# MECAME 2015

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

In the Honour of Svetozar Musić

Hotel Donat, Zadar, Croatia

7-10 June 2015

# BOOK OF ABSTRACTS

**Edited by:**

**Mira Ristić**

**Željka Petrović**

**Stjepko Krehula**

# WELCOME TO MECAME 2015

On behalf of the Organizing Committee I wish to welcome all participants to the first Mediterranean Conference on the Applications of the Mössbauer Effect – MECAME 2015 in Zadar, Croatia, from 7th to 10th June 2015.  The Conference is organized by the Ruđer Bošković Institute which is the largest research institution in Croatia.

The aims of MECAME 2015 are to present new investigations and reviews of the applications of Mössbauer effect, to exchange ideas, to promote collaboration among scientists concerning the future potential of Mössbauer spectroscopy and to enhance the development of Mössbauer spectroscopic research in Mediterranean countries, stimulating closer interaction among scientists in this region of the world.

We expect the MECAME conference will become a regular meeting of the Mössbauer community with the special aim to honour the scientists who gave significant contribution to the development of Mössbauer spectroscopy in their local scientific communities. MECAME 2015 is organized in honour of Dr. Svetozar Musić (Ruđer Bošković Institute, Zagreb, Croatia) on the occasion of his 70th birthday and to celebrate his life-long scientific contribution, particularly for his introduction of Mössbauer spectroscopy as a research technique in Croatia.

The Conference will be held in the Hotel Donat, Zadar. Zadar is one of the oldest cities in Croatia located on the Adriatic coast. Its long and turbulent history is today reflected in the rich and diverse cultural heritage; municipal square The Forum (1st century B.C., Roman era), St. Donatus church which is the symbol of the city (9th century, Byzantine era), St. Anastasia Cathedral (the largest cathedral in Dalmatia, 12th century), the city walls and gates (the largest city-fortress in the Venetian time), and more. Historical treasures are on display in many museums and galleries in the city (Gold and Silver of Zadar, Ancient Glass Zadar, and many others). Zadar is an ancient European university city, with its university founded in 1396 in the Dominican monastery under the name Studium generale, later called Universitas Jadertina. Zadar has one of the most beautiful sunsets, which attract visitors from all over the world. The Greeting the Sun installation and the Sea Organ are among Zadar's top attractions.

We wish that all the participants of MECAME 2015 have a fruitful meeting and wonderful time in Zadar.

Dr. Mira Ristić

Chair of MECAME 2015

## ORGANIZATION AND SPONSORSHIP

MECAME 2015 is organized by the Ruđer Bošković Institute under auspices of Croatian Academy of Sciences and Arts, Department of Mathematical, Physical and Chemical Sciences.

MECAME 2015 is sponsored by PLIVA HRVATSKA d.o.o.

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## Conference Programme *(only presenters are listed)*

## Sunday 07/06/2015

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

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

## Monday 08/06/2015

**09:00 - 09:30  Opening Ceremony** (Chairperson: M. Ristić)

**09:30 - 11:00  Plenary Lectures** (Chairperson: V.K. Sharma)

09:30 - 10:15  <u>Philipp Gütlich</u>: *Spin State Switching in Iron Coordination Compounds - Retrospect, Trends, Perspectives*

10:15 - 11:00  <u>Radek Zbořil</u>: *Iron and iron oxide based nanomaterials for environmental, magnetic and catalytic applications by view of Mössbauer spectroscopy*

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

**11:30 - 13:00  Invited Lectures** (Chairperson: R. Zbořil)

11:30 - 12:00  <u>Virender K. Sharma</u>: *Ferrate and ferryl species: Mössbauer spectroscopy investigations*

12:00 - 12:30  <u>Tetsuaki Nishida</u>: *Characterization and conduction mechanism of highly conductive vanadate glass*

12:30 - 13:00  <u>Denes Lajos Nagy</u>: *Quality assurance in Mössbauer spectroscopy*

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

**14:00 - 15:30  Invited Lectures** (Chairperson: I.S. Lyubutin)

14:00 - 14:30  <u>Elisa Baggio-Saitovitch</u>: *Structural and magnetic properties of Fe-doped Yb films prepared by vapor deposition*

14:30 - 15:00  <u>José Francisco Marco</u>: *Mössbauer studies on $Fe_3O_4$ and $CoFe_2O_4$ thin films*

15:00 - 15:30  <u>Massimo Carbucicchio</u>: *Magnetic thin films and multilayers*

**15:30 - 16:00  Coffee Break**

**16:00 - 17:30  Invited Lecture & Oral Presentations** (Chairperson: M. Reissner)

16:00 - 16:30  <u>Jean Marc Greneche</u>: *Magnetic properties of ferrites and nanoferrites investigated by $^{57}Fe$ Mössbauer spectrometry*

16:30 - 17:00  <u>Cathrine Frandsen</u>: *Magnetic properties of antiferromagnetic nanoparticles and the influence of inter-particle exchange interactions*

17:00 - 17:15  <u>Marko Bošković</u>: *Iron oxide: magnetic hyperthermia and encapsulation*

17:15 - 17:30  <u>Liudmila Dzemiantsova</u>: *Topologically protected magnetic helix imaged with Mössbauer spectroscopy and X-ray polarimetry*

**19:00  Zadar Sightseeing**

## Tuesday 09/06/2015

**09:00 - 10:30  Invited Lectures** (Chairperson: J.M. Greneche)

09:00 - 09:30   Igor S. Lyubutin: *Mössbauer spectroscopy characterization of hollow microcapsules designed for the targeted drug delivery*

09:30 - 10:00   Květoslava Burda: *Role of the intermediate spin state of reduced non-heme iron in bacterial reaction centers of type II*

10:00 - 10:30   Ernő Kuzmann: *Mössbauer, XRD and TEM study on the intercalation and the release of drugs in/from layered double hydroxides*

**10:30 - 11:00  Coffee Break**

**11:00 - 12:00  Invited Lectures** (Chairperson: S.M. Dubiel)

11:00 - 11:30   Michael Reissner: *Investigation of magnetic, electronic and crystallographic structure of $FeSb_2$*

11:30 - 12:00   Cesar Barrero: *Mössbauer spectrometry and the magnetism of Fe-doped and Fe-transition-metal co-doped ZnO and $SnO_2$ nanoparticles*

**12:00 - 13:00  Lunch Time**

**13:30       Conference Excursion** (Krka National Park, Šibenik, dinner in Dalmatian village)

## Wednesday 10/06/2015

**09:00 - 10:30  Invited Lectures** (Chairperson: M. Miglierini)

09:00 - 09:30   Israel Felner: *Synchrotron radiation Mössbauer spectra of a rotating absorber*

09:30 - 10:00   Bogdan Sepiol: *Nanoscale dynamics - an atomistic picture*

10:00 - 10:30   Stanisław M. Dubiel: *Application of the Mössbauer spectroscopy to study spin- and charge-density waves*

**10:30 - 11:00  Coffee Break**

**11:00 - 12:30  Invited Lectures** (Chairperson: C. Barrero)

11:00 - 11:30   Marcel Miglierini: *Surface features of nanocrystalline alloys*

11:30 - 12:00   Adriana Lančok: *Structural transformation in high corrosion resistant steel*

12:00 - 12:30   Kiyoshi Nomura: *Oxygen vacancy and dilute magnetism of $SnO_2$ doped with Fe and metal ions*

**12:30 - 14:00  Lunch Time**

**14:00 - 15:30   Invited Lectures** (Chairperson: K. Nomura)

14:00 - 14:30   Göstar Klingelhöfer: *In-Situ Mössbauer and PIXE analysis of planetary surfaces and small bodies*

14:30 - 15:00   Károly Lázár: *Preparation of iron oxide xero-and aerogels by hydrolysis in aprotic media*

15:00 - 15:30   Satoru Nakashima: *DFT Study on thermal spin-crossover behavior for complexes having Fe(NCS)$_2$(pyridine)$_4$ unit*

**15:30 - 16:00   Coffee Break**

**16:00 - 17:30   Invited Lectures & Oral Presentations** (Chairperson: T. Nishida)

16:00 - 16:30   Shiro Kubuki: *Relationship between structure and visible light activated photocatalytic ability of iron containing aluminosilicate glass prepared by sol-gel method*

16:30 – 16:45   Masashi Kaneko: *Computational study on Mössbauer isomer shifts of some organic-neptunium(IV) complexes*

16:45 - 17:00   Takafumi Kitazawa: *Mössbauer spectroscopic study on Hofmann-like coordination polymer Fe(4-Clpy)$_2$[Ni(CN)$_4$]*

17:00 - 17:30   Mile Ivanda: *Development and applications of SERS techniques*

**17:30        Closing Ceremony**

**18:00 - 19:00   Poster Session**

**21:00        Conference Dinner**


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

Geraldo Magela da Costa: *The multiple dehydroxylation peaks of goethite and the existence of hydrohematite revisited*

Karen E. García: *Mössbauer spectrometry study of corroded steels surfaces submitted to accelerated tests in chloride environments*

Mohamed Y. Hassaan: *Effect of sulfur addition on some physical properties of Li-V-Fe silicate glass and glass-ceramic nano composite*

Juan A. Jaén: *Characterization of magnesium doped lithium iron silicate*

Radina P. Kralchevska: *Mechanism of phosphorus(V) substitution in Fe(III) component lattice*

Stjepko Krehula: *Synthesis and microstructural properties of mixed iron-gallium oxides*

Shiro Kubuki: *Improving the performance of metallic-iron-maghemite nanoparticle system for treating polluted water*

M.G. Moustafa: *Role of sulfur addition as a reducing agent on the ionic state of the transition metals in lithium silicate glass containing Fe and Ni ions*

Ivana Opačak: *The influence of gum arabic on the precipitation of α-FeOOH in a highly alkaline medium*

Marija Perović: *Simultaneous relaxation processes in super spin glass maghemite nanoparticles*

Alex Scrimshire: *Variable temperature Mössbauer spectroscopy study of nano-particle iron carbides*

# Spin state switching in iron coordination compounds – Retrospect, trends, perspectives

## P. Gütlich

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Coordination compounds of transition metal ions with open-shell electron configurations may exhibit dynamic electronic structure phenomena, depending on the nature of the coordinating ligand sphere. Thermal, light- and pressure-induced changes of spin states [1-3], known as spin transition or spin crossover (SCO), are among the most fascinating electronic games encountered in transition metal compounds, particularly of iron(II) and iron(III), which have been under extensive study by chemists and physicists. The characteristic switching properties such as drastic changes of color and magnetic behavior of the different spin states, make such material potential candidates for practical applications in thermal and pressure sensors as well as optical devices. Some highlights of studies of thermal spin transition will be briefly reviewed. Selected examples of thermal spin crossover in mono-, oligo- and polynuclear iron(II) complexes will be discussed, with special emphasis on the importance of cooperative interactions. It will also be shown that switching forth and back between different spin states may be effected by irradiation with light of different wave lengths ("Light-Induced Excited Spin State Trapping (LIESST)"). The effect of pressure on the spin transition behavior in mono- and polynuclear spin crossover compounds will be demonstrated. New activities towards synthesis of systems exhibiting thermal spin transition in combination with other phenomena such as liquid crystalline properties are briefly outlined. Possible practical applications will be discussed.

[1] P. Gütlich, A. Hauser, H. Spiering, Angew. Chem. Int. Ed. Engl. 33 (1994) 2024.
[2] P. Gütlich, H.A. Goodwin (eds.), Top. Curr. Chem., vol. 233, 234, 235, Springer, Berlin, 2004.
[3] P. Gütlich, A.B. Gaspar, Y. Garcia, Beilstein J. Org. Chem. 9 (2013) 342-391.

# Iron and iron oxide based nanomaterials for environmental, magnetic and catalytic applications by view of Mössbauer spectroscopy

## R. Zbořil

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The unique potential of Mössbauer spectroscopy in environmental sciences will be highlighted through environmentally friendly water treatment technologies based on nanonoscale zero-valent iron (nZVI) and ferrate(VI). The principal contribution of the method in analysis of the reaction mechanisms will be demonstrated with examples of nZVI and ferrate reactions in water, but also with technologically important processes of arsenic treatment and heavy metals removal [1-4]. The possibility of distinguishing between magnetite and maghemite, discerning of amorphous iron(III) oxide from crystalline polymorphs or monitoring the sample texture will show a huge applicability of low-temperature, in-field or conversion electron Mössbauer spectroscopy in various fields of catalysis/photocatalysis including magnetically separable catalysts, heterogeneous catalysis and technologies of direct solar splitting of water [5-7]. Finally, the use of the technique for complex structural and magnetic characterization of various iron(III) oxide polymorphs (alpha, beta, gamma, epsilon) involving their mutual thermally or pressure induced polymorphous transformations will be discussed [8-9].

[1] V.K. Sharma, R. Zboril, R.S. Varma: *Ferrates: Greener Oxidants with Multimodal Action in Water Treatment Technologies*, Accounts of Chemical Research 48 (2015) 182-191.

[2] J. Filip, F. Karlicky, Z. Marušák, P. Lazar, M. Cernik, M. Otyepka, R. Zboril: *Anaerobic Reaction of Nanoscale Zerovalent Iron with Water: Mechanism and Kinetics*, The Journal of Physical Chemistry C 118 (2014) 13817-13825.

[3] R. Prucek, J. Tucek, J. Kolarik, J. Filip, Z. Marusak, V.K. Sharma, R. Zboril: *Ferrate(VI)-Induced Arsenite and Arsenate Removal by In Situ Structural Incorporation into Magnetic Iron(III) Oxide Nanoparticles*, Environmental Science & Technology 47 (2013) 3283-3292.

[4] R. Prucek, J. Tuček, J. Kolařík, I. Hušková, J. Filip, R.S. Varma, V.K. Sharma, R. Zbořil: *Ferrate(VI)-Prompted Removal of Metals in Aqueous Media: Mechanistic Delineation of Enhanced Efficiency via Metal Entrenchment in Magnetic Oxides*, Environmental Science & Technology 49 (2015) 2319-2327.

[5] M.B. Gawande, A.K. Rathi, J. Tucek, K. Safarova, N. Bundaleski, O.M.N.D. Teodoro, L. Kvitek, R.S. Varma, R. Zboril: *Magnetic gold (nanocat-Fe-Au) nanocatalyst: catalytic applications for the oxidative esterification and hydrogen transfer reactions*, Green Chemistry 16 (2014) 4137-4143.

[6] K. Sivula, R. Zboril, F. Le Formal, R. Robert, A. Weidenkaff, J. Tucek, J. Frydrych, M. Graetzel: *Photoelectrochemical Water Splitting with Mesoporous Hematite Prepared by a Solution-Based Colloidal Approach*, Journal of the American Chemical Society 132 (2010) 7436-7444.

[7] M. Hermanek, R. Zboril, N. Medrik, J. Pechousek, C. Gregor: *Catalytic efficiency of iron(III) oxides in decomposition of hydrogen peroxide: Competition between the surface area and crystallinity of nanoparticles*, Journal of the American Chemical Society 129 (2007) 10929-10936.

[8] L. Machala, J. Tucek, R. Zboril: *Polymorphous Transformations of Nanometric Iron(III) Oxide: A Review*, Chemistry of Materials 23 (2011) 3255-3272.

