



# 9<sup>th</sup> International Symposium on the Industrial Applications of the Mössbauer Effect

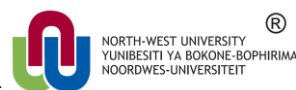
## Cape Town, South Africa

### 4-8 September 2016



**Programme and Abstracts**

**Organized by the North-West University**



**9<sup>th</sup> International Symposium on the Industrial Applications of the  
Mössbauer Effect  
Cape Town, South Africa  
4-8 September 2016**

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## Preface

Dear colleagues and friends. It is a pleasure for the local organising committee to invite participants to the ISIAME 2016 conference (Industrial Symposium on the Applications of the Mössbauer Effect) to be held in Cape Town South Africa from 4-8 September 2016. Due to the financial situation in South Africa and lack of major sponsors, the Symposium almost did not happen. Thanks to all the dedicated Mössbauer researchers that did not want this opportunity to pass and all the positive inputs they gave, it finally came to a reality. A special word of thanks goes to Raquel Richardson from Ap22ude, who kept her cool and supported us in all organizational matters. Special thanks also go to Krish Baruth-Ram who stepped in, in difficult times and ensured that all went well.

Our hearts go out to those who cannot make it due to various circumstances and also to those we have lost recently. The Symposium is organised by the North-West University Potchefstroom, the University of Johannesburg, Johannesburg and Sasol, South Africa.. It follows on previous successful Symposia and will be open to experts, scientists, practitioners and engineers with an interest in recent developments in the field of the Mössbauer Effect and its applications. Invited lectures, oral presentations and poster sessions will form the bulk of the programme with a whole day Cape tour to ensure a scientific and well balanced symposium.



Frans Waanders (Chair ISIAME 2016)  
Professor and Director  
School of Chemical and Minerals Engineering  
North-West University  
Potchefstroom  
South Africa

## Acknowledgements

A special word of thanks goes to the North-West University and Sasol for sponsorships and iThemba labs for the welcome function and Ap22ude for their support.



## Organizing Committee (RSA)

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K Baruth-Ram, Durban University of Technology and iThemba LABS

Antoine Mulaba-Bafubiandi, University of Johannesburg

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## IBAME list as of September 2015

List of IBAME Members as of 9 September 2015

### Executive

			first year	last year	
Nagy	Dénes Lajos		2007	2015	Chair
Greneche	Jean-Marc		2007	2015	Vice Chair
Reissner	Michael		2007	2015	Secretary

### Honorary

			first year	last year	
Gerdau	Erich		2011	no limit	
Gülich	Philipp		2002	no limit	

### Advisory

			first year	last year	
Baggio-Saitovitch	Elisa		2007	no limit	without right of voting
Berry	Frank		2007	no limit	without right of voting
Kalvius	G. Michael		2008	no limit	without right of voting
Langouche	Guido		2009	no limit	without right of voting
Marup	Steen		2007	no limit	without right of voting
Stevens	John		2011	no limit	without right of voting
Wang	Junhu		2011	no limit	without right of voting

### Elected

			first year	last year	
Ahmed	Mamdouh	Egypt	2015	2018	
Al Rawas	Ahmed	Oman	2013	2018	
Balogh	Judit	Hungary	2013	2018	

Barrero Meneses	Cesar Augusto	Colombia	2015	2020	
Bender Koch	Christian	Denmark	2015	2020	
Cadogan	J M Sean	Australia	2012	2017	
Chuev	Mikhail A.	Russia	2013	2018	
Costa	Benilde Oliveira	Portugal	2011	2016	
Diamandescu	Lucian	Romania	2012	2017	
Feiner	Israel	Israel	2015	2020	
Forder	Sue	United Kingdom	2015	2020	
Garcia	Yann	Belgium	2015	2020	
Hägström	Lennart	Sweden	2015	2020	
Jurazsek	Jean	France	2015	2020	
Klingelhöfer	Göstar	Germany	2011	2016	
Kuzmann	Emő	Hungary	2011	2016	
Lančok	Adriana	Czech Republic	2015	2020	
Latka	Kazimierz	Poland	2011	2016	
Lippens	Pierre Emmanuel	France	2013	2018	
Mibu	Ko	Japan	2013	2018	
Miglierini	Marcel	Slovakia	2013	2018	
Passamani Caetano	Fernando	Spain	2013	2018	
Plazaola	Fernando	Spain	2013	2018	
Ristić	Mira	Croatia	2013	2018	
Röhlsberger	Ralf	Germany	2011	2016	
Ryan	Dominic	Canada	2015	2020	
Semenov	Valentin	Russia	2013	2018	
Sejdić	Bogdan	Austria	2015	2020	

Spizzo	Federico	Italy	2013	2018	
Stewart	Silvana	Argentina	2013	2018	
Szymański	Krzysztof	Poland	2013	2018	
Tušek	Jiří	Czech Republic	2015	2020	
Waanders	Frans	South Africa	2013	2018	
Yamada	Yasuhiro	Japan	2013	2018	
Zhang	Tao	China	2013	2018	

## Session Chairs

A preliminary list of session chairs has been put together, but can be changed on request during the Symposium. Massimo Carbucicchio has volunteered to chair the Forum on the matters going forward with the Symposium. Inputs from all participants are needed to ensure that the Industrial Applications Symposium will continue into the future

<b>Session</b>	<b>Monday 5 September</b>	<b>Session</b>	<b>Wednesday 7 September</b>	<b>Thursday 8 September</b>
<b>Opening</b>	F Waanders M Carbucicchio Junhu Wang	<b>Session 4</b>	Junhu Wang	<b>Forum</b> M Carbucicchio
<b>Session 1</b>	E. Kuzmann	<b>Session 5</b>	K Bharuth-Ram	
<b>Session 2</b>	H. P. Gunnlaugsson	<b>Session 6</b>	A. F. Mulaba- Bafubiandi	
<b>Session 3</b>	S. M. Dubiel	<b>Session 7</b>	F Waanders	

## PROGRAMME

	Sun 4 Sept	Mon 5 Sept	Tue 6 Sept	Wed 7 Sept	Thu 8 Sept
8:00		Registration	Whole day Cape tour	Registration	
8:30		Opening Session		Session 4	Forum
9:00		Invited talk 1		Invited talk 7	Announcement ISIAME 2020
9:30		Invited talk 2		Invited talk 8	
10:00		Coffee/Tea		Coffee/Tea and Photo	
10:30		Session 1		Session 5	
11:00		Invited talk 3		Oral 7	
11:30		Invited talk 4		Oral 8	
12:00		Oral 1		Oral 9	
12:30				Oral 10	
13:00		Lunch		Lunch	
13:30		Session 2		Session 6	
14:00	Invited talk 5	Invited talk 9			
14:30	Invited talk 6	Invited talk 10			
15:00	Oral 2	Invited talk 11			
15:30	Coffee/Tea	Coffee/Tea			
16:00	Reception iThemba labs	Session 3		Session 7	
16:30		Oral 3		Poster session and drinks	
17:00		Oral 4			
17:30		Oral 5			
18:00		Oral 6			
18:30		ISIAME SEC meeting			
19:00				Dinner	
	Registration Townhouse hotel				

**Invited talks:** Topics: T1, T4, T5, T9, T10 (2), T11 (2), T12

I-1: Xuning Li, Junhu Wang: Mössbauer studies on the mechanism of Fenton-like reaction catalyzed by Prussian blue analogues and as-derived oxides

I-2: Massimo Carbuticchio Topic 4: Magnetic Materials. Influence of the phenomena occurring at the interface between L1<sub>0</sub>-ordered-FePt and Fe on the coercivity behaviour

I-3: Krish Bharuth-Ram: Search for ferromagnetic behaviour in TM implanted oxides

I-4: J. Galazka-Friedman A. Friedman: The impact of Mössbauer spectroscopy on the understanding of mechanisms of neurodegeneration in Parkinson's disease

I-5: Vadim Ksenofontov Sergii I. Shylin: Application of synchrotron radiation in study of novel superconductors

I-6: V.V. Popov: Emission Mössbauer spectroscopy of grain boundaries in ultrafine-grained materials processed by severe plastic deformation

I-7: F. Sayed, Z. Nehme, K. Brymora, N. Yaacoub, Y. Labaye, F. Calvayrac, J.M. Greneche: Magnetic properties of Fe-based nanoparticles for biomedical applications

I-8: S. M. Dubiel: Microscopic phenomena underlying macroscopic properties of Fe-Cr alloys.

I-9: E. Kuzmann, L. da Silva, S. Stichleutner, M. El-Sharif, Z. Homonnay, Z. Klencsár, L. Sziráki, C.U. Chisholm and Gy.Lak Mössbauer and XRD study of Al-Sn lined steel bimetal alloy

I-10: H. P. Gunnlaugsson: Emission Mössbauer spectroscopy at ISOLDE/CERN

I-11: Michael Reissner, Klaudia Hradil, Walter Steiner, Magnetic and electrostatic hyperfine interactions in FeSb<sub>2</sub>

**Oral talks:** Topics: T3, T4 (2), T6, T8 (3), T12 (3)

O-1: Moulay Tahar Sougrati, Jean-Claude Jumas and Lorenzo Stievano. Review of Mössbauer spectroscopy contribution to design of electrochemical energy conversion and storage systems

O-2: V. Masondo, K. Bharuth-Ram<sup>2</sup>, H. Masenda, T. E. Mølhol, C. Ronning, H. P. Gunnlaugsson, K. Johnston, P. Krastev, D. Naidoo, P.Qi, J. Schell, A. Tarazaga, I. Unzueta, G. Langouche, R. Mantovan, H. P. Gíslason, S. Ólafsson. Fe sites and interactions in C implanted ZnO single crystals studied with Emission Mössbauer Spectroscopy following implantation <sup>57</sup>Mn\*

O-3: Guodong Zheng, Xiangxian Ma, Wang Xu, Yang Li, Limin Ji, Baoguang Shi. Iron speciation by Mössbauer spectroscopy and its implications in various studies on petroleum geosciences

O-4: A. Ladam, L. Aldon, P.E. Lippens, C. Cenac-Morthe, J. Olivier-Fourcade and J.-C. Jumas. How to select a tin based negative electrode for Li-ion batteries: application to Ti-Ni-Sn based composites.

O-5: Raphaël P. Hermann, Moulay T. Sougrati, Ali Darwiche, Laure Monconduit, Lorenzo Stievano, Richard Dronskowski, Xiaohu Liu, Abdelfattah Mahmoud, Marcus Herlitschke, Aamuel Jouen, Transition metal carbodiimides, a new class of anode materials

O-6: Hilary Masenda, Deena Naidoo, Krish Bharuth-Ram, Haraldur P. Gunnlaugsson, Karl Johnston Roberto Mantovan, Torben E. Mølholt, Mehluli Ncube, Sveinn Ólafsson, Seyedmohammad Shayestehaminzadeh, Haflidi. P. Gíslason, Guido Langouche, Gerd Weyer and the ISOLDE Collaboration. Fe behaviour in InN studied by Emission Mössbauer spectroscopy

O-7: Antoine F. Mulaba-Bafubiandi and Niclette Eloko Energy source in macadamia nut shell used in artisanal claybrick making in Dididi village (Venda, Limpopo, South Africa)

O-8: Jakub Navarik, Petr Novak, Jiri Pechousek, Jiri Tucek: The scintillation based Mössbauer detection system optimization.

O-9: Manfred Deicher and the ISOLDE Collaboration. Perturbed angular correlation - a complementary technique to Mössbauer effect in the study of materials for industrial applications

O-10: H. P. Gunnlaugsson. Annealing studies in Emission Mössbauer Spectroscopy using short lived isotopes

**Posters:** Topics: T1, T4 (3), T5, T6 (4), T8, T10 (4), T11 (3)

P-1: Ayyakannu Sundaram Ganeshraja, Junhu Wang, Kiyoshi Nomura, Ferromagnetic Sn-TiO<sub>2</sub> Nanocrystals: <sup>119</sup>Sn Mössbauer and photocatalytic studies

P-2: C. L. Ndlangamandla, K. Bharuth-Ram, B. D. Ngom and M. Maaza. Ru doping of hematite nanorods tracked with XRD and Mössbauer spectroscopy

P-3: T. E. Mølholt, H. P. Gunnlaugsson, K. Johnston, R. Mantovan, J. Röder, V. Adoons, A. M. Gerami, H. Masenda, Y. A. Matveyev, M. Ncube, I. Unzueta, K. Bharuth-Ram, H. P. Gislason, P. Krastev, G. Langouche, D. Naidoo, S. Ólafsson, A. Zenkevich, ISOLDE Collaboration. Charge states and lattice sites of dilute implanted Sn in ZnO

P-4: Luiz Fernando França, Kelly Grace Magalhães, Francisco Assis de Oliveira Nascimento, Erno Kuzmann, Vijayendra Kumar Garg, Aderbal Carlos de Oliveira. A portable, diagnostics system for the Zika virus

P-5: Deena Naidoo, Mehluli Ncube, Hilary Masenda and Harshna Jivan. Annealing studies of holmium substituted bismuth ferrite

P-6: J. Galazka-Friedman, M. Woźniak, P. Duda, Ł. Karwowski, S.D. Forder. Could Mössbauer spectroscopy be an alternative method of the preliminary classification of the ordinary chondrites?

P-7: J.-C. Jumas, N. Bibent, P.E. Lippen<sup>a</sup>, J. Olivier-Fourcad<sup>a</sup>, T. Azi<sup>b</sup>, F. Cueva<sup>b</sup> and M. Latroche. Ni-Sn-Si/C based composite as negative electrode for Li-ion batteries <sup>119</sup>Sn Mössbauer *operando* study

P-8: J. Kohout, T. Kmječ, D. Kubániová, L. Kubíčková, K. Závěta P. Brázda, M. Klementová, E. Šantavá, A. Lančok. The magnetic transition in ε-Fe<sub>2</sub>O<sub>3</sub> nanoparticles: Mössbauer spectroscopy

P-9: Changseok Han, Libor Machala, Ivo Medrik, Radina P. Kralchevska, Dionysios D. Dionysiou. Degradation of the cyanotoxin microcystin-LR using nanoparticulate Fe<sub>2</sub>O<sub>3</sub> photocatalysts under visible light illumination

P-10: R. Konieczny, R. Idczak and J. Chojcan. A study of thermodynamic properties of dilute Fe-Au alloys by the <sup>57</sup>Fe Mössbauer spectroscopy

P-11: Gerrard Peter, Deena Naidoo and Hilary Masenda. A spectroscopic study of iron based cemented carbides

P-12: Antoine F. Mulaba-Bafubiandi, Seke vangu Max, Balue Kumona and Wafula Mifundu, Nyiragongo lava pozzolana material to use in construction applications characterised by X-ray techniques, SEM, FTIR and Mössbauer spectroscopy

P-13: S. Krehula, M. Ristić, M. Reissner, C. Frandsen, S. Musić, <sup>57</sup>Fe Mössbauer study of iron phases in TiO<sub>2</sub> production

P-14: Danny Müller, Christian Knoll, Marco Seifried, Gerald Giester, Peter Weinberger, Michael Reissner, Spin-state determination in rigid iron(ii) tetrazole spin crossover chains

P-15: M. Walter, W.D.C. Schenkeveld, L. Gille, M. Reissner, S.M. Kraemer. Dissolution of chrysotile asbestos and its implications on the fibers' radical forming potential: a complementary ICP-OES, EPR and <sup>57</sup>Fe Mössbauer study

P-16: Z. Klencsár, K. Kovács, F. Fodor, Á. Solti, Gy. Tolnai, Z. Homonnay, E. Kuzmann. Manufactured nanoparticles: potentially toxic agents or nutrient reservoirs for plants?

