover in Transition Metal Compounds I, II and III”, volumes 233, 234, 235, Topics in Current Chemistry, Springer, Berlin, Heidelberg, New York, **2004**.

B2 ordering of mechanosynthesized bcc $(\text{FeCo})_{100-x}\text{Sn}_x$ alloys by annealing at moderate temperatures

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Recent interest in Fe-Co-Sn alloys stems from Heusler alloys. Even when unstable or metastable relative to other phases, Heusler alloys may nevertheless be synthesized by non-equilibrium techniques. This is for instance the case of a Co_2FeSn Heusler alloy. We focus on metastable bcc phases formed in ternary $(\text{FeCo})_{100-x}\text{Sn}_x$ alloys by mechanical alloying in standard experimental conditions of high-energy planetary ball-mills and on their transformations by annealing. In such conditions, the maximum solubility of Sn in mechanically-alloyed near-equiatomic bcc Fe-Co

alloys reaches a value of about 20 at% Sn while the equilibrium solubility of Sn in ordered B2-FeCo is less than 1 at%. Neutron diffraction and ^{119}Sn Mössbauer spectroscopy prove that metastable B2 type structures are formed in bcc Sn-rich Co-Fe-Sn over a significant concentration range by annealing as-milled samples at moderate temperatures, for instance at 673K. In addition, ^{119}Sn Mössbauer spectra reveal that a Sn content of about 15 at% marks the separation between domains with different short-range orders.

Application of Mössbauer spectroscopy for the study of tin(II) fluorides and chloride fluorides

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Tin-119 Mössbauer spectroscopy, when combined with crystallography, is a very helpful tool for understanding the structure and bonding type of tin (II). The presentation will show several cases encountered in our laboratory where crystallography alone was unable to give the crystal structure. Despite the easy availability of good quality single crystals of α -SnF₂, its crystal structure remained unsolved for one and half decades. Mössbauer spectroscopy could have been used to show that one of the tin sites determined from X-ray diffraction was not possible. While highly oriented polycrystalline samples are not suitable for determining crystal structures from diffraction, the Mössbauer spectrum recorded at different orientations of the sample in the γ -ray beam gave an accurate model of the structure of α -PbSnF₄. In the case of disordered systems, diffraction gives an average structure for the atoms/ions that are disordered. Since Mössbauer spectroscopy probes only the Mössbauer nuclide, it gives a picture of the situation at the Mössbauer nuclide, and the influence of its surroundings. Two kinds of tin(II) containing solid solutions were studied. First, the M_{1-x}Sn_xF₂ (M= Ca and Pb) is a high performance fluoride ion conductor for M = Pb. It has a highly symmetric unit-cell (cubic) and crystallography suggests a cubic coordination of tin [1]. The Mössbauer spectra show that this is impossible, and it gives a much more realistic coordination. The most complex case of disordered systems studied in our laboratory is the Ba_{1-x}Sn_xCl_{1+y}F_{1-y} doubly disordered solid solution [2]. This solid solution is shown by X-ray diffraction to have the same structure as unsubstituted BaClF. The absence of superstructure or lattice distortion shows that Sn and Ba are randomly distributed on the Ba site. How could Sn substitute Ba on the same site, taking into account that tin(II) usually forms covalent bonding with F and Cl. This does not seem possible since the BaClF structure is purely ionic. In the unlikely case that tin(II) forms ionic bonding, the Sn²⁺ stannous ion is much smaller than Ba²⁺ and therefore it would be expected to fit too loosely in the Ba²⁺ site to form stable ionic bonding. Mössbauer spectroscopy allows to distinguish

easily between ionic bonding with Sn²⁺ ions and covalent bonding (Table 1, figure 1)

Table 1: Typical Mössbauer parameters for Sn(IV) oxides, Sn²⁺, and covalent Sn(II)

Species	O Num ¹	δ (mm/s) ²	Δ (mm/s) ²	Example
Sn(IV)-O	Sn ⁴⁺	0 (ref. δ)	0-small	CaSnO ₃
Ionic	Sn ²⁺	\approx 4.1	0-small	Ba ₂ SnCl ₆
Covalent	Sn(II)	3.0-3.5	1.0-2.0	SnF ₂

¹O Num = Oxidation number

²The isomer shift δ and the quadrupole splitting Δ can vary widely for covalent Sn(II). They are related to one another (Δ decreases when δ increases) and δ increases with increasing electronegativity of the non-metal it binds to.

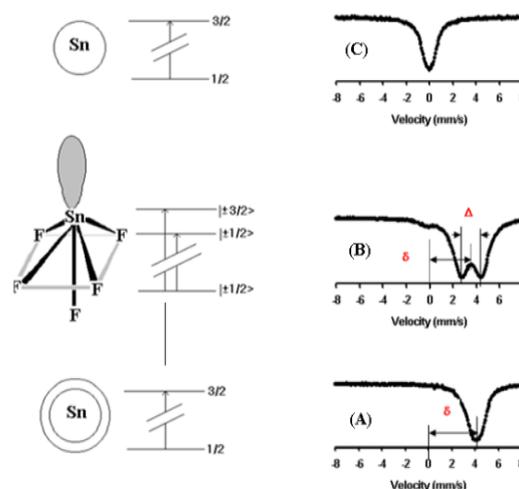


Fig. 1 Typical Mössbauer spectra: (A) Sn²⁺ stannous ion, (B) covalently bonded Sn(II) in MSnF₄ (M = Ba and Pb), (C) Sn⁴⁺ in CaSnO₃.

The type of Mössbauer spectrum, as shown in figure 1, tells unambiguously the type of bonding that tin forms. A stereoactive lone pair (fig. 1(B)) creates an enormous electric field gradient at tin, thereby generating a large quadrupole splitting [3].

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Mössbauer spectroscopic characterization of magnetic, electronic and dynamic properties of selected Frank-Kasper phases

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Frank-Kasper (F-K) phases or topologically close-packed structures are a group of intermetallic compounds with a complex crystallographic structure and physical properties. The most known examples of F-K are: A15, Laves phases (λ), σ , μ , M, P, and R. Characteristic structural feature common to all F-K phases are high coordination numbers ranging between 12 and 16. Their physical properties are characteristic of the phase, and for a given phase they depend on composition. In particular, A15 compounds are known for their superconductivity e. g. Nb₃Sn, Nb₃Zr or Nb₃Ge. F-K compounds containing Fe are suitable for Mössbauer spectroscopic studies [1-6].

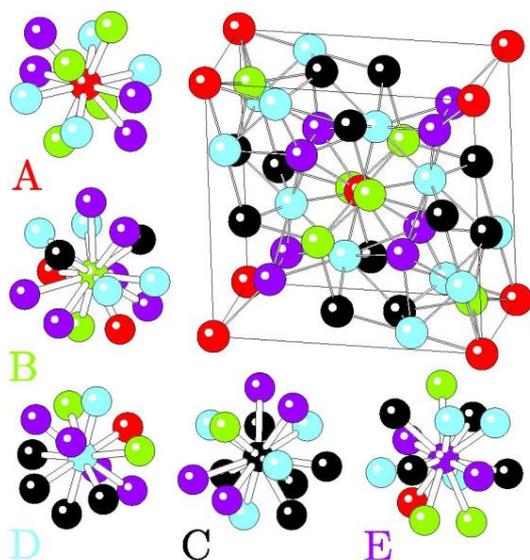


Fig. 1 Unit cell of σ . Five sub lattices designated as A, B, C, D and E and their nearest neighbourhood.

In this contribution presented will be results relevant to magnetic, electronic and lattice-dynamical properties of σ , μ and R in Fe-X (X = Cr, Mo, V) compounds. Concerning magnetic properties, a magnetic ordering temperature, T_C , will be discussed. Electronic properties will be tackled by presenting results on the isomer shift,

whereas the Debye temperature, force constant, mean-square amplitude of vibrations as well as mean-square velocity of vibrations will illustrate the lattice-dynamical properties of the investigated compounds. Notably, T_C in σ -FeV can be changed by two-orders of magnitude by adjusting the composition, the isomer shift can differ by 0.12 mm/s between μ and σ in Fe-Mo having the same composition. Even more spectacular properties were revealed as regards the lattice-dynamical properties. Here, was discovered a strong effect of magnetism on values of the Debye temperature, force constant and the mean-square amplitude of vibrations – see Fig. 2.

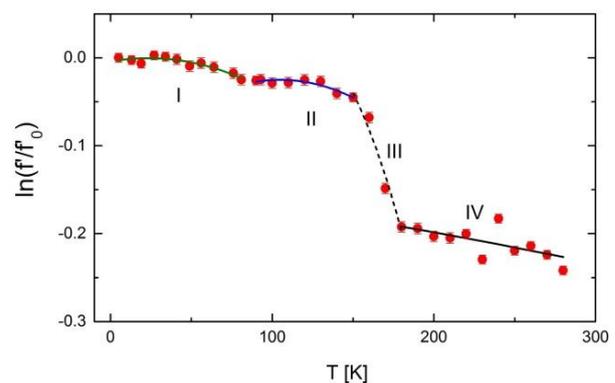


Fig. 2 Ln of a relative recoil-free factor, f/f_0 , versus temperature, T , for a σ -Fe₆₀V₄₀ compound. Four ranges can be distinguished corresponding to paramagnetic (IV), ferromagnetic (III) and spin-glass (I+II) phases.

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Mössbauer spectroscopy and the understanding of the role of iron in neurodegeneration

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The possible role of iron in neurodegeneration is related to oxidative stress, which can be triggered by Fenton reaction:



In this reaction hydroxyl free radical production is generated by divalent iron. Several studies tried to assess the concentration of iron in human brain structures involved in neurodegenerative diseases, which represent a group of disorders related to a progressive death of nervous cells in specific brain locations. Typical neurodegenerative diseases include Parkinson's, Alzheimer and several other disorders. Out of them this is the Parkinson's disease (PD), which was the most studied in regard of the role of iron. Motor symptoms of the disease depend on the destruction of substantia nigra (SN), small structure located in mesencephalon and known for high concentration of iron. The concentration of iron in this structure is of about 200 µg/g wet tissue. Studies aimed to compare the concentration of iron in parkinsonian and control SN gave controversial results. Some groups found an increase of the total iron concentration with high amounts of divalent iron [1], while other did not find any difference between PD and control [2]. The results obtained with the use of various methods gave dispersive values for the concentration of iron in SN ranging from 40 to 400 µg/g wet tissue (a factor of 10!). The history of these research was presented by us in 2012 [3]. The analysis of these discrepancies lead us to the conclusion that the choice of the method is crucial. As the substantive questions were: 1/ what is the concentration of iron in the samples, 2/ what is the proportion of divalent vs. trivalent iron in the samples, and 3/ what is the iron-binding compound, it seemed appropriate to use Mössbauer spectroscopy to answer those questions. Our long-lasting investigations in collaboration with Professor Erika Bauminger allowed to answer unequivocally those questions. We found no difference in the concentration of total iron between

PD and control, with the ratio of iron in PD vs. control being 1.00±0.13. We demonstrated no detectable concentrations of divalent iron, which according to our computerized simulations, could not exceed 5% of the total iron [4]. According to our studies the main iron-binding compound in SN, both in PD and control is ferritin. Our results were summarized in a review paper [5]. Our further studies inspired by Professor Bauminger demonstrated with the use of ELISA (enzyme-linked immunosorbent assay) technique a change in the structure of ferritin in parkinsonian SN with a decrease, compared to control, of L-ferritin. This subunit of ferritin is involved in the safe storage of iron within the ferritin shell. Therefore this significant decrease of L-ferritin detected by us already in the preclinical stage of PD could allow an efflux of iron from the ferritin shell [6] and an increase of non-ferritin iron in PD SN [7]. It is important to note that the concentrations of this non-ferritin iron are of about 1000 times smaller than the concentration of the total iron in SN (~100 ng/mg of wet tissue) [7]. The role of the change of the structure of ferritin as a possible starting point of the whole process of neurodegenerations was presented by us in a review paper [8].

Conclusion: Mössbauer spectroscopy is a very successful and promising technique for the studies of iron mediated oxidative stress in human neurodegenerations.

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Testing time dilation due to acceleration of a rotating Mössbauer absorber using synchrotron radiation

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A cornerstone of Relativity Theory is the Clock Hypothesis (CH) which states that the rate of an accelerated clock is equal to that of a co-moving non-accelerated clock. If the CH is false, the rates of two clocks with different accelerations and equal instantaneous velocities are different, then one expects an additional Doppler-type shift due to this acceleration. Since this expected shift is very small, it can be detected by the shift in the Mössbauer spectrum of an accelerated absorber.

To test the CH, an experiment was performed in 2013 by Y. Friedman, I. Nowik, I. Felner, G. Wortmann and H. -C. Wille under the leadership of Ralf Röslerberger at the Dynamics Beamline P01 of PETRAIII at DESY, Hamburg with the aim to detect the shift in the energy spectrum at two points of incidence A and B of a fast rotating ^{57}Fe Mössbauer foil.

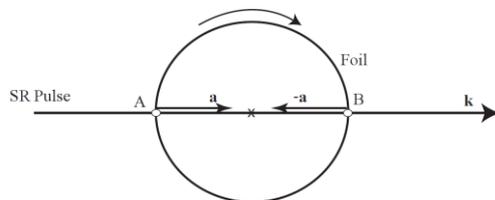


Fig. 1 The experimental setup at PETRAIII

Time-domain interferometry based on nuclear forward resonant scattering was used to measure the time spectrum of the delayed radiation from the rotating system. For a thin foil, the above shift is expressed by the change in the effective thickness of the combined time spectrum due to rotation

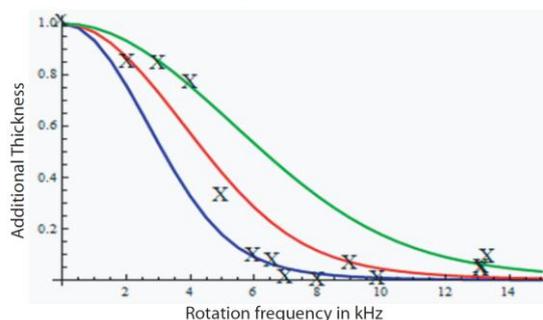


Fig. 2 The measured additional effective thickness relative to that of one foil, at different rotational frequencies

Fig. 2 indicates that acceleration does influence time.

Additional two experiments were performed by the team using the Synchrotron Mössbauer Source at beamline ID18 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France in 2014 and 2015.

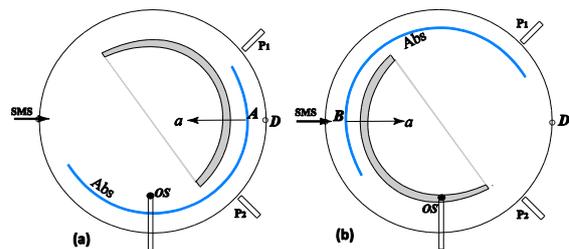


Fig. 3 The experimental setup at ESRF.

Absorption lines for a potassium ferrocyanide single line rotating absorber were obtained by separating the count for states (a) and (b) for each run.