[9] J. Tucek, R. Zboril, A. Namai, S. Ohkoshi: *ε-Fe2O3: An Advanced Nanomaterial Exhibiting Giant Coercive Field, Millimeter-Wave Ferromagnetic Resonance, and Magnetoelectric Coupling*, Chemistry of Materials 22 (2010) 6483-6505.

# Structural and magnetic properties of Fe-doped Yb films prepared by vapor deposition

C. Rojas-Ayala[1,2], E.C. Passamani[3], N.M. Suguihiro[1], F.J. Litterst[1,4]
and <u>E. M. Baggio-Saitovitch</u>[1]

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[2]*Facultad de Ciencias Físicas, Universidad Nacional Mayor de San Marcos, Lima 14, Peru*
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[4]*Institute for Condensed Matter Physics, TU Braunschweig, 38106 Braunschweig, Germany*

Zero-field and in-field Mössbauer spectroscopy, as well as DC and AC magnetization measurements were applied to study the magnetic properties of Fe nanoclusters formed upon vapor co-deposition of ~5.0 at.% of Fe and Yb onto Kapton substrates kept at TS = 80 K or RT. Structural characterization was performed by X-ray diffraction and transmission electron microscopy (TEM).

From our TEM investigations we found that Yb is deposited with fcc structure as major phase, and additional two minor hcp-type phases depending on film thickness. We will present a schematic model for a microscopic description of the microstructure and localization of the fcc- and hcp-type structures as well as the Fe-clusters. For our deposition conditions the Fe-nanoclusters are preferentially located at Yb grain boundaries and their sizes depend on Fe concentration and substrate temperature as well. For very low Fe concentration and substrate temperature, Fe clusters do not magnetically order at low temperature, but for larger Fe contents they are found in a magnetically ordered state. Typical magnetic blocking temperatures are on the order of 5-10 K according to AC susceptibility and in the 10-20 K range for Mössbauer spectroscopy.

In general, we could show that the chosen substrate temperature TS, during the film deposition, has strong influence on the Fe-cluster sizes, with bigger clusters formed at higher TS values. We could demonstrate that the clusters have sizes in nanometer scale and are generally formed by 30-40 atoms that produce an average magnetic moment of about 80 μB and an effective anisotropy constant in the range of 7.7 to $11.7 \cdot 10^5$ J m$^{-3}$, which is higher than the value for bulk Fe. The enhanced values may be related to surface effects and eventually to inter-particle interactions. In fact AC-susceptibilities indicate that the Fe clusters are weakly interacting with frequency dependent Vogel-Fulcher temperatures on the order of only 3 K and less. The Fe clusters reveal a cluster-glass-like magnetic behavior, i.e., they do not have a pure superparamagnetic behavior for 5.0% Fe-doped Yb films.

# Mössbauer spectrometry and the magnetism of Fe-doped and Fe-transition-metal co-doped ZnO and SnO₂ nanoparticles

<u>C. Barrero</u>[1], J. Beltran[1], K. Nomura[2] and A. Punnoose[3]

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[2]*Department of Applied Chemistry, School of Engineering, Tokyo University, Tokyo-Japan*
[3]*Department of Physics, Boise State University, Boise-United States*

Understanding the actual role of iron in the room temperature ferromagnetism (RTFM) of Fe-doped and Fe-Transition Metal (TM)-codoped ZnO and SnO₂ nanoparticles is still one of the most puzzling investigations in materials science. While some studies concluded that the Fe ions participate in the magnetic interaction, others on the contrary do not believe Fe as playing a direct role in the magnetic exchange interaction. In this presentation we will show some examples of the contributions that $^{57}$Fe Mössbauer spectrometry have done to the characterization of Fe-doped ZnO [1], Fe-TM (with TM = Cr, Mn, Co, Ni and Cu) codoped ZnO [1,2] and Fe-doped SnO₂ [3-5] nanoparticles. We will show how this technique has contributed to the: (i) demonstration of the absence of both spurious phases and clustering of ions, (ii) determination of the preferable sites, high or low spin character, and oxidation states of the Fe ions, (iii) identification of the possible preferable location of the ions, either at the surface, at the interior or in the whole nanoparticles, (iv) indirect identification and characterization of possible defects, and (v) determination if the Fe ions are involved in the magnetic ordering or not. An important finding is that the ferromagnetic signal detected in most of our samples do not directly originates from the Fe ions, but from the defects that these ions produce in the samples.

[1] Jailes Beltrán et al., J. Appl. Phys. 113 (2013) 17C308.
[2] Jailes Beltrán et al., J. Phys. Chem. C, 118 (2014) 13203-13217.
[3] Alexander Punnoose et al., J. Appl. Phys. 115 (2014) 17B534.
[4] Jailes Beltrán et al., J. Mater. Sci. 45 (2010) 5002-5011
[5] Kiyoshi Nomura et al., Phys. Rev. B 75 (2007) 184411.

# Role of the intermediate spin state of reduced non-heme iron in bacterial reaction centers of type II

K. Burda[1], A. Halas[1], V. Derrien[2], A. Chumakov[3], P. Sebban[2], T. Slezak[1],
J. Korecki[1] and A. Orzechowska[1]

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Non-heme iron (NHFe) is a preserved component of the photosynthetic reaction centers of type II. It was already present in primitive photosynthetic bacterial organisms about 3.8 billion years ago. Our aim was to study its influence on the activity of the $Q_A$ – Fe – $Q_B$ complex located on the acceptor side of the photosynthetic bacterial reaction centers of type II. The role of NHFe still remains unclear, especially in the stabilization of the $Q_A$ and $Q_B$ binding sites of the primary and secondary quinone acceptors, respectively, as well as the primary electron transfer between these quinone acceptors. This step of the electron transfer is activated at temperatures $\geq 160$ K and at this temperature fast collective motions of the protein matrix in the vicinity of NHFe appear [1-3]. Mössbauer spectroscopy, nuclear resonant inelastic scattering of X-ray radiation (NIS) and nuclear forward scattering (FNS) using synchrotron radiation are unique methods allowing to monitor the relationship between the spin and valence state of NHFe and the local flexibility of bacterial reaction center (BRC) core proteins in the vicinity of the iron-quinone complex. Various spin states of reduced NHFe were found in different mutated bacterial reaction centers of Rb. sphaeroides. For the first time an intermediate spin state of $Fe^{2+}$ was observed in photosystems of type II. Its relevance to the photosynthetic activity of the studied systems will be discussed. The role of NHFe in coupling of the reorganization of BRC core proteins and triggering of electron and proton transfer on its acceptor side is suggested.

[1] P. Eisenberger et al. Biophys. J. 37 (1982) 523–538.
[2] K. Burda, Cell Biochem. Biophys. 47 (2007) 271–284.
[3] A. Halas et al. Biochim. Biophys. Acta 1817 (2012) 2095-2102.

# Magnetic thin films and multilayers

## M. Carbucicchio

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Recently, increasing attention is addressed to nanoscale systems whose properties are largely depending on the low dimensionality and on the phenomena occurring at the interface between different nanometric layers or between film and substrate. The Mössbauer spectroscopy is a very powerful technique to study the surface and interface phenomena occurring in nanocomposites, in particular it allows to understand and correlate them to the macroscopic structural, electric and magnetic properties of the systems. New generations of magnetic recording devices require to combine nanocomposite materials having very different properties and exchange coupled at their interfaces. The intermixing phenomena and the surface morphology are not only fundamental properties of the final device but become parameters that have to be tuned and controlled. In this work the results obtained on two thin multi-layered systems Fe/Co and Fe/Cr will be presented. These two systems have very different magnetic behaviours characterized by the establishing of an exchange coupling interaction at the interface of the elemental layers which favours a parallel and an antiparallel alignment of the magnetic moments respectively for Fe/Co and Fe/Cr. These media, therefore, can be considered as model systems representing the exchange spring and exchange-biased systems. Both multilayers were grown by electron beam evaporation onto different substrates: monocrystalline (100)-MgO, naturally oxidised (100)-silicon and amorphous glass substrates. The samples have been characterized by high resolution transmission electron microscopy (HR-TEM) and atomic/magnetic force microscopy (AFM/MFM). The interface phenomena have been analysed by conversion electron Mössbauer spectroscopy (CEMS). The magnetic properties have been studied using magneto-optical Kerr effect magnetometer (MOKE) applying the magnetic field at different angle into the sample plane. The thickness of the elemental layers and the growing temperature have been changed in order to study their effect on the structural and the magnetic properties.

# Application of the Mössbauer spectroscopy to study spin- and charge-density waves

S.M. Dubiel

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Relevance of the Mössbauer spectroscopy (MS) in a study of spin-density waves (SDWs) and charge-density waves (CDWs) will be presented. CDWs exist in 1D and 2D chalcogenides e. g. $TaS_3$, $NbSe_3$, $TaS_2$, $VS_2$, and $NbSe_2$, while SDWs in 3D metals e. g. $\omega$-Zr, Cr. SDWs were also suggested to occur in iron-pnictides. SDWs are usually accompanied by CDWs.

The potential of MS pertinent to SDWs and CDWs will be outlined in the first part of the talk. In particular, it will be shown that (a) commensurate structures can be distinguished from incommensurate ones, and (b) amplitude and sign of higher-order harmonics, hence shape of SDWs and/or CDWs, can be determined.

Applications of MS using the effect on $^{119}$Sn nuclei (chromium and its alloys) and on $^{57}$Fe nuclei (Fe-pnictides) will be shown in the second part. In particular, it will be demonstrated that Mössbauer spectra are very sensitive to size of grains, presence of foreign atoms and strain. In other words, to obtain the proper information on virgin properties of SDWs and/or CDWs single-crystalline, strain-free samples are needed.

[1] S.M. Dubiel, J. Cieslak, in Mössbauer Spectroscopy and Transition Metal Chemistry, by Ph. Gütlich, E. Bill, A.X. Trautwein, 2011, Springer Verlag.
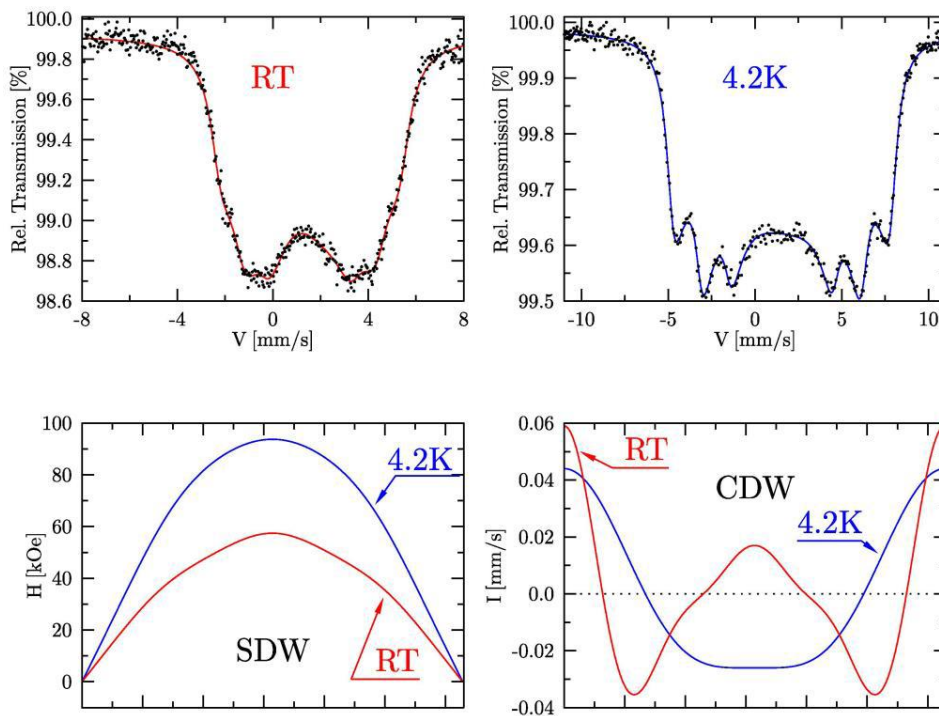
Fig. 1  (top) $^{119}$Sn Mössbauer spectra recorded at 4.2 K and 295 K on a $^{119}$Sn-implanted single-crystal chromium, and (bottom) shapes of the spin-density waves (SDW) and charge-density waves (CDW) derived from the spectra [1].

# Synchrotron radiation Mössbauer spectra of a rotating absorber

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In the sixties many Mössbauer spectroscopy experiments have been performed with rotating absorbers, in order to measure the second order Transverse Doppler Shift, to test the validity of the Einstein Time Dilation formula. In most of these experiments the source and absorber were at rest relative to each other in the Rotating Coordinate system, and the counting rate change was recorded as a function of rotation frequency (f). All these studies claimed agreement with Relativity Theory (RT) predictions. In all those studies it was assumed that the absorption line width does not depend on f. Kündig (1963, Phys. Rev. **129**, 2371) was able to measure the full absorption spectrum as a function of f, and shows large changes in absorption line width. His most reliable experimental results were reanalyzed by Kholmetskii et al. (2008, Phys. Scr.**, 77**, 035302) to show that Kündig's results **disagree** with RT. Moreover, they performed an elegant two absorber experiment, (2009, Phys. Scr.**, 79**, 065007), by which they claim to prove again the disagreement with RT.

In our recent experiment we used a Synchrotron Mössbauer Source (SMS) from the $^{57}$Fe SMS ID18 beam-line of ESRF, with a 304 stainless steel 50 µm absorber, attached to a rotating disc. For such a configuration, one expects absorption line broadening as predicted by Friedman and Nowik (Phys. Scr.**, 85**, 2012, 065702). We confirm (Friedman et al, Journal of Synchrotron Radiation 2015, to appear) that: The broadening is linearly proportional to the rotation frequency f, and to the beam line width (Slit) at the position of the rotation axis. With a slit installed at the rotation axis, the effective beam width decreased from 15.6 µm to 5.4 µm, and enabled to obtain meaningful spectra up to 300Hz. Our next ESRF experiment, July 2015, will use an enriched absorber of $K_4Fe(CN)_6$ and a slit down to 1-2 µm. This will enable an accurate test to Einstein's time dilation formula.

# Magnetic properties of antiferromagnetic nanoparticles and the influence of inter-particle exchange interactions

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Magnetic dipole interactions may be negligible between antiferromagnetic nanoparticles due to the particles' almost zero net magnetic moments [1,2]. However, inter-particle exchange interactions can be established between magnetic surface ions of neighboring particles [2] and lead to a suppression of superparamagnetic relaxation [2-4] and/or spin reorientation [5,6]. The interaction effects depend very much on the exact particle attachment [3-6]. In aqueous suspensions, nanoparticles may attach into larger structures, where water can be expelled from the interface. The particles may thereby form larger crystalline structures [7], where the resulting morphology and crystallinity may differ from that of larger crystals grown "classically" by addition of ions [7]. It has been shown by Mössbauer spectroscopy in combination with transmission election microscopy that magnetic properties of antiferromagnetic nanoparticles are indicative of how the particles are attached together [3-6], e.g., whether the particles are attached with perfect oriented attachment [3], with low-angle grain dislocations [4], with larger crystalline angles, or with a more random aggregation [5,6].