P-17: E. Kuzmann, L. da Silva, S. Stichleutner, M. El-Sharif, Z. Homonnay, Z. Klencsár, L. Sziráki, C.U. Chisholm and Gy.B. Lak. Mössbauer and XRD study of hot dip galvanized alloy

P-18 C.J. Masina, L. Lodya, J.H. Neethling, E.F. Oliver, S. Manzini, W. Barnard and E. du Plessis. Synthesis and characterisation of 2- and 6-line ferrihydrite nanoparticles



## I-1. Topic 1: Catalysis

### MÖSSBAUER STUDIES ON THE MECHANISM OF FENTON-LIKE REACTION CATALYZED BY PRUSSIAN BLUE ANALOGUES AND AS-DERIVED OXIDES

Xuning Li<sup>a,b</sup> Junhu Wang<sup>a,\*</sup>

<sup>a</sup>Mössbauer Effect Data Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China, <sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, China, \*Corresponding author: [wangjh@dicp.ac.cn](mailto:wangjh@dicp.ac.cn)

Nowadays, the scarcity of fresh water resources and the ever-growing environmental pollution have been attracting increased concern. The Fenton-like process has been widely investigated due to its high efficiency in removing persistent organic contaminants by in-situ production of  $\text{SO}_4^{\bullet-}$  or  $\text{HO}^{\bullet}$  radicals. However, limited mechanism understanding hinders the breakthroughs in Fenton chemistry.

We focus on the development of novel nano-sized catalytic materials towards environmental purification and energy application & conversion. We understand the structure-activity relationship and the catalytic mechanism of the developed nano-catalysts mainly by Mössbauer spectroscopy in combination with various advanced conventional techniques.<sup>1</sup> Here we systematically report our research advance in investigating the mechanism of Fenton-like reactions. Firstly, Prussian blue/ $\text{TiO}_2$  nanocomposites were designed to explore the synergistic effects between photocatalyst and Fenton-like system.<sup>2</sup> Then, two kinds of Fe-Co Prussian blue analogues (Fe-Co PBAs) with different iron valence state,  $\text{Fe}_3[\text{Co}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$  and  $\text{Fe}[\text{Co}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ , were developed as novel photo-Fenton catalysts for in-depth investigation of the heterogeneous Fenton reaction mechanism.<sup>3,4</sup> Finally, considering that although  $\text{CN}^-$  is closely associated with stable  $[\text{Co}(\text{CN})_6]^{3-}$  complex, one may prefer to use oxide in place of cyanide catalysts.  $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$  nano-cages derived from Fe-Co PBAs were also developed as excellent catalysts for removal of bisphenol A by activation of peroxydisulfate (PDS).<sup>5</sup> All through these researches,  $^{57}\text{Fe}$  Mössbauer spectroscopy plays a crucial role to determining the oxidation state and the coordination environment of iron species in

the catalysts, which is critical for understanding the mechanism of Fenton-like reactions

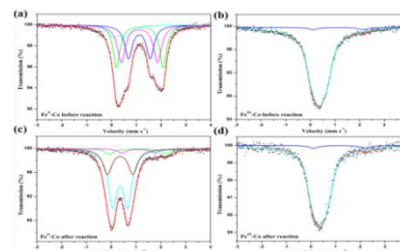


Fig.1  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Fe}^{\text{II}}$ -Co PBA (a) before, (c) after;  $\text{Fe}^{\text{III}}$ -Co PBA (b) before, and (d) after photo-Fenton reactions.

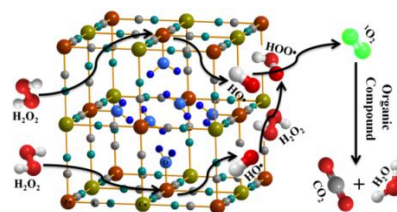


Fig.2. Mechanism of photo-like process on Fe-Co PBAs.

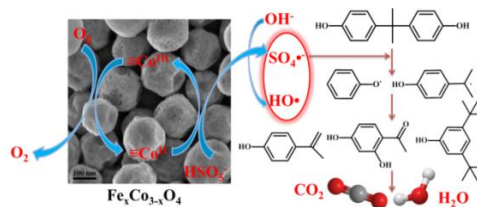


Fig.3. Schemes of BPA degradation catalyzed on  $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$  by activation of PMS

1. K. Liu, A. I. Rykov, J. Wang, T. Zhang, Adv. Catal., 2015, 58: 1.
2. X. Li, J. Wang, A.I. Rykov, V.K. Sharma, H. Wei, C. Jin, X. Liu, M. Li, S. Yu, C. Sun, D.D. Dionysiou, Catal. Sci. Technol. 2015, 504.
3. X. Li, J. Liu, A.I. Rykov, H. Han, C. Jin, X. Liu, J. Wang, Appl. Catal. B 2015, 196.
4. X. Li, A.I. Rykov, J. Wang, Catal. Commun. 2016, 32.
5. X. Li, Z. Wang, B. Zhang, A.I. Rykov, M. A. Ahmed, J. Wang, Appl. Catal. B 2016, 788.

## I-2. Topic 4: Magnetic Materials

### INFLUENCE OF THE PHENOMENA OCCURRING AT THE INTERFACE BETWEEN L1<sub>0</sub>-ORDERED-FePt AND Fe ON THE COERCIVITY BEHAVIOUR

Massimo Carbucicchio

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As known, the materials for magnetic recording devices are to be characterized by large values of the maximum energy product (BH)<sub>max</sub> which represents the density of information that can be stored in a magnet.

In this field, the exchange spring magnets are very promising materials. They are nanocomposites constituted by a hard phase with a large uniaxial anisotropy and a soft phase with a very large saturation magnetization. If a strong exchange coupling establishes at the interface between the different phases, the system can behave as single phase hard magnet having simultaneously a large value of both the coercivity and the saturation magnetization.

Exchange-spring magnets having a single phase magnetic behaviour can only be obtained with a fine control of the growth allowing to preserve a good crystallographic coherence and adhesion between the different phases.

Contrary to what expected, i.e. a decrease of coercivity by increasing the soft layer thickness, an initial slight increase in coercivity has been often found in systems where the soft layer thickness is comparable to that of the hard one. In principle, this peculiar behaviour could be justified considering the phenomena occurring at the hard/soft interfaces.

In order to verify this assumption, L1<sub>0</sub>-ordered FePt/Fe thin bi-layers were grown using a molecular beam epitaxy systems onto (100)-MgO substrates changing the soft Fe layer thickness. The study of the intermixing phenomena occurring at the hard/soft interfaces was carried out using surface Mössbauer spectroscopy (CEMS). For increasing the CEMS sensitivity to the compounds that eventually form at the interfaces, the FePt was grown using natural iron, while iron highly enriched with <sup>57</sup>Fe isotope was

used for growing the soft layer. The magnetic properties of the samples were analyzed with a magneto-optical Kerr effect (MOKE) magnetometer. The surface morphology and the magnetic domains were analyzed with an UHV atomic and magnetic force microscopy (AFM/MFM) in tapping and lift mode respectively.

The present work clearly demonstrates that the degree of interface intermixing and reactions is the responsible for the coercivity behaviour in exchange-spring magnets.

### **I-3. Topic 4: Magnetic Materials and Superconductive Materials**

#### **SEARCH FOR FERROMAGNETIC BEHAVIOUR IN TM IMPLANTED OXIDES**

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*Materials Research Division, iThemba LABS, South Africa*

While there have been several reports of the observation of ferromagnetic behaviour in metal oxides doped with low concentrations of transition metal ions, the origin of the observed effects has been the subject of much debate. In this presentation the results of our recent experiments at the ultra-low ( $<10^{-3}$  at. %) and low ( $\leq 8$  at. %) dopant concentrations will be reviewed.

The ultra-low concentration systems were studied in  $^{57}\text{Fe}$  - emission Mössbauer Spectroscopy (eMS) measurements following the implantation of radioactive parent isotope  $^{57}\text{Mn}^*$  at the ISOLDE facility, CERN. Systems implanted with up to 8 at. % Fe, Co and Mn ions were studied in conventional conversion electron Mössbauer Spectroscopy (CEMS) measurements. The results will be discussed in the light of complimentary magnetization measurements.

#### *Acknowledgements:*

The results to be presented were obtained in projects undertaken within the Mössbauer Collaboration at ISOLDE/CERN and the DFG-NRF Joint S & T Research Collaboration.

## I-4. Topic 5: Biology and Biomedicine

### THE IMPACT OF MÖSSBAUER SPECTROSCOPY ON THE UNDERSTANDING OF MECHANISMS OF NEURODEGENERATION IN PARKINSON'S DISEASE

J. Galazka-Friedman<sup>1</sup>, A. Friedman<sup>2</sup>

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<sup>2</sup>*Department of Neurology, Medical University of Warsaw, Poland*

Parkinson's disease (PD) is related to a progressive loss of neurons mostly in substantia nigra (SN) of the human brain. SN is a small neuronal structure of about 500 mg, located deeply in the brain stem. The mechanism of this process remains unknown, although several hypotheses are discussed. Among them the oxidative stress plays an important role. According to this theory the death of neurons is caused by an over production of free radicals mediated by Fenton reaction  $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^\cdot + \text{OH}^-$ . In this reaction divalent iron plays a crucial role. If the theory is correct several questions should be answered: 1/ is there an increase of the concentration of iron in parkinsonian SN?, 2/ which iron is increased – total or only divalent iron?, 3/ what is the source of the iron available for Fenton reaction?

The assessments of iron in Parkinson's disease started with a study by Earle [1] who detected, using X-ray fluorescence, almost 2 times more iron in SN from parkinsonian brains compared to controls. The study was followed by Sofic et al [2], in which with the use of spectrophotometry, high increase of the total iron together with high concentrations of divalent iron were described. Others studies did not find any increase of the concentration of total iron in parkinsonian SN [3, 4]. In general the studies showing a significant increase of the total iron in SN were using methods related to destruction of the tissue for measurements. Therefore it seemed appropriate to use Mössbauer spectroscopy (MS) for determination of the total concentration of iron and also for the assessment of the ratio  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the tissue. Various studies tried also to determine the source of iron for the Fenton reaction. According to some authors iron, which could trigger the reaction was bound to ferritin, while others suggested that the source of this iron may be neuromelanin. We suggested that MS could be a good tool to answer this question too. There is also another important advantage of the MS – the method does not need any pretreatment of samples. Therefore the samples may be used later for other investigations.

Our first systematic MS results were published in 1996 [5] and up to now we measured 20 PD 29 control SNs. The concentration of total iron did not differ between the pathological and control tissues and the concentration of iron was of about 180 mg/g in both, with the ratio PD vs. control being  $1.00 \pm 0.13$  [6]. On the other hand MS applied to SN samples obtained from brains of patients affected by another form of Parkinsonism – progressive supranuclear palsy – did show a significant increase of the concentration

of total iron with the concentration of total iron being of about 300 ng/mg [7].

Our measurements did not detect any divalent iron and the computer simulation to assess how much of divalent iron could escape identification demonstrated that it could not be more than 10% of the total iron. Concerning the source of iron our measurements identified iron present in SN both in PD and control as ferritin-like iron. We compared the spectra obtained from the native SN tissue to those obtained from synthetic neuromelanin and neuromelanin isolated from 22 control SNs. The spectra differ significantly [6].

Although application of Mössbauer spectroscopy to human brain samples is difficult because of small amounts of iron in the samples, which demand iron free counter and cryostat windows, Mössbauer spectroscopy is an important tool for studies aimed to determination of the role of iron in Parkinson's disease and other neurodegenerations. Further studies with the use of this method in diseases like Alzheimer could lead to a better understanding of mechanisms leading to iron mediated oxidative stress.

References:

- [1] Earle KM. J. Neuropathol. Exp. Neurol. 27 (1968) 1-13
- [2] Sofic et al. J. Neural. Trans. 74 (1988) 199-205
- [3] Loeffler et al. J. Neurochem. 65 (1995) 710-716
- [4] Uitti et al. Can. J. Neurol. Sci. 16 (1989) 310-314
- [5] Galazka-Friedman et al. Mov. Disord. 11 (1996) 8-16
- [6] Galazka-Friedman et al. Hyperfine Interact. 165 (2005) 285-288
- [7] Galazka-Friedman J et al. Acta Phys Pol. 115 (2009) 431-433

## I-5. Topic T9: Applications using Synchrotron Radiation

### APPLICATION OF SYNCHROTRON RADIATION IN THE STUDY OF NOVEL SUPERCONDUCTORS

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

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

Doping of small amounts of Cu into the FeSe matrix suppresses superconductivity and introduces local static moments at the Fe sites, evidenced by glassy magnetic interactions. Application of pressure leads to restoration of superconductivity in Cu-doped FeSe [4]. High-pressure studies of non-superconductive  $\text{Fe}_{0.97}\text{Cu}_{0.04}\text{Se}$  using the SMS revealed that pressure suppresses the static spin-glass state. Apparently only nano-scale phase separation of insulating vacancy-ordered antiferromagnetic and metallic non-magnetic FeSe-similar domains provides conditions for coexistence of static magnetism and SC [5].

Observation of high- $T_C$  SC with onset temperature of 203 K in H<sub>2</sub>S in a pressure range of 150-190 GPa [6] was recently independently confirmed by  $^{119}\text{Sn}$  Mössbauer spectroscopy

applying SMS [7]. This new possibility to study SC at extreme conditions is due to the expulsion of the applied magnetic field from the superconducting sample (Meissner Effect) where nonmagnetic  $^{119}\text{Sn}$  as a highly sensitive nuclear probe is placed. In the cited study, the magnetic field at the  $^{119}\text{Sn}$  sensor was monitored using Nuclear Resonance Scattering (NRS) of synchrotron radiation. The presence of the magnetic field at tin nuclei in normal state of H<sub>2</sub>S above  $T_C$  was identified by quantum beats in the time spectra of NRS. Obviously, using of NRS to record superconducting transitions could be applied to study many important systems including superconducting metallic hydrogen which presumably exists in the mega bar pressure range [8].

[1] S. Medvedev et al., Nature Mater. 8, 630 (2009).

[2] V. Ksenofontov et al., Phys. Rev. B 81, 184510 (2010).

[3] S. I. Shylin et al., Europhys. Lett., 109, 67004 (2015).

[4] L. M. Schoop et al., Phys. Rev. B, 84, 174505 (2011).

[5] V. Ksenofontov et al., Phys. Rev. B, 84, 180508(R) (2011).

[6] A.P. Drozdov, et al., Nature 525 (2015) 73.

[7] I.A. Troyan, et al., Science 351 (2016) 1303.

[8] N.W. Ashcroft, Phys. Rev. Lett. 92 (2004) 187002.

## I-6. Topic 10: Nanotechnology

### EMISSION MÖSSBAUER SPECTROSCOPY OF GRAIN BOUNDARIES IN ULTRAFINE-GRAINED MATERIALS PROCESSED BY SEVERE PLASTIC DEFORMATION

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Along with the ultrafine-grained (UFG) structure one of the most important features of materials processed by severe plastic deformation (SPD) is the specific state of their grain boundaries (GBs), which, on the opinion of many researchers, play a crucial role in the unique properties of these materials [1]. Such grain boundaries are often referred to as the non-equilibrium ones in order to distinguish them from the grain boundaries in annealed polycrystals (which are in the meta-stable equilibrium) [2]. A specific feature of non-equilibrium GBs is an excess free volume. In the present study capabilities of the emission gamma-resonance (NGR) spectroscopy for revealing the non-equilibrium state of GBs in the materials processed by SPD are analyzed.

The technique of the emission NGR (Mössbauer) study of GBs is described in [3]. In order to obtain a Mössbauer specimen-source, a specimen is coated with  $^{57}\text{Co}$  Mössbauer radionuclide in an amount of 30–40 MBq using electrolytic precipitation. Then the specimen is annealed at such temperatures when the volume diffusion is frozen, and the Mössbauer isotope atoms diffuse only along grain boundaries. The last step consists in the removal of the non-diffused isotope from the surface together with a thin surface layer in which the radioisotope atoms could penetrate not only by diffusion along high-angle boundaries but by dislocations and low-angle boundaries. A Mössbauer spectrum is taken from an as-prepared specimen. Then the specimen is annealed at higher temperatures and after every annealing a spectrum is taken. The difference between the NGR spectra of UFG materials processed by SPD and well-annealed polycrystalline materials of the same composition enables to judge on the non-equilibrium state of GBs of the former.

According to the investigations carried out in the present study, at relatively low annealing temperatures there are two components in the spectra of UFG materials, one of which – component 1 – is formed by the Mössbauer atoms localized in grain boundaries proper, whereas another one – component 2 – by the atoms located in the near-boundary areas of crystallites. Analogous spectra were observed in all the previously studied coarse-grained materials [3]. However, the isomer shifts of both spectral lines in the SPD-processed materials are substantially lower than in coarse-grained materials annealed at the same temperatures, which obviously results from an excess free volume of the non-equilibrium GBs formed under the SPD and their near-boundary areas.