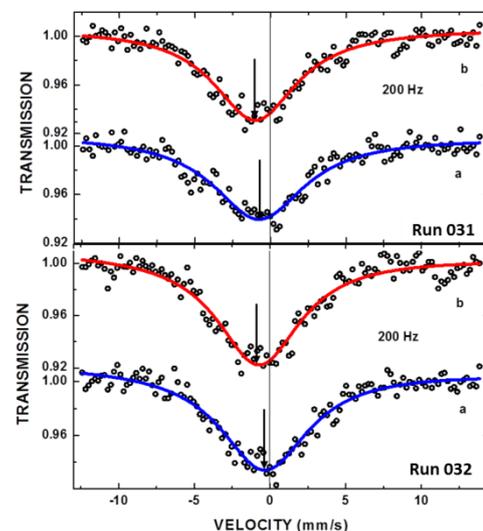


Fig. 4 The observed relative shift between absorption lines for states (a) and (b) in two runs at 200Hz

This also indicates the influence of acceleration on time.

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Mössbauer spectroscopy - a useful method for classification of meteorites

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Ordinary chondrites are the most popular meteorites (77% of observed falls). There are 3 types of ordinary chondrites: LL, L and H. They differ in the amount of iron (the highest amount of iron is in H-type, the lowest in LL-type). In Fig. 1 typical Mössbauer spectra of these types of meteorites are presented.

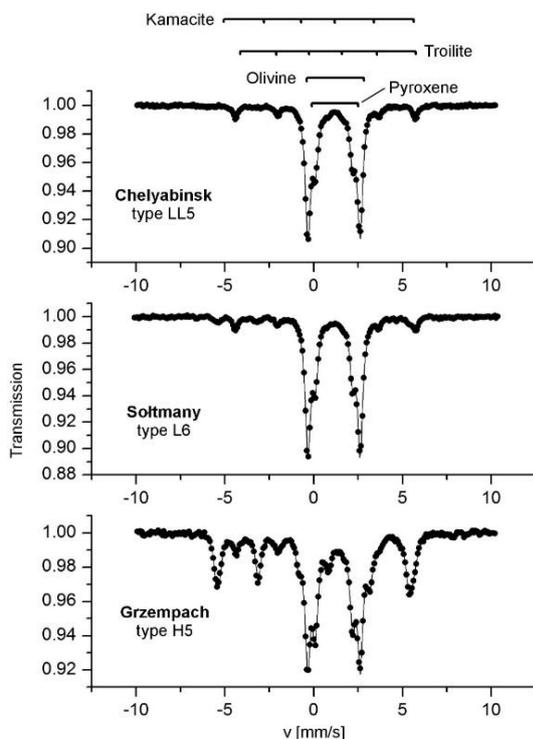


Fig. 1. Mössbauer spectra of ordinary chondrites type LL, L, and H types.

The first suggestion of the application of Mössbauer spectroscopy to the classification of stony meteorites was made by W. Herr and B. Skerra [1] in 1969. It was strictly connected with the classical method of classification of meteorites and was based on the precise determination (from the Mössbauer spectra) of the concentration of the different mineralogical phases in various types of the meteorites. This idea was abandoned because of difficulties related to the determination of the amount of iron in the investigated samples.

In early 2000 a Mössbauer group from India started systematic studies on the possibility of the application of Mössbauer spectroscopy to the classification of ordinary chondrites [2, 3, 4]. Using different types of plots such as “areas for metallic phases vs. areas for nonmetallic phases”, “areas for metallic phases vs. areas for silicate phases” and “areas for pyroxene vs. areas for olivine” this group determined regions for H, L and LL types of the meteorites. Using this method they were able to classify the meteorite Itawa-Bhopij fallen in India in 2000 as ordinary chondrite type L.

Our preliminary analyses on the possibility of the application of Mössbauer spectroscopy to the simplified classification of the ordinary chondrites were presented in a paper published in 2014 [5].

Now we came to the conclusion that the best method of the classification of the meteorites based on Mössbauer spectroscopy should apply all four values of the spectral areas connected with olivine, pyroxene, troilite and metallic phase. To calculate the probability of the identity of the specific meteorite to LL, L or H type we will use special statistical methods.

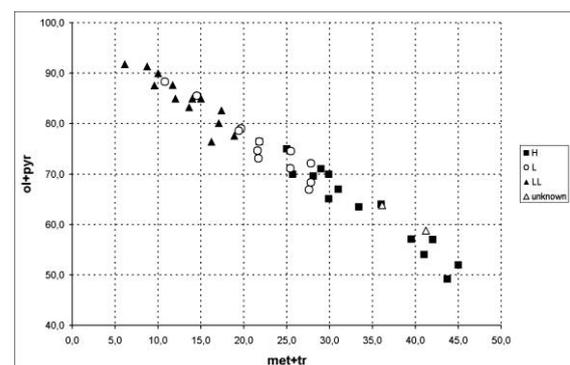


Fig. 2. Plot of spectral areas (olivine + pyroxene) vs. (troilite + metallic phase) for ordinary chondrites.

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Spin crossover in hybrid nanomaterials

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Iron(II) spin crossover (SCO) complexes continue to attract a great deal of interest,^[1,2] due to their potential technological applications, for instance as pressure sensors.^[3] SCO nanomaterials have emerged as an appealing class of materials considering nanostructuring processes and size reduction effects.^[4] Although sophisticated and expensive techniques can be used for the preparation of SCO nanoparticles, we have introduced a botanic biomembrane as a soft and green support for deposition of SCO micro and nanocrystals, which were used for transfer printing on various solid inorganic supports.^[5] More recently, we investigated the SCO properties of a hybrid nanomaterial,^[6] based on a metal organic framework embedding the mononuclear SCO complex [Fe(HB(pz)₃)₂], earlier studied by Grandjean *et al.* and recently reinvestigated by Bousseksou *et al.*^[7] We have also studied the composite material made of MCM-41 and 1D selected Fe(II) 1,2,4-triazole coordination polymers.^[8] This later class of SCO materials, which were shown to present the LIESST effect,^[9] afforded recently the first 1D chain with 1,2,4-triazole ligands displaying a thermally induced two-step spin conversion.^[10] This compound was discovered in the frame of our general investigation of a new range of porous metal organic frameworks including 1,2,4-triazole ligands built from amino acids building blocks.^[11] Within the same family, we recently isolated a 1D SCO chain switching at room temperature with a wide bistability domain of 60 K, which will be discussed in detail.^[12]

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Mesoporous structures and Metal Oxide Frameworks (MOFs) investigated by Mössbauer spectrometry

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Metal Oxide Frameworks (MOF) have been widely investigated for the last 20 years: indeed, large efforts in their preparation gave rise to well understand the role of both polyfunctional organic linkers and inorganic skeleton. In addition, they allow control the structure, the morphology and the chemical composition of these hybrid nanostructures to be well controlled, together with their magnetic properties, electronic, optical or transport. Such a fundamental approach makes these materials suitable for some applications in gas storage, drug delivery, ...

The main structural families will be first detailed as well as their different physical properties in relation with their applications. Then we focused on the role ^{57}Fe Mössbauer spectrometry in investigating such hybrid materials.

The structural and chemical properties of Fe-containing MOFs can be better modelled by ^{57}Fe Mössbauer spectrometry which provides valuable information, complementary to diffraction

techniques. Indeed, Mössbauer spectrometry remains an excellent tool to investigate the influence of different parameters such as: i) the presence of fluorine (used as a mineralizer agent during synthesis), ii) the presence of water molecules trapped in the porous matrix, iii) the changes in the organic ligand with different functional groups, iv) the structure, since the distances and atomic environments may change because of the flexibility of these porous solids, and v) to follow *in situ* the insertion of Li and the reversibility of both redox and sorption properties. Both the stability and the degradation can be followed by *in situ* measurements to understand the evolution of the structure and composition depending on temperature and pressure conditions including the chemical environment. Illustrative example of the relevance of Mössbauer spectrometry is also given from nanocomposites resulting from nanoparticles grafted on MOFs.

Application of Mössbauer spectroscopy in industrial heterogeneous catalysis

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In a supported catalyst system, phase specific mixed metal oxides have recently attracted great interest for use as catalyst and catalyst supports, since these materials give rise to well dispersed and stable metal particles on the surface of the support materials and consequent improved catalytic performance. In this regard iron (III) oxide catalysts, which have catalytic characteristics similar to those of CeO₂ but are considerably cheaper to produce, have attracted particular interest as catalysts for the preferential oxidation of carbon monoxide (CO PROX).

Iron oxides supported precious metal catalysts have been proven to be very effective for low-temperature CO oxidation. However, the high cost and limited availability restrict their use. In searches for an alternative, recent studies have found that Fe³⁺ had a promotional effect on the activity of Cu-Ce catalysts used for CO oxidation. The Cu-based oxide catalysts have good catalytic performances for CO-PROX, which coupled with their low fabrication costs make them an efficient alternative to the precious metal catalysts.

The influence of Fe loading in Cu-Fe phases and its effect on carbon monoxide (CO) oxidation in H₂-rich reactant streams were investigated with the catalyst material phases characterized by field emission scanning electron microscopy, X-ray diffraction (XRD) studies and Mössbauer spectroscopy. There was no change in the oxidation state of the Fe ions with copper or iron loading. In addition to the formation of the CuFe₂O₄ phase, the Fe and Cu were found to be incorporated into a Cu-Fe super saturated solid solution which improved CO oxidation activity, with carbon dioxide and water produced selectively with a high catalytic activity in depleted hydrogen streams. A relatively high conversion of CO was obtained with high Fe metal loading.

In the copper-iron composite system, the primary active phase is CuFe₂O₄. However, the role of CuFe₂O₄ on CO oxidation has not been explored

yet, and it is still a challenge to develop a Cu-Fe composite material for the desired enhancement of catalytic performance. Obviously, to prepare the effective catalysts for the CO-PROX reaction, one could apply solution routes and a low temperature treatment for combining the Fe and Cu oxides in the one sample. In this study, Cu-Fe/Al₂O₃ and Cu and Fe loaded CuFe₂O₄, were synthesized (with a 5 wt. % of Cu and 5 wt. % of Fe loading) and the role of Fe species on the active phase and in the activity of the catalyst were investigated.

The effect of the FePO₄ material phase transformation in the direct selective oxidation of methane to methanol was studied using various oxidants, *i.e.* O₂, H₂O and N₂O. The phases of the heterogeneous catalyst applied, before and after the reactions, were characterized by Mössbauer spectroscopy. The main reaction products were methanol, carbon monoxide and carbon dioxide, whereas formaldehyde was produced in rather minute amounts. The Mössbauer spectra showed the change of the initial catalyst material, FePO₄ (tridymite-like phase (tdm)), to the reduced metal form, iron(II) pyrophosphate, Fe₂P₂O₇, and thereafter, the material phase change was governed by the oxidation with individual oxidizing species. Mössbauer spectroscopy measurements applied along with X-ray diffraction (XRD) studies on fresh, reduced and spent catalytic materials demonstrated a transformation of the catalyst to a mixture of phases which depended on operating process conditions. Generally, activity was low and should be a subject of further material optimization and engineering, while the selectivity towards methanol at low temperatures applied was adequate. The proceeding redox mechanism should thus play a key role in catalytic material design, while the advantage of iron-based heterogeneous catalysts primarily lies in them being comparably inexpensive and comprising non-critical raw materials only.

Microbiological applications of the ^{57}Co emission and ^{57}Fe transmission variants of Mössbauer spectroscopy and their 'crossroad'

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People believe that they govern the world... However, in the reality, our world – from the formation of minerals to human health and, finally, to decomposition of organic matter – is governed by the tiny sub-world of microorganisms. Therefore the extremely diverse and complicated field of microbiology has long been increasingly attracting the attention of researchers. Nevertheless, the most impressive progress in microbiology has been achieved with the involvement of modern physicochemical instrumental techniques which allow molecular-level studies to be performed.

Mössbauer spectroscopy in its conventional ^{57}Fe transmission variant (TMS) has been applied for decades to studying various aspects of iron transformation, metabolisation and mineralisation by microbial cells [1–3]. Along with ^{57}Fe TMS, the ^{57}Co emission variant of Mössbauer spectroscopy (EMS) is also useful in monitoring metabolic transformations of cobalt in microbial cells and its chemical state in various biological samples [3–7]. However, the potentials of ^{57}Co EMS in this field have so far been significantly underestimated (see reviews [3, 5]), although the emission variant is ca. 10^4 -fold more sensitive than ^{57}Fe TMS.

In this talk, some recent representative examples will be discussed illustrating the applicability and high sensitivity of ^{57}Co EMS in studying cobalt(II) binding (at its trace concentrations in the medium) and metabolisation in live bacteria [5–7], as well as possibilities of ^{57}Fe TMS in monitoring the state of the microbial cellular iron pool [1–3]. The latter (formed, e.g. from $^{57}\text{Fe}^{\text{III}}$ complex used as an iron source, reductively assimilated by live bacteria from the medium) includes high-spin Fe^{II} and paramagnetic Fe^{III} complexes (featured by quadrupole doublets with typical parameters) at varying ratios, as well as nanocrystalline ferric oxyhydroxide-containing constituents of the core of bacterial ferritin (iron storage protein) [2, 3].

There is a particularly interesting 'crossroad' of ^{57}Co EMS and ^{57}Fe TMS related to the involvement of Co^{2+} in *de novo* synthesis and/or repair of [Fe-S]

clusters in bacterial cells as a basis of Co^{2+} toxicity for bacteria [3]. As was found by using ^{57}Co EMS [7], one of the spectral components (with specific Mössbauer parameters) in emission spectra of bacterial cells after their contact with $^{57}\text{Co}^{2+}$ coincided by its isomer shift (0.89 mm/s vs. $\alpha\text{-Fe}$) and quadrupole splitting (1.97–2.00 mm/s; $T = 80$ K) with the specifically coordinated Fe site in the $[\text{4Fe-4S}]^{2+}$ cluster of LytB protein, the last enzyme in the methylerythritol phosphate (MEP) pathway [3]. These Mössbauer parameters of the site (25% of the whole spectral area) correspond to high-spin Fe^{2+} with three S donor atoms and additional three (or two) O and/or N donor atoms in its first coordination sphere. The same parameters of the spectral component found in ^{57}Co emission spectra of bacterial cells (after their contact with $^{57}\text{Co}^{2+}$) are likely to reflect the incorporation of $^{57}\text{Co}^{2+}$ in a Fe-S cluster at a site with similar coordination.

Acknowledgements

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Mössbauer spectroscopic characterization of spin crossover 2D Hofmann-like coordination polymer materials

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The ⁵⁷Fe Mössbauer spectroscopic research field associated with spin crossover (SCO) behavior in Hofmann-type coordination polymer compounds might be going to be potentially related with valuable smart materials, promising materials for applications as components of memory devices, displays and sensors so on. In coordination chemistry, metal ions of 3-d electrons with d⁴-d⁷ configuration in an octahedral crystal field allow a possibility of SCO phenomena between the low spin (LS) and the high spin (HS) states, being accompanied by color changes. Octahedral iron(II) SCO systems with 3d⁶ which can be transitioned between the diamagnetic (t_{2g})⁶ and the paramagnetic (t_{2g})⁴(e_g)² configuration might be widely and deeply investigated as smart materials.