For 7 nm $\alpha$-$Fe_2O_3$ particles with oriented attachment, the crystalline order continues perfectly across particle interfaces, and the magnetic properties correlate to the increased particle size [3]. In a study of $\alpha$-FeOOH with low-angle grain boundaries, the magnetic mismatch at these grain boundaries lead to a weakened magnetic coupling, and magnetic properties which are neither nano- nor bulk-like are observed [4]. For more randomly aggregated 7 nm $\alpha$-$Fe_2O_3$ particles, magnetic spins may rotate up to 18° out of their easy plane due to inter-particle exchange coupling [5]. In aggregates of $\alpha$-$Fe_2O_3$ and NiO nanoparticles, spin rotations up to 70° have been observed [6].

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# Magnetic properties of ferrites and nanoferrites investigated by $^{57}$Fe Mössbauer spectrometry

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The microcrystalline ferrites have been widely investigated in the last century for their chemical, electrical and magnetic properties while attention was recently paid when they are nanostructured. Both micro- and nanoferrites exhibit unusual and interesting magnetic properties which are strongly dependent not only on their morphology and their chemical composition but also on their local chemical order. It is also clear that the elaboration and/or the synthesis and post-treatment of these materials have a significant role on their chemical and physical nature as well as the design of new functional nanoarchitectures. This procedure is quite important to get reproducible systems with tunable properties to be applied them in various fields such as recording media, GMRs, MRI contrast agents, nanocareers for drug delivery, magnetic hyperthermia fluids.

The structural and magnetic properties of any ferrite can be completely investigated by using several complementary techniques as diffraction, electron microscopy, magnetic measurements to correlate the structural and static and dynamic magnetic properties. In addition to these large scale approach techniques, $^{57}$Fe Mössbauer spectrometry appears as an excellent complementary tool. Indeed, this local probe technique usually contributes to investigate in situ local atomic order and magnetic properties: indeed, it is able to first discriminate surface and bulk effects in addition to oxidation and spin states of Fe species and then contributes to follow the hyperfine magnetic properties and their dynamics in correlation with superparamagnetic relaxation phenomena.

We first discuss the role of some relevant parameters in magnetic nanostructures and then we illustrate how zero-field and in-field $^{57}$Fe Mössbauer spectrometry contribute to better understand static and dynamic magnetic properties from selected examples based on microcrystalline and nanostructured ferrites, nanoparticles and functionalized nanoparticles.

# Development and applications of SERS techniques

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Introduction of silver nanocrystals in the porous silicon is promising for Surface Enhanced Raman Spectroscopy (SERS). Here we present the results on preparation of stable and uniform SERS solid substrates using macroporous silicon (pSi) with deposited silver and on the devices based on heterojunctions of porous silicon formed by adonization in HF-based electrolytes and organic thin films formed by vacuum evaporation. Macroporous silicon is produced by anodisation of p-type silicon in hydrofluoric acid. The as prepared pSi is then used as a template for Ag depositions. The noble metals were deposited in three different ways: by immersion in silver nitrate solution, by drop-casting silver colloidal solution and by pulsed laser ablation (PLA). Substrates obtained by different deposition processes are evaluated for SERS efficiency using methylene blue and rhodamine 6G at 514.5, 633 and 785 nm. Substrate concentrations detected in most of the cases were in the nanomolar range suggesting that it may be possible to detect lower analyte concentrations when using porous instead of crystal silicon template.The possibility of histamine detection in fish by Surface Enhanced Raman Spectroscopy was examined. Four different silver colloids were used as SERS substrates in combination with different aggregation agents. Excitation wavelength, aggregating agent concentration and time of data acquisition have been optimized in order to obtain maximum enhancement of histamine signals. The obtained results show a potential for development of new histamine detection method in fish and fish products.

# In-Situ Mössbauer and PIXE analysis
# of planetary surfaces and small bodies

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The miniaturized Mössbauer spectrometer MIMOS II [1] and the Alpha-Particle X-ray spectrometer (APXS) [3] are off-the-shelf instruments with proven flight heritage. They were successfully during NASA's Mars Exploration Rover (MER) mission [2] and on-board the UK-led Beagle 2 and the Russian Phobos-Grunt missions, as well as on the ESA comet mission Rosetta [3].

MIMOS II consists of a sensor head and an electronics board. The sensor head can be mounted on e.g. a robotic arm and needs to be brought in contact with the sample to be analyzed. No sample preparation is necessary. The sensor head carries the radiation source (57-Co) and detector system. The electronics board holds data acquisition and instrument control units (CPU + FPGA), voltage converters, and electrical and data interfaces to the spacecraft.

Mössbauer spectroscopy determines oxidation states of the element Fe and Fe-bearing mineralogy, and quantifies the distribution of Fe between oxidation states and mineral phases. This information is vital to assess the habitability of Mars: The Fe sulphate hydroxide jarosite [3], for example, provides evidence for past liquid water at the surface albeit at low pH, while (Fe,Mg)-carbonates are evidence of abundant liquid water at neutral pH. Meteorites were discovered on the surface of Mars on the basis of their metallic Fe content during the MER mission. Asteroids are the parent bodies of most meteorite group, and their Fe mineralogy is important to understand their and the Solar System's evolution.

The Alpha Particle X-Ray Spectrometer (APXS) is one of the 9 scientific instruments on board Philae, the Rosetta mission´s lander. Rosetta reached comet 67P/Churyumov-Gerasimenko after a 10-year cruise in August 2014. Philae landed on October 12th, following a 7-hour descent. Philae did not get anchored to the surface at first touchdown and bounced off twice before coming to rest at its not yet precisely known final position., The APXS was deployed during the first science sequence to reach the comet's surface and determine its chemical composition.

The APXS combines an alpha mode for alpha backscattering spectroscopy and an XRF mode for X-ray fluorescence and PIXE (particle induced X-ray emission) spectroscopy in one single instrument. The target is irradiated by Curium 244 sources exciting characteristic X-rays of the elements present in the surface. The alpha mode allows detecting low-Z elements like C and O and groups of elements with a higher Z. The X-ray-SD-detector allows the detection of most of the elements from Na up to Ni and above. The design of the Rosetta APX spectrometer is based on the experience gained with the APXS instruments built for the Russian Mars 96 spacecraft and NASA's Mars Pathfinder and Mars Exploration Rover missions.

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# Relationship between structure and visible light activated photocatalytic ability of iron containing aluminosilicate glass prepared by sol-gel method

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Anatase type $TiO_2$ is well known as a photocatalyst when activated only by UV light. For technical application, it would be more effective to develop a photocatalyst that can be activated by visible light. Recently, Takahashi *et al.* reported that iron silicate glass prepared by sol-gel method showed photocatalytic effect due to the precipitated hematite in the glass host [1]. On the other hand, it was reported that aluminate glass is transparent for light in the visible and infrared (IR) region [2]. It is expected that the photocatalytic ability of iron silicate glass might be increased by introduction of $Al_2O_3$ due to the high IR transmittance. In this study, we report the relationship between visible light activated photocatytic effect and the structure of iron containing aluminosilicate glass with the composition of $40Fe_2O_3 \cdot (60-x)SiO_2 \cdot xAl_2O_3$ (abbreviated as FS*x*A, *x* is in mass %) prepared by sol-gel method. $^{57}$Fe-Mössbauer spectra (FeMS) were measured in order to identify iron containing phases precipitated in the glass system. Methylene blue (MB) degradation tests were applied to check catalytic activity. UV-VIS spectra of MB during the degradation were recorded between 200 and 800 nm under irradiation of visible light in the range of 420 to 750 nm. As shown in Fig.1 (a) and (b), FeMS of heat treated FS15A was composed of a paramagnetic doublet with isomer shift (I.S.) of 0.25 mms$^{-1}$ and quadrupole splitting (Q.S.) of 0.99 mms$^{-1}$ due to distorted $Fe^{III}O_4$ tetrahedra, and a magnetic sextet with I.S. of 0.37 mm s$^{-1}$ and, Q.S. of -0.19 mm s$^{-1}$, and Internal magnetic field ($H_{int}$) of 51.7 T assigned hematite. In addition, FeMS of FS0A was composed of two other doublets due to fayalite, and FS15A contained a relaxed sextet due to $Fe_{1.833}(OH)_{0.5}O_{2.5}$ [3]. As a result of the MB degradation tests, the first order rate constant ($k$) for heat treated FS0A and FS15A were calculated to be $2.18 \times 10^{-3}$ and $6.66 \times 10^{-3}$ min$^{-1}$, respectively. These results prove that addition of alumina into iron silicate glass could improve the visible light-photocatalysis caused by hematite and $Fe_{1.833}(OH)_{0.5}O_{2.5}$ in the glass matrix.

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# Mössbauer, XRD and TEM study on the intercalation and the release of drugs in/from layered double hydroxides

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Layered double hydroxides (LDHs), also known as anionic clays, are found in Nature, but for use, they are most often synthesised [1]. Most representatives belong to the hydrotalcite supergroup, in which those containing Ca(II) and a trivalent metal form the hydrocalumite subgroup. These materials consist of positively charged layers with heptacoordinated Ca(II) and octahedral Al(III) or Fe(III) as the most frequently occurring trivalent metal. The interlayer space contains neutralising anions as well as H-bonded water molecules. LDHs are one of the very important nano-carriers for drug delivery, due to their many advantageous features, such as the ease and low-cost of preparation, low cytotoxicity, good biocompatibility, protection for the intercalated drugs, and the capacity to facilitate the uptake of the loaded drug in the cells. In our previous studies, Mössbauer spectroscopy [2-4] was applied to monitor structural changes occurred during the incorporation of Fe(III) in MgFe- and CaFe-LDHs and the intercalation of various organic compounds in anionic form. Recently, we have successfully elaborated a protocol for the intercalation and release of indol-2-carboxylate and L-cystinate in CaFe-LDH. The corresponding structural changes in the LDH samples were studied by XRD, HRTEM and $^{57}Fe$ Mössbauer spectroscopy. The Mössbauer spectra reflected small but significant changes upon both the intercalation and the release of drugs. The changes in the basal distances could be followed by XRD measurements, and HRTEM images made these changes visible.

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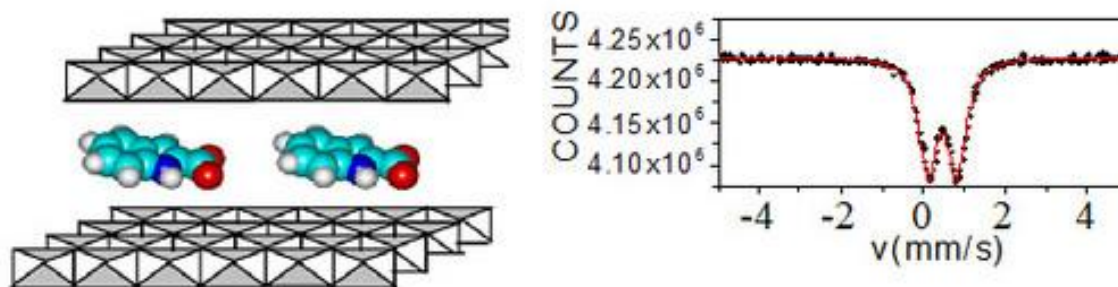
Fig. 1   Structure of LDH with an intercalated drug and its 78K $^{57}Fe$ Mössbauer spectrum.

# Structural transformation in high corrosion resistant steel

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The long-term reliability of construction materials operating in nuclear facilities under harsh conditions such as intense irradiation, high temperature, and in the presence of corrosion agents is a serious technologic, economic, and environmental demand. In this work, we elucidate the structural features of a novel advanced corrosion resistant LC 200N steel, possessing large and stable hardness up to relatively high temperatures and excellent wear resistance. High Cr and N content provide high hardness and wear resistance of this perspective material which can be considered for possible applications in nuclear installations.

We have employed Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) and micro X-ray fluorescence analysis (XRF) for sample characterization and check of the element composition. The samples were investigated both in the as-prepared state, i.e. in form of disks (thickness ~0.5 mm, diameter 22 mm) after electro-erosive cutting from original rods as well as after polishing of both surfaces. SEM/EDS unveiled regions with different Cr concentrations in the steel – lower Cr concentration (~ 15 at. %) was found in the bulk material and considerably higher Cr concentration (~50 at. %) was determined in precipitates.

Mössbauer spectrometry was chosen as a principal method of investigation. Surface as well as bulk properties were studied using CEMS (Conversion Electron Mössbauer Spectrometry) and transmission techniques, respectively. Structural arrangement was checked by scanning electron microscopy and transmission electron microscopy. Chemical composition was inspected by X-ray fluorescence technique as well as by neutron activation analysis. The impact of cutting upon the surface of the specimens is also discussed. Apart from the declared chemical composition, presence of residuals from the cutting process was identified. After a consequent removal of the affected layers, the original structural and magnetic characteristics of the base material were resumed.

# Preparation of iron oxide xero-and aerogels
# by hydrolysis in aprotic media

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Preparation of iron oxide xerogels and high surface area aerogels in particular got a renewed impetus recently. A simple possible procedure is the controlled hydrolysis performed in aprotic media by using water in restricted amounts. The tuning of the process can be provided by an appropriate proton scavanger (propylene oxide or epichlorohydrine). A suitable choice can be hydrolyzing iron from $FeCl_3 \cdot 6H_2O$ in dimethyl sulfoxide (DMSO) or in dimethyl formamide (DMFA) media without any further additional water, only by using the six stoichiometric water molecules present in the crystals of the starting iron salt. A dense gel forms within a few hours after mixing the components. Aerogel can be prepared from the gel in a further stage by extraction of solvents with supercritical carbon dioxide [1].

In our recent study the first stages of hydrolysis were followed by recording spectra of frozen reaction mixtures taken at various intervals after mixing the reactants and solvent. Replacement of ligands in the coordination sphere of iron,

formation of transitional species could be followed. For example, five different components were identified by hydrolyzing $FeCl_3 \cdot 6H_2O$ in DMFA. The change of their relative spectral contributions in dependence of time is shown in Fig. 1.

Similar procedure has also been performed in DMSO media, and aerogel was prepared by supercritical $CO_2$ extraction. The product is characterized by 671 $m^2$ $g^{-1}$ specific BET surface area, 3.7 $cm^3$ $g^{-1}$ pore volume values, and a pore size distribution with maximum at 17 nm. High resolution transmission electron microscopy studies were also performed on the samples. The aero- and xerogels are typically composed from nanoparticles with diameter less than 5 nm. Reflection rings with 0.212 and 0.245 nm characteristic distances were observed. These and some further information suggest that the main constituent of the aerogel is ferrihydrite.
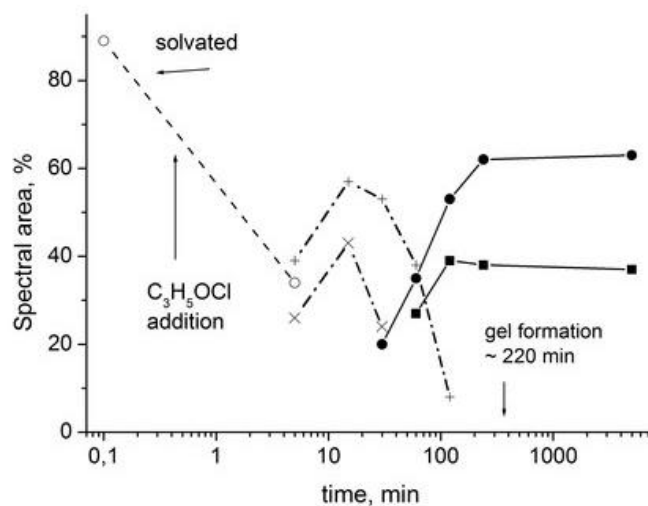
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Fig. 1   Time dependence of relative spectral contributions of different iron species formed in the $FeCl_3 \cdot 6H_2O$ / DMSO / epichlorohydrine mixture.