When the annealing temperature is increased, two more components, denoted as 3 and 4, appear in the spectra of the UFG materials. The isomer shifts of these components are much higher than those of components 1 and 2, and are close to the values obtained in the coarse-grained materials

with GBs of recrystallization origin. The appearance of these two additional lines obviously results from the recovery processes in GBs formed under the SPD and their near-boundary areas, due to which the excess free volume decreases. Besides, they can result from the migration of GBs by small distances (their straightening), due to which the segregation of interstitial impurities connected with GBs and their near-boundary areas decreases. Thus, it can be suggested that component 3 is formed by the Mössbauer atoms localized in GBs which recovered and migrated by small distances, and component 4 by the atoms located in the near-boundary areas of these boundaries. With the increase of the annealing temperature, the intensities of components 3 and 4 increase, and those of components 1 and 2 decrease up to the complete vanishing of the latter, which indicates the disappearance of non-equilibrium GBs.

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[1] R.Z. Valiev. *Nature Mater.* **3** (2004) 511.

[2] V.N. Chuvildeev. *Non-equilibrium grain boundaries in metals. Theory and applications.* Moscow, FIZMATLIT, 2004 [in Russian].

[3] V.V. Popov. *Phys. Met. Metallogr.* **113** (2012) 1257.

## I-7. Topic 10: Nanotechnology

### MAGNETIC PROPERTIES OF Fe-BASED NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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Great attention has been paid during the last decades to the synthesis of nanoparticles (NPs) and the control of their chemical, morphological and physical properties and their reproducibility. In addition, the correlations between the structure, the local chemical order and the magnetic properties have to be well understood in order to tune and to optimize the nature of NPs according to their applications. Indeed, various topics such as recording media, MRI contrast agents, nanocarriers for drug delivery, magnetic hyperthermia fluids are promising.

In the case of Fe-based NPs, both  $^{57}\text{Fe}$  transmission zero-field and in-field Mössbauer spectrometry appear as excellent local probe techniques providing relevant structural and magnetic information. Indeed, they are suitable (i) to investigate *in situ* local atomic order and magnetic properties, (ii) to discriminate surface and bulk effects in addition to oxidation and spin states of Fe species and (iii) then to follow the hyperfine magnetic properties and their dynamics as a function of temperature in correlation with super paramagnetic relaxation phenomena. But it is important to emphasize that it remains also necessary to investigate NPs by means of complementary techniques as X-ray diffraction, Transmission Electron Microscopy, field-cooled and zero-field cooled (FC-ZFC) magnetic measurements, X-ray magnetic circular dichroism. Consequently, we report first the structural and magnetic properties of NPs, functionalized NPs and hollow NPs. Then, we discuss the role of some relevant parameters in magnetic NPs and we illustrate how zero-field and in-field  $^{57}\text{Fe}$  Mössbauer spectrometry contribute to better understand static and dynamic magnetic properties from selected examples based on assemblies of ferrites NPs, hollow NPs and functionalized NPs. In addition, we report some relevant results

obtained by means of computer modelling including Monte Carlo and *ab initio* calculations to model the magnetic configurations of both NPs and hollow NPs and the chemical interactions between NPs and grafted molecules.

## I-8. Topic 11: Metals and Alloys

### MICROSCOPIC PHENOMENA UNDERLYING MACROSCOPIC PROPERTIES OF FE-CR ALLOYS.

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The basic ingredient of technologically important stainless steels (SS) are Fe-Cr alloys. Ferritic–martensitic (F–M) steels which contain 7–12% Cr are regarded as good candidates for structural materials in Gen-IV reactors due to their low ductile–brittle transition temperature shift, low swelling and reduced creep rate under 600 °C. Long-term annealing and irradiation they undergo in service deteriorates their macroscopic properties causing, among other, enhanced embrittlement (EE). EE is caused by precipitation of: (i) Cr-rich phase ( $\alpha'$ ), and (ii) foreign phases like  $\sigma$ ,  $\lambda(\epsilon)$ ,  $\chi$ , G,  $M_6C$  to name the most important. As the precipitates have a microscopic nature, microscopic techniques are the most appropriate tools to study the issue. Among them the Mössbauer spectroscopy (MS) plays a crucial role which will be outlined and exemplified in this presentation. In particular, the following issues will be addressed:

(a) determination of the solubility limit of Cr in iron, (b) kinetics of the phase decomposition, (c) kinetics of the  $\sigma$ -phase formation, (d) short-range ordering, (e) effect of irradiation with different ions.

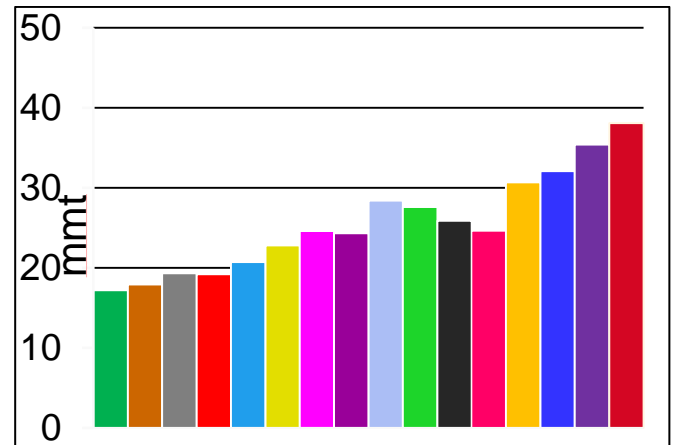


Fig. 1 Global production of stainless steels in years 1998-2013.



## I-9. Topic 11: Metals and Alloys

### MÖSSBAUER AND XRD STUDY OF Al-Sn LINED STEEL BIMETAL ALLOY

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Bearings manufactured from cold roll bonded Al/AlSn/Al/steel composite materials possess superior tribological wear and strength characteristics making them the ideal choice for both passenger car and truck vehicle bearings in the automotive manufacturing industry. The Al-Sn alloy is cold roll bonded to the steel via an aluminium foil (Fig. 1). The aluminium foil surface layer serves to provide a good bonding agent between the aluminium alloy and the steel. However the bearings unique properties can be influenced by the many steps applied during the complex industrial manufacturing process [1]. Steps such as surface preparation and condition, contaminants and oxides formation lead to a possibility of slight changes in elemental composition which could contribute to bond failure.

The aim of the present work was to perform phase analysis in order to elucidate the possible formation of oxide phases at the surface or at the interfaces, when water was sprayed on to the surface of the steel pre cold roll bonding or when finishing debris was deliberately introduced to the surface of the finished steel pre cold roll bonding.



Fig. 1 Micro section of an annealed bimetal sample.

An aluminium alloy free CS1 type steel (0.06 wt% C, 0.45 wt% Mn) and samples of cold roll bonded steel bimetal alloys (MAS15 and MAS16) were fabricated at different conditions at MAHLE Engine Systems UK Ltd., Kilmarnock, U.K. The samples were investigated by X-ray diffraction (XRD), <sup>57</sup>Fe and <sup>119</sup>Sn conversion electron Mössbauer spectroscopy (CEMS) at room temperature.

XRD has revealed only the existence of the steel phase in the steel only sample, while no impurity or oxide phases in this sample were detected. XRD identified steel and metallic Al and Sn constituent phases in the bimetallic alloys which confirm the phase composition according to CS1 steel and MAS15 or MAS16 alloys and interface Al layer. Beside the main phase composition XRD revealed a minor phase(s) in the bimetallic alloys “water spray” and “deliberate debris”

which may probably be connected with Al substituted magnetite.

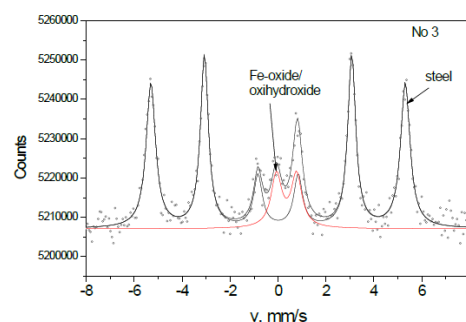


Fig. 2 <sup>57</sup>Fe CEMS of Al-Sn bimetal/steel cold roll bonded sample with deliberately added excess debris.

<sup>57</sup>Fe Mössbauer spectroscopy revealed the presence of 4% secondary iron-bearing phase attributed mainly to iron oxide/ oxyhydroxides (ferrihydrite) besides the steel matrix on the surface of the steel sample. A significant difference between the occurrences of the secondary phase of differently prepared bimetal alloys found in their <sup>57</sup>Fe CEM spectra (Fig. 2) allowed identifying the main phase of debris as different iron oxide/ oxyhydroxides. <sup>119</sup>Sn CEM spectroscopy revealed the presence of tin only in metallic form in all bimetal alloys.

[1] L. da Silva, Technical Report KTP 01003, MAHLE Engine Systems UK Ltd., Kilmarnock, 2012.

## **I-10. Topic 12: Methodology and Instrumentation**

### **EMISSION MÖSSBAUER SPECTROSCOPY AT ISOLDE/CERN**

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Emission Mössbauer spectroscopy (eMS) gives several new additions to conventional Mössbauer spectroscopy. It allows making use of the chemical properties of parent atoms beyond the Mössbauer isotope, enhancing the use of the technique. Samples can be prepared with extreme dilution ( $<0.01$  at.%), making it possible to use the parent to study intrinsic properties of the host material. Some parents have recoil, which enables study of interstitial defects.

In recent years, the interest of eMS at ISOLDE has increased significantly. The Mössbauer collaboration has six on-going experiments, including studies of metal impurities in silicon, metal dopants in oxide semiconductors, and many more.

Currently we apply eight isotopes for five different Mössbauer transitions. In my presentation, I will present the experimental possibilities at ISOLDE/CERN, ideas for future extensions, and show examples of results relevant to industrial applications of the technique, that can give ideas for future experimental proposals

## I-11 Topic 6: Mineralogy

### MAGNETIC AND ELECTROSTATIC HYPERFINE INTERACTIONS IN FeSb<sub>2</sub>

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Because of its colossal Seebeck coefficient [1] and its rather high charge carrier mobility [2], FeSb<sub>2</sub> is a candidate for several interesting applications like thermoelectrics and high speed electronics. Magnetically FeSb<sub>2</sub> shows a quite unusual behaviour. At low temperatures susceptibility is constant with a value near to zero, pointing to a nonmagnetic ground state. Above approximately 90 K susceptibility increases and magnetization curves point to paramagnetic behaviour. This temperature induced magnetism is usually explained either by a small gap insulator with an semiconductor – metal transition around 90 K [3] or by a near ferromagnetic ground state [4]. FeSb<sub>2</sub> crystallizes in the marcasite structure type with only one crystallographic Fe site. The Fe is surrounded by slightly distorted Sb octahedra, which are corner shared in the ab-plane and edge sharing along the c-axis. The distortion is a squeezing of the octahedron along the apical axis. This is in good agreement with <sup>57</sup>Fe Mössbauer measurements, which can be explained by only one subspectrum (Fig. 1).

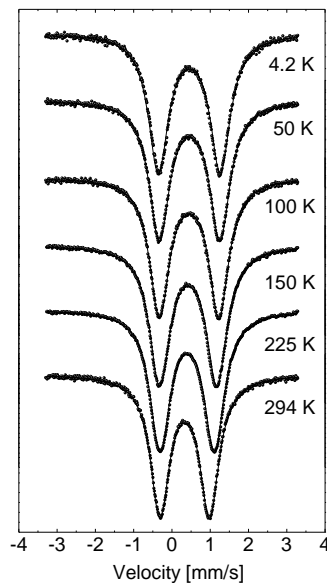


Figure 1

In contrast to this, Mössbauer spectra taken in external magnetic fields cannot be explained by only one

subspectrum. The obtained spectra are extremely complex (Fig.2) [5].

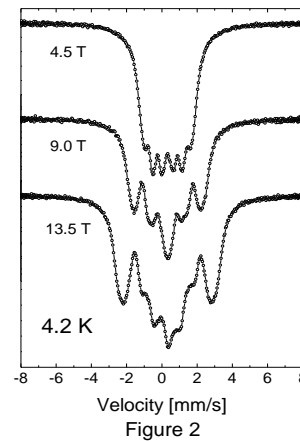


Figure 2

Several subspectra are necessary to explain the measured spectrum. From a thorough structural investigation by X-ray and neutron diffraction measurements it is concluded that approximately 30% of the Fe atoms are shifted out of the center of the octahedron. A closer look to the structure shows that the two Fe atoms in the unit cell, which are in the average structure crystallographically identical, are not the same in case of the electronic structure, because the apical axis of the octahedra is not perpendicular to the basal plane but tilted by approximately two degrees. The distortion of the Sb octahedron as a consequence of the off-site position of part of the Fe atoms lead to distribution of isomer shift, large spread in quadrupole splitting and rather large asymmetry parameter. Analysis of the magnetic hyperfine fields show that those Fe atoms which are still in the center of the octahedrons have no hyperfine field, whereas those shifted out of the center show a small ferromagnetic like hyperfine field.

- [1] Bentien A et al, 2007 *EPL* **80** 17008
- [2] Hu R et al, 2008 *APL* **92** 182108
- [3] Petrovic C et al, 2003 *Phys. Rev. B* **67** 155205
- [4] Lukoyanov A V et al, 2006 *Eur. Phys. J. B* **53** 205
- [5] Farhan A et al, 2009 *J. Phys. Conf. Ser.* **215** 012142



## O-1. Topic 8: Electrochemistry, batteries, sensors

### REVIEW OF MÖSSBAUER SPECTROSCOPY CONTRIBUTION TO DESIGN OF ELECTROCHEMICAL ENERGY CONVERSION AND STORAGE SYSTEMS

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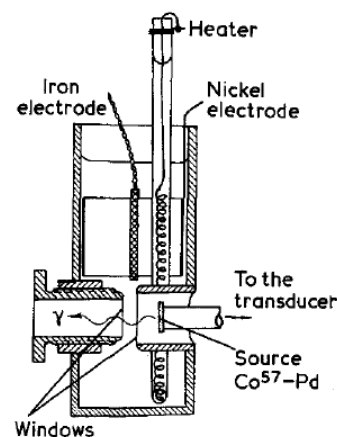
A huge number of electrochemical systems used to convert and store energy are designed with materials including the most common Mössbauer elements; iron and tin. Since its childhood, Mössbauer spectroscopy has been successfully employed to elucidate the impact of electronic and structural changes of the performances of electrochemical systems. The sensitivity of this technique has been a key point in investigating redox reactions as well as tinny lattice changes. Also, its versatility and the ease of its implementation have paved the way to the development of *in situ* and *operando* uses. The pioneering *in situ* studies of batteries have been reported in early seventies by different groups<sup>1-3</sup>.

This current presentation aims to review the Mössbauer spectroscopy contribution in the last decades with a focus on the last fifteen year. The first uses of Mössbauer spectroscopy in the investigation of primary batteries will be illustrated in details with lithium iron sulfur system. Fe<sup>3+</sup>-Fe<sup>6+</sup> chemistry has been also investigated with aim of building high density batteries as will be exemplified with the case of K<sub>2</sub>FeO<sub>4</sub>. In the field of Li and Na-ion secondary batteries, Mössbauer spectroscopy has been widely used in the elucidation of reaction mechanisms of iron fluorides, phosphates, sulfates, fluorsulfate and intermetallics. Remarkable examples will be highlighted.

In their seek of affordable alternatives to platinum group metals, researchers have focused on transition metal materials to prepare new catalysts that can be used in the conversion of chemical energy to electrical energy. Hence many iron based systems are proposed as serious candidates to make next generation fuel cell electrodes. After a general review of iron based fuel cell materials, a more detailed overview of

the Fe-N-C system considered as the most promising one will be given.

Finally, a short review will concern the super capacitors made with iron based materials.



One of the pioneering Mössbauer in situ cells developed in the early seventies by Geronov et al.

#### References

- (1) Geronov, Y.; Tomov, T.; Georgiev, S. *Journal of Applied Electrochemistry* **1975**, 5, 351-358.
- (2) Kennedy, J. H.; Sammells, A. F. *Journal of The Electrochemical Society* **1974**, 121, 1-7.
- (3) Tomov, T.; Ruskov, T.; Georgiev, S.; Pavlov, N.; Kwachkov, R. *Proceedings of the Conf. on Mössbauer Spectrometry, Dresden* **1971**, p508.