Coordination polymer materials with bistable systems between the LS and the HS states, usually triggered by external stimuli, such as temperature, light, pressure and guest molecule inclusion, are a family of potential candidates for smart materials because the change of the crystal cell volume between the HS and LS states is very large. Various SCO iron(II) coordination compounds, especially those with polymeric 1D, 2D and 3D frameworks, have been intensively investigated since their polynuclear geometries linked framework structures enhance cooperative effects which work among the SCO species resulting in SCO behavior with large hysteresis and transition temperature ranges around RT.

Since the typical SCO behavior of the fundamental Hofmann-like coordination polymer Fe(pyridine)₂Ni(CN)₄ was found using ⁵⁷Fe Mössbauer spectroscopy and SQUID magnetometry in 1996,[1] SCO Hofmann-like metal-organic frameworks containing 2D layers[2] and 3D structures, with octahedral iron(II) ions linked by cyanidometallates along the in-plane directions, have interesting magnetic behaviors and have been studied thoroughly for the developing new SCO materials in order to obtain potential applications in smart materials.[3,4] Using square-planar geometry [M(CN)₄]²⁻ units and linear [M(CN)₂]⁻ units allow two crystallographic types of Hofmann-

like SCO coordination polymer compounds respectively: cyano-bridged Hofmann-like 2D frameworks realized using square-planar tetracyanometallate units in the general formula Fe(L)₂[M(CN)₄] (M = Ni²⁺, Pd²⁺, Pt²⁺; L is a monodentate ligand), and complexes using linear dicyanometallate units forming 2D frameworks in the general formula Fe(L)₂[M(CN)₂]₂ (M = Ag⁺, Au⁺; L is a monodentate ligand).[5,6] Using bidentate ligands such as pyrazine allow 3D frameworks in the general formula FeL[M(CN)₄] and FeL[M(CN)₂]₂ (L is a bidentate ligand) respectively, which can be accommodated with guest molecules.

In this context, we report the preparation of new cyanide (CN)-bridged Fe-M (M = Ni, Pd, Pt) coordination polymers using Ethyl Isonicotinate; Fe(Ethyl Isonicotinate)₂M(CN)₄. The crystal structures of Fe(Ethyl Isonicotinate)₂M(CN)₄ (M = Pd or Pt) have been determined from the single-crystal X-ray diffraction (XRD). The structure shows that the Fe(II) ions coordinate to Ethyl Isonicotinate ligands in trans geometry at axial sites and bridged by the cyanidometallate in equatorial sites. The crystal structure of Fe-Ni complex was similar to those of Fe-Pd and Fe-Pt ones from the powder XRD analysis. From the measurements of magnetic susceptibility (χ_MT), spin transition temperature and χ_MT in high spin states of Fe-Pd and Fe-Pt complexes were almost the same, but higher than that of Fe-Ni one. We will discuss the preparation methods and spectroscopic characterizations using ⁵⁷Fe Mössbauer spectroscopy which is a very powerful tool for SCO compounds

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In-Situ Mössbauer and PIXE analysis of planetary surfaces, comets, and asteroids

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The miniaturized spectrometers for Mössbauer (MIMOS II) and X-ray spectroscopy (APXS) for extraterrestrial Solar System Exploration have been included already in the exploration of the planet Mars (Mars-Exploration-Rover missions Spirit and Opportunity; Beagle 2 lander), and the in-situ investigation of a comet (ROSETTA mission) [1-5]. Both instruments are part of the payload of proposed space missions to different Solar System bodies. These include Asteroids, comets, Martian moons, the Earth Moon, Mars, Venus, and Mercury. Because of the very different environmental conditions, for each Solar System target the instruments have to be modified and adapted to those specific situations. We will discuss some examples of mission projects, and how instruments have to be modified for different cases. First results will be presented and discussed.

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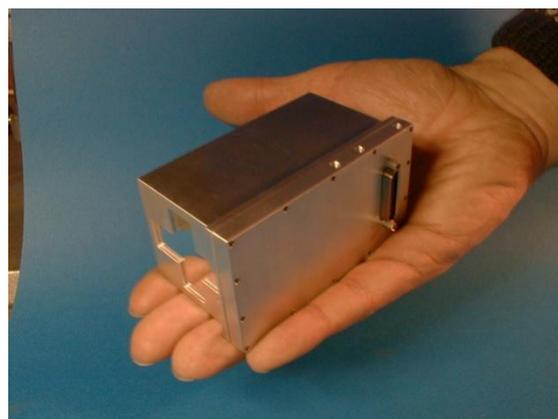


Fig. 1. The miniaturized Mössbauer Spectrometer MIMOS II

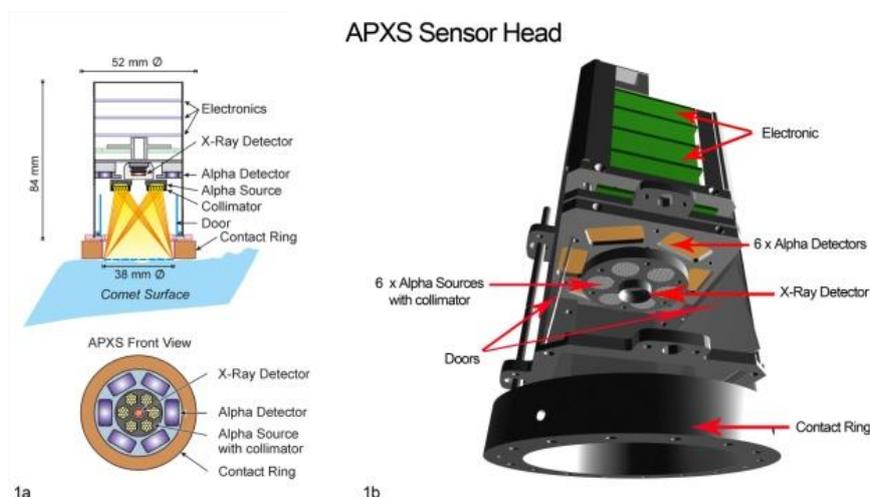


Fig. 2. The X-ray Fluorescence Spectrometer APXS for chemical analysis of planetary surfaces, comets, and other solar system bodies

Tuning magnetism and magneto-transport by cluster organization in Fe based nano-globular thin films

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Since the discovery of giant magnetoresistance effect, ferromagnetic multilayers and nanogranular thin films have attracted much research interest due to both fundamental and technological striking queries. Different magnetic and magneto-resistance effects have been reported in the two geometrical structures, e.g. the case of superparamagnetic clusters dispersed in conductive metallic matrices and in case of thin ferromagnetic layers sandwiching conductive metallic layers, respectively. However, no trials for a complex investigation involving a quasi-continuous change of the cluster organization, starting from almost randomly distribution to almost lamellar organization, has been considered.

The present work reports on the possibility to tune the magnetic and magnetoresistive properties of Fe-Au granular thin films by controlling the morphology and organization of magnetic clusters into the conductive metallic matrix via specific processing conditions. Fe-Au granular thin films of different Fe concentrations have been prepared by rf-magnetron sputtering technique at different temperatures of the substrate. The morphology, size distribution and organization of the magnetic clusters have been investigated by Scanning Electron Transmission Microscopy (in section) whereas the local magnetic structures with the involved atomistic configurations and local interactions were analysed via ⁵⁷Fe Conversion Electron Mössbauer Spectroscopy. Magnetic anisotropy and texture as well as specific relaxation effects were also investigated by vector Magneto-Optic Kerr Effect and Superconducting Quantum Interference Device magnetometry. Different magneto-resistance scattering mechanisms in the considered nanoglobular thin films were studied by the linear four probe method under variable fields/

temperatures and further discussed in relation to their specific magnetic peculiarities (Figure 1). Theoretical estimations of the involved macro-spin structures have been considered in the frame of the OOMMF (Object Oriented Micromagnetic Framework) public domain software, developed by the Applied and Computational Mathematics Division of NIST, being shown that the experimentally observed magnetoresistance effects can be explained by the magnetic interactions between the Fe nanoclusters as imposed via their specific organization.

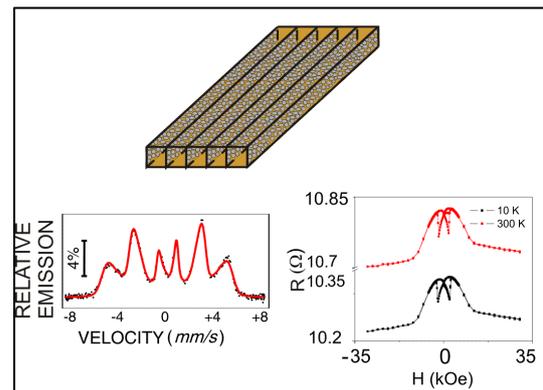


Fig. 1 A lamellar organization of Fe clusters (about 3 nm average size) in the Au matrix was evidenced in the Fe₃₀Au₇₀ nanoglobular film, involving a specific local magnetic configuration and electron scattering mechanism.

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Mössbauer and XRD investigations of electrodeposited novel binary, ternary and quaternary alloy coatings

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Electrodeposition processes have the potential to facilitate the deposition of alloys or alloy phases which are non-existent in the thermal equilibrium diagram and cannot be prepared by thermal methods. Electrodeposition has the potential to yield amorphous alloys, which are non-equilibrium and thermodynamically metastable, and they have different structures, and, hence, different properties from those obtained from a thermal process giving metallurgical equilibrium conditions. These phases can be very important in relation to their potential for technological applicability. For example, electrodeposited tin-based alloys at the nanometer scale are viewed as important electrode materials for future battery applications and environmentally acceptable corrosion resistant materials. The use of electrochemical deposition processes to produce compositionally modulated materials are often the simplest, the most cost effective. Another important feature of modern electrodeposition is the ability to develop electrolytes for the process which are environmentally acceptable.

The one of the aims of our investigations was to examine a suitable electrolyte for the potential deposition of tin based alloys containing Fe and/or Co and/or Ni and to study the effects of the major plating parameters, such as current density, deposition time, deposition temperature and pH, on the phase composition and the structure of the resulting deposits using techniques as ⁵⁷Fe and ¹¹⁹Sn conversion electron Mössbauer spectroscopy (CEMS), and X-ray diffraction (XRD). Gluconate based electrolyte using a constant current technique ensured the metal codeposition. Metal codeposition together with strong hydrogen evolution enhanced the formation of the random structure. DC and pulse plating conditions have been established at which adherent, bright, uniform amorphous Sn-Fe binary, Sn-Co-Fe and Sn-Ni-Fe ternary and Sn-Fe-Co-Ni quaternary alloys can be electroplated from gluconate- and peptone containing bath onto Cu substrate.

XRD results revealed the amorphous character of the novel binary, ternary and quaternary alloy coatings electroplated at stated conditions.

⁵⁷Fe and ¹¹⁹Sn CEMS proved to be an excellent tool to characterize the phase composition and short range order of electrodeposited tin based iron, cobalt and nickel containing alloys and to establish the suitable parameters for electroplating of novel binary, ternary and quaternary alloy coatings. A review of our previous [1-7] and new results will be given.

The typical ⁵⁷Fe Mössbauer spectra of the amorphous coatings showed a dominant magnetically split sextet with broad lines and a minor doublet, assigned to ferromagnetic and paramagnetic amorphous alloy phases. For the interpretation of derived hyperfine field distributions a nearly random distribution of alloying elements can be considered as a model of short-range order in the amorphous phases.

Magnetically split ¹¹⁹Sn Mössbauer spectra reflecting transferred hyperfine field were observed in the case of amorphous ferromagnetic binary, ternary and quaternary alloy coatings.

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Mössbauer spectroscopy characterization of $[\text{Fe}(\eta^6\text{-C}_6\text{H}_{6-n}\text{Me}_n)_2]^{2+}$ dications

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Iron is one of the most abundant elements on the Earth and also in Mössbauer research. The present study is a part of our search for novel iron compounds that now play an important role in the development of specific areas of metalloorganic and metallocarborane chemistry of iron [1].

As a part of the chemistry these complexes, a short review on the synthesis of bis-(arene) iron complexes and reactions associated with direct and indirect replacement of arene ligands in these complexes is presented. These reactions lead to a broad variety of novel iron sandwich compounds that now play an important role in the development of specific areas of metalloorganic and metallocarborane chemistry of iron. The review comprises recent synthetic routes and approaches to iron sandwich complexes, of which the most significant have been arene and cyclohexadienyl ferradica- and ferratricarba-boranes, together with new types of piano-stool structured compounds. The reader will also find references to methods of structural characterization of individual compounds in this area of chemistry.

At the room temperature reaction between polymethylated arenes $\text{C}_6\text{H}_{6-n}\text{Me}_n$ ($\text{Me} = \text{CH}_3$) and FeCl_2 is shown in [1, 2]. The presence of AlCl_3 in heptane for 24-36 hours proceeded with the formation of the samples. The details of the formation of series of the $[\text{Fe}(\eta^6\text{-C}_6\text{H}_{6-n}\text{Me}_n)_2]^{2+}$ dications were described in [2, 3].

To characterize the thermal behaviour and compositional/structural evolution we used the Mössbauer spectroscopy, XRD and SEM techniques.

Mössbauer spectroscopy has been chosen as a further tool of structural characterization. Mössbauer effect experiments were performed with a constant acceleration spectrometer using a $^{57}\text{Co}/\text{Rh}$ source. Calibration was done using a thin ($12.5 \mu\text{m}$) $\alpha\text{-Fe}$ foil at room temperature. Hyperfine parameters including isomer shift, quadrupole splitting, and relative areas revealed differences in the samples with varying amount of methyl groups. At the room temperature MS were fitted by several doublets which corresponded to Fe^{2+} and to Fe^{3+} . The Fig. 1 shows the evolution of Mössbauer

spectra of the sample from without methyl groups ($n=0$) to the sample with six methyl groups ($n=6$).

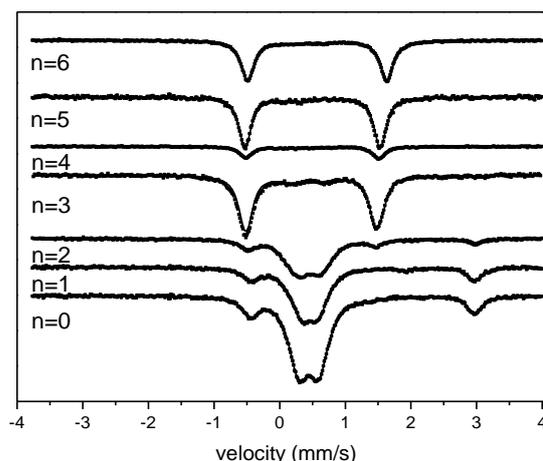


Fig. 1 The evolution of the Mössbauer spectra of the sample from without methyl groups ($n=0$) to the sample with six methyl groups ($n=6$)

The reader will also find references to methods of structural characterization of individual compounds in this rapidly developing area of iron-sandwich chemistry. It is readily seen that for the doublet ascribed to Fe^{3+} the isomer shift, equal to $\sim 0.5 \text{ mm/s}$, does not change while the quadrupole splitting varies with the number of arene methyl groups (n). It can be concluded that the effects of the Me-substituents (Fe) on the arene ligands are transmitted via the arene ring onto the iron centre. The effect can be employed for useful inter-comparisons among iron environments that differ in the number of substituents.