# Mössbauer spectroscopy characterization of hollow microcapsules designed for the targeted drug delivery

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A great attention is now paid to the application of magnetic nanostructures in biology and medicine and focused mainly on the targeted drug delivery, hyperthermia treatment, magnetic resonance imaging (as contrast media), separation of biochemical products and gene manipulation and immunoassays. In our study, hollow microcapsules from biodegradable polyelectrolytes were fabricated by layer-by-layer adsorption technique. The capsule shells were modified with the maghemite nanoparticles by in situ synthesis (Fig. 1). Such capsules can be assigned for the target drug delivery. The Mössbauer spectroscopy along with several other complementary techniques was used for the evaluation of their structural, physicochemical, and magnetic properties. An average diameter of the capsule is about 6.7 micrometer while the average thickness of the capsule shell is 0.9 micrometer. A particular effort was devoted to distinguish between magnetite $Fe_3O_4$ and maghemite $\gamma$-$Fe_2O_3$ nanoparticles as well as to study the effect of the size and coating on the magnetic behavior of the nanoparticles. Mössbauer spectroscopy, XRD, HRTEM and Raman spectroscopy data revealed that the iron oxide nanoparticles have the crystal structure of maghemite $\gamma$-$Fe_2O_3$ [1]. The nanoparticles were highly monodisperse with medium size of 8 nm. The superparamagnetic behavior of the nanoparticles was established up to room temperature, and the microcapsules can be handled by an external magnetic field, which is important for target drug delivery.

In addition, the poly(MMA-co-MAA) microspheres were used as a core template to synthesize the hollow $SiO_2$/$CoFe_2O_4$ composite spheres using chemical co-precipitation, followed by the sol-gel method and then calcination. The size control and magnetic properties of the $CoFe_2O_4$ nanoparticles can be tuned at the stage of calcination. The Mössbauer and magnetic measurement data indicate that the samples display ferromagnetic and superparamagnetic behavior at room temperature depending on the size of particles.

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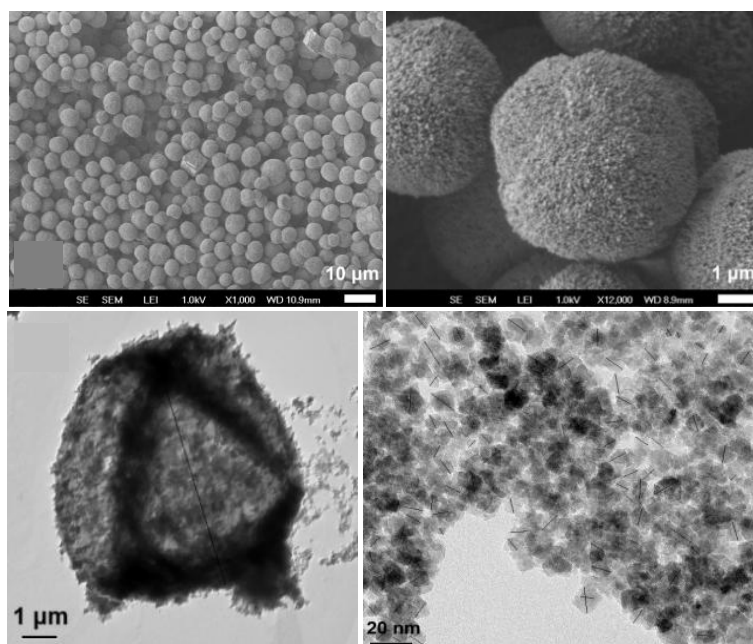[1]　I.S. Lyubutin, et al., J. Mater. Sc & Eng C. 45 (2014) 225-233.

Fig. 1　The scanning (SEM) and transmission (HRTEM) electron microscopy images of microcapsules.

# Mössbauer studies on $Fe_3O_4$ and $CoFe_2O_4$ thin films

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Magnetite is a classic functional material that has been often used in catalysis and magnetic applications. It has a spinel structure, shared with many ternary oxides, and in particular, cobalt ferrite (CFO). While magnetite has a high bulk magnetic moment of 4.0 $\mu_B$ and a low anisotropy that favours <111> magnetic easy axes at room temperature, cobalt ferrite has a lower magnetic moment of 3.4 $\mu_B$ and a much higher magnetic anisotropy which favours <100> ones. Both have been considered promising materials for spintronic applications as spin-injectors or as part of a spin-valve. Although cobalt ferrite has often been combined with ferroelectric perovskites to couple the high magnetostriction of cobalt ferrite with materials such as $BaTiO_3$ or $BiFeO_3$, in such case the two components are immiscible. Instead, magnetite and cobalt ferrite form a solid solution that extends from pure cobalt oxide to pure magnetite. This has been employed to tune the magnetic and electric properties of intermediate cobalt ferrites both in the bulk and in thin films. Thin films with successive layers of the two spinels have also been grown although interdifussion across their interface remains a concern. It is thus expected that growth of mixtures of both spinel phases that retain their individual characteristics would be difficult, although for the Co-rich phase diagram a miscibility gap exists. Such system would be interesting to study the coupling between the magnetically soft magnetite and the hard cobalt ferrite, and to try to incorporate the best properties of both components in a single film.

We focus here on the growth of films of magnetite and magnetite/cobalt ferrite on $SrTiO_3$ substrates. Such substrates have the advantage of being available in doped form so the substrate conductivity can be tuned while keeping the same strain state in the films. We report here on the high-quality magnetite films we have grown by infrared-pulsed laser deposition, thus reducing the oxidation state from the target $Fe^{3+}$ to the magnetite combination of $Fe^{3+}$ and $Fe^{2.5+}$. We also show in the present work the possibility of growing mixed magnetite cobalt ferrite films by employing similar conditions for cobalt ferrite targets. PLD with wavelengths in the ultraviolet range has often been employed to grow both magnetite and cobalt ferrite. The use of IR-PLD as presented in this work is more unusual, and we complement it with a full structural and chemical characterization.

# Surface features of nanocrystalline alloys

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Metallic glasses (MGs) belong to a class of amorphous materials that, though introduced already couple of decades ago, are still attractive because of their unique magnetic [1] as well as mechanical [2] properties. Some MGs are used as precursors for preparation of nanocrystalline alloys (NCAs) that exhibit magnetic parameters superior to those of the original MGs [1]. NCAs represent a new class of nanocomposite materials the physical properties of which can be tailored not only by controlling their chemical composition but also by varying the size of crystalline grains, their morphology and structural arrangement. They attract a lot of scientific interest because, contrary to their amorphous counterparts, their magnetic parameters do not substantially deteriorate at elevated temperature during their practical exploitation.

Fe-based NCAs are routinely investigated by $^{57}$Fe Mössbauer spectrometry which provides direct identification of all structurally different regions of the resonant atoms that are located in nanocrystalline grains, the residual amorphous matrix and/or in between these two phases. As NCAs are usually in a form of thin (~20 micro) ribbons, in this contribution we discuss their surfaces. Due to the preparation procedure which consists of rapid quenching of a melt upon a wheel and subsequent heat treatment, two distinct sides can be identified in the NCA ribbons. They are denoted as the wheel and the air side as they were in contact with the quenching wheel and the surrounding atmosphere, respectively. They differ namely in the degree of the surface crystallization.

In this presentation, we report on the use of surface sensitive Mössbauer effect techniques like Conversion Electron Mössbauer Spectrometry (CEMS) and Conversion X-Ray Mössbauer Spectrometry (CXMS) to follow the structural variations that are observed at both sides of the ribbons. CEMS and CXMS provide information from subsurface regions that extend to the depth of 200 nm and ~5 micrometres, respectively. Immediate surfaces are investigated by the help of AFM and MFM. Structural modifications demonstrate themselves also via macroscopic magnetic parameters such as temperature dependence of magnetization, Curie temperature, and hysteresis loops that are followed by conventional magnetic measurements.

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# Quality assurance in Mössbauer spectroscopy

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Quality assurance (QA) in industry, i.e. the way of preventing mistakes or defects during production is a concept dating back to the forties of the last century. Since several decades, QA has gradually become a standard requirement for many services, too. Generally speaking, QA ensures that the customer may trust the producer without having its special knowledge. Nowadays, QA is a common practice in material testing and analysis as well as in other scientific services. Until the early nineties, Mössbauer experiments were, as a rule, performed by professional Mössbauer groups so that the supplier and the recipient of the service was the same and, accordingly, there was no need to elaborate a QA scheme for Mössbauer spectroscopy. However, during the last two decades, this has completely changed and currently many chemists, materials scientists, mineralogists, life scientists, etc. are applying Mössbauer spectroscopy without really knowing details of its theory and methodology. The result is a flood of improperly performed experiments, data reduction exercises and, consequently, of partly inconclusive publications. Clearly, there is a need to set up QA scheme for Mössbauer spectroscopy. The presentation will summarise the key elements of such a scheme for laboratory experiments. Experimental aspects include properly choosing the velocity range, optimising the geometry and drive frequency of the experiment, avoiding dead-time effects of the detector and the analogue electronics, optimising and properly measuring the non-resonant background. The appropriate choice of the thickness of the sample, especially if granularity cannot be avoided, is a crucial part of planning the experiment. A prerequisite of correct data reduction is the proper calibration of the velocity scale taking into account the nonlinearity of the drive, specifying details of the experimental geometry, as well as the geometry and the age of the radioactive source the latter being necessary for taking into account the source selfabsorption. The correct method of fitting a theory to the spectrum is calculating the transmission integral, an approach no more limited by its computation time demand and included, at least as an option, in up-to-date Mössbauer programs. A critical test of the reliability of spectrum fitting is the correlation matrix of the fitted parameters. Finally, implications of the Mössbauer spectroscopy QA scheme to a future network of Mössbauer laboratories in frames of an international distributed research infrastructure as well as to re-structuring the international Mössbauer community will be briefly discussed.

# DFT Study on thermal spin-crossover behavior for complexes having Fe(NCS)$_2$(pyridine)$_4$ unit

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Fe(II) spin-crossover (SCO) phenomena described as the switching behavior of two spin ground states between high-spin (HS) and low-spin (LS) have inspired lots of chemists due to their application possibilities. These possibilities come from the response abilities to several external field stimuli such as temperature, pressure and light-illumination. The investigations of coordination polymers by introducing bridging ligands have suggested not only the controlling these responsivities of SCO behavior, but also the additional potentials for fundamental and applied fields in chemistry.

The framework of coordination polymers [Fe(NCS)$_2$L$_2$]$_n$, which have *trans*-Fe(NCS)$_2$ unit bridged by 4,4'-bipyridine type ligands (L), have provided the several types of SCO-on/off results. Since their assembled structures have the vacancies, which can incorporate the guest molecules, due to the systematic construction of Fe$^{II}$ octahedral sphere, the guest dependency of these compounds has been studied extensively. These dependencies of SCO-on/off behaviors on the selection of guest molecules are of great worth from the viewpoint of controlling the switching of bistable two quantum states, leading to the industrial application such as the molecular-based memory.

Temperature-dependent spin transition behavior has been understood as the thermodynamic reaction with the energy difference between HS and LS. If the difference between them of zero-point corrected energy ($E_0$) including total energy ($E_{tot}$) and zero-point energy ($E_{ZPE}$), $\Delta E_0^{HL} = (E_{tot}^{HS} + E_{ZPE}^{HS}) - (E_{tot}^{LS} + E_{ZPE}^{LS})$, is negative, its spin state remains HS state (SCO-off). If $\Delta E_0$ is positive, SCO transition occurs (SCO-on). Theoretical investigations of SCO behavior have been achieved successfully by applying density functional theory to the mono-nucleus model.[1]

In the present study, we present the density functional investigation to coordination polymers and evaluate the validity of iron mono-nucleus model. Estimating the energy difference between HS and LS for calculation models based on coordination polymers [Fe(NCS)$_2$L$_2$], we discuss the reproducibility of our procedure to SCO-on and -off behaviors for several complexes including mono-nucleus complex.

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# Characterization and conduction mechanism
# of highly conductive vanadate glass

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Isothermal annealing of barium iron vanadate glass, *e.g.* $20BaO \cdot 10Fe_2O_3 \cdot 70V_2O_5$, at temperatures higher than glass transition temperature ($T_g$) or crystallization peak temperature ($T_c$) causes a marked increase of conductivity ($\sigma$) from the order of $10^{-7}$ to $10^{-1}$ $Scm^{-1}$ [1-3]. It is noted that we can easily "*tune*" the conductivity by the heat treatment. These "highly conductive" vanadate glasses show a marked decrease in the activation energy for conduction ($E_a$), *e.g.*, from 0.38 to 0.13 eV, suggesting an increased carrier density in the conduction band (CB) [2,3]. Mössbauer study of "highly conductive" vanadate glasses shows a marked decrease of $\Delta$, *e.g.* from 0.70 to 0.55 $mms^{-1}$ (Fig. 1), which reflects a decreased $eq_{lat}$ or an increased symmetry of $FeO_4$ and $VO_4$ units.

It is expected that effective shielding of nuclear charge by 3d-electrons increases the mobility of carriers. In this paper, $20BaO \cdot xMO \cdot (10-x)Fe_2O_3 \cdot 70V_2O_5$ glasses (M: Ni, Cu, Zn) were studied in order to elucidate the effect of $3d^8(Ni^{II})$, $3d^9(Cu^{II})$ and $3d^{10}(Cu^I$ or $Zn^{II})$. Annealing of $20BaO \cdot 5ZnO \cdot 5Fe_2O_3 \cdot 70V_2O_5$ glass at 450 °C for 30 min caused a marked increase of $\sigma$ from $2.5 \times 10^{-6}$ to $2.3 \times 10^{-1}$ $Scm^{-1}$ at *RT*. These experimental results suggest that 3d-electrons occupying the outermost orbital of "d-block elements" could effectively shield the nuclear charge, and that the mobility of carriers in the CB (mostly 4s-band) increased remarkably. We can conclude that conductivity of these "highly conductive" vanadate glasses is associated with *n-type semiconductor model*, which is predominant over the *small polaron hopping theory*.
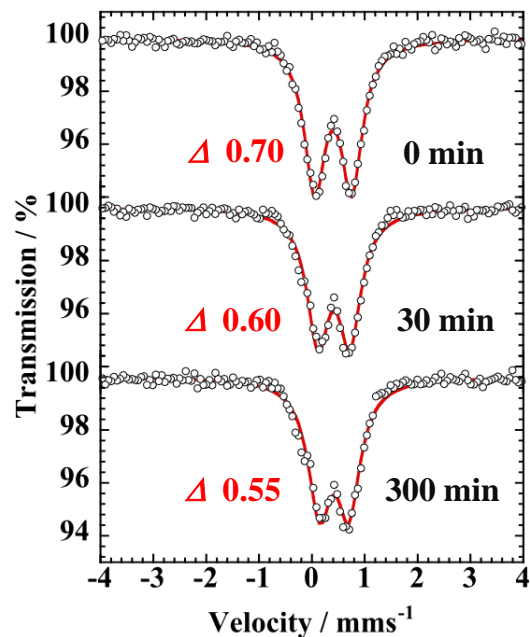


**Fig. 1** *RT*-Mössbauer spectra of $20BaO \cdot 10Fe_2O_3 \cdot 70V_2O_5$ glass annealed at 450 °C.

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# Oxygen vacancy and dilute magnetism of $SnO_2$ doped with Fe and metal ions

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To develop room temperature (RT) ferromagnetism in semiconductors, we have studied on transparent oxide semiconductors doped with magnetic ions. Interesting phenomena have been reported for these systems previously [1].