## O-2. Topic T4: Magnetic Materials and Superconductive Materials

### Fe SITES AND INTERACTIONS IN C IMPLANTED ZnO SINGLE CRYSTALS STUDIED WITH EMISSION MÖSSBAUER SPECTROSCOPY FOLLOWING IMPLANTATION OF $^{57}\text{Mn}^*$

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Theoretical studies on room temperature ferromagnetism (RTFM) in transition metal doped ZnO [1,2] and the wide range of potential application of such systems prompted intense research activity in attempts to realise RTFM in ZnO implanted with TM and other potential dopant ions. In C incorporated ZnO (ZnO:C) ferromagnetic behaviour in thin films has been reported, with the observed behaviour shown to depend on the method of film growth and/or carbon ion incorporation [1-4]. In bulk ZnO single crystals implanted with C ions, a strong decrease in resistivity is observed after C implantation which is attributed to interstitial C ions and the complex defects that are formed [5].

Prompted by these observations, we have prepared ZnO:C samples by implanting ZnO single crystals with 15 keV C ions to concentrations of 4, 1 and 0.4 at. %. Emission Mössbauer Spectroscopy measurements were conducted on the samples following the implantation of 50 keV radioactive parent isotopes  $^{57}\text{Mn}$  ( $t_{1/2} = 1.5$  min) at the ISOLDE facility, CERN. The samples were held at temperatures in the range 299K – 780 K in an implantation chamber, and EMS data was collected with a parallel plate avalanche counter, with one electrode consisting of stainless steel enriched in  $^{57}\text{Fe}$ , mounted on a velocity drive outside the implantation chamber. In order to minimise Mn/Fe precipitation, the Mn fluence was kept extremely low, corresponding to a local Fe concentration of approx. 10-4 at. %.

The spectra of the 4 and 1 % implanted samples showed no evidence of ferromagnetic effects, but displayed considerable implantation induced lattice damage. The spectra were analysed in terms of two components, attributable to substitutional Fe (in the 2+ charge state) and to Fe in lattice defects. While the substitutional Fe made a significant contribution to the spectra of sample ZnO:C1 at RT, in the case of ZnO:C4 this was evident only at temperatures above 416 K.

The 0.4% implanted ZnO sample, on the other hand, showed magnetic features at RT, attributable to high

spin Fe+3 in implantation induced lattice defects. This component showed strong enhancement at low temperatures and at higher temperatures displayed paramagnetic relaxation as observed in EMS studies on virgin ZnO.

- [1] H. Pan et al., Phys. Rev. Lett. 99 (2007) 127201
- [2] S. Zhou et al., Appl. Phys. Lett. 93 (2008) 232507
- [3] T. S. Herng et al., Appl. Phys. Lett. 95 (2009) 012505
- [4] S. Akbar et al., Sol. State Commun. 151 (2011) 17
- [5] Y. Izawa et al., AIP Conf. Proceedings 1399 (2011) 69
- [6] H.P. Gunnlaugsson et al., Appl. Phys. Lett. 92 (2010) 142501

### **O-3. Topic 6: Mineralogy**

#### **IRON SPECIATION BY MÖSSBAUER SPECTROSCOPY AND ITS IMPLICATIONS IN VARIOUS STUDIES ON PETROLEUM GEOSCIENCES**

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As the fourth most enriched element in the crust and being chemically active, iron is generally significant to the studies of Earth sciences. Mössbauer spectroscopy is one of the reliable and valuable techniques to measure iron species by far and implied in various fields such as petroleum geology and geochemistry, particularly in the research on oil and gas generation, migration, and accumulation, the properties of petroleum reservoir rocks, and even the net-path for oil and gas releasing etc.

Key words: iron speciation, Mössbauer effect/spectroscopy, oil and gas geochemistry



## O-4. Topic 8: Electrochemistry, batteries, sensors

### HOW TO SELECT A TIN BASED NEGATIVE ELECTRODE FOR Li-ION BATTERIES: APPLICATION TO Ti-Ni-Sn BASED COMPOSITES.

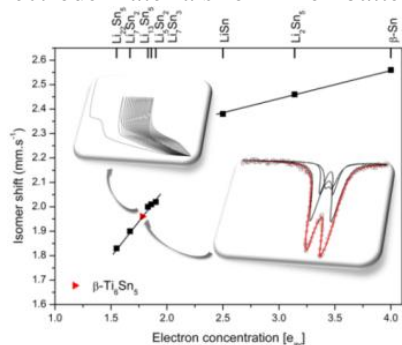
A. Ladam<sup>a</sup>, L. Aldon<sup>a</sup>, P.E. Lippens<sup>a</sup>, C. Cenac-Morthe<sup>b</sup>, J. Olivier-Fourcade<sup>a</sup> and J.-C. Jumas<sup>a</sup>

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Improvement of Li-ion batteries is essential for the development of autonomous systems and especially for space applications. Some elements such as Si or Sn can be used in negative electrode materials and provide high specific capacity (1000 – 4000 Ah.kg<sup>-1</sup>). They reversibly form alloys with lithium during charge-discharge cycling. Unfortunately, they induce strong volume variations that break electrical contacts within the electrode ending in the death of the battery.

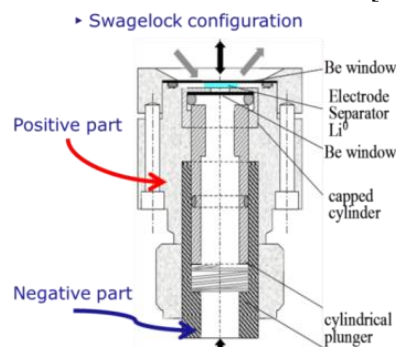
The use of intermetallic electrode materials can reduce the effect of volume variations and significantly improves the cycle life. <sup>119</sup>Sn Mössbauer spectroscopy can be used to select the best Sn-based intermetallic. It has been previously established from an empirical relation between isomer shift (IS) and the Hume-Rothery electron concentration  $e_{av}$  that tin based materials with  $1.5 < e_{av} < 2$  do not undergo drastic structural modifications upon lithiation [1,2]. Based on this result, we have found that IS average value is of particular interest to predict the electrochemical behaviour of tin based compounds or alloys as negative electrode materials for Li-ion batteries.



**Figure 1:** Empirical relation between isomer shift and electron concentration and schematic representation of the <sup>119</sup>Sn Mössbauer spectrum and electrochemical curves of β-Ti<sub>6</sub>Sn<sub>5</sub> based electrode (inset).

In addition, <sup>119</sup>Sn Mössbauer spectroscopy can be used to understand the electrochemical mechanisms, such as conversion or alloying reactions, occurring during lithiation and delithiation. This technique allows characterizing changes in the local environment of tin and can be combined with X-ray diffraction (XRD) that provides information on long-range structural order. Such a combination is very powerful when used in operando mode during charge-discharge cycles of

batteries. An experimental setup including lab-made cell (Fig. 2) has been developed for simultaneous XRD/Mössbauer *in situ* measurements [3,4].



**Figure 2:** Sectional view of the *in-situ* cell used for combined XRD/Mössbauer measurements.

In this work, we present the application of both IS- $e_{av}$  relation and combined XRD/Mössbauer technique to composites obtained from the Ni-Ti-Sn system which presents some compositions of shape memory alloys as negative electrode materials for Li-ion batteries. We show that it is possible to predict the optimal compositions in this ternary system for electrochemical applications and we propose an analysis of the complex reaction mechanisms with Li<sup>+</sup> ions based on XRD/Mössbauer *in-situ* measurements.

#### References

- [1] S. Naille, J.-C. Jumas *et al*, J. Power Sources **189**, 814 (2009)
- [2] A. Ladam, L. Aldon *et al*, Hyperfine Interact. **237**, 51 (2016)
- [3] J.-C. Jumas, L. Stievano *et al*, Brevet Français, n° de dépôt 12 58086 (30/08/2012), PCT/FR2013/051981 (28/08/2013)
- [4] J.-C. Jumas, M.T. Sougrati, *et al*, Hyperfine Interactions, **217** (2013) 107.

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## O-5. Topic 8: Electrochemistry, batteries, sensors

### TRANSITION METAL CARBODIIMIDES, A NEW CLASS OF ANODE MATERIALS

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Moulay T. Sougrati, Ali Darwiche, Laure Monconduit, Lorenzo Stievano, Institut Charles Gerhardt, Montpellier, France, Richard Dronskowski, Xiaohui Liu, RWTH Aachen University, Germany, Abdelfattah Mahmoud\*, Université de Liège, Belgium, Marcus Herlitschke\*, DESY, Hamburg, Germany, Samuel Jouen, Normandie University UMR CNRS 6634, France

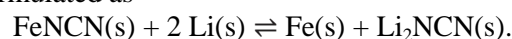
Battery technology is central to the development of improved transportation and communication systems. The market is hungry for improved energy storage devices which motivate sustained efforts in finding new anode, cathode, or electrolyte materials. In this context it is thus surprising to stumble across entirely uncharted territory as happened with our work on iron carbodiimide, FeNCN. Transition metal carbodiimides have been investigated only in the last fifteen years, although the material class is known since CaNCN was first synthesized in 1877. CaNCN is still the best known family member and has been used intensively as fertilizer. The transition metal carbodiimides can be thought of as equivalent to transition metal oxides, where the  $O^{2-}$  is replaced by the  $(-N=C=N-)^{2-}$  moiety. The rigid character of this carbodiimide group leads to unique structural properties, and, amazingly, for some transition metals, magnetism survives.

The intriguing magnetic properties of FeNCN led us to investigate this material by iron-57 Mössbauer spectroscopy [1]. A quite complex spectrum is observed below the Néel temperature of 345 K. The spectrum consists of 5 visible lines and simplifies to an asymmetric doublet upon further cooling to 6 K, see Fig. 1, left. An in depth analysis reveals that the magnetic hyperfine field is perpendicular to the principal axis of the electric field gradient and decreases with temperature because the orbital contribution is reduced through thermal depopulation. The interesting rather open framework of the structure, of NiAs type with As replaced by NCN, with prominent diffusive channels prompted us to investigate electrochemical properties.

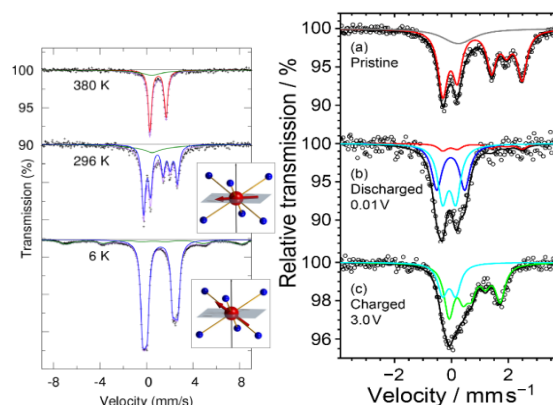
The result of the electrochemical testing with combined *in-situ* XRD and Mössbauer spectroscopy reveals an outstanding reversible capacities of 600 and 400 mAh/g against Li and Na respectively and excellent resilience against high current rate cycling (9 A/g at 32 C) [2].

The scenario that emerges from combining XRD, Mössbauer and infrared spectral data is that the material undergoes a conversion mechanism that can

be formulated as



Interestingly, although the diffractograms after cycling do not exhibit any peak of the starting FeNCN material, Mössbauer spectral data confirms that a magnetic FeNCN spectrum is recovered. These observations indicate nanometric crystalline FeNCN as the endpoint.



**Fig. 1** (left) Temperature dependent Mössbauer spectra of FeNCN with the temperature induced hyperfine field reorientation (inset). (right) Evolution of the Mössbauer spectrum of FeNCN upon discharge and charge against Li.

Several  $M_x(\text{NCN})_y$  carbodiimides with  $M = \text{Mn}, \text{Cr}, \text{Zn}$  were investigated electrochemically and exhibit similar promising performance and cyclability. This investigation thus opens the way to the design of a whole novel family of anode materials where O is replaced by NCN and a corresponding patent[3] has been filed.

#### References

- [1] M. Herlitschke, *et al.*, New J. Chem. 2014, 38, 4670–4677.
- [2] M. T. Sougrati, *et al.*, Angew. Chemie Int. Ed. 2016, 55, 5090-5095.
- [3] M. T. Sougrati, *et al.*, Metal Carbodiimides and Metal Cyanamides as New Active Electrode Materials, EP15305888 (2015), European Patent pending.

#### Acknowledgments

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## O-6. Topic 4: Magnetic materials and Superconductive Materials

### Fe BEHAVIOUR IN InN STUDIED BY EMISSION MÖSSBAUER SPECTROSCOPY

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<sup>8</sup>*Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, 8000 Aarhus, Denmark,*

<sup>†</sup> **Corresponding Author: Hilary Masenda; hilary.masenda@wits.ac.za; (011) 717 6888**

Recent reports of ferromagnetic behaviour in undoped<sup>[1]</sup> and Cr doped<sup>[2]</sup> InN has prompted our study of the lattice sites and valence states of Fe ions in InN using <sup>57</sup>Fe emission Mössbauer spectroscopy (eMS). Radioactive <sup>57</sup>Mn<sup>+</sup> ( $T_{1/2} = 1.5$  min.) ions were implanted with 50 keV energy at ISOLDE/CERN into an InN epilayer grown on a GaN/Al<sub>2</sub>O<sub>3</sub> substrate by hydride vapour phase epitaxy (HVPE), and eMS is conducted at the 14.4 keV <sup>57</sup>Fe Mössbauer state following the <sup>57</sup>Mn  $\beta^-$  decay. By performing eMS at room temperature and at different angles between the sample and the ion beam, it is found that the majority of the Fe ions are in the 2+ valence state, located on near-substitutional In sites and/or associated with N vacancy type defects (Fe<sub>C</sub>). A small fraction of Fe (Fe<sub>D</sub>) are attributed to Fe in implantation induced lattice defects.

No evidence of magnetically split sextets are apparent in the spectra, similarly as reported for GaN and AlN<sup>[3]</sup>, implying the absence of high-spin Fe<sup>3+</sup> in InN. Instead, a spectral line (Fe<sub>S</sub>) with an isomer shift of 0.08(2) mm/s is observed, which is typical for Fe<sup>3+</sup> (S=1/2) or Fe<sup>4+</sup> (S=1) or Fe<sup>2+</sup> (S=0). We argue that this line is due to the 4+ state of Fe in InN.

Temperature dependence of the relative areas show that a decrease in Fe<sub>C</sub> component is connected with an increase in Fe<sub>S</sub>, indicative of the probe atom occupying purely substitutional sites, resulting from the mobility of vacancies.

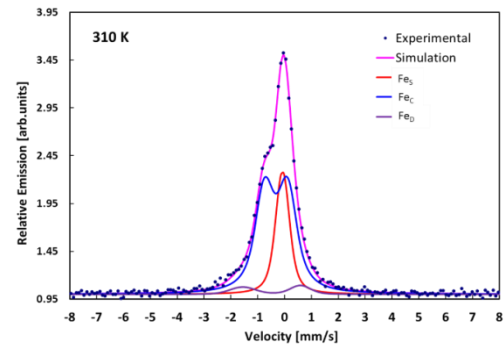


Figure 1: Room temperature <sup>57</sup>Fe emission Mössbauer spectrum obtained at 310 K for InN after implantation of <sup>57</sup>Mn\* at  $\theta_r = 60^\circ$ .

## References

- [1] Xie, Q.Y. et al.: *AIP Advances*, **2** (2012) 012185.
- [2] Chen et al.: *J. Cryst. Growth*, **269** (2004) 66.
- [3] Masenda, H. et al.: *J. Magn. Magn. Mater.*, **401** (2016) 1130.