Acknowledgment

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Vaporization of steel by electric wire explosion in water: phase transitions and oxidation

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Electric wire explosion (EWE) is a known method for production of nanoparticles in various gases and liquids. In most of cases pure metals are vaporized, e.g. Al, Cu, Au, Fe, preferably in water. The process is rather complex, a series of steps results in the final product(s). A few reports have also been published on EWE of alloys. In the present communication comparison of products of vaporization of a low carbon and an austenitic steel (ASI 304; 18 % Cr, 10 % Ni, 68 % Fe) is presented.

Steel wires with ca. 0.2 and 0.3 mm diameters were exposed to max. 7 kA impulses for ca. 6 microseconds in water. Core-shell structured, metal and metal oxide sol is formed, sedimentation takes place in several days afterwards. Different fractions were collected and analysed by Mössbauer spectroscopy, XRD, SEM (with EDX) and HRTEM (with electron diffraction).

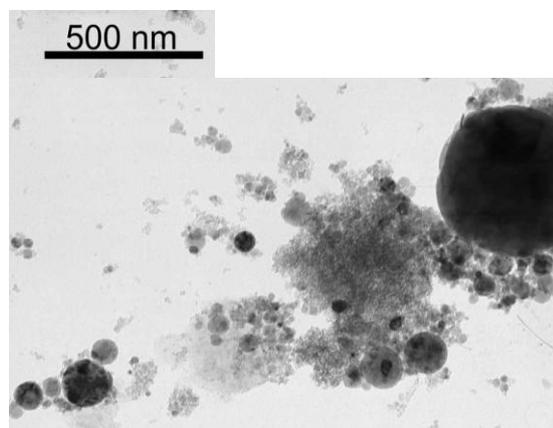


Fig. 1 TEM image of products from ASI 304 steel wire

Sizes of the formed metallic globuli cover a wide range (from nanometres to microns, Fig. 1). Mössbauer spectrum of the fine fraction of the low carbon steel displays the expected shape, i.e. magnetic splitting of bcc phase is combined with some oxide (Fig. 2.a). In contrast, four components can be identified in the fine fraction of products of the austenitic steel, namely singlet of the original fcc phase, an iron oxide (~wüstite), sextet of an iron rich phase (~33 T) and a distribution of hyperfine fields (centered at ~30 T) originated from Fe,Cr,Ni alloy with local compositions.

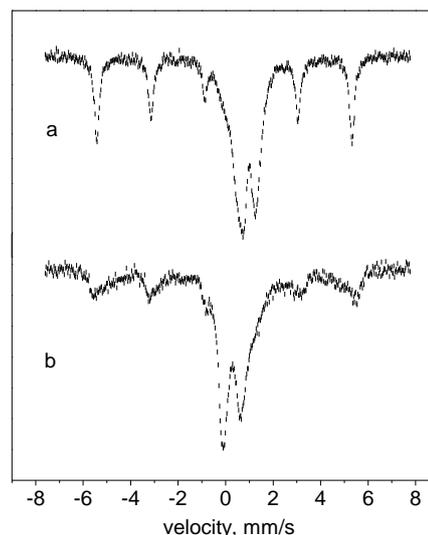


Fig. 2 Mössbauer spectra of the fine fractions of the vaporized steels, ferritic (a – top), austenitic (b – bottom)

The applied electric discharge results in melting and evaporation. A part of the excited metal vapour interacts with water immediately, water is decomposed, oxides are formed. The other, non-interacting part of the metal vapour is condensed, spheres of various sizes are formed, with compositions deviating from that of the original steel in an extent. Various stages of these processes are clearly manifested in XRD patterns (presence of different phases), in SEM (surface morphology and composition of oxides on metallic spheres) and in HRTEM images (high resolution images and electron diffractograms of oxides) as well. Thus, comparison of the products of the vaporization of two steel samples reveals that nanoparticles of pure metals can be prepared by EWE. In contrast, vaporization of alloy wires and condensation afterwards may result in significant compositional changes and structural phase transformations as well.

Acknowledgement

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Si or Sn in high capacity anode materials for Li-ion batteries?

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Lithium-ion batteries are now widely used as electrochemical energy storage systems because of their high energy density and good cycle life. However, new applications as portable electronic devices, electric vehicles or intermittent energy sources require improved performances and much effort has been devoted to the search for new electrode materials.

Concerning the negative electrodes, carbon is currently used but exhibits moderate specific capacity (372 mAh g^{-1}) due to the insertion mechanism that involves only 1 Li per 6 C. There are also safety problems due to the operating voltage close to that of metallic lithium. Increasing the electrode capacity requires considering other electrochemical mechanisms such as alloying or conversion reactions. This is the case of some elements, like Sn and Si, that reversibly alloy with Li at room temperature. For the theoretical maximum value of 4.4 Li per atom, tin and silicon based anode materials have specific capacities of 1 Ah g^{-1} and 4.2 Ah g^{-1} , respectively, strongly increasing the energy density compared to carbon. The average potential for these two materials is higher than $0.2 \text{ V vs Li}^+/\text{Li}^0$, avoiding lithium plating process. Unfortunately, they both suffer for large volume variations during charge-discharge cycles, leading to the loss of mechanical cohesion and electrical contacts and to instabilities of the surface electrolyte interphase (SEI). Different approaches have been proposed to minimize the effects of volume variations, including the use of nanomaterials, composites, oxides, intermetallic compounds and surface coating.

This talk concerns the comparison and the possible combination of Si and Sn in based anode materials. The attention will be focused on different intermetallic compounds MSn_x and MSi_x (where M represents transition metals) [1] and Si-enriched composites containing such compounds [2]. The materials were obtained by mechanosynthesis and characterized by different experimental tools. The analysis of the electrochemical reactions with Li was performed by operando experimental techniques including X-ray diffraction (Figure 1) and Mössbauer spectroscopy (Figure 2). For all the materials, the first lithiation (discharge) is irreversible and consists in a restructuring step that transforms the pristine material into a composite which should be considered as the real starting

material for cycling. The performances strongly depend on the microstructure of the lithiated material obtained at the end of this process but also on some changes observed during cycling. This can be related to the mechanical and electrical cohesion of the composite electrode and to interfacial reactions with the electrolyte. These different aspects and their influence on the anode performances will be discussed.

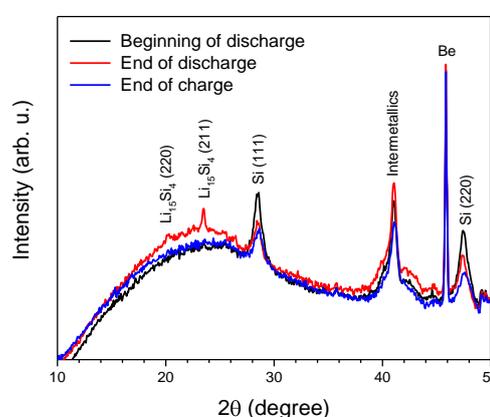


Fig. 1 Comparison between operando X-ray diffraction patterns obtained at different stages of the first galvanostatic cycle for $\text{Ni}_{0.12}\text{Ti}_{0.12}\text{Si}_{0.76}$ composite.

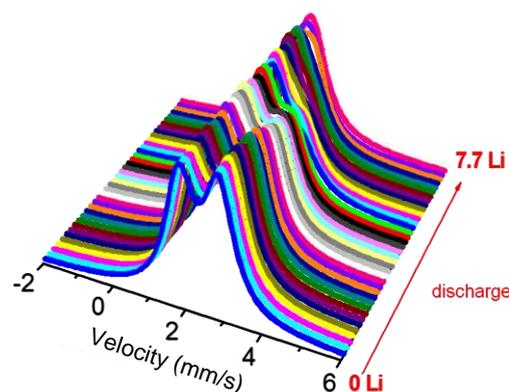


Fig. 2 Evolution of the operando ^{119}Sn Mössbauer spectra obtained during the first galvanostatic discharge of MnSn_2 .

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Mössbauer and EXAFS studies of bulk and thin film CoFe_2O_4 : cation distribution at room and low temperatures

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Cobalt ferrite, CoFe_2O_4 (CFO) is a remarkable oxide with the highest magnetocrystalline anisotropy of any spinel ferrite¹. It has an spinel structure, an fcc anion lattice with Co and Fe cations in tetrahedral (A) and octahedral (B) sites. Formally, it is expected to have a formula of $(\text{Fe}^{3+})_A(\text{Co}^{2+}\text{Fe}^{3+})_B\text{O}_4$. But the particular cation distribution can differ from the canonical one in real samples. In turn, the electronic and magnetic properties depend strongly on the cation distribution. The Fe cationic distribution has been probed by Mössbauer spectroscopy. Experiments have been reported indicating that thermal treatments of a given sample can affect the distribution².

But one issue with variable temperature Mössbauer experiments of CFO^{3,4} is that the spectra evolve strongly in the temperature range from 100 K to 300 K. In fact, the two sextets corresponding to Fe^{3+} in tetrahedral and octahedral positions change their relative areas by a factor of 3. This

evolution can be interpreted in terms of a different Debye characteristic temperature for Fe^{3+} in each site, or by a change of the cation population with temperature. Although at low temperature it is more natural to ascribe it to the former, it is still unusual. For example, in magnetite (iron spinel), there is nearly no difference between the Debye characteristic temperatures of both sites. In order to determine the origin of the observed changes we will compare Mössbauer spectra and extended x-ray absorption fine structure spectra acquired in single crystals and powder samples.

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Optimizing Fe²⁺ molecular switches by Mössbauer spectroscopy

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Switchable molecular compounds are in the forefront of research as potential candidates in the design of new, quick switching devices and high-density data storage systems. One of the most important family of these materials is formed by transition metal, especially Fe²⁺ centered organometallic complexes of medium ligand-field strength, the so called spin-crossover systems which – under certain circumstances – can undergo spin-state switching between low-spin (LS) and high-spin (HS) states. Regarding their room-temperature functionality, they became even more hopeful since the discovery of the light-induced excited-spin-state trapping (LIESST) phenomenon [1] which allows for switching the molecules back and forth using light pulses of different wavelengths.

One of the most promising candidate for practical usage is the tridentate polypyridine ligand containing [Fe(tpy)₂]²⁺ (tpy: 2,2':6',2''-terpyridine) complex which has, in spite of its strong ligand field, – at low temperatures and in certain matrices – a 10 orders of magnitude longer lived light-induced HS state than other similar strong-field complexes like [Fe(bipy)₃]²⁺ (bipy: 2',2''-bipyridine). In this complex the iron(II) center is surrounded by two pairs of 3 N donor atoms in D_{2d} symmetry as, due to geometrical constraints, the 6 N atoms cannot form an ideal octahedron around it. However, as proposed by McCusker and coworkers [2], releasing this geometric constraint may lead to a more relaxed and close-to-ideal local structure with enhanced ligand-field strength, a key requirement to get longer-lived excited states thus a real potential for room-temperature applications.

The tpy ligand can be modified based on both chemical intuition and quantum chemical calculations to design new, even more efficient molecular switches. The iron(II) complex of 2,6-di(quinolin-8-yl)pyridine (dqp) where an extra (condensed) side ring shifts the donor atoms further out thereby allowing for a less strained coordination is a probable candidate. The new molecules can be tested by various methods including Mössbauer spectroscopy. We present detailed comparison of the local symmetry, electronic structure and vibrational behavior of the tpy, tpy-OH and dqp complexes of iron(II) with SO₄²⁻ and PF₆⁻ counter ions based on the analysis of hyperfine interactions (HFI), second-order Doppler shift δ_{SOD} and the temperature dependence of the Lamb–Mössbauer factor f_{LM} as

taken from ⁵⁷Fe transmission Mössbauer spectra in the 77 K ≤ T ≤ 300 K temperature range.

Density-functional theory (DFT) calculations using the COSMO-B3LYP functional [3] show, in case of all complexes and counter ions investigated, excellent and fair correlation between experiment and theory for the isomer shift (IS) and the quadrupole splitting (QS), respectively.

The Debye model of lattice vibrations describes well the experimental temperature dependence of f_{LM} and δ_{SOD} . Nevertheless, with the fitted values of the Debye temperatures Θ_{D} , the temperature dependence of δ_{SOD} cannot be explained. This is the consequence of the fact that the temperature dependence of f_{LM} is related to $\langle x^2 \rangle$ and determined by acoustic phonons while that of δ_{SOD} is related to $\langle v^2 \rangle$ and determined by optical vibration modes.

DFT is also capable of predicting vibration modes of a molecule. Nuclear inelastic scattering (NIS) active modes were calculated for all complexes so that a) the dispersion (intra-molecular van der Waals) interaction was taken into account, b) the effect of the counterion was neglected and c) no effect of the crystal beyond the molecule was accounted for. A ‘multi-Einstein’ model based on 12–19 modes identified below 700 cm⁻¹ for the three complexes describes well the temperature dependence of δ_{SOD} , however it fails to explain that of f_{LM} . Indeed, the true NIS-active phonon density of state (DOS) consists of an additional low- Θ_{D} Debye-like part corresponding to the ‘acoustic’ lattice modes and a multi-Einstein part corresponding to the ‘optical’ molecular modes broadened by the lattice modes [4,5]. Evaluation of the experimental data in terms of this combined model is in progress.

In conclusion, by combining the HFI data and the temperature dependence of f_{LM} and δ_{SOD} from laboratory Mössbauer experiments with DFT calculations, a better understanding of switching phenomena, a basis for ligand design and further development of molecular switches can be reached.

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Biomedical applications of Mössbauer spectroscopy: The past, the present and future trends

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It is well-known that iron is a metal of life. Iron containing biomolecules play vitally important roles in the living systems. Tetrameric hemoglobins are responsible for reversible oxygen binding and transport in the red blood cells while monomeric myoglobins are the oxygen storage proteins in muscles. Some other heme proteins demonstrate various enzyme functions. Iron transport in mammals is realized by transferrin and lactoferrin while iron storage in the body is implemented by means of ferritins and hemosiderins. Various tissues, especially liver and spleen, contain ferritin and hemosiderin. Therefore, these iron containing proteins and tissues can be studied using ^{57}Fe Mössbauer spectroscopy that is why biological application of the technique was started at the early stage of the Mössbauer effect since 1960. Further these studies related to the normal proteins were extended to the study of iron containing proteins during some pathological states of organisms. Moreover, various investigations of pharmaceutical compounds containing ^{57}Fe , ^{119}Sn and ^{197}Au have been started using Mössbauer spectroscopy. Therefore, by nowadays a lot of studies can be considered as biomedical applications of Mössbauer spectroscopy (further we will limit these wide range of research as a proper biomedical within the framework of the comparative studies of normal and pathological states or the effect of factors caused diseases as well as the studies of developed and commercial pharmaceutical compounds).