Ferromagnetism was observed by doping of dilute Fe ions into $SnO_2$ although only paramagnetic doublets were observed in $^{57}Fe$ Mössbauer spectra [2]. The magnetization decreased after annealing for many hours in air. Co-doping with Sb into Fe doped $SnO_2$ induced further ferromagnetism [2]. Broad peaks of $SnO_2$ were observed by $^{119}Sn$ Mössbauer spectrometry under a magnetic field [3]. This magnetic behavior may be due both to the lattice deformation and to the oxygen vacancies introduced by doping Fe. The isomer shift (*IS*) and quadrupole splittings (*ΔQ*) obtained by the experiments are shown in Fig. 1. The experimental values are grouped as follows: I1, I2 and I3 due to $Fe^{3+}$ and I4 due to $Fe^{2+}$. The groups I1 and I2 are observed with high and low peak intensity, respectively. The groups I3 and I4 are observed in only samples prepared by ion implantation and ball milling, respectively.

Substituting $Sn^{4+}$ by $Fe^{3+}$ favors the formation of oxygen vacancies. The *ab-initio* calculations were performed for the following model structures: $Sn_{15}FeO_{31}$ with nearest oxygen vacancy (Fe-VO1), with second nearest oxygen vacancies (Fe-VO2) and with third nearest oxygen vacancy (Fe-VO3), $Sn_{14}Fe_2O_{31}$ with the different configurations of two substituted Fe and one oxygen vacancy (Fe-VO-Fe) and $Sn_{14}Fe_2O_{30}$ with two substituted Fe ions and two oxygen vacancies (Fe-2VO-Fe). The calculated *IS* and *ΔQ* are also shown in Fig.1.

Bound magnetic polarons (BMP) are formed by two Fe ions linked with an oxygen vacancy, the Fe moments are aligned parallel to each other. However, two BMP become antiferromagnetically ordered, as the formation energy, $E_{anti}$ - $E_{ferro}$ = ΔE = -0.05 eV. When doping with extra electrons, such as with $Sb^{5+}$, ΔE = + 0.3 eV is obtained, that is ferromagnetic coupling between two BMP.

Therefore, oxygen vacancies and electron doping play an important role in the magnetism of Fe doped $SnO_2$.

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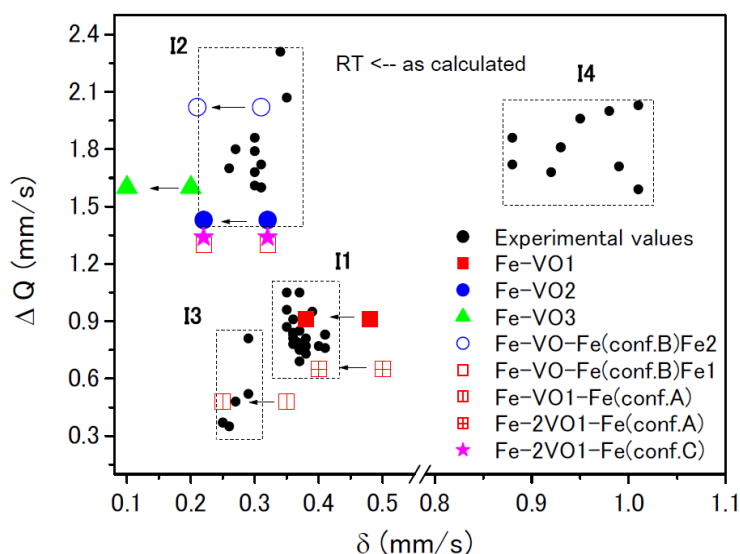[4] A.M.M. Navarro et al., J. Phys. Chem. C 119 (2015) 5596.

Fig. 1  *IS* (δ) and *ΔQ* obtained by the experiments and *ab initio* calculation (ref. 4). *IS* values at RT are shifted by about -0.1 mm/s from the as calculated ones.

# Investigation of magnetic, electronic and crystallographic structure of FeSb$_2$

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FeSb$_2$ is investigated since several decades [1], because of its interesting magnetic and electronic properties. It crystallizes in the *Pnnm* marcasite structure type, where Fe occupies only one crystallographic site, surrounded by slightly distorted Sb octahedral, which are corner shared in the *ab*-plane and edge shared along the *c*-axis, thus forming piles of tilted octahedral in *c*-direction. This is in agreement with Mössbauer spectra, which can be fitted by only one sub-spectrum. Whereas in a simple ionic picture iron has a low spin Fe$^{4+}$ ($t_2g^4 e_g^0$) ground state, because in this model the $t_2g$ levels split in a higher lying $d_{xy}$ and two lower lying $d_{yz}$ and $d_{xz}$ levels, a high spin ferric ground state was suggested from some Mössbauer investigations [2]. In contrast Mössbauer spectra taken in high magnetic fields are rather complex. An interpretation in terms of only one sub-spectrum can only explain approximately 60 to 70% of the spectrum. At least five subspectra are necessary to explain the in-field spectra [3].

In this work we present results of a reinvestigation of FeSb$_2$ by both zero and high-field $^{57}$Fe Mössbauer spectroscopy. The structure was investigated by neutron and X-ray diffraction. Electronic and magnetic properties were investigated by specific heat and dc-magnetic measurements.

The thorough investigation of the structure of the compound by neutron and X-ray investigation, both on powder and single crystal shows that approximately 30% of the iron atoms are shifted out of the center of the octahedra. This shift takes place in the basal plane of the octahedra. The relation of this shift to the analyses of the in-field Mössbauer spectra will be discussed.

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# Nanoscale dynamics - an atomistic picture

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How do metal atoms diffuse in ordered intermetallic alloys? What is the consequence in new material types, like thin films, or epitaxial ultra thin layers? The accepted view is that diffusion takes place by random jumps of atoms between nearest-neighbor sites. But what happens when the structure is highly anisotropic like a tetragonal $L1_0$ phase? We have carried out extensive studies on epitaxial $L1_0$-ordered FePt thin films which show exemplary and exceptional behavior.

Firstly, we have studied thin films of an isotopic altering multilayer superstructure containing alternate layers $Fe^{56}$ and $Fe^{57}$ isotopes using synchrotron radiation Mössbauer spectroscopy - nuclear resonant scattering (NRS) under grazing incidence. The measurements reveal the decay of the isotopic superstructure due to diffusion driven by successive annealing steps [1,2]. This superstructure decay can be seen with atomic resolution. The well-defined orientation of the lattice in FePt-thin films allows us to resolve the strong anisotropy of diffusion in the tetragonal structure, see Fig. 1 left.

Secondly, we have studied order-order transitions again on $L1_0$-ordered FePt thin films using CEMS [3]. We found that the films exhibiting the c-axis of the tetragonal structure perpendicular to the surface orient towards a-axis perpendicular to the film surface by annealing at 500 °C. This process is again driven by atomic diffusion. The ordering starts from the film surface, while a c-axis oriented re-ordering starts at the same time from the epitaxial interface, see Fig 1, right. The total film ordering runs towards an equilibrium state specified by the annealing temperature. We could analyze the transitions using an advanced Johnson-Mehl-Avrami formalism [3], showing the time constant, activation energies and ordering dynamics. The activation energies we find for the c-variant ordering are the same we found from the atomic diffusion studies.

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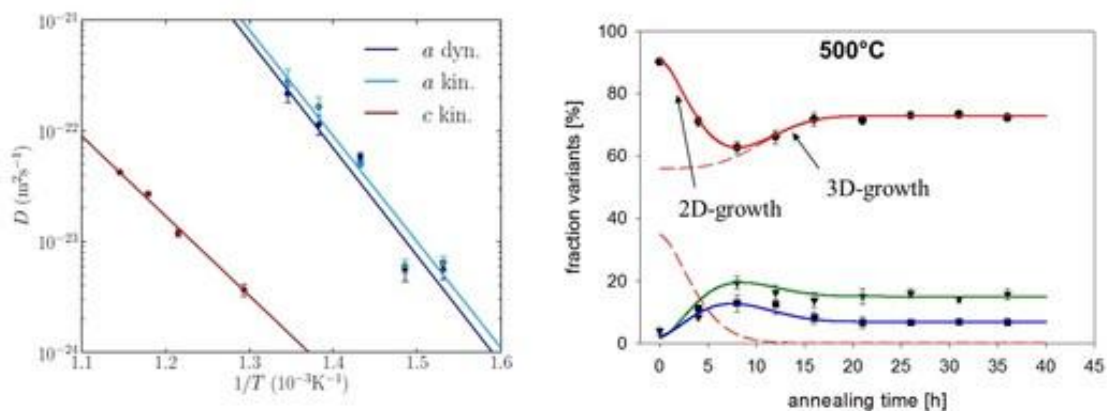
Fig. 1   Left: diffusion constant D as a function of the inverse temperature measured for diffusion along the c-axis direction [1] and a-direction, evaluated by kinematical (a kin.) [1] and dynamical (a dyn.) [2] scattering theory, respectively. Right: order-order-transitions in epitaxial grown FePt thin films, showing the time evolution of the ordered states, investigated by means of CEMS [3].

# Ferrate and ferryl species: Mössbauer spectroscopy investigations

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Access to safe drinking water in the 21st century requires effective and sustainable water treatment technologies. Among the various treatment methods, iron-based processes are attractive treatment technologies because iron materials are environmentally friendly and also earth-abundant as well as are magnetic. Hence, these materials can be recycled or separated after the water treatment and thus make the materials more sustainable. In recent years, high-valent iron oxo species, ferrates ($Fe^{VI}O_4^{2-}$, Fe(VI)) have emerged as greener oxidants in treatment technologies. Other high-valent oxo species ($Fe^{V}O_4^{3-}$, Fe(V) and $Fe^{IV}O_4^{4-}$) may also be exploited to transform extremely resistant contaminants such as perfluorooctanesulfionate (PFOS) and perfluorooctanoic acid (PFOA). The oxidation capacity of Fe(VI) depends whether Fe(VI) goes through either one-electron or two-electron transfer process (Figure 1). Oxygen atom transfer process during the electron-transfer steps of the mechanism can be evaluated by theoretical relationships of rates with redox potentials and by experimental observations in the Mossbauer spectroscopy measurements of rapid freeze reactant mixtures. The Mossbauer spectroscopy results were combined with other spectroscopic techniques to confirm steps of the mechanism shown in Figure 1. Examples of different reactions of environmental importance (i.e. water treatment) will be given in the presentation.

High valent oxoiron(IV) species ($Fe^{IV}=O$), commonly called ferryl may also be involved in Fenton and Fenton-like reactions. More importantly, ferryl species play imperative roles in oxidation reaction of biological importance. Numerous studies have been performed in the past decade to characterize the ferryl species in many model systems. Mossbauer spectroscopy played a pivotal role in characterizing oxoiron(IV) complexes. A work on perferryl species ($Fe^{V}=O$) is also in progress because of their possible involvement in oxidative transformations in enzymatic reactions (eg. Rieske dioxygenases). Results from the literature will be used to present Mossbauer spectroscopy investigation of the ferryl and perferryl species in aqueous and non-aqueous solutions.

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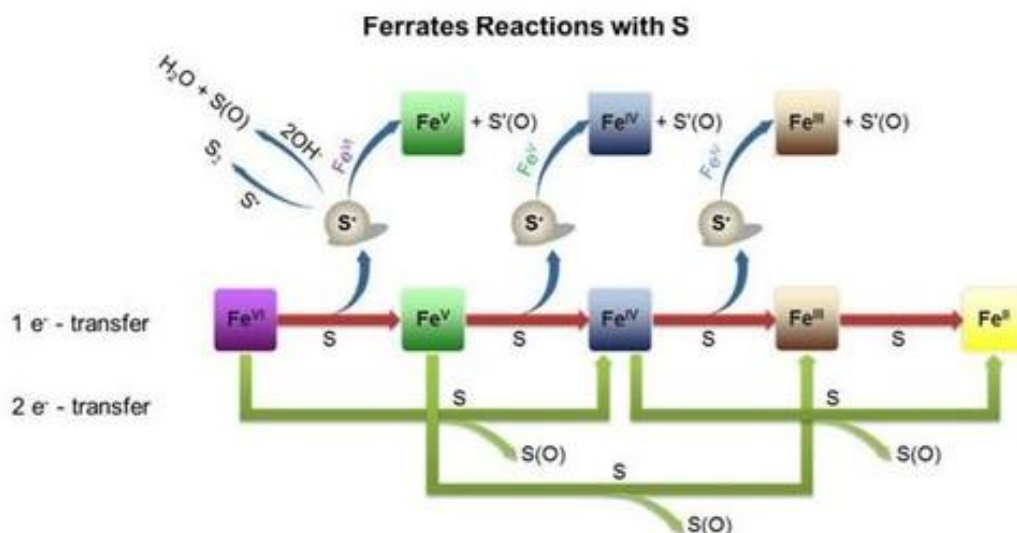[3] Achintesh Biswas et al. J. Am. Chem. Soc. 137 (2015) 2428-2431.

Fig. 1  Transformation steps during the oxidation of substrate (S) by Fe(VI).