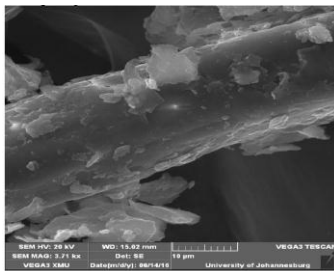
## O-7. Topic 3:Environment

### ENERGY SOURCE IN MACADAMIA NUT SHELL USED IN ARTISANAL CLAYBRICK MAKING IN DIDIDI VILLAGE (VENDA, LIMPOPO, SOUTH AFRICA)

Antoine F. Mulaba-Bafubiandi,\* and Niclette Eloko

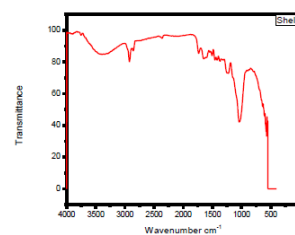
*Mineral processing and technology research center, department of metallurgy, School of mining, metallurgy and chemical engineering, faculty of engineering and the built environment, University of Johannesburg, amulaba@uj.ac.za, +27 11 5596635*

In the view to get the two ends of month meet local communities in the Vhembe district, Thulamela municipality, Limpopo exploit the available clayey soil around the Dididi dam. Artisanal clay bricks production and trade constitute one of their main activities contributing to an apparent increase to the house hold income. Externally humidified clayey soil dug in the vicinity of the dam is given a 8 cm x 22 cm brick shape from a wooden mould. After sun a 24 hours sun drying (in summer), the raw clay brick is stuck in 20 000 piles genuinely arranged to allow some openings at the bottom as tuyeres where a mixture of firewood and crushed macadamia nut shells are pushed in as source of calorific energy. While rural communities have being using firewood in cooking meals and heating at the evening family gatherings around fire spots, clay brickmaking trade skilled individuals add the use of macadamia nut shells to the artisanal making of the clay bricks. It was the aim of this paper to extricate the heat ability of these macadamia nut shells as informed by analytical techniques including Mossbauer spectroscopy. Proximate analysis of macadamia nut shells shows a fixed carbon of 9dry wt.% 70.5 wrt to coal (55.8%) with a ash content of 0.8% wt.% while coal would have 10.3wt%. [1].The fibrous morphology of the macadamia nut shell components, Figure 1, facilitates the transfer of heat upon ignition.

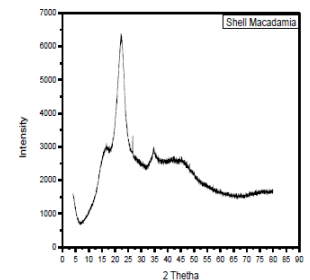


**Figure 1.** SEM micrograph of the macadamia nut shell showing the fibrous shape of the components

This allows a good heat transfer. The organic content of the macadamia nut shell is confirmed by the intense C-H bands in their infrared spectroscopy spectra around 2918.63cm<sup>-1</sup> and 2850.50cm<sup>-1</sup>. (Figure 2) as confirmed by the EDS of the fibre with C=67%; O=32.3% and K= 0.1% and the XRF data.



**Figure 2.** FTIR spectrum of the fibre showing a C-H band at 2918Cm<sup>-1</sup>.



**Figure3.** XRD pattern of crystallite.

While XRD of the powdered nut shell shows the peak of crystallites formed by the agglomeration of the exfoliated fibre skin as the grinding proceeds, their noisy Mossbauer spectra reveal a noticeable absence of structural iron [2]. This makes the materials to burn easily and produce less ash as the propensity of the slagging is related to the amount of iron oxide in the ash content. [3].

[1] D.L.Klaas, Academic Publishers, 1998, ISBN 13-978-0-12-410950-6

[2] G.L Long and F. Grandjean, Vol 1Springer Science + Business media LLC1993.

[3] E. Raask, Hemisphere publishing, Springer-verlag, 1985, p.280.

### THE SCINTILLATION BASED MÖSSBAUER DETECTION SYSTEM OPTIMIZATION

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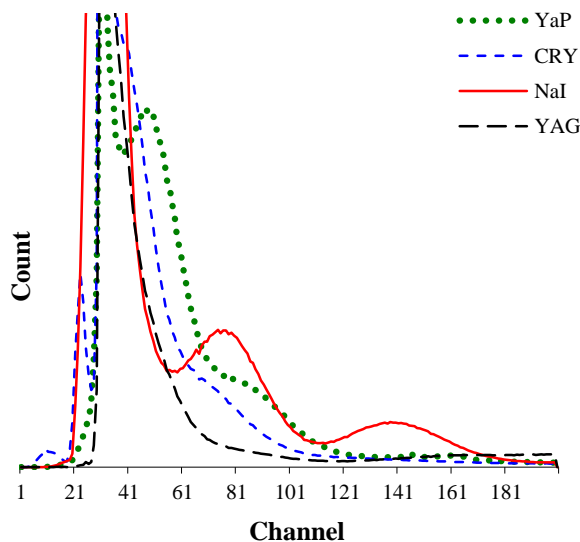
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According to the long-term experiences in the field of Mössbauer spectroscopy instrumentation development the new version of the Mössbauer spectrometer was designed.

Especially the quality of the detection system is the crucial parameter for the measurement precision (Mössbauer effect).

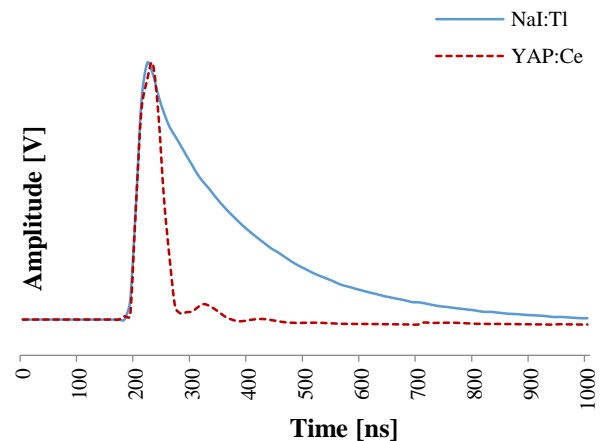
The new design of detection system, with high degree of electronics integration, was successfully developed and implemented to the MS96 – The third Generation Mössbauer spectrometer.

The first step of the development was to compare different scintillation materials (YAP:Ce, NaI:Tl, YAG:Ce and CRY-018) and determine the suitability for the Mössbauer spectroscopy. For this purpose, the examination of the 14.4 keV photo-peak position and count rate comparison was carried out. All of these parameters will be presented in details.



**Fig. 1:** The Multi-channel analysis of the YAP:Ce , CRY-018, NaI:Tl and YAG:Ce scintillation materials.

As the result of this examination, the YAP:Ce (Yttrium aluminum perovskite activated by cerium) was chosen for the further usage.



**Fig. 2:** The comparison of the 14.4keV impulse for the NaI:Tl and YAP:Ce scintillation materials.

#### Acknowledgement:

The authors acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. LM2015073.

#### References

- [1] *Precise compact system for ionizing radiation detection and signal processing with advanced components integration and electronic control*, Jakub Navařík, Petr Novák, Jiří Pechoušek, Libor Machala, Dalibor Jančík and Miroslav Mašláň, *Journal of Electrical Engineering*, Vol. 66, No. 4, 2015, 220-225.
- [2] *Setup of Mossbauer Spectrometers at RCPTM*; Pechousek J., Jancik D., Frydrych J., Navarik J., Novak P.; in *Mössbauer Spectroscopy in Materials Science*, AIP Conference Proceedings, 2012, Vol. 1489, pages 186-193.
- [3] *Patent CZ 25467 U1; System for detection of ionizing radiation*; Palacky University Olomouc: Navarik J., Novak P., Pechousek J., Jancik D., Machala L., Mashlan M.; Application number CZ20130028339U 20130820.

## O-9. Topic Methodology and Instrumentation

### PERTURBED ANGULAR CORRELATION - A COMPLEMENTARY TECHNIQUE TO MÖSSBAUER EFFECT IN THE STUDY OF MATERIALS FOR INDUSTRIAL APPLICATIONS

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Radioactive atoms have been used in solid state physics and in material science for many decades. Besides their classical application as tracer for diffusion studies, nuclear techniques such as Mossbauer Effect (ME) and perturbed  $\gamma\gamma$  angular correlation spectroscopy (PAC) have used nuclear properties via hyperfine interactions to gain microscopic information on the structural and dynamical properties of defects in solids [1]. The availability of many different radioactive isotopes as a clean ion beam at facilities like ISOLDE/CERN [2] has triggered an era involving methods extremely sensitive to the structural and electronic properties of defects in solids.

This sensitivity is especially important in the field of semiconductor physics [3,4]. Progress in semiconductor technology requires a thorough understanding and control of defects responsible for the properties of semiconducting materials, both of intrinsic defects, such as vacancies, self-interstitials, or anti-sites, and of extrinsic defects, such as dopants and impurity atoms. Depending on the material and the structural size used in a device, the electrical and optical properties can be significantly altered by a defect which is present at a concentration as low as  $10^{12} \text{ cm}^{-3}$ .

In this contribution, a short introduction of PAC spectroscopy will be given and the advantages and disadvantages of PAC compared to the much better-known Mössbauer effect will be described.

One focus will be to identify applications where PAC and ME can be complementary. One special feature of PAC is that its sensitivity is independent of temperature, there is no Debye-Waller factor involved. With PAC, diffusion

processes, detected i.e. by the reorientation of an electric field gradient (EFG), are easily distinguished from static inhomogeneous EFG distributions. Last but not least, the isotopes suitable for PAC often complement the ones used by ME leading to a more complete understanding of a certain material.

This contribution will highlight a few examples to illustrate the potential of radioactive isotopes in combination with hyperfine interaction techniques like PAC and ME for solving various problems connected to defects in semiconductor physics.

The financial support by the German BMBF under contract 05K13TSA is gratefully acknowledged.

- [1] G. Schatz and A. Weidinger, *Nuclear Condensed Matter Physics* (Wiley, Chichester, 1995).
- [2] <http://isolde.web.cern.ch/>
- [3] Th. Wichert and M. Deicher, *Nuclear Physics A* **693** (2001) 327.
- [4] M. Deicher, G. Weyer, Th. Wichert, and the ISOLDE Collaboration, *Hyperfine Interactions* **151/152** (2003) 105.



### ANNEALING STUDIES IN EMISSION MÖSSBAUER SPECTROSCOPY USING SHORT LIVED ISOTOPES

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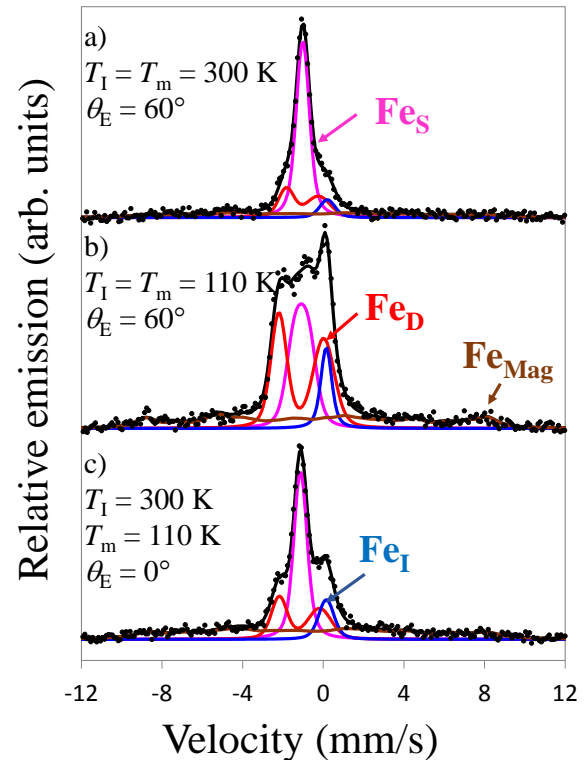
*Mössbauer collaboration at ISOLDE/CERN, CERN, EP div. CH-1211 Genève 23, Switzerland*

The Mössbauer collaboration at ISOLDE/CERN [1] applies implantation of short lived parent isotopes ( $^{57}\text{Mn} \rightarrow ^{57}\text{Fe}$ ,  $T_{1/2} = 1.45$  min. and  $^{119}\text{In} \rightarrow ^{119}\text{Sn}$ ,  $T_{1/2} = 2.4$  min.) for emission Mössbauer spectroscopy (eMS) within material sciences. Beyond the usual information from Mössbauer spectroscopy (MS), eMS allows for measurements in the extremely dilute regime ( $\sim 10^{-4}$  at. %), to make use of the chemical nature of the (implanted) parent atom and to make use of recoil to create/study interstitial defects.

In our usual setup, the implantation temperature is the same as the measurement temperature, owing to the short lifetime of the parent. However, in many cases, the spectra obtained below room temperature are dominated by Fe/Sn in defect regions and/or amorphous zones and implantation/measurements have to be conducted at elevated temperatures to allow for the annealing of these sites during the lifetime of the parent.

In some cases, the physics of interest are at low temperatures, or we are interested in measurement under sample conditions that are not easily achieved in an implantation chamber. This motivated the construction of an addition to our existing implantation facilities to allow for fast removal of samples from a heated finger for off-line measurements.

In this contribution, we describe the experimental setup and show examples where we have conducted implantations/measurements in selected oxides at temperatures above 300 K while off-line measurements are performed at 110 K. The data gives additional information on the annealing of implantation damage and better information on the properties of different spectral components.



**Figure 1:** Example  $^{57}\text{Fe}$  eMS obtained after implantation of  $^{57}\text{Mn}$  into MgO single crystal. The spectra a) and b) are obtained at the implantation temperature, while spectrum c) is obtained after implantation and “quenching”

[1] The Mössbauer collaboration at ISOLDE/CERN, <http://e-ms.web.cern.ch/>, retrieved 1/1 2016



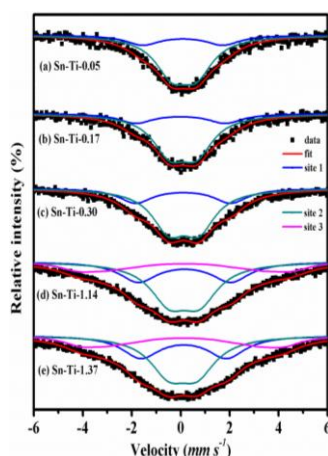
## P-1. Topic 1: Catalysis

### FERROMAGNETIC Sn-TiO<sub>2</sub> NANOCRYSTALS: <sup>119</sup>Sn MÖSSBAUER AND PHOTOCATALYTIC STUDIES

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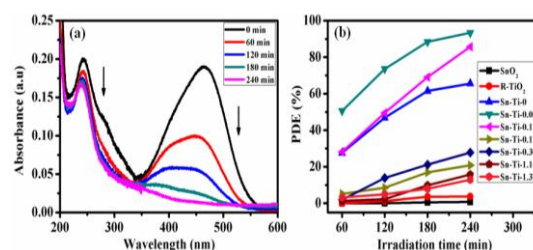
Sn-TiO<sub>2</sub> nanocrystals were synthesized by the simple hydrothermal method without any surfactant and dispersant material. We first time prepared these materials from titanium(IV) nitrate and SnCl<sub>4</sub> solutions as titanium and tin source materials, respectively. The X-ray diffraction (XRD) study obtained the formation of the anatase phase, anatase-rutile mixed phase and rutile phases for the small level to high level tin doping. Due to synergetic effect, a larger optical band gap for as-synthesized materials was found. Vibrating sample magnetometer (VSM) result demonstrates the low level tin doped TiO<sub>2</sub> samples exhibit perfect room temperature ferromagnetism (RTFM) but high level Sn doped samples show ferromagnetism with diamagnetic contribution. We obtained interesting magnetic results from <sup>119</sup>Sn Mössbauer spectroscopy study, low level doped samples shows two doublets and high level doped samples obtained one additional magnetic doublet as shown in Figure 1. Two doublets are due to SnO<sub>2</sub>-d and Sn(Ti)O<sub>2</sub>-d, respectively. It is reasonable that both isomer shift values are similar because Ti is also valence state of 4+.



**Figure 1** <sup>119</sup>Sn Mössbauer spectra for Sn-TiO<sub>2</sub> nanocrystals at room temperature.

Hence, the ionic radius of Sn<sup>4+</sup> is different from that of Ti<sup>4+</sup>, in high level doped samples, large doublet, which may be due to different configurations of Sn(Ti)O<sub>2</sub>-d with more oxygen defects or with 2Ti atoms substituted at 2Sn atom sites. The ferromagnetic property of the material was initiated with the help of oxygen vacancy or structural defects sites. The amounts of oxygen vacancy present in the samples

were identified from the photoluminescence spectroscopy and the value of oxygen vacancy decreased with increasing Sn concentration. However, the doublets have too very high quadrupole splitting (QS) values as Sn oxides. And so we may consider the magnetic component. This could be due to defect induced magnetism. Hence, the broad peaks are consists of two doublets and one magnetic components.