Basing on the numerous results obtained in the field of biomedical applications of Mössbauer spectroscopy we can consider the main directions as follows [1–3]:

- studies of the quantitative changes of iron containing biomolecules related to pathological processes;
- studies of the qualitative changes in iron containing biomolecules related to pathological processes;

- studies of the effect of various environment factors (physical, chemical and biological) on iron containing biomolecules;

- studies of metabolic processes by means of analysis of the Mössbauer nuclides pathways in organisms;

- studies of dynamic processes;

- studies of pharmaceutical compounds and blood substitutes containing Mössbauer nuclides;

- miscellaneous studies.

The knowledge about the iron electronic structure and stereochemistry is very important because a number of iron containing enzymes and heme proteins contain iron in the active site. Therefore, it is also possible to consider studies of iron containing proteins for revealing so called the “drastic” and “small” changes with respect to the iron electronic structure. The drastic changes of the iron electronic structure could be related to the change of the iron valence/spin state resulting from protein transformation and/or destruction (the latter accompanied by the lack of protein functions mainly). The small changes of the iron electronic structure could be related to small stereochemical differences resulting in variations of the energy spectrum of the electron terms. In this case there is no protein destruction while it is possible some change of protein functions.

On the basis of analysis of the past and the present results of biomedical applications of the Mössbauer effect some future trends in the field are considered.

Acknowledgment:

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Spin state switching effects observed by Mössbauer spectroscopy: Stimuli-Responsive Drug Release

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A special focus is devoted to the problem of medical application of magnetic nanoparticles and molecular switches, such as spin crossover compounds in nanoscopic fibers. Spin crossover compounds attracted a great deal of interest for a potential application as switchable units in smart drugs. We approached several ways (1,2).

In order to meet this problem, we integrated spin crossover compounds into nanoscopic polymer fibers produced by electrospinning. In this contribution, we used the widely studied spin crossover compound $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and as well as Polyacrylonitrile (PAN) as polymer matrix. The synthesized systems were characterized by different microscopic and spectroscopic methods. Mössbauer spectroscopy, SEM, EDS and TEM display the integration of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ into fibers with a diameter of about 50 nm in average. Temperature-dependent IR spectroscopy and SQUID magnetometry reveal that the spin transition could be retained.

An approach for a stimuli-responsive drug release is presented. We show electrospun fibers consisting of PLA-PEG and biotinylated (Vitamin H, B7) albumin, which enables immobilization of avidin.

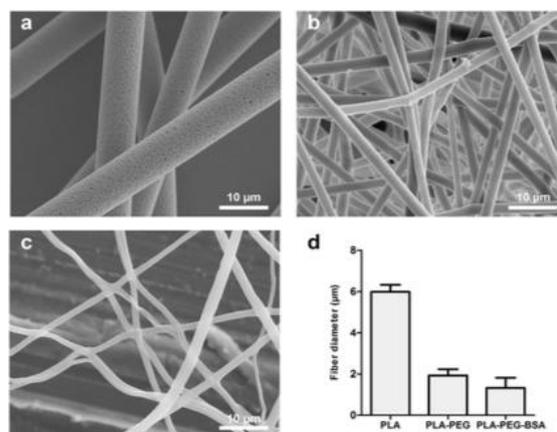


Fig. 1 Scanning electron micrographs for electrospun (a) PLA fibers (b) PLA-PEG blend fibers (c) Biotinylated PLA-PEG blend fibers (d) and their average diameter distribution.

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Infrared and Mössbauer spectroscopies as complimentary tools to study protein electric field

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Heme proteins are intensively used to study relationship between the structure, dynamics and function of proteins. It was shown that the protein electric field affects spectroscopy and functions of these proteins, see for example^{1,2}. Earlier we studied the effect of the protein electric field on the C-O vibrational frequency of carbonmonoxyheme proteins^{1,3} and showed that both position of the C-O vibrational band and its shape are controlled by the protein structure and dynamics, respectively.

Also, we used quantum chemical calculations (DFT) to find out to what extent the electric fields can affect the quadrupole splitting (ΔE_Q) of the excited nuclear state of iron isotope ^{57}Fe , which is observed in Mössbauer spectra. We computed effects of the model electric fields on ΔE_Q of the high-spin iron-porphin-imidazole complex and of electric field of the heme distal environment of the heme on ΔE_Q of deoxymyoglobin. The results of the computations showed that ΔE_Q is substantially

affected by both the model and protein electric fields. We showed that ΔE_Q depends on the strength of the axial component of the field, and, as such, can be used to estimate magnitude of the electric field in the heme pocket of deoxyheme proteins.

Acknowledgements

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Defects enhanced photocatalytic performance and magnetism on $\text{MO}_x(\text{N})\text{-TiO}_2$ nanocrystals

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The $\text{MO}_x(\text{N})\text{-TiO}_2$ (where MO_x = metal oxide coupled and doped and/or N codoped; M is Fe or Sn) nanocrystals were prepared by a simple hydrothermal method and nitridation treatment. We are currently studying how defects (structural, surface, oxygen vacancy) influence on photocatalytic and magnetic properties of $\text{MO}_x(\text{N})\text{-TiO}_2$ nanocrystals. We use conventional and synchrotron based techniques such as X-ray absorption spectroscopy, as well as magnetization techniques (VSM or SQUID) in order to study the structure and magnetism of the materials. On the other hand, we employ ^{57}Fe and ^{119}Sn Mössbauer spectroscopies as a fundamental tool to characterize Fe and Sn doped materials, respectively. The $\text{MO}_x(\text{N})\text{-TiO}_2$ microspheres exhibit altered compositional, optical, electrical, magnetic and photocatalytic properties with respect to vary dosage of iron or tin in the titania matrix. Especially $(\text{Sn},\text{N})\text{TiO}_2$ enhanced visible light photocatalytic activity for the degradation of Rhodamine B in aqueous solution, and the room-temperature ferromagnetism (RTFM). We initiated the photovoltaic study of Sn-TiO_2 and $(\text{Sn},\text{N})\text{TiO}_2$ microspheres to confirm the photovoltaic properties of Perovskite solar cells (PSCs) application. The $(\text{Sn},\text{N})\text{TiO}_2$ microspheres showed the relatively large saturation magnetization and high photocatalytic activity. The following main reasons were considered: (a) band-edge absorptions evidently shift toward the visible region, (b) the reasonable oxygen vacancy concentration can influence the spin relaxation between Ti^{3+} to Sn^{4+} states, and (c) influence the formation of electron-hole pairs under visible light irradiation by $\text{MO}_x(\text{N})$ in TiO_2 lattice. The important issues, such as (i) enhancement in the photocatalytic activities of titania, (ii) effects of structural, optical, electrical and magnetic properties of $\text{MO}_x(\text{N})\text{-TiO}_2$, and (iii) photocatalytic degradations of model organic dyes in aqueous suspension were systematically investigated. It concludes that $\text{MO}_x(\text{N})$ could

influence the magnetic and photocatalytic behavior of TiO_2 microspheres. The results signify the clear details of the RTFM and the photocatalytic activity of $\text{MO}_x(\text{N})\text{-TiO}_2$ microspheres.

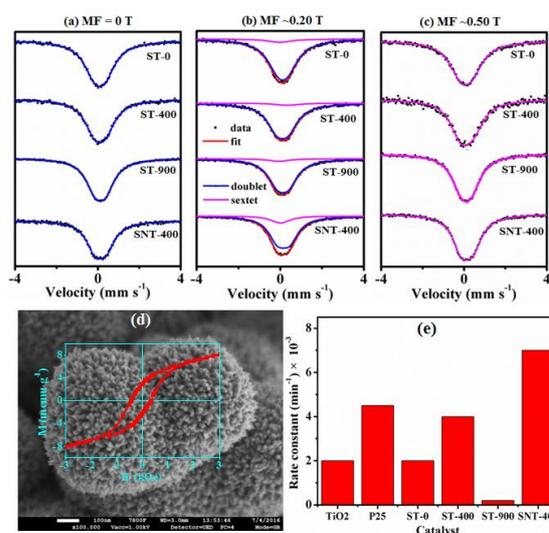


Fig. 1 Room temperature ^{119}Sn Mössbauer spectra of ST-x (Sn-TiO_2 ; x = calcination temperature) and SNT-400 ($(\text{Sn},\text{N})\text{TiO}_2$ calcinated at 400°C) samples in absence (a) and presence of weak (b), strong (c) external magnetic fields. HRSEM images (inset shows hysteresis loop) (d), photocatalytic rate constant (e).

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Mössbauer studies of Fe-based superconductors

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Within the novel Fe-based superconductors, FeSe could be a clue compound for the understanding of the mechanisms of superconductivity (SC) in these systems. In particular, the dramatic increase of T_C under pressure from 8.5 K at ambient pressure to 36.7 K at 9 GPa [1] points to a new superconductivity mechanism in these systems. Application of nuclear inelastic scattering (NIS) of synchrotron radiation to study of the local phonon DOS in FeSe-based SC as function of temperature and pressure could prove that electron-phonon interactions could not be the main mechanism for superconductivity in these systems [2]. We determined and compared the energy position of acoustic and optical phonon modes in several Fe-based superconductors as function of temperature and pressure, especially above and below T_C . Together with conventional ^{57}Fe -Mössbauer spectroscopy, we can conclude an important role of antiferromagnetic spin fluctuations which can mediate superconductivity acting as “glue” for Cooper pairs in Fe-based SC.

Our Mössbauer studies of FeSe intercalated with Li/NH_3 ($T_C = 43$ K) demonstrate that parallel with the superconducting transition a magnetic subspectrum of dynamic nature appears in the ^{57}Fe spectra [3]. Conductivity measurements demonstrate that T_C decreases with increasing pressure. Pressure measurements with ^{57}Fe -Synchrotron Mössbauer Source (SMS) revealed that both the amount of magnetic fraction and the frequency of the hyperfine magnetic field fluctuations do follow the variation of T_C with pressure confirming that the superconducting pairing in FeSe-based superconductors is mediated by the antiferromagnetic spin fluctuations.

Recent magnetic, structural and Mössbauer studies of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ observe first an increase of T_C from 13.5 to 19.5 K, and then a decrease and

disappearance of T_C , accompanied by the occurrence of a new hexagonal phase [4]. Previous studies of superconducting $\text{Rb}_{0.8}\text{Fe}_{1.6}\text{Se}_2$ have demonstrated the high resolution power of the ^{57}Fe -resonance for a phase analysis of the dominant magnetic and the superconducting minority phase as function of temperature and pressure [5,6].

Observation of high- T_C SC with onset temperature of 203 K in H_2S in a pressure range of 150-190 GPa [7] was recently independently confirmed by ^{119}Sn Mössbauer spectroscopy applying SMS [8]. This new possibility to study SC at extreme conditions is due to the expulsion of the applied magnetic field from the superconducting sample (Meissner Effect), in which a nonmagnetic ^{119}Sn foil was placed as highly sensitive nuclear probe. In the cited study, the magnetic field at the ^{119}Sn sensor was monitored using Nuclear Resonance Scattering (NRS) of synchrotron radiation. The presence of the magnetic field at tin nuclei in normal state of H_2S above T_C was identified by quantum beats in the time spectra of NRS. Obviously the use of ^{119}Sn -NRS to record superconducting transitions could be applied to study many important systems including superconducting metallic hydrogen, which presumably exists in the megabar pressure range [9, 10].

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Metallic condensates from an iron meteorite impact

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Impact cratering is the most recently recognised geological process affecting solid planetary bodies. The energy for the process is derived from conversion of the kinetic energy of colliding bodies into thermal energy and work. Modelling of the extreme pressure and temperature regimes involved indicates peak shock pressures of 1000 GPa and peak temperatures of 10000 K. These figures indicate that materials from the impactor and the planetary body may potential both melt and evaporate. Impactites are a general class of rocks forming by these processes and containing impact-metamorphed materials. Understanding the processes leading to the formation of the minerals in the impactite is a major source of knowledge about the impact process itself.

In an attempt to unravel the peak temperature details of the impact the impactite from a small scale- but high energetic- impact involving an iron meteorite and a simple sandy sediment was studied. The quartz-containing sand from the sediment has been ion-implanted by molecular metals where the iron locally has taken a glass-like coordination. The metallic components from the iron meteorite are

dominantly found as metallic phases exhibiting broad-lined sextet components in the Mössbauer spectra. Analysis indicates that the Si has been added to the meteoritic components. This most likely happened in the gas phase, and thus the solid metallic components are condensates from the impact.

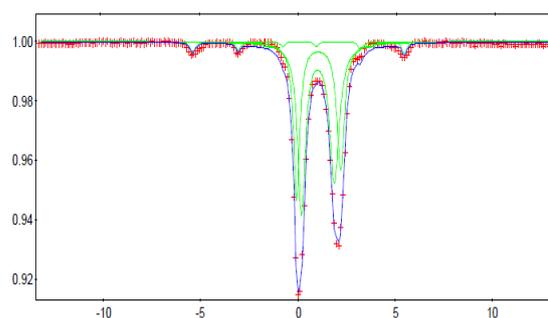


Fig. 1 Mössbauer spectrum of the studied impactite measured at room temperature. Prominent components are a glass-like ferrous component and an iron-alloy.

Metal atom dynamics in host-guest inclusion compounds

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Due to their potential use as drug delivery systems as well as related pharmacological and catalytically active processes, inclusion compounds have enjoyed a recent upsurge in study, and a large literature has developed in this field. In particular, since the pioneering work of Behrend the cucubiturils CB[7] and CB[8] have been the subject of numerous investigations [1]. These matrices can serve as “host” structures for a variety of “guest” species, including neutral and charged moieties. In the present study inclusion compounds involving neutral ferrocene (Fc), ferricinium hexafluorophosphate (Fc^+PF_6^-) and neutral 1,1 dimethyl ferrocene have been subjected to temperature-dependent Mössbauer Effect (ME) spectroscopy to elucidate the hyperfine interactions and metal atom dynamics of these systems.

Using standard transmission geometry ME Spectroscopy over a significant temperature range, it is found that for neutral “guest” species such as ferrocene and 1,1’ dimethyl ferrocene in CB[7] and CB[8] there is little specific bonding interaction between guest and host. The hyperfine parameters of the guest species are similar (within experimental error) to those noted for the neat guest moieties. On the other hand, ferricinium PF_6^- which gives rise to an expected broad asymmetric resonance, Fig. 1, in both CB matrices also reflects changes in the mean-square-amplitudes-of vibration of the metal atom compared to the neat species. A graphical summary is shown in Fig. 2. More comprehensive comparisons of the ME spectra will be discussed in detail.