# Iron oxide: magnetic hyperthermia and encapsulation

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Iron oxide is currently material of choice for many medical applications. The main reason is its presumed nontoxicity, as relatively large quantity of iron already exists in organism. Here we present research on application of iron oxide nanoparticles in magnetic hyperthermia. Nanoparticles of iron oxide were synthesized using Massart's method and were subsequently coated with different surfactants, polyethylene glycol or citric acid, to ensure their colloidal stability. Measurements of heating losses in AC magnetic field were conducted on polyethylene glycol coated nanoparticles where attention was given to influence of their size distribution and field amplitude. Citric acid coated nanoparticles were encapsulated in human serum albumin microspheres. Here albumin serves as carrier platform as it can be easily functionalized with medicaments or radionuclides.
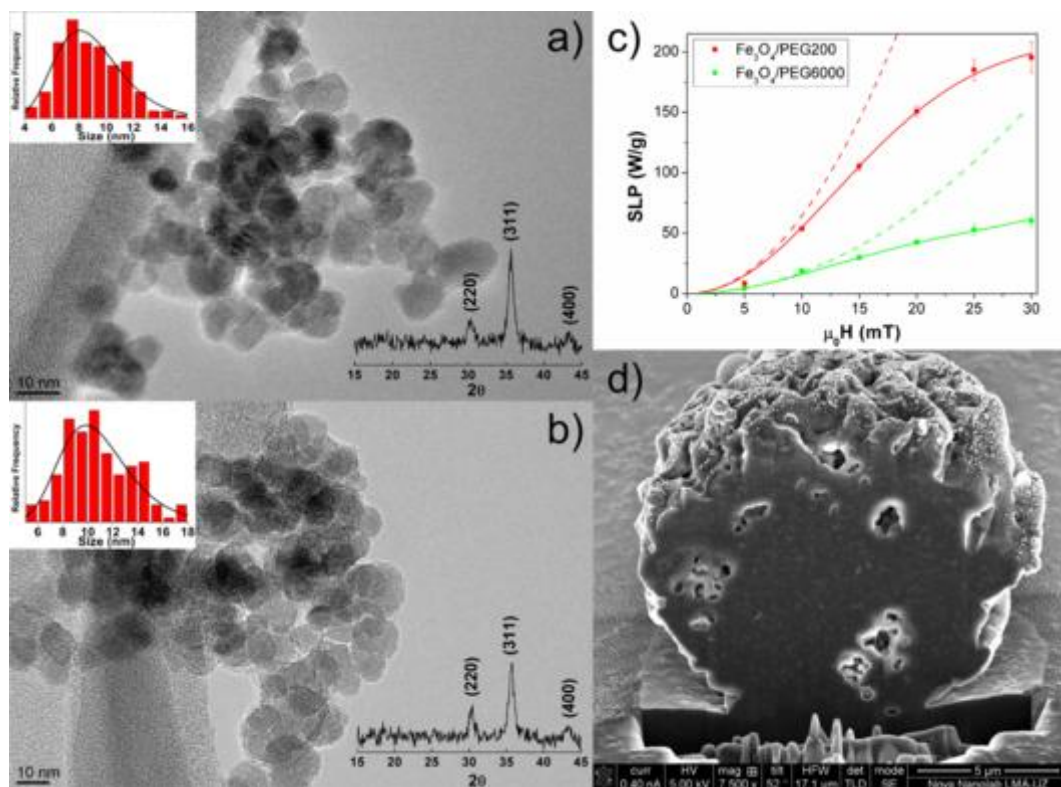
Fig. 1   a) and b): TEM images of $Fe_3O_4$/PEG200 and $Fe_3O_4$/PEG6000 nanoparticles; c) SLP field dependence; d) SEM image of albumin microsphere loaded with iron oxide nanoparticles

# Topologically protected magnetic helix imaged with Mössbauer spectroscopy and X-ray polarimetry

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Based on micromagnetic simulations, we report on a novel helical magnetic structure in a soft magnetic thin film that is sandwiched between and exchange-coupled to two hard magnetic layers with different anisotropies (Fig. 1a). We show that such a structure initially twisted in an external magnetic field, stays topologically stable even without the presence of the external field (Fig. 1b). Our simulations show that this topological helix stores magnetic energy of a few kJ/m$^3$. Interestingly also, the ferromagnetic resonances are dramatically modified compared to those in a ferromagnetic state. Using the package CONUSS, [1] we predict that the topological helix can be imaged with Mössbauer spectroscopy and high resolution X-ray polarimetry. In particular, the in-plane angular distribution of magnetic moments in the film can be derived from Mössbauer spectra (Fig. 1d) and time spectra (Fig. 1c) whose intensities differ for the helical and the ferromagnetic state, when the film is rotated in its plane. Thin films with a stable helical order provide a new route to store magnetic energy, and can generate high frequency signals on the smallest scale.

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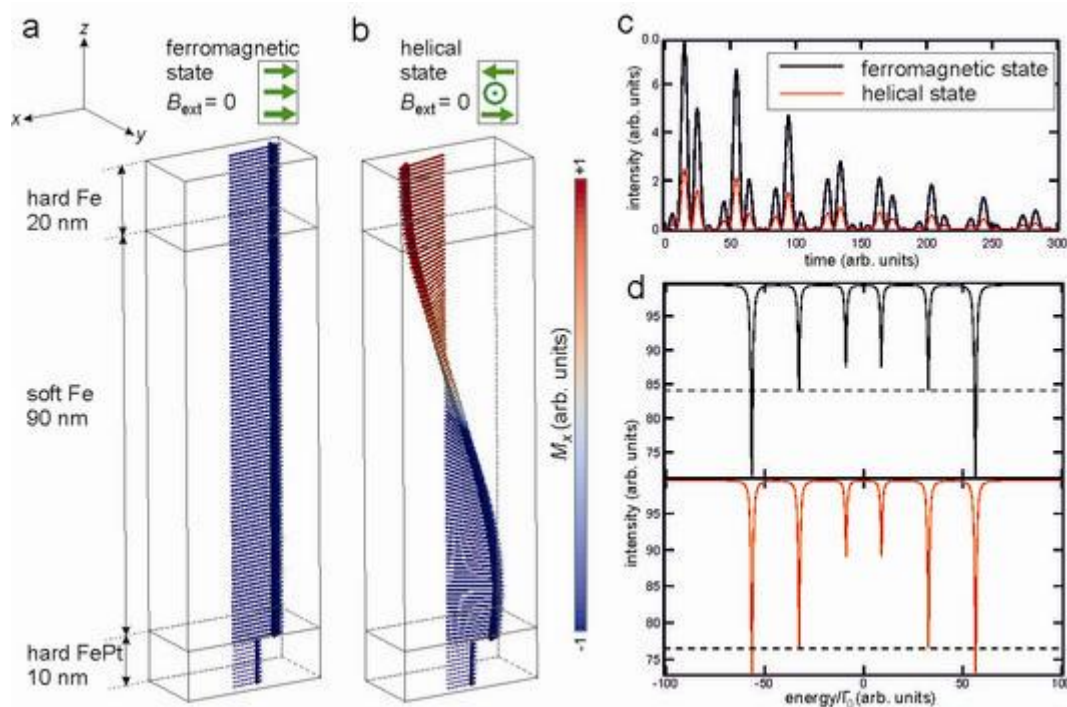
Fig. 1    3D representation of micromagnetic simulations of a stack with magnetic moments (arrows inside slabs) arranged into the (a) ferromagnetic and (b) helical state. (c) Time spectra and (d) Mössbauer spectra calculated for a thin Fe film.

# Computational study on Mössbauer isomer shifts of some organic-neptunium(IV) complexes

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The bonding investigation for f-block compounds has been desired due to its importance in fundamental and applied fields of chemistry. Although quantum chemical calculation has been very useful tool for understanding the electron state on f-block compounds[1], the quantitative investigation for bonding property of them, especially actinide compounds, has not been performed well. The $^{237}$Np Mössbauer isomer shifts of some organic-neptunium complexes $[Np^{IV}Cp_3X]^0$ (Cp $= \eta^5$-$C_5H_5$; X = Cl, OR and alkyl) have been reported[2]. As the results, it has been indicated that the covalency between Np ion and ligands decreased in order of X = Cl, OR and alkyl. Our purpose is to understand this tendency from the viewpoint of bonding analysis for molecular orbitals obtained by density functional calculation. We have shown successfully the validity of the quantum chemical computation for f-block compounds [3]. In our computation, we employed the ZORA-B2PLYP/SARC theory which showed the best performance for the Mössbauer isomer shifts of Eu and Np complexes. The calculation models were employed for X = Cl, O$^t$Bu and $^n$Bu and constructed by substituting U with Np for UCp$_3$X crystal structures. As the results of geometry optimization, the calculated structures are consistent with the experimental structures and are obtained without imaginary frequencies of normal vibration modes, indicating that all structures are in local minima. The results of single point calculation show that the calculated isomer shifts of $^{237}$Np are 7.5, 6.8 and 3.4 mms$^{-1}$ for X = Cl, O$^t$Bu and $^n$Bu, respectively and reproduce the experimental tendency which was 14, 8.6 and 2.7 mms$^{-1}$ for X = Cl, O$^t$Bu and $^n$Bu, respectively. Performing the partial density of states (PDOS) analysis of f-electron in Np atom, we find that the 5f$^3$-electron is distributed to –12 ～ –9 eV region (Figure 1). We also perform the overlap population (OP) analysis which is the indicator of bonding interaction. Calculating the OP between Np and donor atoms,

we obtain the difference in bonding and anti-bonding OP among X = Cl, O$^t$Bu and $^n$Bu systems. Figure indicates that focusing on the 5f-electron region, there is no distribution of anti-bonding OP shown by broken-line in X = Cl, whereas the contribution of anti-bonding OP increases in order of X = O$^t$Bu and $^n$Bu compared to that of bonding OP shown by dotted line. These results suggest that the variation of the experimental $^{237}$Np isomer shifts reflects the difference in the bonding interaction between f-electron in Np and ligands. We also indicate that the balance of the contribution of f-electron to bonding or anti-bonding determines the covalency in organic-Np complexes.
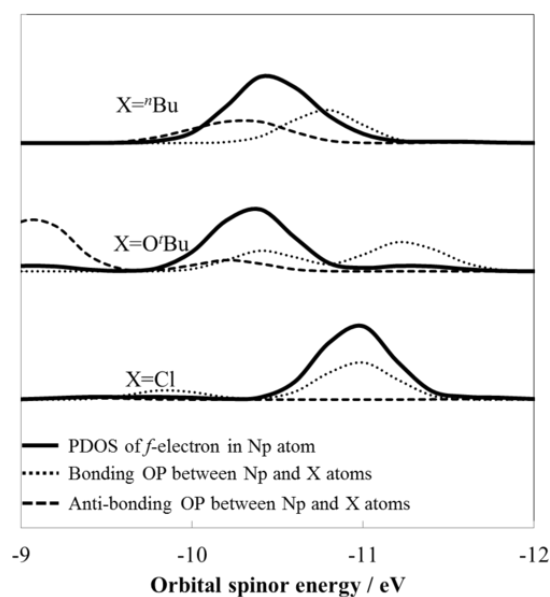


Fig. 1   Partial density of states (PDOS) and overlap population (OP) analyses for NpCp$_3$X complexes.

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# Mössbauer spectroscopic study on Hofmann-like coordination polymer Fe(4-Clpy)$_2$[Ni(CN)$_4$]

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Hofmann-like coordination polymer materials are potentially wide interest for chemical applications. Extensively attention is currently much paid to Hofmann-like coordination polymer iron(II) SCO compounds acting cooperative behaviour because they can manifest sensory and memory functions. The prototype Hofmann pyridine coordination polymer Fe(py)$_2$Ni(CN)$_4$ **1** demonstrates iron(II) SCO behaviour, revealed by [57]Fe Mössbauer spectroscopy and SQUID technique [1]. Emission Mössbauer spectroscopic study [57]Co-labelled analogous [57]Co(py)$_2$Ni(CN)$_4$ has been reported in the nuclear-decay-induced excited spin state trapping (NIESST) [2]. The effect on the spin crossover of Cl and CH$_3$ replacements located at different positions on the pyridine ring were also studied. The related spin crossover coordination compounds have been developed. We previously reported two kinds of 2D coordination polymer iron(II) spin crossover complexes containing 3,5-lutidine with ideal formula Fe(3,5-lutidine)$_2$Ni(CN)$_4$· n(H$_2$O)m(3,5-lutidine), whose host framework is similar to that of **1** [3]. We report here [57]Fe Mössbauer spectroscopic study on the spin crossover coordination polymer Fe(4-Clpy)$_2$Ni(CN)$_4$. Mössbauer spectra at RT and 80 K shows main doublets correspond to the iron(II) high spin states, indicating the Fe(4-Clpy)$_2$Ni(CN)$_2$ is not a spin crossover compound. The minor doublet with a small $\Delta E_Q$ may correspond to the iron(III) high spin state.

[1] Kitazawa, T., Gomi, Y., Takahashi, M., Takeda, M., Enomoto, M., Miyazaki, A., Enoki, T.: J. Mater. Chem. 6, 119 (1996).

[2] Sato, T., Ambe, F., Kitazawa, T., Sano, H., Takeda, M.: Chem. Lett. 1287(1997).

[3] Kitazawa, T., Takahashi, Mi., Hyperfine Interact.,226, 27(2014).

# The multiple dehydroxylation peaks of goethite and the existence of hydrohematite revisited

### G.M. da Costa and C.C.R.F. da Cunha

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The water contents of several synthetic and natural goethite-bearing samples were determined by the loss-of-mass method and by the Karl-Fischer titration. It was found that temperatures above 200 °C are required to completely remove the adsorbed water. In one experiment, the differential scanning calorimetric runs of a synthetic goethite were interrupted at 240, 260, 290 and 330 °C, and the decomposition products were investigated by Mössbauer spectroscopy. The results showed no hematite after heating at 240 °C, and only 5% was formed after heating at 260 °C (Fig. 1). Hence, the multiple peaks observed in the thermogravimetry and differential scanning calorimetry measurements are not due to the dehydroxylation of goethite, but are due to the release of adsorbed water. The water contents of another synthetic goethite were determined by the Karl Fischer titration after heating the samples at 400 °C and 900 °C, and were found to be the same within the experimental errors. Therefore, there is no occluded water in the hematite formed at high temperature, suggesting the absence of hydrohematite.
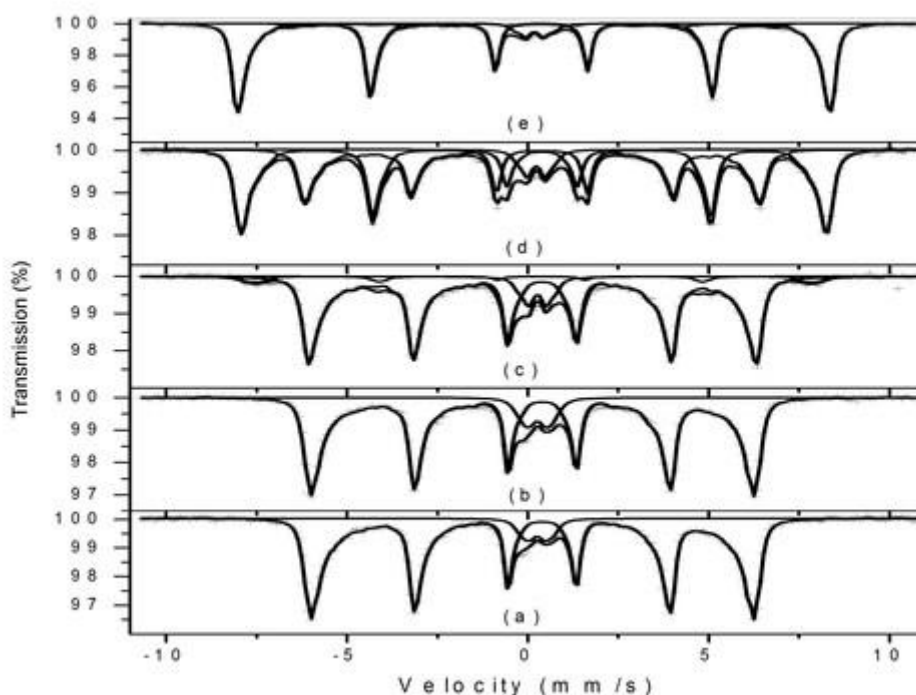
Fig. 1  Mössbauer spectra at room temperature of the synthetic goethite (a) and its decompositions products at 240 °C (b); 260 °C (c); 290 °C (d); 330 °C (e).