**Figure 2** (a) Repetitive scan spectra of photocatalytic degradation of methyl orange with Sn-Ti-0.05 and (b) PDE of SnO<sub>2</sub>, TiO<sub>2</sub> (rutile) and Sn-TiO<sub>2</sub> samples at various irradiation times under visible light in water.

Photocatalytic degradation of methyl orange and phenol derivatives (RPhOH) were studied under visible and UV light irradiation in water, respectively. Among all the samples, anatase phases of low Sn content in TiO<sub>2</sub> samples were performed good photocatalytic activity as shown in Figure 2. This study could point out a potential way to develop new and more efficient RTFM metal oxides coupled photocatalysts for the waste water treatment.

1. A. S. Ganeshraja, A. S. Claraa, K. Rajkumara, Y. J. Wang, Y. Wang, J. Wang, K. Anbalagana, Appl. Surf. Sci. 2015,353,553.
2. A. S. Ganeshraja, S. Thirumurugan, K. Rajkumar, K. Zhu, J. Wang, K. Anbalagan, RSC Adv. 2016,6, 409.

*This work was supported by National Natural Science Foundation of China (11079036, 21476232) and the CAS President's International Fellowship Initiative (PIFI) programme (No. 2016PT023).*



## P-2. Topic 10: Nanotechnology

### **Ru DOPING OF HEMATITE NANORODS TRACKED WITH XRD AND MÖSSBAUER SPECTROSCOPY**

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Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a photo anode material with an electronic band gap suitable for efficient absorption of visible light in a photo electrochemical cell (PEC), and, hence, for hydrogen production by solar water splitting. Further, its earth abundance and chemical stability has driven the search for low cost synthesis and refinement of hematite for applications in an efficient, cost-effective solar energy economy.

In the present contribution, we present results of our studies on the production of hematite nanorods (NRs) doped with different concentrations of ruthenium. The NRs were deposited on fluorine doped tin oxide (FTO) glass substrates and the Ru concentration was controlled by varying the Ru concentration in the Ru<sub>x</sub>Cl<sub>3</sub>.xH<sub>2</sub>O precursors.

Scanning Electron Microscopy confirmed the formation of the nanorods. X-ray diffraction and Mössbauer spectroscopy (MS) data provided clear evidence of the incorporation of ruthenium in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorod structure. The band gap of the Ru-doped hematite NRs estimated from the UV-Vis curves, were found to be directly related to the Ru concentration. For concentrations in the range 0.006g - 0.030g the band gaps are in the range well suited to drive the water splitting process in a PEC without application of an external bias.

### P-3. Topic 4: Magnetic materials and Superconductive Materials

#### CHARGE STATES AND LATTICE SITES OF DILUTE IMPLANTED Sn IN ZnO

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ZnO is naturally found to be  $n$ -type and producing  $p$ -type material remains challenging. The need for  $p$ -type doping to be successfully realised has hampered its potential as a technologically viable material in many applications, including optoelectronics and spintronics. Sn has been proposed as an efficient  $n$ -type dopant in ZnO, due to the observed decrease in the resistivity with increasing Sn concentration [1-3]. This has been attributed to the presence of  $\text{Sn}^{4+}$  substituting the  $\text{Zn}^{2+}$ , which results in two extra free electrons [4]. The common charge states of Sn ( $[\text{Kr}]4d^{10}5s^25p^2$ ) are 2+ and 4+. While charge neutrality considerations favour 2+ to be the natural charge state of Sn in ZnO, there are several reports suggesting the 4+ state to be the natural charge state. In order to investigate the lattice sites, charge states and the effect of the ion implantation process of dilute Sn atoms in ZnO, we have performed  $^{119}\text{Sn}$  emission Mössbauer spectroscopy on a ZnO single crystal samples following ion implantation of radioactive  $^{119}\text{In}$  ( $T_{1/2} = 2.4$  min.) at temperatures between 96 K and 762 K and complemented this with perturbed angular correlation measurements on  $^{111\text{m}}\text{Cd}$  implanted ZnO. Our results show that while the 2+ state is the natural charge state for Sn in defect free ZnO the 4+ charge state is stabilized by acceptor defects created during the implantation process. We demonstrated that the implantation of ZnO crystals with Sn creates acceptor-type of defects ( $\text{V}_{\text{Zn}}$ ) which stabilize  $\text{Sn}^{4+}$  over  $\text{Sn}^{2+}$ . The acceptor defect anneals above 700 K, restoring the natural  $\text{Sn}^{2+}$  state in defect free ZnO. The increased conductivity in Sn doped ZnO, is therefore probably not only related to Sn in the 4+ state as suggested in the literature.

These results open new possibilities to stabilize or tune  $p$ -type conductivity in ZnO at temperatures of potential interest for applications.

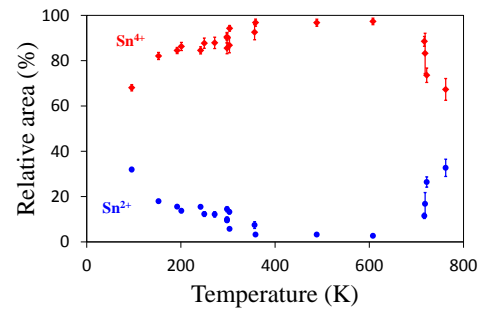


Fig.1. Relative spectral areas of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  in ZnO as a function of temperature obtained from the analysis of the  $^{119}\text{Sn}$  Mössbauer spectra.

[1] G. B. Palmer et al. Chem. Mater. 9 (1997) 3121.

[2] A. Bougrine et.al Mater. Chem. Phys. 91 (2005) 247.

[3] Saliha Ilcan et al. Applied Surface Science 256 (2010) 7204–7210.

[4] M. Ajilia et al. Super. Micro 53 (2013) 213.

**A PORTABLE, DIAGNOSTICS SYSTEM FOR THE ZIKA VIRUS**

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This work presents an effective and portable diagnostics solution for the Zika Virus, to attend patients at the point of care (POC). The device uses a variation of the ELISA standard biochemical process. Through the coupling of the biochemical module with a software and hardware component, it is possible to reach effective diagnostics within 10 minutes [1].

Super paramagnetic nano iron oxide particles have been used to produce an effective diagnostics modifying ELISA test. Super paramagnetic nano particles are being utilized to track down the viruses using a small robotic arm. These particles vary from 100nm to 1µm because of the size of the viruses. Mossbauer Spectroscopy has been used to certify the quality of super paramagnetic iron oxide nano particles and to assure conformity in the functionalization, interaction with the architecture of the microchip and the environment created (varying solutions and distinct agents such as enzymes and antibodies). The aim of the present work was to perform a portable diagnostics solution for the Zika virus at POC.

[1] Wang, S., Tasoglu, S., Chen, P. Z., Chen, M., Akbas, R., Wach, S., . . . Demirci, U. (2014). Micro-a- fluidics ELISA for Rapid CD4 Cell Count at the Point-of- Care. Sci. Rep. Scientific Reports, 4.

ANNEALING STUDIES OF HOLMIUM SUBSTITUTED BISMUTH FERRITE

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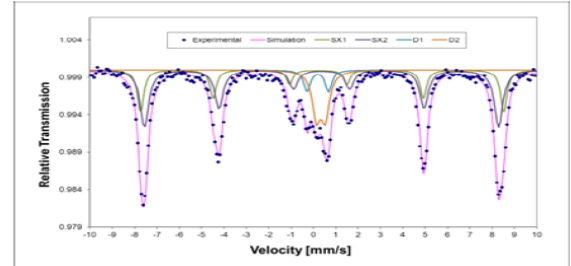
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Perovskite materials have generated much attention in recent years, particularly as they exhibit a wide variety of fundamental properties, from magnetism to ferroelectricity [1]. Such materials seem to be promising candidates for magnetoelectronics and spintronics with potential technological applications as electromagnets, sensors and optical storage devices. Subsequent to the discovery of large electric and magnetic polarization effects in thin bismuth ferrite (BiFeO<sub>3</sub>) films [2], much focus has been devoted to BiFeO<sub>3</sub> because of its long range magnetic ordering. The unique magnetic and electric properties of BiFeO<sub>3</sub> can be modified by substitutional doping at the Bi and/or Fe sites with lanthanide elements like Ho.

In this presentation, we report on X-ray Diffraction (XRD) and <sup>57</sup>Fe Mössbauer spectroscopy investigations of Bi<sub>1-x</sub>Ho<sub>x</sub>FeO<sub>3</sub> ( $x = 0.05, 0.10$  and  $0.15$ ) which were synthesised by the solid state reaction method [3] described in [4]. The XRD patterns revealed a rhombohedrally distorted perovskite structure of  $R3m$  space group with bismuth ferrite impurity phases as described in [4]. Mössbauer measurements were performed at room temperature on the as-synthesized samples and after annealing in Argon atmosphere up to 600 K. The spectra exhibits broadened features due to hyperfine field distributions related to the local variation of the neighbourhood of Fe and the magnetic hyperfine splitting patterns are indicative of magnetic ordering mostly probably screwed or slightly antiferromagnetic ordering as indicated by the Mössbauer spectrum for the as-synthesized Bi<sub>0.95</sub>Ho<sub>0.5</sub>FeO<sub>3</sub> sample in Figure 1. The spectra have been analysed in a simultaneous fit with four spectral components: dominated by two sextets (SX1 and SX2), and two superimposed quadrupole-split doublets (D1 and D2). The hyperfine parameters of sextet SX1 were determined as  $B_{hf} = 50.3$  T,  $\Delta E_Q = 0.17$  mm.s<sup>-1</sup> and  $\delta = 0.31$  mm.s<sup>-1</sup> which is assigned to rhombohedral BiFeO<sub>3</sub> [5] and the spectral component, SX2 component is characteristic of an undoped BFO spectrum with hyperfine parameters of  $B_{hf} = 49.1$  T,  $\Delta E_Q = -0.001$  mm.s<sup>-1</sup> and  $\delta = 0.37$  mm.s<sup>-1</sup>. Both components are typical of magnetically ordered Fe<sup>3+</sup> due to the presence of hyperfine fields  $B_{hf}$  acting on the nuclear spin.



**Figure 1: Mössbauer spectrum for the as-synthesized Bi<sub>0.95</sub>Ho<sub>0.5</sub>FeO<sub>3</sub> sample.**

The isomer shifts of D1 and D2 were deduced as 0.20 and 0.33 mm.s<sup>-1</sup>, respectively with quadrupole splitting values of 0.97 and 0.40 mm.s<sup>-1</sup>. The D1 component is assigned to tetrahedrally coordinated high spin Fe<sup>3+</sup> whilst D2 is typical for high spin Fe<sup>3+</sup> octahedrally co-ordinated by oxygen which have been identify by [6] in their temperature dependent studies of Bi<sub>2</sub>(Fe<sub>x</sub>Al<sub>1-x</sub>)<sub>4</sub>O<sub>9</sub> ( $0.1 \leq x \leq 1$ ) [6]. Our XRD results confirm the existence of the impurity Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> phase typical of a disordered and amorphized system. The annealing behaviour and the variation of the hyperfine parameters of spectral components with increasing Ho concentration will be presented. The results indicate that the magnetic properties in chemically substituted (Ho) BiFeO<sub>3</sub> are related to the structural distortions of the lattice.

#### References

- [1] Filippetti A. and Hill N.A., *Phys. Rev.*, vol. B 65, p. 195120, (2002).
- [2] Pokatilov V.S. et al., *Bulletin of Russian. Academy of Scie.: Phys.*, vol. 74, pp. 347-351, (2010).
- [3] Pradhan S.K. et al., *Journal of Physics and Chemistry of Solids*, vol. 71, pp. 1557-1564, (2010).
- [4] Ncube M. et al., *Hyp. Int.*, Vol 219, pp 83-88 (2013).
- [5] Blaauw, C. and Van der Woude, F.: *J. Phys. C. Solid State Phys.* 6, 1422-1431 (1973).
- [6] Weber S.U. et al., *Int. J. Mat. Res.* 103 4 (2012) 430-437

**COULD MÖSSBAUER SPECTROSCOPY BE AN ALTERNATIVE METHOD OF THE PRELIMINARY CLASSIFICATION OF THE ORDINARY CHONDRITES?**

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The first suggestion of the application of Mössbauer spectroscopy to the classification of stony meteorites was done by W. Herr and B. Skerra [1] in 1969. It was strictly connected with the classical method of classification of the meteorites and was based on the precise determination (from the Mössbauer spectra) of the concentration of the different mineralogical phases in various types of the meteorites.

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

Our suggestion of the application of Mössbauer spectroscopy to the classification of the ordinary chondrites is based on the simplified method of the determination of the percentage of the different mineralogical phases present in ordinary chondrites and the construction of the parameter sensitive to different types of the meteorites.

The Mössbauer spectrum of the non-weathered ordinary chondrites is composed from 4 subspectra: two doublets connected with olivines and pyroxenes and two sextets connected with metallic phases and troilite. When the process of weathering begins in the meteorite, the fifth subspectrum of the trivalent iron appears. We will take into consideration only those meteorites in which this trivalent doublet is smaller than 5%.

Our preliminary analyses on the possibility of the application of the Mössbauer spectroscopy to the simplified classification of the ordinary chondrites were presented in papers published in 2014 [5,6]. Now we come to the conclusion that the best parameter to assess different types of the ordinary chondrites is the value  $(ol+pyr)/met$ , where  $ol$  – the area of the olivine subspectrum,  $pyr$  – the area of the pyroxene subspectrum and  $met$  – the area connected with the metallic subspectrum.

Let us name this value  $olpmet$ . The average value of the  $olpmet$  parameter for LL type of ordinary chondrite was 84.5 (2 meteorites), for L6/L5 type was 11 (11 meteorites)

and for H6/H5 type was 4.9 (8 meteorites). It seems that the value of the  $olpmet$  parameter differentiates very well LL, L, and H types of meteorites.

In our laboratory, studies on the application of Mössbauer spectroscopy to the classical method of the classification of the meteorites were initiated. The calibration curve for the determination of the amount of the total iron in the meteoritic sample from its Mössbauer spectrum was obtained. In the future we plan to use the Mössbauer spectroscopy to the classical classification of meteorites as was suggested by W. Herr and B. Skerra [1].

**References:**

1. Herr and Skerra. In: Meteorite Research Vol.12 of the series Astrophysics and Space Science Library, 1969
2. Paliwal et al. Meteorit. Planet. Sci. 35 (2000) 639
3. Verma et al. Hyperfine Interact. 142 (2002) 643-652
4. Verma et al. Meteorit. Planet. Sci. 6 (2003) 963-967
5. J.Gałazka-Fiedman et al. Hyperfine Interact.226 (2014) 593-600
6. K. Szlachta et al. Acta Soc. Meteorit. Polonorum, 5 (2014)

## Ni-Sn-Si/C BASED COMPOSITE AS NEGATIVE ELECTRODE FOR Li-ION BATTERIES <sup>119</sup>Sn MÖSSBAUER *operando* STUDY

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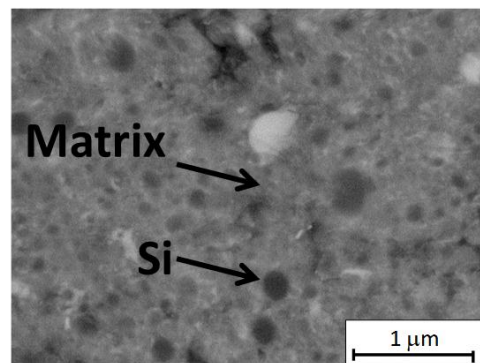
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New electrode materials and battery design are required to improve the electrochemical performances of Li-ion batteries. Some metals like Al, Si or Sn can form alloys with Li by reversible electrochemical reactions and can be used as negative electrodes of high specific capacities (600 - 4000 Ah/kg) for high density Li-ion batteries. However, alloying reactions cause large volume variations resulting in the loss of electronic percolation and SEI instability at the origin of the usually observed poor cycle life of such materials.