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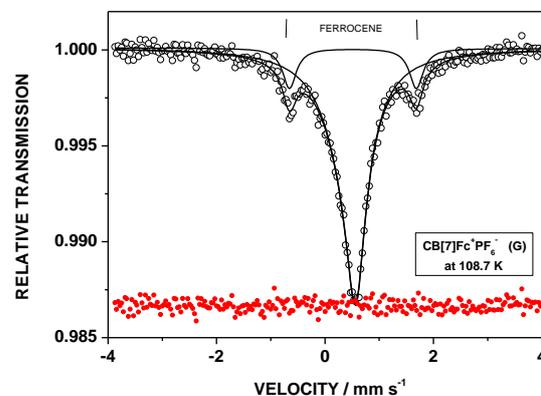


Fig. 1 ME spectrum of $\text{CB}[7]\text{Fc}^+\text{PF}_6^-$ at 108.7 K. The diamagnetic impurity is presumably ferrocene.

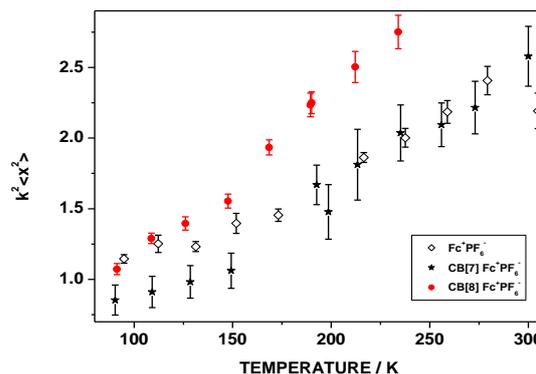


Fig. 2 The $k^2\langle x^2 \rangle$ parameters for two Inclusion Compounds and Fc^+PF_6^- .

Microstructural properties and OER activity of hydrothermally prepared Ni-Fe (oxy)hydroxides

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Mixed Ni-Fe (oxy)hydroxides have been intensively investigated in recent years because of excellent electrocatalytic properties for oxygen evolution reaction (OER) of Fe-doped Ni hydroxide, Fe-doped Ni oxyhydroxide and Ni-Fe layered double hydroxide [1,2], as well as good adsorption and catalytic properties of Ni-doped goethite (α -FeOOH) [3,4]. Natural Ni-doped goethite has also been investigated for the understanding the sorption mechanism of metal cations in goethite [5,6] In this work, the influence of Ni doping on the properties of goethite and influence of Fe doping on the properties of Ni hydroxide were systematically investigated.

Mixed Ni-Fe (oxy)hydroxide samples were synthesized by a hydrothermal precipitation in a highly alkaline medium and investigated using X-ray diffraction (XRD), Mössbauer spectroscopy, magnetic measurements, thermal analysis, FE-SEM, EDS, FT-IR and UV-Vis-NIR spectroscopy.

Ni-for-Fe substitution in goethite was confirmed from the shifts in the position of XRD lines and from a decrease in the hyperfine magnetic field observed by Mössbauer spectroscopy. A significant influence of Ni doping on different properties of goethite was also observed.

Fe doping in β -Ni(OH)₂ caused the formation of an interstratified structure with β -Ni(OH)₂ and α -Ni(OH)₂ structural units interconnected inside the same structural layers and in the same crystallites. This is accompanied with incorporation of nitrate ions and water between Ni hydroxide layers. Mossbauer spectra (Fig. 1) showed the presence of some Fe³⁺ ions located in the highly distorted octahedral sites, presumably at the boundary between α -Ni(OH)₂ and β -Ni(OH)₂ structural units.

Electrochemical measurements showed significantly higher OER activities of Ni-doped goethite and Fe-doped Ni hydroxide compared to pure phases.

Acknowledgment

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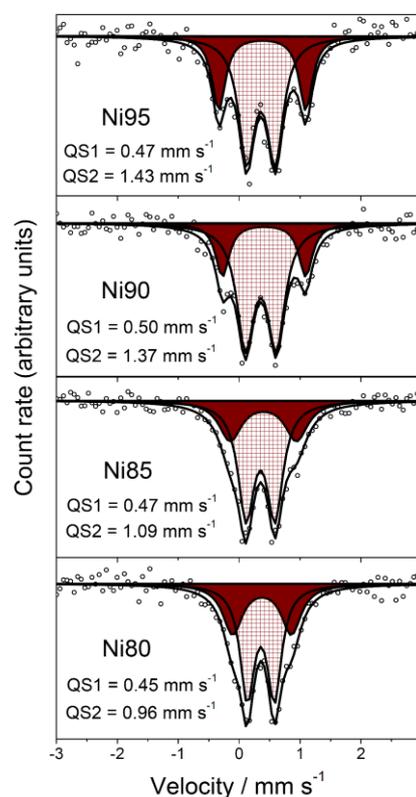


Fig. 1 ⁵⁷Fe Mössbauer spectra of Fe-doped Ni hydroxide samples recorded at 20 °C. Quadrupole splitting values obtained by fitting are given.

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Application of Mössbauer spectroscopy for the study of the oxidation of tin(II) fluoride and chloride fluoride solid solutions at ambient temperature

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Divalent tin fluorides and chloride fluorides have a quite a low recoil-free fraction, although usually high enough to give a reasonably strong Mössbauer spectrum at ambient temperature. Most of these compounds appear to be stable relative to oxidation to tetravalent tin at ambient temperature. However, although their X-ray diffraction pattern shows only the line of the tin(II) compound, the ¹¹⁹Sn Mössbauer spectrum of all the tin(II) polycrystalline samples has a small broad peak at ca. 0 mm/s. For example, the Mössbauer spectrum of polycrystalline α -SnF₂, even if prepared by grinding single crystals, shows the weak broad peak at 0.0 mm/s due to SnO₂, while the spectrum of a large single crystal polished sufficiently thin enough to allow the γ -ray beam through and to avoid giving rise to line broadening by saturation, shows only the tin(II) doublet, with no SnO₂ peak at 0 mm/s [1 & 2]. This shows that there is surface oxidation of each solid particle, to give a thin amorphous layer of SnO₂ stannic oxide. However, the Mössbauer peak of SnO₂ does not grow with prolonged exposure to air at ambient temperature, therefore it must be assumed that the layer of SnO₂ has a passivating effect and it prevents contact of the tin(II) compound to air, the same way as does a layer of paint, however oxidation increases at higher temperatures [3].

In this work, we have investigated the passivating effect of a layer of SnO₂ in two types of solid solutions: (i) in the fluorite type $M_{1-x}Sn_xF_2$, where the amount of tin at low x values is not sufficient to provide full coverage of the surface of the particles, and (ii) in the PbClF type doubly disordered solid solution, $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ [4 & 5]. There is never any crystalline SnO₂ detected by X-ray diffraction in either type of solid solution. On the other hand, due to the very high recoil-free fraction of tin(IV) oxide, compared to that of tin(II) halides, and since Mössbauer spectroscopy is a local probe and it detects amorphous or nanocrystalline species as well as crystalline material, it allows the detection of very small amounts of SnO₂, regardless of crystallinity. In addition, the peak for tin(IV) bonded to oxygen ($\delta \approx$

0 mm/s) is very well separated from tin(II) peaks ($\delta \approx 3-4$ mm/s). $M_{1-x}Sn_xF_2$ solid solutions passivate well, despite the insufficient amount of tin to provide full coverage of the particles by SnO₂. On the other hand, passivation does not work as well for the $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ and it is strongly dependent on the method of preparation and the mode of bonding, and also on the tin(II) recoil-free fraction. The solid solution prepared by precipitation passivates best. When prepared by the dry method, covalently bonded tin(II) passivates best, and the lower the tin(II) recoil-free fraction, the faster tin(II) is oxidized to tin(IV) (fig. 1).

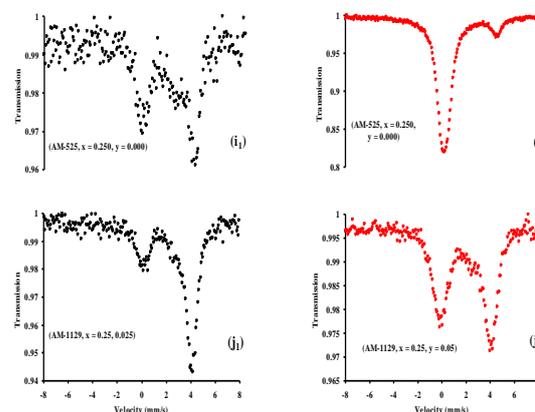


Fig. 1 Mössbauer spectra of two samples (equal amounts of sample and equal x = equal amount of tin) of $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ prepared by the dry method for $x = 0.250$, before (on the left) and after (on the right) spontaneous oxidation at RT in air. Top spectra: $y = 0.000$, freshly prepared and aged 18 months; bottom spectra: $y = 0.050$, freshly prepared and aged 19.7 months.

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Mössbauer parameters of troilite present in ordinary chondrites type H, L and LL

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The Mössbauer spectrum of the non-weathered equilibrated ordinary chondrites is composed of 4 subspectra: two doublets from olivines and pyroxenes and two sextets from metallic phases and troilite. When the process of weathering begins in the meteorite, a fifth subspectrum of trivalent iron appears.

The analysis of Mössbauer parameters of troilite (FeS) obtained in different laboratories was made in a study devoted to Mössbauer studies of the meteorite Baszkówka [1]. A large spread of these parameters was noticed. In our opinion neglecting of the angle between EFG and H_{eff} (the theta angle) was the reason of this dispersion.

In ideal FeS axial symmetry exist [2] and coefficient of asymmetry $\eta=0$. In natural troilite a only very small η can be expected

In Fig. 1 Mössbauer spectrum of Pultusk meteorite is shown. In this case the sub-spectrum of troilite was fitted including theta angle. Fig. 2 shows the influence of the neglecting of theta angle on the quality of the fit.

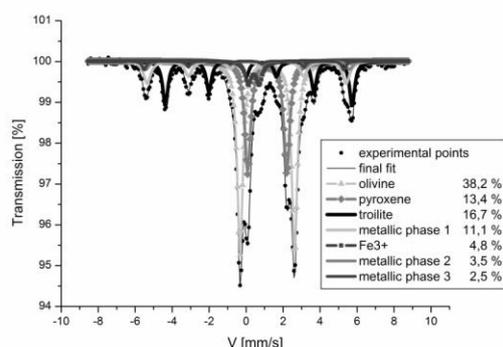


Fig. 1. Mössbauer spectrum of Pultusk meteorite obtained at RT and fitted with theta angle not equal zero.

To check if Mössbauer parameters of troilite in different type of ordinary chondrites (or. ch.) are the same, samples of 6 or. ch. type H (Goronyo, Juancheng, Carancas, Cosina, Tamdakht, Pultusk), 9 or. ch. type L (Pervomaisky, Saratov, Hyatt Ville, Beni Mhira, Elenovka, Katol, Mreira, Bjurbole,

Battle Mountain) and 10 or. ch. type LL (Oued, NWA 8590, NWA 8602, Benguerir, NWA 7733, NWA 7313, Chelabynsk, Sulagiri, NWA 4841) were measured at RT.

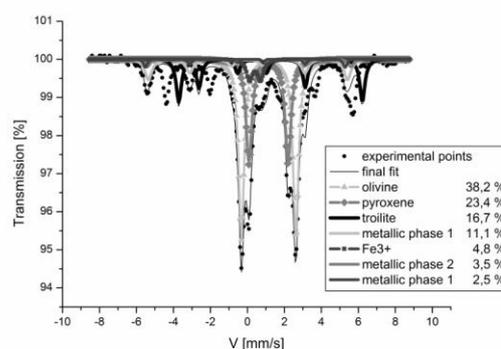


Fig. 2. Mössbauer spectrum of Pultusk meteorite obtained at RT and fitted with theta angle equal zero (quadrupole interaction fixed at true value)

For all measured samples Mössbauer parameters of troilite were very similar. The only significant difference was noticed for 2 samples of ordinary chondrites type LL. It was meteorite NWA 7733 and meteorite NWA 4841. The values of Mössbauer parameters of troilite obtained for investigated samples are shown in Table 1. The meaning of this finding will be discussed.

Table 1. Mössbauer parameters of troilite present in ordinary chondrites

Type of or. ch.	IS [mm/s]	H[T]	QS [mm/s]	Theta angle [°]
H	0.74-0.77	30.7-31.1	0.78-1.10	61-66
L	0.74-0.76	30.8-31.0	0.98-1.05	61-62
LL	0.74-0.78	30.8-31.2	0.81-1.04	58-67
NWA7313	0.73	31.2	0.38	68
NWA4841	0.74	31.2	0.36	78

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Mössbauer investigation of FeCl₃ sediment after model water treatment by different aluminosilicate reagents

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Structure and properties of nanoparticles with that determine a wide range of applications, are still the subject of studies of condensed matter physics. Since many of the nanoparticles contain the Iron, Mössbauer spectroscopy of ⁵⁷Fe nuclei is one of the most useful method for investigating last ones.

The aim of this work is to reveal the results of the interaction of the aluminosilicic coagulant-flocculant (produced by “JSC Aquaservice” in our laboratory, Moscow, Russia) [1] and aluminosilicate coagulant (produced by “TRIVEKTR” in Per'm city, Russia) with iron compounds FeCl₃ 18 mg/l contained in the water. To do this Mössbauer spectroscopy is used which allows to determine the valence of iron atoms as in crystalline and as in amorphous materials.

Table 1 present the Mössbauer spectrum parameters of FeCl₃ sediment after water treatment by aluminosilicic coagulant-flocculant. After fitting this spectrum shows the presents of iron in prevalence state (doublets D_1, D_2 and D_3).

Table 1. Mossbauer parametrs of FeCl₃ sediment by aluminosilicic reagent. T= 293 K

Phase	IS, mm/s	QS, mm/s	S, %	G, mm/s
D_1	0.34	0.80	44	0.52
D_2	0.36	1.00	35	0.65
D_3	0.35	0.54	21	0.23

Table 2 present the Mössbauer spectrum parameters of FeCl₃ sediment after water treatment by aluminosilicate coagulant. This spectrum after fitting shows the presents of iron in prevalence state (doublets D_1, D_2 and D_3).

Table 2 Mossbauer parametrs of FeCl₃ sediment by aluminosilicate reagent. T= 293 K

Phase	IS, mm/s	QS, mm/s	S, %	G, mm/s
D_1	0.36	0.89	51	0.49
D_2	0.32	0.91	35	0.71
D_3	0.36	0.55	14	0.28

For investigating of the Iron in amorphous state the DISTRI program was used.

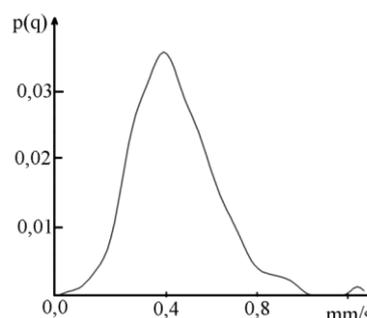


Fig. 1 Quadrupole distribution of the sediment by aluminosilicic reagent at 293 K

The result of fitting is next. The local state of iron atoms can be amorphous. Added to this the liquid nitrogen temperature of sediment didn't give the presence of superparamagnetic particles. Thus at this stage the conclusion might be the wide range of local iron state in sediment produced by both reagent.