# Mössbauer spectrometry study of corroded steels surfaces submitted to accelerated tests in chloride environments

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We review a RT and 77 K Mössbauer spectrometry study of corrosion products of carbon and weathering steels submitted to total immersion, dry-wet cycles and outdoor tests in chloride environments [1,2]. To determine the protective characteristics of the rust layers adhered to the steel surfaces in these experiments, we have used the ternary rust diagram proposed by Hara et al. [3]. This diagram compares the so-called protective ability index, PAI = G/(A+L+S), and the ratio of (A+S)/(A+L+S), where G, A, L and S are the relative phase abundances of $\alpha$-FeOOH, $\beta$-FeOOH, $\gamma$-FeOOH and spinel phases, respectively. Hara et al. [1] proposed that the rust layers are: (i) protective if PAI > 1, (ii) non-protective but active if PAI < 1 and (A+S)/(A+L+S) > 0.5, and (iii) non-protective but inactive if PAI < 1 and (A+S)/(A+L+S) < 0.5. We have also calculated the atomic fraction of iron species coming from the steels that after the corrosion processes form part of the adherent rust, i.e. the so-called $\alpha$ parameter. This parameter is characterized for $0 \leq \alpha \leq 1$; in such

a way that when $\alpha = 0$, all corroded iron is lost; when $\alpha = 1$, all corroded iron is contained into the adherent rust; and when $\alpha < 1$, part of the corroded iron is lost. We have quantitatively demonstrated by using Mössbauer spectrometry that the conversion of metallic ions into adherent rust is incomplete, at least for steels submitted to accelerated corrosion tests in chloride environments and that the rust layers were mostly non-protective and active. Moreover, with the physical properties retrieved from the analysis of the hyperfine parameters, it was possible to discuss possible mechanisms of formation and therefore to contribute to the understanding of the deterioration progress.

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[3] Shuichi Hara et al., Corros. Sci. 49 (2007) 1131-1142.

# Effect of sulfur addition on some physical properties
# of Li-V-Fe silicate glass and glass-ceramic nano composite

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Some physical properties of glass and heat-treated glass of composition $LiO_2$-$[(−Fe_2O_3 + −V_2O_5)(2-x)SiO_2]$ with $x = 0.5$ were prepared by well mixing and then fired the raw mixture in an electric furnace at 1350 °C in a platinum crucible in air for one hour. The melted sample was quenched into a copper plate. A part of the produced glass was heat treated (HT) for one hour near its $T_c$ which was obtained using DTA. The as-quenched and HT samples were investigated using Mössbauer effect (ME), FTIR, XRD, density, DC conductivity measurements. Another glass sample with the same composition was also prepared in the same conditions after adding 5 wt% sulfur to the raw mixture. The as-quenched sample was also HT as mentioned before. Then the two samples (as-quenched and HT) were measured by the same techniques as mentioned before. ME spectra showed one doublet of $Fe^{3+}$ tetrahedra in both the as-quenched and HT samples. While in the glass sample of sulfur addition, the above doublet appeared along with another doublet observed in the ME spectra. The latter doublet represents $Fe^{2+}$ ions. This result was confirmed by the DC conductivity measurements, where the conductivity of the samples containing sulfur showed enhancement of the electrical conductivity values compared to that of sulfur-free sample. This is due to the presence of $Fe^{2+}$ and $Fe^{3+}$ ions. The XRD results in the glass samples confirm the glassy state formation, while it showed diffraction peaks in the HT samples due to precipitation of lithium silicate phase in the glass network with particle size in the nano range. The results of the other techniques were discussed and correlated to each other.

# Characterization of magnesium doped lithium iron silicate

<u>J.A. Jaén</u>[1], J. Iglesias[2], A. Muñoz[3], J.A. Tabares[4] and G.A. Pérez Alcázar[4]

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[2]*Laboratorio de Análisis Industriales y Ciencias Ambientales, Universidad Tecnológica de Panamá, Panamá*
[3]*Departamento de Física, Universidad de Panamá, Panamá*
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Lithium iron silicate ($Li_2FeSiO_4$) is a material that had drawn considerable attention to improve energy density in cathode materials for lithium ion batteries [1]. This material has good electrochemical activity and high cycling stability, but poor electronic conductivity and lithium ion mobility. $Mg^{2+}$ doping can efficiently improve the cathode materials electrochemical properties of the $Li_2FeSiO_4$ cathode particles. In this work, the effect of doping Mg on the structure of the orthosilicate was investigated [1]. The samples were prepared by ball milling, followed by calcination at 650°C. $Li_2SiO_3$ and $FeC_2O_4 \cdot 2H_2O$ were used as precursors of the orthosilicate, $Mg(CH_3COO)_2 \cdot 4H_2O$ was the doping agent. The amount of the precursors and doping agent were varied according to the proportions Li:Fe:Mg:$SiO_4$  2:1-x:x:1 (x=0, 0.10 and 0.15). The resulting material was characterized by Mössbauer spectroscopy (MS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), magnetic measurements and scanning electron microscopy (SEM). Mössbauer spectroscopy is well known to be suitable for differentiating valence states and detecting impurities of Fe within a material. Mössbauer spectroscopy measurements at room temperature of all samples are shown in Figure 1. A dominant symmetric doublet is observed, with hyperfine parameters IS = 0.94 - 0.95 mm s$^{-1}$ and QS = 2.38 – 2.43 mm s$^{-1}$, is typical for $Fe^{2+}$ in ionic compounds. Out of the different polymorphs of $Li_2FeSiO_4$ proposed [2], both the pristine and doped materials consist of the monoclinic structure $P2_1 / n$. This result is supported by the XRD and FTIR analysis. In addition to the $Fe^{2+}$ doublet, a small absorption area in the center of each of the Mössbauer spectrum was also observed, associated to a $Fe^{3+}$ phase. This phase could be attributed to nanoparticles of metal oxides ($Fe_3O_4$) and/or delithiated orthosilicate $LiFeSiO_4$, impurities imperceptible or hardly detected by XRD or in the FTIR spectra. A small contribution coming from a sextet is observed for samples with equal or exceeding 10% mol doping metal. Data clearly show that Mg doping is accompanied by reduction of $Fe^{2+}$ to BCC iron (saturated solid solution of magnesium in iron), with a Mössbauer hyperfine field varying from 32.9 T to 32.4 T with increasing Mg doping, a magnetic phase segregates. The quantity of this magnetic phase increases monotonically in samples with more than 10% mol Mg doping, according to results that are not presented in this report. Magnetization measurements indicate that some soft ferromagnetic or ferrimagnetic component is present in these materials. Additionally, no change is observed in the paramagnetic nature of the $Li_2FeSiO_4$ after doping with magnesium.



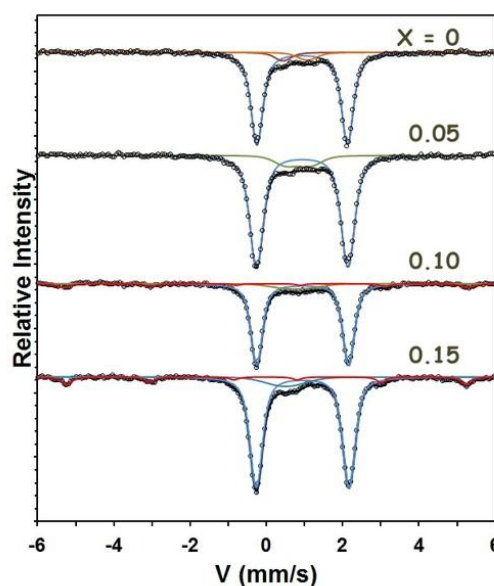Fig. 1: Room temperature Mössbauer spectra of Mg doped $Li_2FeSiO_4$ samples

[1] A. Nytén et al., Electrochem. Commun. 7 (2005) 156-160.
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# Mechanism of phosphorus(V) substitution in Fe(III) component lattice

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Zero-field (5K, 0T) and in-field (5K, 5T) low-temperature $^{57}Fe$ Mössbauer spectroscopy analysis was applied for exploration of the P(V) substitution mechanism into the structure of Fe(III) nanoparticles. The particles were synthesized via "in-situ" and "ex-situ" procedures [1]. Both types of samples showed rather similar looking zero-field low-temperature Mössbauer spectra. In a presence of external magnetic field, the samples showed the resonant lines splitting to three sextets (Figure 1). Two of these sextets had Mössbauer hyperfine parameters corresponding to tetrahedral (T) and octahedral (O) sites of $\gamma$-$Fe_2O_3$, and one sextet had Mössbauer hyperfine parameters values typical for antiferromagnetic $\gamma$-FeOOH (lepidocrocite). Microscopic analyses as well as SQUID magnetization measurements confirmed that the nanoparticles are having core-shell structure. The core consists of $\gamma$-$Fe_2O_3$ phase, which is covered by $\gamma$-FeOOH surface layer. The "ex-situ" sample exhibits spectral tetrahedral/octahedral (T/O) ratio close to 0.63, which is very near to the (T/O = 0.6) for perfectly stoichiometric $\gamma$-$Fe_2O_3$, with vacant positions at O sites [2]. In opposite, the "in-situ" sample showed (T/O) ratio ~0.80, which is significantly higher than the theoretical value. This can be explained with the fact that P(V) induces formation of vacations in the octahedral positions to compensate the charge and for this reason the number of vacations is different than in case of stoichiometric maghemite. Comparison of the effective hyperfine magnetic field ($B_{eff}$) values at T sites and O-sites for the "in-situ" and "ex-situ" samples might be also used as confirmation for the substitution of P(V) for Fe(III). While the values for all the "in-situ" samples at O sites (43.8 T; 44.7 T and 44.9 T) are quite similar, the "ex-situ" sample shows increased ($B_{eff}$) value 46.7 T. Concerning the tetrahedral positions, analogical enhancement is observed with "in-situ" samples values (47.7 T; 48.1 T; 48.3 T) and "ex-situ" sample ($B_{eff}$) value 50.0 T. This indicates that P(V) enters both O- and T-sites. $\gamma$-FeOOH phase is also probably affected by the P(V) incorporation, since the "ex-situ" sample demonstrates again higher

effective hyperfine magnetic field value (43.6 T), in comparison of the parameters concerning the "in-situ" samples (39.7 T; 40.6 T; 40.9 T). Thus the in-field low-temperature Mössbauer spectra of the "in-situ" samples illustrate that certain amount of P(V) ions is incorporated into the crystal structure of $\gamma$-$Fe_2O_3$/$\gamma$-FeOOH core-shell nanoparticles.
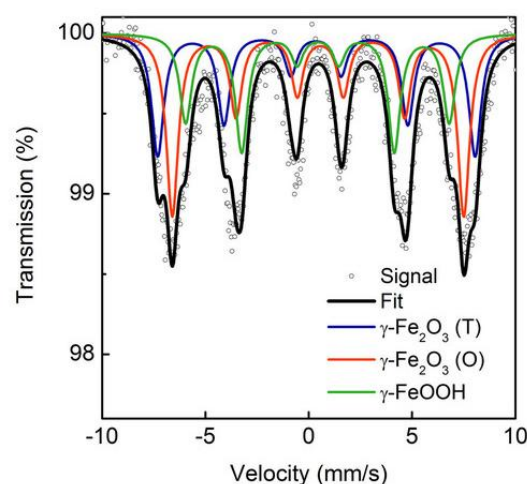


Fig. 1. In-field low-temperature (5K, 5T) Mössbauer spectrum of the "in-situ" sample, illustrating three sextets components corresponding to (i) tetrahedral (T), (ii) octahedral $\gamma$-$Fe_2O_3$, and (iii) $\gamma$-FeOOH.

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# Synthesis and microstructural properties of mixed iron-gallium oxides

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Iron and gallium oxides have been intensively investigated in the last years due to their specific properties, which are suitable for a number of advanced applications (magnetic materials, catalysts, photocatalysts, photoanodes, gas sensors, luminescent materials, etc.). These properties can be improved or tuned by modification of the particle size and shape, as well as by incorporation of foreign cations into their structure. Due to the same charge and a similar ionic radius, $Fe^{3+}$ and $Ga^{3+}$ have a high potential for mutual substitution in the oxide structure [1-5]. Mixed Fe-Ga oxides were prepared by calcination of mixed Fe-Ga oxyhydroxide precursors ($\alpha$-Fe$_{1-x}$Ga$_x$OOH, $0 \leq x \leq 1$) [6] at 500 or 1000 °C. Isostructural oxides $\alpha$-Fe$_2$O$_3$ (hematite) and $\alpha$-Ga$_2$O$_3$, as well as their solid solutions $\alpha$-Fe$_{2-x}$Ga$_x$O$_3$ ($x = 0, 0.4, 1, 1.6, 2$) were prepared by calcination at 500 °C. An increase in Ga content in $\alpha$-Fe$_{2-x}$Ga$_x$O$_3$ caused a reduction of the unit-cell, a change of the particle shape and size, a reduction of the hyperfine magnetic field, a shift in the position of IR bands to higher wavenumbers, and a decrease in intensity of all absorption bands in the UV-Vis-NIR spectra. Calcination of the Fe-Ga oxyhydroxides at 1000 °C resulted with the formation of a rhombohedral $\alpha$-Fe$_{2-x}$Ga$_x$O$_3$ phase for $x = 0$ and 0.4, an orthorhombic GaFeO$_3$ phase for $x = 1$ (Figure 1) and a monoclinic $\beta$-Ga$_x$Fe$_{2-x}$O$_3$ phase for $x = 1.6$ and 2. Monoclinic $\beta$-Ga$_{1.6}$Fe$_{0.4}$O$_3$ phase showed two strong luminescence peaks in the blue region of the PL spectrum.

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[3] T. Arima, D. Higashiyama, Y. Kaneko, J. P. He, T. Goto, S. Miyasaka, T. Kimura, K. Oikawa, T. Kamiyama, R. Kumai, Y. Tokura, Phys. Rev. B 70 (2004) 064426.
[4] S. Ohkoshi, S. Kuroki, S. Sakurai, K. Matsumoto, K. Sato, S. Sasaki, Angew. Chem. Int. Ed. 46 (2007) 8392-8395.
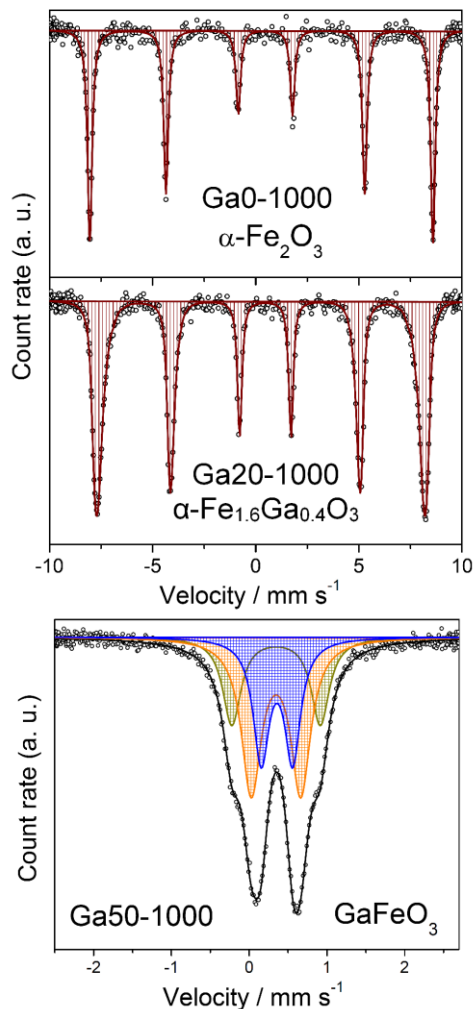
Fig. 1   The [57]Fe Mössbauer spectra (recorded at 20 °C) of Fe-Ga oxides prepared by calcination of Fe-Ga oxyhydroxides at 1000 °C.