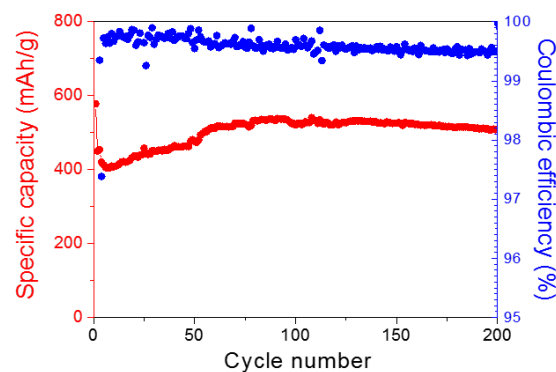
Different approaches were considered to overcome these problems based, for example, on the nanostructuration of the active material, the dispersion of the particles and the use of intermetallics or composites [1]. Recently, we have proposed a family of new composite materials formed by Si nanoparticles dispersed within a tin based intermetallic matrix Ni<sub>3</sub>Sn<sub>4</sub> that exhibits high specific capacity and coulombic efficiency [2]. In order to improve the performances and reduce the cost of such composites, we propose now a new material with a lower tin content with the overall composition Ni<sub>0.15</sub>Sn<sub>0.14</sub>Si<sub>0.26</sub>Al<sub>0.04</sub>C<sub>0.41</sub>.

The synthesis method, the material characterization and the electrochemical performances will be presented. We will show that the composite is formed by Si nanoparticles embedded in a matrix composed of Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn<sub>4</sub> particles (Figure 1). The specific capacity after 200 cycles is of about 500 Ah/kg (Figure 2), which is surprisingly close to that obtained by the Ni<sub>3</sub>Sn<sub>4</sub> based composite. To understand this results, X-ray diffraction and <sup>119</sup>Sn Mössbauer spectroscopy were combined to explore *in situ* (*operando* mode) the reaction mechanisms that reveal the electrochemical activities of the different components of the composite. The Ni<sub>3</sub>Sn<sub>2</sub> phase does not participate in the reversible capacity but contributes to the nanostructuring of the system and improves its electrochemical properties (coulombic efficiency and lifetime).

In this communication, we will see how Mössbauer Spectroscopy has become a key technique to characterize new composite materials and their electrochemical mechanisms in the field of Li-ion batteries. Through this example, we will illustrate the importance of this technique for battery domain.



**Figure 1** SEM image of Si/Ni<sub>3</sub>Sn<sub>2</sub>-Ni<sub>3</sub>Sn<sub>4</sub>/Al/C composite as negative electrode for Li-ion batteries.



**Figure 2** Specific capacity and coulombic efficiency vs. cycle number for the Si/Ni<sub>3</sub>Sn<sub>2</sub>-Ni<sub>3</sub>Sn<sub>4</sub>/Al/C composite at C/10 galvanostatic regime

### References

- [1] D. Larcher, S. Beattie, M. Morcrette, K. Edström, J.C. Jumas, J.M. Tarascon, *J. Mater. Chem.* **17**, 3759 (2007)
- [2] Z. Edfouf, F. Cuevas, M. Latroche, C. Georges, C. Jordy, T. Hézèke, G. Caillon, J. C. Jumas, M.T. Sougrati, *J. Power Sources*, **196**, 4762 (2011)

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**THE MAGNETIC TRANSITION IN  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> NANOPARTICLES: MÖSSBAUER SPECTROSCOPY**

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Magnetic nanoparticles (NPs) have found broad applications in medicine, in particular for cell targeting and transport, and as contrast agents in MRI. The preparation of our samples of  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> NPs consisted of the preparation of mesoporous amorphous SiO<sub>2</sub> template, impregnation of this template by aqueous solution of iron(III) nitrate nonahydrate, annealing at temperatures of about 1050 °C [1] which lead to the formation of  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> in the pores. The silica template was then leached off by NaOH leaving thus the isolated particles that were further coated with silica layer in order to reduce their toxicity and tendency to aggregation. This preparation method of impregnation the matrix does not produce  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>, improving thus the phase purity of NPs. The distribution of the particle sizes was determined from the TEM pictures (see Figure 1) giving the average size  $\sim$  20 nm. The particles were characterized by the XRD and DC magnetic measurements. The system of NPs consisted mainly of the  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> with admixtures of <1% of the  $\gamma$  phase. The temperature dependence of the magnetization indicated a two-step magnetic transition of the  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> NPs spread between  $\sim$  100 K and  $\sim$  150 K [2] and the hysteresis loops displayed coercivities of  $\sim$  2 T at room temperature.

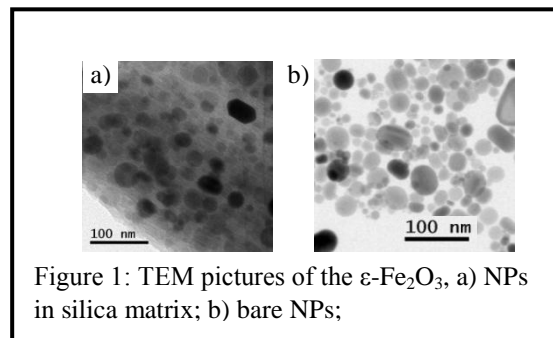


Figure 1: TEM pictures of the  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>, a) NPs in silica matrix; b) bare NPs;

The transmission Mössbauer spectra were acquired in a spectrometer with the <sup>57</sup>Co(Rh) source moving with constant acceleration and calibrated by  $\alpha$ -Fe at room temperature. The in-field spectra were taken in the external magnetic fields up to 6 T covering the temperature range of both above and below the indicated transition at  $\sim$ 100 K. From the spectra the hyperfine parameters for one tetrahedral and three octahedral sites of  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> structure were identified. Their dependence on temperature and external magnetic field points to the fact that the magnetic transition is related to the change of the magnitude and/or orientation of the local magnetic moments in the sublattices.

The authors thank for the support under the grants GACR 16-04340S.

[1] P. Brázda, J. Kohout, P. Bezdička and T. Kmječ: *Crystal Growth & Design*, 2014, 14, 1039–1046A

[2] J. Kohout, P. Brázda, K. Závěta, D. Kubániová, T. Kmječ, L. Kubičková, M. Klementová, E. Šantavá and A. Lančok: *Journal of Applied Physics* 117, 17D505

## P-9. Topic 10: Nanotechnology

### DEGRADATION OF THE CYANOTOXIN MICROCYSTIN-LR USING NANOPARTICULATE $\text{Fe}_2\text{O}_3$ PHOTOCATALYSTS UNDER VISIBLE LIGHT ILLUMINATION

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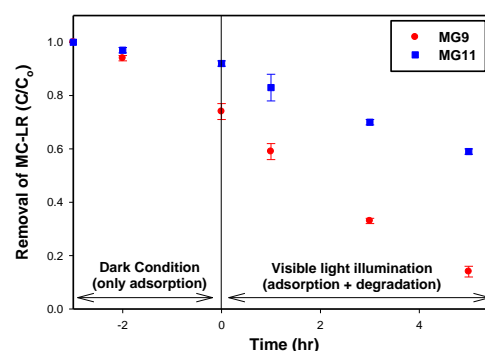
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Iron(III) oxides are known as ubiquitous, chemically stable, cheap and nontoxic compounds. Their low bandgap energy (approx. 2.2 eV) enables them to collect up to 40 % of the solar spectrum energy and are thus used, among other applications, as photocatalysts in water splitting and water treatment. There are many studies where  $\alpha\text{-Fe}_2\text{O}_3$  thin films were successfully applied as semiconducting electrodes for photocatalytic water splitting and hydrogen production. Both  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$  can be applied as photocatalysts for degradation of organic and inorganic pollutants, which are present in water as well as in air. Moreover, ferrimagnetic behavior of  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  gives a possibility to recycle the catalyst by applying external magnetic field, e.g. using a permanent magnet. On the other hand, the photocatalytic performance of iron oxides can be limited by low diffusion lengths of holes, poor conductivity, and high recombination rate of electrons and holes. These difficulties can be significantly overcome by forming nanostructured iron oxides.

Microcystins (MCs) are the most common toxins produced by harmful cyanobacteria, which can be present in natural water. Microcystin-LR (MC-LR) is mostly found in various water bodies among MCs. Up to now, several approaches of photocatalytic degradation of MC-LR have been investigated mostly based on the application of  $\text{TiO}_2$ -based nanostructures, such as highly ordered  $\text{TiO}_2$  nanotubes,  $\text{Ag}/\text{AgCl}/\text{TiO}_2$  nanotube arrays, nanostructured nitrogen doped  $\text{TiO}_2$ , C-N co-doped  $\text{TiO}_2$  films, Bi-doped  $\text{TiO}_2$ , N-F co-doped  $\text{TiO}_2$  films, and sulfur doped  $\text{TiO}_2$  films. Generally, a shift of the bandgap toward visible light was achieved by various kinds of doping of  $\text{TiO}_2$ . Besides  $\text{TiO}_2$  based nanomaterials,  $\text{AgCl}/\text{iron oxide}$  composites were tested for MC-LR photocatalytic degradation.

In this study, iron(III) oxide nanopowders with particle sizes of 5-20 nm were successfully synthesized for the removal of microcystin-LR (MC-LR) by visible light-

induced photocatalysis. Two iron(III) oxide samples (MG-9 calcined at 200 °C for 5 h and MG-11 calcined at 180 °C for 16 h) were prepared by thermal decomposition of ferrous oxalate dihydrate in air. The samples were characterized by X-ray powder diffraction,  $^{57}\text{Fe}$  Mössbauer spectroscopy, transmission electron microscopy, and BET specific surface area analysis. The samples show similar phase composition (a mixture of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$ ), particle size distribution (5-20 nm), particle morphology, and degree of agglomeration, but differ in specific surface area (234  $\text{m}^2/\text{g}$  for MG-9 and 207  $\text{m}^2/\text{g}$  for MG-11). The results confirmed higher photocatalytic activity of the sample with higher specific surface area. The highest photocatalytic activity for the degradation of MC-LR was observed at the solution pH of 3.0 and the catalyst loading of 0.5  $\text{g L}^{-1}$ . The visible light-induced photocatalytic activity of samples was achieved without any further processing (doping, making a composite) of the  $\text{Fe}_2\text{O}_3$ . Ferrimagnetic behavior of  $\gamma\text{-Fe}_2\text{O}_3$  gives a possibility for an easy separation of the catalysts after their use.



**Figure 1.**

The removal of MC-LR for MG-9 and MG-11 samples at pH 5.8 with a 500  $\mu\text{g L}^{-1}$  of MC-LR and the catalyst loading of 0.5  $\text{g L}^{-1}$ .



# A STUDY OF THERMODYNAMIC PROPERTIES OF DILUTE Fe-Au ALLOYS BY THE $^{57}\text{Fe}$ MÖSSBAUER SPECTROSCOPY

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The room temperature Mössbauer spectra of  $^{57}\text{Fe}$  were measured for  $\text{Fe}_{1-x}\text{Au}_x$  solid solutions with  $x$  in the range  $0.010 \leq x \leq 0.048$ . The spectra are presented in Fig. 1. They were analyzed in terms of parameters of their components related to unlike surroundings of the iron probes, determined by different numbers of gold atoms existing in the neighbourhood of iron atoms [1]. Basing on intensities of the spectrum components we determined binding energy  $E_b$  between two gold atoms. The latter was done for properly annealed samples using the extended Hryniewicz-Królas idea [2, 3]. It was found that the energy is positive which speaks in favour of the suggestion that gold atoms interact repulsively in  $\alpha$ -iron (bcc) matrix.

The extrapolated value of  $E_b$  for  $x = 0$  was used for computation of the enthalpy of solution  $H_{\text{Fe-Au}}$  of Au in Fe [4];

$$H_{\text{Fe-Au}} = -z \cdot E_b(0)/2$$

where  $z$  is the coordination number of the crystalline lattice and for  $\alpha$ -Fe it is 8. The obtained value of  $H_{\text{Fe-Au}}$  was compared with corresponding one derived from calorimetric studies [5] and that resulting from the cellular atomic model of alloys by Miedema [6]. All the mentioned  $H_{\text{Fe-Au}}$  data are displayed in Table I.

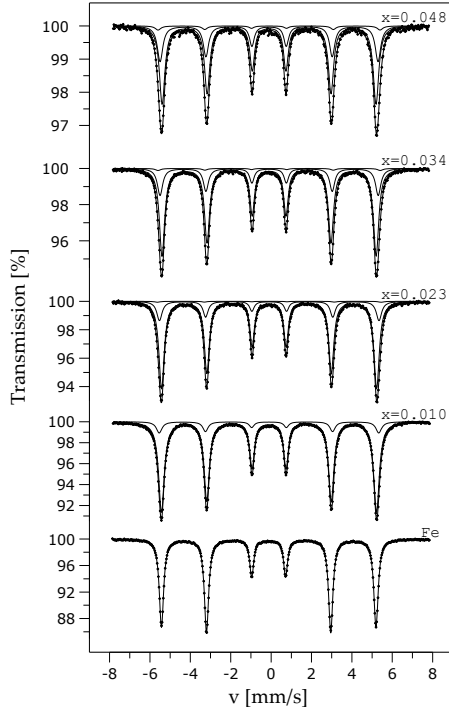


Figure 1. The room temperature  $^{57}\text{Fe}$  Mössbauer spectra for  $\text{Fe}_{1-x}\text{Au}_x$  alloys prepared in an arc furnace filled with argon and then cold-rolled to the final thickness of about 0.04 mm, annealed in vacuum at 1270 K for 2 h and finally slowly cooled to room temperature during 6 h.

Table I: The enthalpy  $H_{\text{Fe-Au}}$  [eV/atom] of solution of gold in iron.

Calorimetric data [5]	Miedema's model [6]	This work
0.498	0.377	-0.186(40)

Finally the value of enthalpy  $H_{\text{Fe-Au}}$  was used to predict the mixing enthalpies  $H_{\text{mix}}(x)$  for the Fe-Au solid solutions. It was done on the basis of the following relationship [7]

$$H_{\text{mix}}(x) \approx H_{\text{Au-Fe}} x^2(1-x) + H_{\text{Fe-Au}} x(1-x)^2,$$

where  $H_{\text{Au-Fe}}$  is the enthalpy of solution of Fe in Au. We calculated the  $H_{\text{mix}}(x)$  dependence using also the  $H_{\text{Au-Fe}}$  value obtained by us in the past [8] as well as that computed with the Miedema's model [6]. The results are presented in Fig. 2 together with corresponding findings obtained on the basis of calorimetric measurements [5, 9].

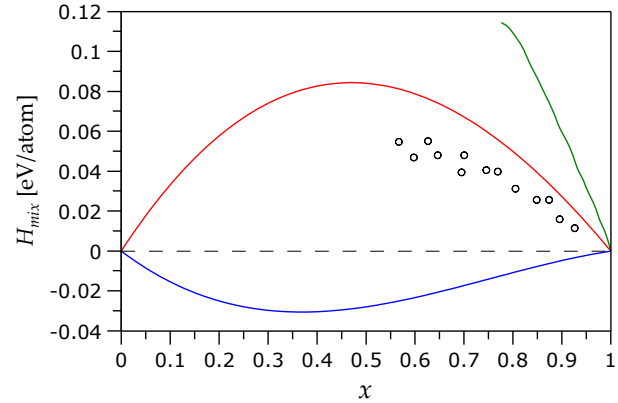


Figure 2. Mixing enthalpy  $H_{\text{mix}}$  for  $\text{Fe}_{1-x}\text{Au}_x$  alloys obtained in this work (blue line), resulting from Miedema's model (red line) and derived from calorimetric measurements: Hultgren – green line, Topor – circles.

- [1] A. Błachowski, K. Ruebenbauer, J. Przewoźnik, J. Żukrowski, J. Alloy Compd. 458, 96 (2008).
- [2] A.Z. Hryniewicz et al., Phys. Rev. B 28, 1864 (1983).
- [3] J. Chojcan, J. Alloys and Comp. 264, 50 (1998).
- [4] K. Królas, Phys. Lett. A 85, 107 (1981).
- [5] R. Hultgren et al., Selected Values of Thermodynamic Properties of Binary Alloys, American Society for Metals, Metals Park (1973).
- [6] A.R. Miedema, Physica B 182, 1 (1992).
- [7] M. H. F. Sluiter, Y. Kawazoe, Europhys. Lett. 57, (2002) 526.
- [8] R. Idczak, R. Konieczny, J. Chojcan, Nukleonika 58(1), 93 (2013).
- [9] L. Topor, O. J. Kleppa, Metallurgical Transactions B, 15B, 573 (1984).