Acknowledgements

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Iron state in nanoparticles in zirconium alloys with small and large iron contents

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Zirconium alloys have found wide application in engineering. Alloys are used both with a low iron content, as well as with an increased content, where zirconium enters as a doping additive. To obtain the necessary properties of the alloys, alloying elements are added therein and thermomechanical treatments are carried out. In zirconium alloys, precipitates are formed, which can be various intermetallic compounds of complex and variable composition.

The iron powder (99.9% pure) with approximate particle size of <math><75\mu\text{m}</math> and zirconium powder (98% pure) with approximate similar particle size was loaded into an ampoule of tool steel in an atmosphere of pure argon with balls of 6.4 and 7.9 mm diameter, 440 °C into a mill with ball bearings in stainless steel and the ratio of the weight of the balls to the weight of the powder equal to 10:1. The initial weight of the sample charge was 5 grams. Thus, the behaviour of the growth of pure-iron grain and two iron-zirconium alloys is investigated. Fe + 5 wt.% Zr and Fe + 10 wt.% Zr. The used powder was ground for 24 hours in a SPEX Model 8000 mill shaker, which was cooled to a temperature of approximately 50 °C.

At low iron concentrations in alloys quenched from beta-field, supersaturated solid solutions of iron and particles of intermetallic compounds are formed. The parameters of the Mössbauer spectra of a supersaturated solid solution are close to those of a solid solution of iron in alpha-zirconium. During annealing process, the supersaturated solid solution decomposes into a solid solution and intermetallic compounds. Unlike conventional metal systems, in which only solid substitution solutions are formed in zirconium alloys, the formation of interstitial solid solutions is also possible. The rate of the decay process depends on the presence of the third elements in the alloy and, as a rule, in the presence of the third element, it decreases. When mechanical grinding of iron with additives of zirconium, nano-sized crystals are formed. Additives of zirconium affect the growth

processes of nanoparticles and the activation energy of particle growth. It is shown that during annealing in alloys, both with a small and a high iron content, structural-phase transformations

Table 1. Grain sizes after thermomechanical treatment take place. A change in the activation energy of particle growth when zirconium is added to iron is revealed. Mossbauer data suggest that in alloys with a high iron content, zirconium is released from grain kernels in iron nanocrystals.

T / K	Time / s	Average grain size / nm		
		Fe	Fe+5%Zr	Fe+10%Zr
825	300	63	18	18
	1200	60	20	19
	3600	97	20	20
725	600	35	15	12
	3000	39	16	15
	10500	41	15	14

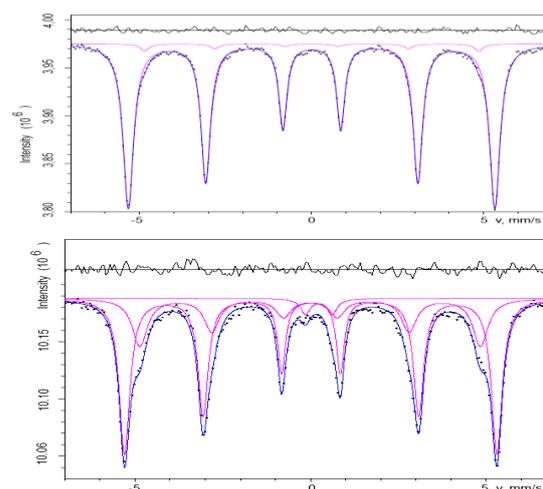


Fig. 1. Mossbauer spectra after milling-Fe (top) and Zr+5%Fe (down)

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Temperature effect on cationic migration in $\text{CoFe}_2\text{O}_4@Z\text{nO}$ composites

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Dipole-dipole interactions in nanoparticles cause spin glass and superferro-magnetism. Exchange interaction among different magnetic species expands the scope of application of magnetic materials. Combinations of different magnetic species are mostly among antiferromagnetic (AFM), ferromagnetic (FM), ferrimagnetic (F), paramagnetic (P) and diamagnetic (D) materials. The coupling of the magnetic moments of the interface atoms of two different magnetic species leads to huge increase in the coercivity. Diffusion of cations or anions across the interface modifies the magnetism.

In the present work, CoFe_2O_4 nanoparticles were decorated with diamagnetic ZnO by co-precipitation. The magnetic properties with respect to temperature are traced using Mössbauer and VSM.

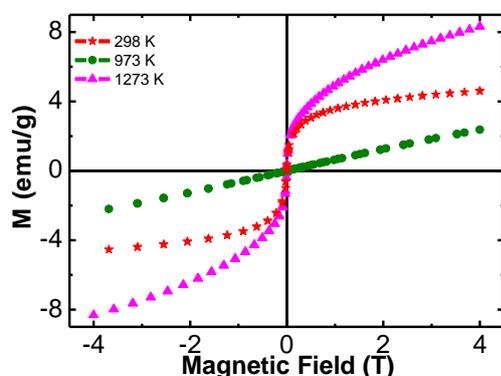


Fig. 1 MH loop of as synthesized, after annealing at 973 K and 1273 K.

The structural information derived from XRD shows, the as-synthesized and annealed nanoparticles consist of CoFe_2O_4 and hexagonal ZnO. M-H loop of the as-synthesized nanoparticles indicates the superparamagnetic nature. Annealing at 973 K shows a non-saturating linear paramagnetic curve. M-H loop of the sample annealed at 1273 K is observed to have a ferromagnetic nature.

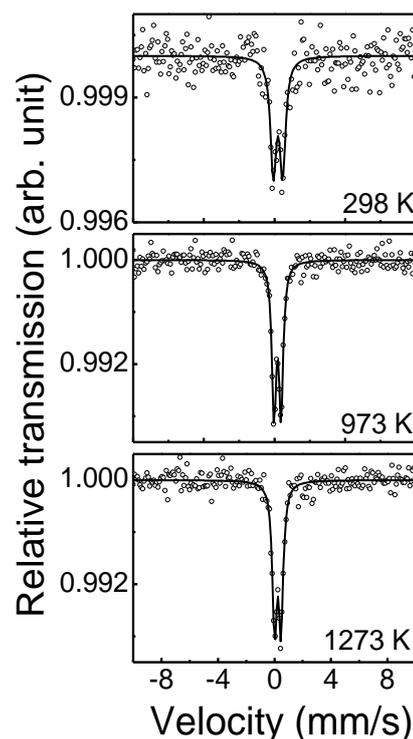


Fig. 2 Mössbauer spectra of as synthesized, after annealing at 973 K and 1273 K.

Mössbauer spectrum (Fig. 2) of the as-synthesized nanoparticles consists of a superparamagnetic doublet ($IS = 0.35$ mm/s & $QS = 0.65$ mm/s). Annealing at 973 K and 1273 K transformed the superparamagnetic Fe-based compound to paramagnetic. The transformation to paramagnetic is due to the formation of ZnFe_2O_4 as Zn diffuse from ZnO to CoFe_2O_4 , knocking out Co from the lattice. IS remains around 0.33 mm/s, but the QS decreases to 0.50 mm/s and 0.45 mm/s as the annealing temperature increases from 973 K to 1273 K. The QS of the nano ZnFe_2O_4 after annealing at 973 K is 0.35 mm/s. The high QS observed after annealing is contributed due to the presence of Co in the interstitials of ZnFe_2O_4 .

Mössbauer spectroscopy characterization of Fe/Au multilayers structures fabricated by pulsed laser deposition

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Mössbauer spectroscopy is very suitable techniques to examine the structural properties of the iron containing materials at the atomic level. To increase the sensitivity of this method in case of ultrathin films and interfaces of nanostructures one has to use ⁵⁷Fe for sample preparation. Unfortunately the high price of this isotope causes limits to use the standard techniques such as magnetron sputtering or Chemical Vapour Deposition. The aim of this work is to demonstrate ability of the pulsed laser deposition techniques to fabricate the special Au/Fe multilayers structures and study the structural properties of the nanometric size and interfaces by Mössbauer spectroscopy.

The pulsed laser deposition (PLD) technique is based on the rapid evaporation by the target materials by focused ns or fs laser pulses in vacuum chamber (see Fig.1). To eliminated the contamination from residual atmosphere we performed the experiments in ultrahigh vacuum system with the based pressure $<10^{-8}$ Pa monitored by mass spectrometry

Fe/Au multilayers were deposited by PLD on MgO single-crystalline (100) substrate using Nd:YAG laser operating at 266 nm wavelength with the repetition rate of 10 Hz and providing energy of 130 mJ in 5 ns light pulses. The laser beam was focused on the target by means of quartz lens to a spot with 3 mm diameter. The laser energy density on targets was ~ 2.6 J/cm². At this condition the 4×10^{14} atoms of ⁵⁷Fe was evaporated per laser pulse and so the thickness of the growing films was precisely controlled. Moreover the laser plasma plume (Fig.1) is always perpendicular to the target and well-focused, so the amount of used ⁵⁷Fe target is very small.

The samples were in situ characterised by spectral ellipsometry and ex situ after deposition by the scanning electron microscope Tescan Ferra,

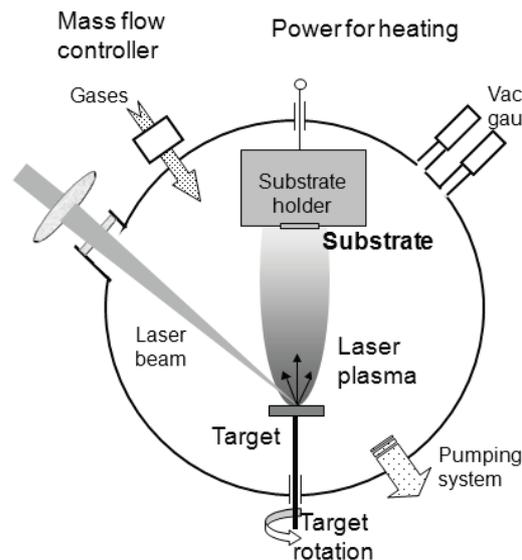


Fig. 1 Pulsed Laser Deposition system

EDX, by conventional XRD, XPS and by Mössbauer spectroscopy.

Mössbauer spectra were acquired at room temperature in the transmission and conversion electron geometry with constant acceleration of the ⁵⁷Co(Rh) source. The calibration of velocity scale was performed with natural α -Fe at room temperature.

The structure Au/⁵⁶Fe/⁵⁷Fe/⁵⁶Fe/Au was fabricated by target alternating in one deposition cycles without breaking of vacuum. The thickness of ⁵⁶Fe films varied from 0 up to 3 nm keeping (⁵⁶Fe+⁵⁷Fe) thickness approximately equal of 10 nm.

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^{57}Fe Mössbauer spectroscopy in the study of selected iron ores

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Selected iron ores (goethite, hematite and siderite) from known deposits in Hungary, Bosnia and Herzegovina, and Albania were investigated with XRD, ^{57}Fe Mössbauer, FT-IR and FE-SEM/EDS. XRD and ^{57}Fe Mössbauer of limonite from Budapest location showed goethite ($\alpha\text{-FeOOH}$) crystal structure. The formation of this limonite can be related with the chemical weathering process of primary minerals such as FeS_2 (pyrite and marcasite). Weathering of FeS_2 with water may produce FeSO_4 or/and hydronium jarosite which in the next step, depending on the geochemical conditions precipitate goethite, hematite or magnetite. This mechanism can be simulated under laboratory conditions [1]. RT Mössbauer spectrum of goethite from Omarska/Ljubija region (Northwest Bosnia and Herzegovina) showed also the presence of smaller fraction of hematite. RT Mössbauer spectrum of siderite from Omarska/Ljubija region showed asymmetric quadrupole doublet and this effect is discussed in the sense of Goldansky-Karyagin and/or texture effect (Fig.1). XRD and Mössbauer spectroscopy that iron ore from Vareš region (Bosnia and Herzegovina) consisted goethite and hematite phases. Low temperature Mössbauer spectrum was also recorded. The Mössbauer spectrum of iron ore from Korçë region in Albania showed superposition of one sextet corresponding to hematite, one collapsing sextet corresponding to goethite and also one central quadrupole doublet.

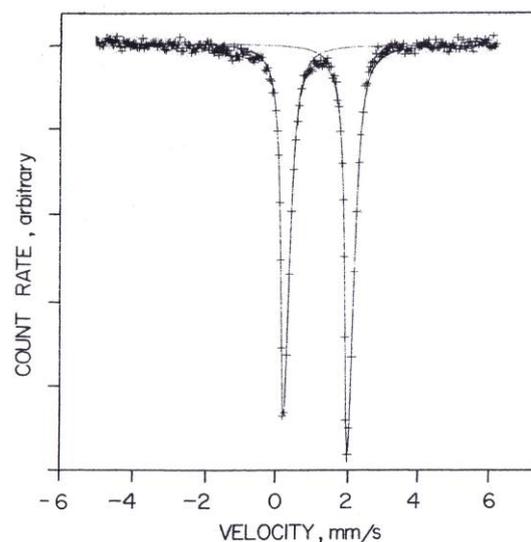


Fig. 1. RT Mössbauer spectrum of siderite (FeCO_3) ore showing an asymmetric quadrupole doublet.

Small amounts of Mg, Al, Si and Cr found with EDS could be used to support the formation of this ore by the chemical weathering mechanism which involved the precursors such as chromites of Fe^{2+} and Mg^{2+} , hercynite (FeAl_2O_4) and quartz (SiO_2) or some silicates.

Acknowledgment

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High spin to low spin transition in thermal plasma synthesized Fe-Ni alloy nanoparticles probed by Mössbauer spectroscopy

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Here, present work deals with the synthesis and characterization of Fe-Ni alloy having composition close to invar composition i.e. in the range of Fe 60-70% and Ni 40-30 %, respectively, using thermal plasma route. This particular range is of great interest of researchers due to their various properties such as low thermal expansion coefficient for Fe₆₆Ni₃₄. The high spin to low spin transformation is observed from Fe₆₀Ni₄₀ to Fe₇₀Ni₃₀ and which is conformed to Mössbauer spectroscopy[1][2].

The invar alloy nanoparticles were synthesized by gas phase condensation followed by rapid quenching inside the thermal plasma reactor. Fe and Ni metal powders were used as precursors, whose thermal properties are close to each other. The Fe-Ni precursors were mixed together in required proportion and co-evaporated using a thermal plasma plume having length of 50-70 mm. As a result of rapid thermal quenching the growth of the Fe-Ni particles is restricted, which results into formation of nanoparticles. The particles so formed are collected from the inner surface double walled water cooled chamber in which plasma torch is housed. Further the nanoparticles are characterized for structural and magnetic properties. Structural investigation reveals that FCC phase as a prominent one, however, in case of Fe₇₀Ni₃₀ presence of BCC phase is also significant. The magnetization of the alloy nanoparticles found to decrease from Fe₆₀Ni₄₀ to Fe₇₀Ni₃₀. The as synthesized samples were investigated using Mossbauer spectroscopy. The as obtained spectra were then fitted with SITE and DIST modes in WinNorms for Igor. Room temperature Mössbauer spectra of the as synthesized alloy nanoparticles show an interesting behaviour from Fe₆₀Ni₄₀ to Fe₇₀Ni₃₀. The sextet observed at Fe₆₀Ni₄₀ transferred into singlet for Fe₇₀Ni₃₀. The fitting parameters obtained from the SITE fit are listed in Table1.