[5] C. Lefevre, F. Roulland, A. Thomasson, C. Meny, F. Porcher, G. Andre, N. Viart, J. Phys. Chem. C 117 (2013) 14832−14839.
[6] S. Krehula, L. Kratofil Krehula, S. Musić, J. Alloys Compd. 581 (2013) 335–343.

# Improving the performance of metallic-iron-maghemite nanoparticle system for treating polluted water

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Water and soil pollutions with the volatile organic compounds (VOC) are very serious worldwide problem. The $Fe^0$ + maghemite ($\gamma$-$Fe_2O_3$) mixture have already been proved as efficient in decomposition of TCE, as well as in bleaching tests using methylene blue (MB) [1, 2]. [57]Fe-Mössbauer spectroscopy is very useful technique in monitoring the chemical and structural changes of $Fe^0$ + $\gamma$-$Fe_2O_3$ mixture caused by their catalytic activity. In this study, nanoparticles (NPs) of $Fe^0$ and $\gamma$-$Fe_2O_3$ were synthesized in reference to the already described procedures [3] and the appropriate ratio of $Fe^0$ NPs to $\gamma$-$Fe_2O_3$ NPs for MB degradation was studied by [57]Fe-Mössbauer spectroscopy, X-ray diffractometry (XRD), transmission electron microscopy (TEM) and ultraviolet-visible absorption spectroscopy (UV-Vis). MB degradation test was performed with $20.0 \times 10^{-3}$ mM MB aqueous solution and NPs of $Fe^0$ + $\gamma$-$Fe_2O_3$ nanocomposite (1:1-4 molar ratio). TEM photographs showed the sizes of $Fe^0$ NPs and $\gamma$-$Fe_2O_3$ NPs in the range of 50-100 nm and 10-40 nm, respectively. Before the MB degradation test, the relaxed sextets were confirmed from [57]Fe-Mössbauer spectra, both for $Fe^0$ and $\gamma$-$Fe_2O_3$ NPs. The MB degradation test using $Fe^0$ + $\gamma$-$Fe_2O_3$ nanocomposite with 1:1 molar ratio changed the color from blue to yellow after 10 days as shown in Fig. 1a. The high absorption at low wavelength was caused by the dissolution of Fe(III). Compared to 1:1 molar ratio, UV-Vis spectra of MB degradation test using 1:3 molar ratio showed remarkable decrease in concentration from $20.0 \times 10^{-3}$ to $0.85 \times 10^{-3}$ mM after 10 days (Fig. 1b). This result indicates that NPs of $Fe^0$ + $\gamma$-$Fe_2O_3$ (1:3) nanocomposite is favorable for MB degradation.
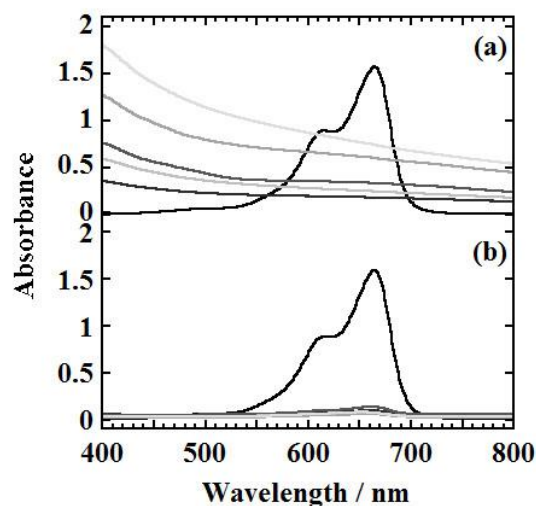


Fig. 1. UV-Vis spectra of MB before and after degradation test using mixture $Fe^0$ NPs and $\gamma$-$Fe_2O_3$ NPs having the molar ratio of (a) 1:1 and (b) 1:3 for 10 days.

[1] S. Kubuki, K. Shibano et al., J. Radioanal. Nucl. Chem. 295 (2013) 23–30.
[2] S. Kubuki, K. Shibano et al., Hyperfine Interact. 218 (2013) 47-52.
[3] S. Kubuki, Y. Watanabe et al., AIP Conference Proceedings. 1622 1 (2014) 134-141.

# Role of sulfur addition as a reducing agent on the ionic state of the transition metals in lithium silicate glass containing Fe and Ni ions

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$Li_2O – (0.25 Fe_2O_3 + 0.25 Ni_2O + 1.5 SiO_2)$ is the composition of the investigated glass. The mixture was divided into two portions, the first is sulfur free while 5 wt% of sulfur was added to the second portion. Each portion was fired at 1350 °C in an electric furnace in air using two platinum crucibles along one hour, then quenched onto a copper plate. A part from each two as prepared glasses was heat treated (HT) along one hour near its $T_c$ as obtained from DTA data. The four samples were investigated using Mössbauer Effect (ME), FTIR, XRD, density and dc conductivity techniques. ME spectra gave the ionic states of iron and XRD patterns demonstrate the glassy state formation for the two glass samples either with or free of sulfur. The HT samples showed precipitated lithium silicate phase with particle size in the nano range. The results of the other techniques were discussed and correlated to each other.

# Influence of gum arabic on the precipitation of α-FeOOH particles in a highly alkaline medium

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Influence of gum arabic (GA) on the precipitation of α-FeOOH in a highly alkaline medium was investigated using XRD, $^{57}$Fe Mössbauer, FT-IR and FE-SEM. In absence of GA long α-FeOOH rods with nanosize width (~30 nm), as a single phase, were produced. The lateral aggregation of two or more α-FeOOH rods is visible. A very strong effect of GA on the precipitation of α-FeOOH in a highly alkaline medium was noticed. At a prolonged time of autoclaving time the ferrihydrite-like phase transformed to α-FeOOH and α-Fe$_2$O$_3$. The formation of α-Fe$_2$O$_3$ as the end product of this precipitation process was controlled by the dissolution/recrystallization mechanisms. The effect of GA addition to the precipitation system of Fe(ClO$_4$)$_3$ salt in a highly alkaline medium was assigned to the surface interactions of GA with nuclei and crystallites (particles) formed during the kinetics investigated. It was assumed that a thick layer of GA biopolymers suppressed the formation of α-FeOOH from the ferrihydrite-like phase, which is generally a fast process in the absence of GA. In such a way the conditions for nucleation and crystal growth of α-Fe$_2$O$_3$ are created and with a prolonged autoclaving time the reactions were shifted to the formation of α-Fe$_2$O$_3$ as end-product.

# Simultaneous relaxation processes
# in super spin glass maghemite nanoparticles

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Spherical $\gamma$-$Fe_2O_3$ nanoparticles with the narrow size distribution of $(5 \pm 1)$ nm were synthesized by the method of thermal decomposition from iron acetyl acetonate precursor. X-ray diffraction, Transmission Electron Microscopy, Fourier Transform Infrared and Mossbauer Spectroscopy techniques were employed in detailed characterization of the obtained sample. Comprehensive study of the magnetic behavior of interacting $\gamma$-$Fe_2O_3$ nanoparticles by means of SQUID magnetometry, showed that collective super spin glass behavior governed the magnetic relaxation dynamics of the particle system in a temperature interval below freezing temperature, $T_f$. The collective behavior of the investigated system was manifested through the appearance of zero field cooled (ZFC) memory effects, aging, and slow magnetic relaxation. However, the picture which emerged from three different experiments for probing magnetization relaxation (single-stop and multiple stop ZFC memory effects, ZFC magnetization relaxation, and AC susceptibility measurements) revealed the peculiar change in relaxation regime at the lowest temperatures. Possible interpretation of the observed effect takes into account the magnetic relaxation of weakly interacting ('individual') particle moments that occurs simultaneously with the hierarchically constrained collective relaxation of correlated moments. Complementarity of the applied measurements was utilized in order to single out distinct relaxation processes as well as to elucidate complex relaxation mechanisms in the investigated interacting nanoparticle system. Measurements of ZFC magnetic relaxation, and in particular ZFC memory effects, turn out to be an excellent tool to investigate the relaxation dynamics in interacting nanoparticle systems. AC susceptibility data, discussed in terms of Cole–Cole model, allowed the deeper insight into the possible scenario for the underlying relaxation processes.

[1] V. Nikolic et al., J. Nanopart. Res. 17 (2015) 139.

[2] M. Perovic et al., J. Phys. D Appl. Phys. 46 (2013) 165001.

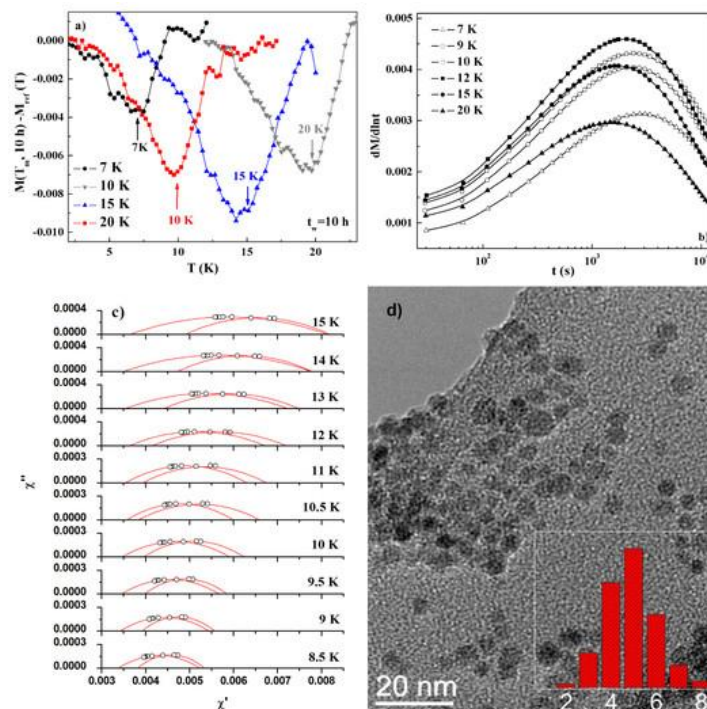Fig. 1   a) ZFC memory effect at 7,10,15 and 20 K after tw = 10 h; b) Relaxation rates derived from ZFC magnetization relaxation curves; c) Cole–Cole plots at different temperatures; d) TEM micrograph of $\gamma$-$Fe_2O_3$ nanoparticles and nanoparticle size distribution

# Variable temperature Mössbauer spectroscopy study of nano-particle iron carbides

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With fossil fuel sources and reserves in decline, and increased consciousness of harmful greenhouse gas emissions and their effects on the environment, there is a great desire to harness the full potential of cleaner burning, renewable fuel sources. While sources such as solar, wind and geothermal may be capable of generating electricity, the generation of liquid fuels used in transportation and heating is sought using other processes. One process through which a liquid fuel can be generated is Fischer-Tropsch synthesis, which converts carbon monoxide and hydrogen into hydrocarbons; gaseous, liquid and solid. Through this process it is possible to generate biofuels that burn with reduced greenhouse gas emissions, and their feedstock sources are renewable, such as vegetable oil or animal fats [1]. Although biodiesel has a slightly lower energy density than conventional diesel, its price can be much lower due to its availability and abundance of feedstock, and with its greatly reduces greenhouse gas emission, it is of high interest. The catalysts used in Fischer-Tropsch synthesis are most commonly cobalt, ruthenium or iron based, with iron carbides having high potential due to their cost effectiveness and competitive activity and selectivity. The focus of our research is the activity and deactivation of iron carbides used in Fischer-Tropsch synthesis, and to construct a comparative study between various nano-particulate iron carbides undergoing the same service lives regarding environments and exposure durations. To do this we are principally using variable temperature 57-Fe Mössbauer spectroscopy. We are studying the nano particle iron carbides as fresh materials, following various reaction regimes, for the Mössbauer spectroscopy at various temperatures, and the effects of support systems for the iron carbides. The aim is to identify the most active and therefore most desirable iron carbide phase to use in Fischer-Tropsch, and then to promote this phase to remain present and active through long exposures to Fischer-Tropsch reactions by exploring support systems. It is believed that $Fe_5C_2$ is the most active iron carbide phase for Fischer-Tropsch synthesis [2], however other iron carbides will be studied independently, and in combination, to observe the effects of multiple carbide systems on the catalytic performance. The Mössbauer spectra provided show the room temperature 57-Fe analysis of a) $Fe_5C_2$ and b) $Fe_3C$, which are distinctly different to one another which allows characterisation in mixed iron oxide nano particles. Low temperature studies of these carbides are currently underway from a temperature of 10 K to room temperature, in order to identify transition temperatures, such as the Néel temperature, whereby a magnetic field forms as thermal energy is removed and paramagnetic becomes antiferromagnetic [3].

[1] G.W. Huber et al. Chem. Rev. 106 (2006) 4044-4098.
[2] T.H. Pham et al. ACS Catal. 5 (2015) 2203−2208.
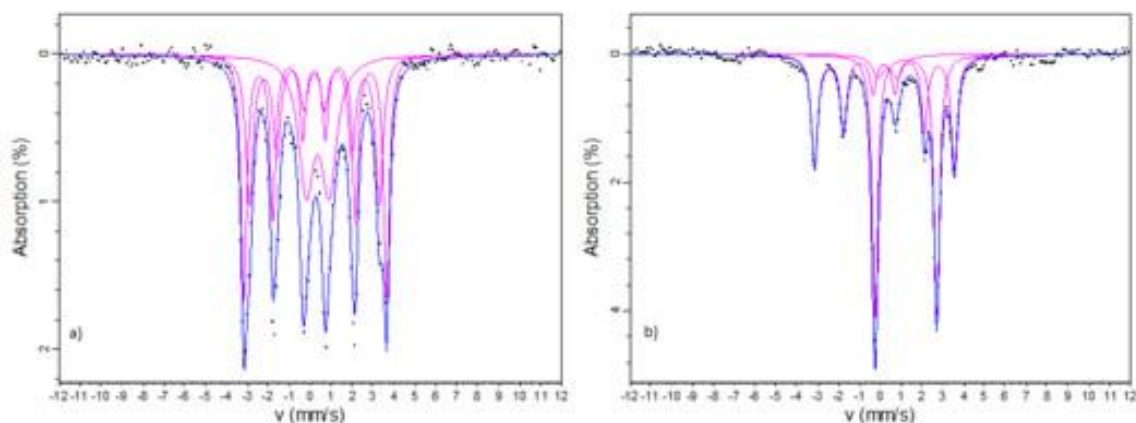[3] Kittel, Charles (2005). Introduction to Solid State Physics (8th ed.) 340-344.

Figure 1: Room temperature Mössbauer spectra of a) $Fe_5C_2$ and b) $Fe_3C$ with IS relative to soft (alpha) iron.

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