Table 1: Mossbauer fitting parameters for as synthesized alloy nanoparticles (SITE mode)

Sample	Sub-Spectrum	Bhf(T)	IS (mm/s)	Q S(mm/s)	Area (%)
Fe ₆₀ Ni ₄₀	Sextet	31.50	-0.073	-0.081	29
	Sextet	29.61	-0.070	0.064	70
	Sextet	30.39	-0.049	-0.034	41
Fe ₆₆ Ni ₃₄	Sextet	25.52	-0.027	0.14	45
	Doublet	-	0.10	1.14	14
	Sextet	26.08	-0.005	-0.012	85
Fe ₇₀ Ni ₃₀	Singlet	-	-0.17	-	15

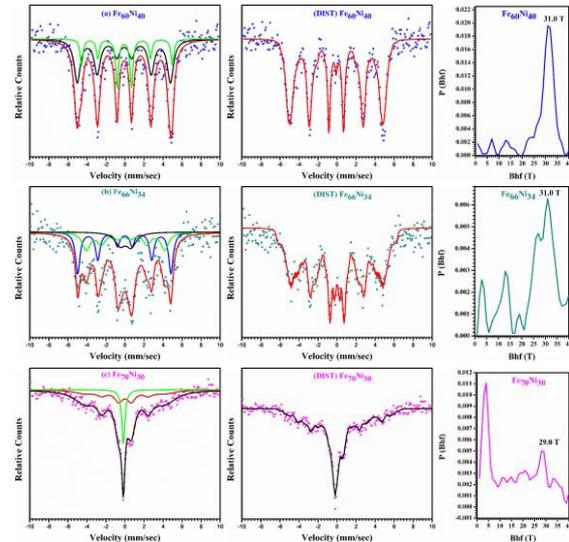


Fig.1 Mossbauer spectroscopy data for composition Fe₆₀Ni₄₀, Fe₆₆Ni₃₄ and Fe₇₀Ni₃₀

From Fig. 1 it is seen that, Fe₆₀Ni₄₀ shows high spin structure which favour ferromagnetism and high value of magnetization with respect to parent elements. The nature of the Mössbauer spectrum recorded for the samples under investigation transfers from prominently sextet to singlet with increasing concentration of Fe from 60 to 70 %. Hyperfine field distribution is sharp in case of Fe₆₀Ni₄₀, it broadens for Fe₆₆Ni₃₄ and completely shifted towards lower side for Fe₇₀Ni₃₀ which is attributed to high spin to low spin transition of magnetic moments in Fe-Ni system.

In summary analysis of Mössbauer spectra recorded on the Fe-Ni alloy nanoparticles synthesized by thermal plasma route indicates high spin to low spin transition of magnetic moment at room temperature for the Fe-Ni alloy nanoparticles, in the vicinity of invar composition. The above discussion is well supported by x-ray and magnetic data (not shown).

Acknowledgment:

Author wishes to thank NRB Delhi, India for funding research project (DNRD/05/4003/NRB/303).

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Magnetic properties and thermal stability of 1D Fe(IO₃)₃ particles

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Most metal iodates show pyroelectric, piezoelectric and non-linear optical (NLO) properties which make the physical basis for their possible technological applications. One of the most interesting metal iodates is Fe(IO₃)₃ which possesses noncentrosymmetric crystal structure. In this work 1D Fe(IO₃)₃ particles in the form of nanorods were synthesized following the procedure of von Endredy [1]. The sample prepared was characterized using XRD, FT-IR, DTA, ⁵⁷Fe Mössbauer spectroscopy, magnetic measurements and FE-SEM/EDS. The RT Mössbauer spectrum of Fe(IO₃)₃ sample was characterized with single line (IS = 0.41 mm s⁻¹; QS = 0.38 mm s⁻¹) (Fig.1), whereas hyperfine magnetic splitting was completely developed at ~ 4.3 K.

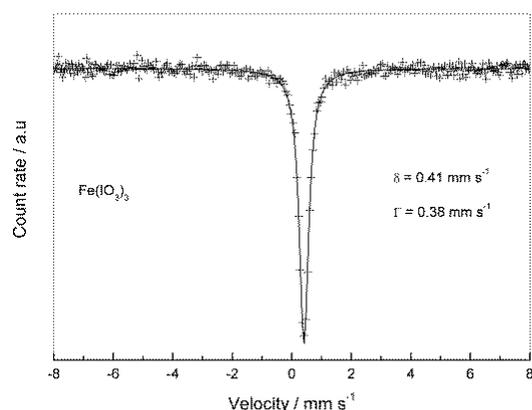


Fig. 1. ⁵⁷Fe Mössbauer spectrum of Fe(IO₃)₃ nanorods recorded at RT.

The maximum magnetization of 12 emu g⁻¹ was obtained in the magnetic field of $\mu_0 H = 9$ T (Fig. 2).

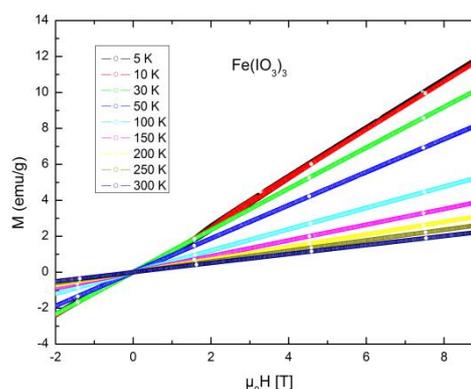


Fig. 2. Magnetization of Fe(IO₃)₃ nanorods at different temperatures versus applied magnetic field.

In DTA curve, very small endothermic peaks at 340 and 400 °C appeared besides of very strong endothermic peak at 515 °C. Mössbauer spectroscopy showed that Fe(IO₃)₃ particles are stable in air up to 370 °C. Heating of 1D Fe(IO₃)₃ particles at 520 and 800 °C produced 1D α -Fe₂O₃ particles. 1D α -Fe₂O₃ particles produced at 800 °C were decreased in length and increased in width.

Acknowledgment:

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Mössbauer investigation of iron phospho-silicide as negative electrode for Li-ion batteries

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Numerous iron based phases have been reported as serious positive electrode material candidates for Li-ion batteries [1]. In this work, we report on the performance and the reaction mechanism of iron phospho-silicide as negative electrode material for both Li- and Na-ion batteries. FeSi₄P₄ is prepared by milling a stoichiometric mixture of pure silicon, iron and red phosphorous powders. The whole diffraction pattern is indexed in the P1 space group in agreement with reported data [2]. The crystallographic cell is built on octahedral FeSi₃P₃ units (Fig. 1). Two metal-free overlapping tetrahedra share a common axis: one SiP₄ tetrahedron with four P corners overlaps one PSi₄ tetrahedron with four Si corners. Each octahedron is completely isolated from its neighbors.

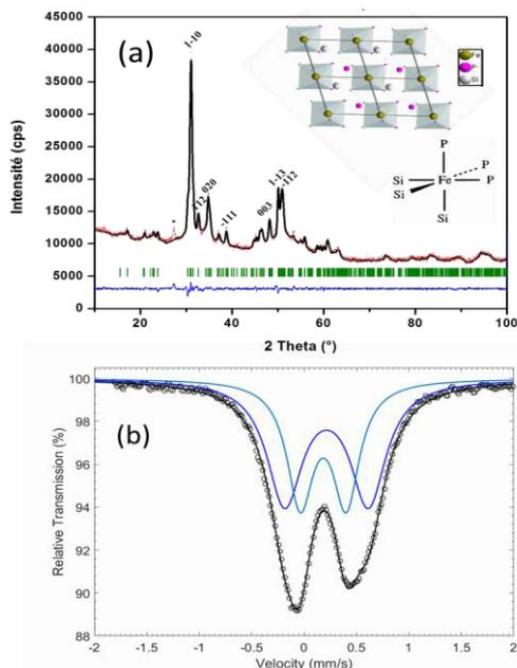


Fig. 1. XRD pattern with indexed peaks of FeSi₄P₄ and crystallographic description (a). Room temperature Mössbauer spectrum of the as prepared FeSi₄P₄ (b).

The room temperature ⁵⁷Fe Mössbauer spectrum of FeSi₄P₄ is shown in figure 1b. Contrary to crystallographic predictions, Mössbauer data cannot be fitted with a single component (i.e., a single iron site) but at least two broadened doublets are

needed. This can be explained by the presence of defects due to the preparation method (high energy ball milling) known to lead to less well crystallized particles with structural defects. An alternative explanation could be a variable first shell coordination of the iron centers, which can be described as Fe-Si_{3-x}P_{3+x} with -3 < x < 3 instead of the theoretical Fe-Si₃-P₃ configuration. The galvanostatic profile is shown in fig. 2, the first discharge shows the reaction of about 24 Li per FeSi₄P₄ unit which corresponds to the experimental value of 2200 mAh/g a value close to the theoretical capacity. 19 Li are de-inserted during the charge (1750 mAh/g) and a capacity of 1120 mAh/g is retained after 40 cycles.

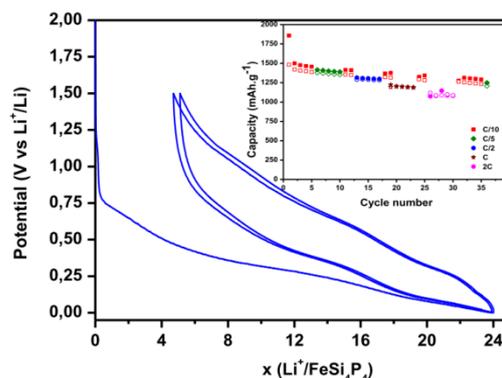


Fig. 2. Galvanostatic curve (C/2 rate) and rate capability of FeSi₄P₄/Li.

In situ ⁵⁷Fe Mössbauer spectroscopy was used to monitor the electronic changes around the iron centers. The whole series of *operando* Mössbauer spectra (90 spectra) were first globally analyzed using a statistical method based on Principal Component Analysis (PCA) (Fig. 2). The variance obtained from PCA analysis shows that more than 99.3 % of the variance of the Mössbauer spectra can be described using 3 principal components. The obtained Mössbauer results are discussed in the light of *ex situ* magnetic analyses obtained at the charged and discharged states.

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Thermal reaction of sonochemically prepared amorphous Fe/C

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The sonochemical synthesis is a useful method to produce new materials in a solution. The cavitation bubbles have high-temperature and high-pressure to decompose reagents, and the fragments cool down rapidly in a solution. We have previously reported the production of Fe/C amorphous by the ultrasonication of ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) in diphenylmethane [1]. The as-prepared precipitate was amorphous, and the heating of the amorphous sample produced iron carbide or metal particles. In this paper, we report the results obtained after annealing at higher temperatures up to 1200 °C. It was found that carbon nanotubes (CNT) was synthesized by a solid phase reaction.

The experimental setups used in this study were almost the same as that reported in our previous literature [1]. Briefly, a mixture of 15 mmol of ferrocene and 45 mL of diphenylmethane was kept at 20 °C. Ultrasonication was performed with high-intensity ultrasonic Ti-horn (Branson Sonifier 450, working frequency: 20 kHz, tip diameter: 6.4 mm, immersion depth: 20 mm) under an argon flow for 6 h. The products were centrifuged, washed with hexane under an argon atmosphere and dried under vacuum. The obtained amorphous was heated at desired temperatures using an infrared image furnace (ULVAC, MILA-5000) under the argon flow for 2 h. The products were investigated using Mössbauer spectroscopy ($^{57}\text{Co}/\text{Rh}$ source), X-ray diffraction (XRD; Rigaku, RINT2000), and transmission electron microscopy (TEM; Hitachi, H-9500).

The sonolysis of ferrocene in diphenylmethane produced a black precipitate. Mössbauer spectra of the precipitate were measured at room temperature (Fig. 1a), which showed a paramagnetic doublet. XRD patterns of the sample did not show any peak corresponding to iron-based materials. The precipitate was assigned to the paramagnetic amorphous composed of the mixture of Fe and C atoms. The amorphous Fe/C precipitate samples were heated at 900, and 1200 °C for 2 h under argon.

The sample obtained after heating of the amorphous sample at 900 °C for 2 h was the combination of α -Fe and Fe_3C (Fig. 1b), while the sample obtained after heating the sample at 1200 °C was the combination of α -Fe and γ -Fe (Fig. 1c). It has been reported that Fe-C alloys exhibit a tendency toward phase separation at high

temperature, which leads to the precipitation of carbon and γ -Fe.

TEM images of the samples were measured. The TEM image of the as-prepared sample did not show any particles, showing the shape of amorphous. The sample obtained after annealing at 900 °C consisted of spherical particles with ~50 nm diameters. The Fe and C atoms migrated by heating to form the adequate compositions according to the Fe-C phase diagram, and the particles stabilized while cooling down to room temperature. The sample obtained after annealing at 1200 °C consisted of spherical particles with ~80 nm diameters. Besides the particles, there observed the image of CNT. The CNT were not straight but bend showing tangled shapes. It is well known that Fe or Fe_3C nanoparticles play a role as a catalyst for synthesis of CNT from carbon hydride gasses.

It was demonstrated that Fe_3C and iron metal (α -Fe and γ -Fe) particles were produced by the heating of Fe/C amorphous. The reaction was accompanied by the formation of CNT catalyzed by the Fe particles.

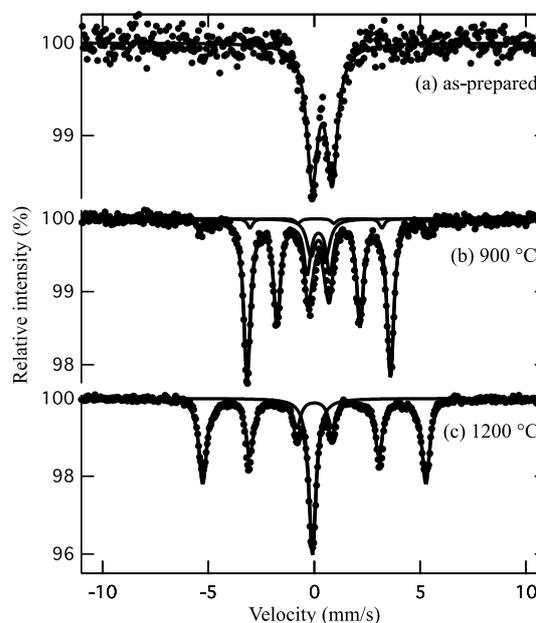


Fig. 1 Mössbauer spectra measured at room temperature of (a) as-prepared Fe/C amorphous and the samples after annealing at (b) 900 °C and (c) 1200 °C.

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