## P-11. Topic 11: Metals and Alloys

### A SPECTROSCOPIC STUDY OF IRON BASED CEMENTED CARBIDES

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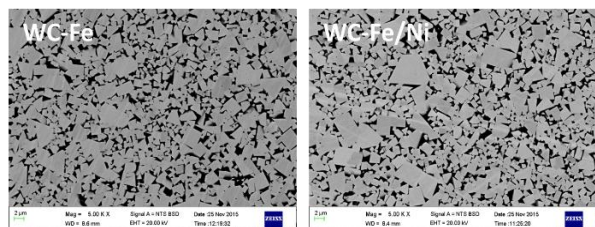
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In the cemented carbide industry, there are increasing demands to produce tungsten carbide (WC) tools with higher cutting speeds, in addition to improved wear and corrosion resistance. Currently there are concentrated research efforts in the cemented carbide industry to find an alternative binder to cobalt (Co) in WC-Co alloys, due to its toxicity, availability and strong price fluctuations. Iron (Fe) and nickel (Ni) binder alloys are envisaged as suitable replacements for Co, and are currently only used in very limited applications, which still warrants further research <sup>[1, 2]</sup>.

Materials were prepared by ball milling WC powder with 10 wt.% Fe and Fe-Ni, respectively. The milled powders were pressed into compacts and vacuum sintered at three different temperatures (1340, 1430 and 1510°C). The structural properties of the materials were characterised using Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), density, hardness, magnetic saturation and coercivity measurements. X-ray Diffraction (XRD) was used to determine the phases present in the materials.

Visual inspection of SEM micrographs show a more homogeneous binder distribution for the samples sintered at the highest temperature, 1510°C. There is however, a slight coarsening of the WC grains, especially in the WC-Fe/Ni material as shown in Figure 1. This is confirmed by the decrease in coercivity and hardness



values.

**Figure 1:** Microstructures of the WC-Fe and WC-Fe/Ni cemented carbides at 5000x.

The materials sintered at the different temperatures were within the stoichiometric range for Fe based cemented

carbides as evident in X-ray diffraction and magnetic saturation data. X-ray diffraction results show WC and the metal binder phase present in the materials. The WC-10Fe grade has the highest hardness ranging from 1282 to 1320 Hv<sub>30</sub>, across the sintering temperatures.

Mössbauer spectroscopic investigations were carried out to determine the Fe charge states/complexes and hyperfine interaction parameters with the aim of understanding the role of different phases, structural changes and magnetic effects of the binder alloy. This may be useful in elucidating information on the fabrication process and/or material design. Transmission Mössbauer Spectroscopy (TMS) spectra for all the as-milled powder samples exhibit a ferromagnetic feature identified as  $\alpha$ -Fe with hyperfine interaction parameters of  $\delta = 0.001$  mm/s,  $\Delta E_Q = -0.002$  mm/s and  $B_{hf} = 33$  T with no evidence of iron oxide phases. Conversion electron Mössbauer (CEM) spectra for the sintered WC-Fe hard metals show the presence of the  $\alpha$ -Fe phase, whilst the WC-Fe/Ni material was characterised by a single line with an isomer shift of 0.13 mm/s corresponding to the austenite Fe-Ni phase and a broad magnetic component structure with a very low hyperfine field ( $< 20$  T). The results obtained from SEM, EDS, XRD, Mössbauer Spectroscopy and magnetic measurements on the samples sintered at different temperatures will be compared and collaborated with literature.

#### References:

- [1] Norgren, S., Garcia, J., Blomqvist, A., & Yin, L. (2014). Trends in the PM hard metal industry. *International Journal of Refractory Metals and Hard Materials*, 31-45.
- [2] Prakash L, Article review (2013). Global R&D Trends in the PM Hardmetals Industry - Part 2. <http://www.ipmd.net/articles/002341.html>

NYIRAGONGO LAVA POZZOLANA MATERIAL TO BE USED IN CONSTRUCTION APPLICATIONS, CHARACTERISED BY X-RAY TECHNIQUES, SEM, FTIR AND MÖSSBAUER SPECTROSCOPY

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The Nyiragongo with an altitude of 3470 m, is one of the eight volcanoes which compose in the Virunga region, the Western Branch of the East African Rift System. The eruptions of the Nyiragongo volcano are of Hawaiian type characterized by effusive lava fountains and flows. The volcano has two types of eruptions; one is fissure and another intra-crater eruption. Huge amount of volcanic materials has accumulated in the area since the first volcanic eruption. It constitutes visual pollution. The paper will discuss results from a study which aimed at characterizing these volcanic materials for their possible application in construction. X-Rays techniques, SEM, FTIR and Mossbauer spectroscopy were used. The main results shows the materials of a pyroxene type as confirmed by Bowen et al., in [1] with a very high silica content, Table 1. The Nyiragongo material was found to be potassic. FTIR results were in agreement with the XRF findings while the XRD confirmed the amorphous nature of the lava. The paper will additionally elaborate on the mechanism and kinetics of the reactions during the pozzolanic reaction of the materials with calcium hydroxide and water. These results will lead to the determination of the Los-Angeles coefficient of rocks essential ingredient in the characteristics requirements of concretes.

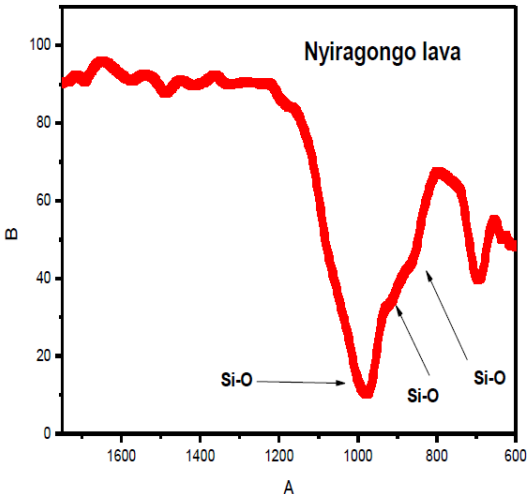


Figure 1. FTIR results of the Nyiragongo lava showing the presence of Si-O stretching bands around 1000Cm-1. 1600 1400 1200 1000 800 600 0 20 40 60 80 100 Si-O Si-O B A Nyiragongo lava Si-O

Table 1. XRF results of Nyrangongo material showing the potassic characteristic of the lava.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MnO
38.63	9.89	13.35	14.70	11.09	2.41	2.61	3.23	0.18

[1] G.L Long and F. Grandjean, Vol 1Springer Science + Business media LLC1993, p.151

## P-13. Topic 6: Mineralogy

### <sup>57</sup>FE MÖSSBAUER STUDY OF IRON PHASES IN TiO<sub>2</sub> PRODUCTION

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TiO<sub>2</sub> white pigment [1] has found important applications in catalysis, printing inks, plastics, papers, solar cells and pharmaceuticals. In the manufacture of TiO<sub>2</sub> pigments two technologies are used. Ilmenite ore is used in the production of TiO<sub>2</sub> pigment by sulphate process, whereas rutile ore is used in the production of TiO<sub>2</sub> pigment by chloride process. In the present work the possibilities of Mössbauer spectroscopy in analysis of Fe-bearing phases which appear in the manufacture of TiO<sub>2</sub> pigment by sulphate process will be shown and discussed. XRD, FE-SEM/EDS and magnetometry were also used as supporting techniques.

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

In the manufacture of TiO<sub>2</sub> by sulphate process a significant amount of copperas (FeSO<sub>4</sub>·7H<sub>2</sub>O) crystallizes as a by-product. In the technology mentioned copperas is calcined with the aim to produce H<sub>2</sub>SO<sub>4</sub> acid which is returning to the process of ilmenite ore digestion. The RT Mössbauer spectrum of calcined copperas showed the superposition of one sextet corresponding to hematite and one central quadrupole doublet of small relative intensity. However, the Mössbauer spectrum of the magnetic fraction separated from calcined copperas with permanent magnet also showed the presence of substoichiometric magnetite (Fe<sub>3-x</sub>O<sub>4</sub>). Sulphur detected by EDS analysis of calcined copperas was a result of incomplete oxidation of copperas.

Copperas produced as a by-product undergoes oxidation at ambient conditions and this can be also monitored by Mössbauer spectroscopy. Copperas can be utilized in the manufacture of yellow pigment ( $\alpha$ -FeOOH) with the aim to optimize the cost of TiO<sub>2</sub> pigment production.

[1] G. Auer, Titanium dioxide, in *Industrial inorganic pigments* (Eds.: G. Buxbalm, G. Pfaff), Wiley- VCH, Weinheim (2005), pp. 51-81

[2] D. Jancik, M. Mashlan, R. Zboril, J. Adetunji, K. Nomura, *Czechoslovak, J. Phys.* 55 (2005) 803-811.

[3] B. Saensunon, G.A. Stewart, R. Pax, *Int. J. Miner. Process.* 86 (2008) 26-32

## P-14. Topic 4: Magnetic materials and Superconductive Materials

### SPIN-STATE DETERMINATION IN RIGID IRON(II) TETRAZOLE SPIN CROSSOVER CHAINS

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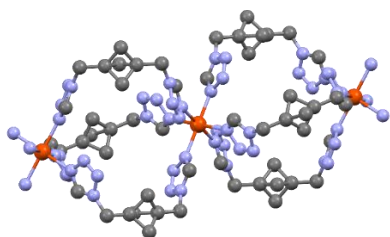
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Spin crossover (SCO)-materials are considered as promising candidates for a future technological application in switching, sensing and magneto-optic devices.

One crucial requirement for application is a complete, sharp and abrupt spin transition. Extensive ligand design studies and crystal engineering led to the conclusion, that 1-dimensional SCO chains are promising candidates for the quested type of spin transition behaviour.

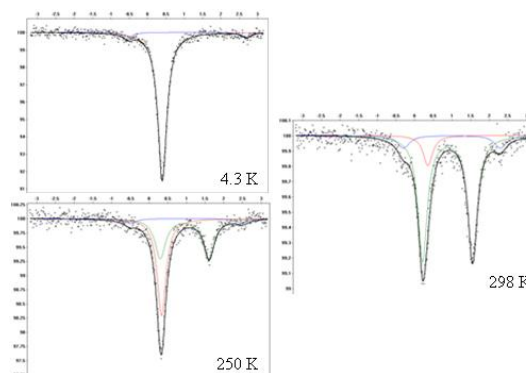
These studies were continued in our group, leading to different types of Fe(II) SCO chains, based on bridging, rigid tetrazole-ligands (see fig.1)



**Fig.1** Molecular structure of a propellane-based 1D-Fe(II)-SCO chain

A major task in the characterization of such materials is a precise and independent characterization of the spin transition temperature, as well as the transition curve. Besides determination of the magnetic susceptibility

temperature dependent <sup>57</sup>Fe-Mößbauer measurements are highly suitable, especially. From the <sup>57</sup>Fe-Mößbauer experiments not only a transition curve is determined, but even more for every measurement the exact HS-LS ratio is obtained. This seemingly trivial information is of utmost relevance for a technological application, as completeness and Fe<sup>(II)</sup><sub>HS</sub>-Fe<sup>(II)</sup><sub>LS</sub> coexistence are key information in assessing the suitability of a SCO-material.



**Fig.2** Temperature dependent <sup>57</sup>Fe-Mößbauer study of a p-xylene based 1D-Fe(II)-SCO chain

Finally, the influence of several weak coordinating anions and different solvents on the molecular arrangement and, therefore, the switching behaviour was investigated. Quantum chemical calculations were used to provide further insights into the solvents' and anions' influence on the spin transition.



## P-15. Topic 6: Mineralogy.

### DISSOLUTION OF CHRYSOTILE ASBESTOS AND ITS IMPLICATIONS ON THE FIBERS' RADICAL FORMING POTENTIAL: A COMPLEMENTARY ICP-OES, EPR AND $^{57}\text{Fe}$ MÖSSBAUER STUDY

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Chrysotile-asbestos [ $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ], a fibrous sheet silicate consisting of octahedral Mg and tetrahedral Si layers, is a carcinogenic mineral that for long has been used as a construction material.

Apart from the fibrous mineral habit and its persistency in vivo, Fe substituted in the asbestos structure plays a key-role with regard to its health risks due to its ability to undergo Fenton like redox reactions and generate radicals which can damage DNA and proteins. To test that, pristine fibers and artificially altered fibers are analyzed with respect to their Fe content and speciation. Among other techniques Mössbauer- and EPR Spectroscopy can be applied for this purpose. Mössbauer spectra of commercial pristine chrysotile fibers (Shijiazhuang Mining IMP&EXP Trade Co. LTD, Hebei region, China) were fitted with one  $\text{Fe}^{2+}$  and two  $\text{Fe}^{3+}$  doublets and had a  $\text{Fe(II)/Fe(III)}$  ratio of 1:1.  $\text{Fe}^{2+}$  substituted in the Mg octahedra had an isomer shift of approximately 1 mm/s (rel. to  $^{57}\text{CoRh}$ ) and a big quadrupole splitting ( $eQV_{zz}/2$ ) of approximately 2.6 mm/s. The isomer shifts of the two  $\text{Fe}^{3+}$  doublets are only slightly different, but quadrupole splitting showed bigger differences: The more intense  $\text{Fe}^{3+}$  doublet had an isomer shift of approximately 0.3 mm/s and a quadrupole splitting of approximately 0.8 mm/s, originating from  $\text{Fe}^{3+}$  substituted in Mg octahedra. The second less intense  $\text{Fe}^{3+}$  doublet had an isomer shift of approximately 0.1 mm/s and a quadrupole splitting of only 0.4 mm/s, originating from  $\text{Fe}^{3+}$  substituted in Si tetrahedra. Mössbauer spectra were well comparable with UICC (Union internationale contre le cancer) reference Mössbauer spectra of chrysotile.

Incubation of 1 g/l pristine fibers in a buffered pH=3 solution for two weeks (blank) mobilized 16.9 % Mg, 6.8% Si and 1.6% Fe, whereas the presence of a high Fe-affinity ligand (1 mmol/l DFOB (desferrioxamine B)) in the same treatment mobilized 38.5% Mg, 21.0% Si and 26.7% Fe of the total Mg, Si and Fe content, measured by ICP-OES. EPR spectroscopy was used to quantify the concentration of hydroxyl-radicals generated by Fe from the fibers via Fenton-like redox reactions in the presence of  $\text{H}_2\text{O}_2$  by applying a spin-

trapping technique with 5-5'-dimethyl-1-pyrroline-N-oxide (DMPO) as trapping agent: The same altered fibers showed a decrease in the radical forming potential of 70% (blank) and 83% (DFOB) relative to pristine fibers. Regarding the different amount of Fe mobilized from the fibers in both treatments, we hypothesize that this similar decrease in radical forming potential can be either achieved by complexing Fe away from the fiber surface (DFOB) or forming secondary, Fenton inactive Fe precipitates (blank).

Mössbauer spectra of the same two altered fiber specimens support this hypothesis: There were no clear differences in the Mössbauer spectra of both altered fiber specimens (DFOB and blank) compared to the pristine fibers, suggesting that not the Fe bulk speciation of the altered fiber, but rather the surface Fe speciation (secondary precipitates) or the absence of Fe on the fiber surface due to complexation (DFOB) determined the decrease in the radical forming potential.

Correlations in speciation (coordination and oxidation state of Fe) and the radical forming potential (spin trapping method) between pristine and altered fibers contribute to understand and estimate the overall health hazard of pristine and altered chrysotile fibers.

## MANUFACTURED NANOPARTICLES: POTENTIALLY TOXIC AGENTS OR NUTRIENT RESERVOIRS FOR PLANTS?

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On account of their peculiar and advantageous physicochemical properties, the magnitude and importance of production and industrial utilization of manufactured nanoparticles (MNPs) has been increasing rapidly in the last decade [1]. According to global estimates [2], worldwide production of nanomaterials exceeded the order of 10<sup>5</sup> t/year already in 2012. It is to be expected that a considerable fraction of MNPs will finally find its way from the industry and consumer products to different environmental compartments such as air, water and soil [1]. Despite growing concerns regarding the environmental risks of MNPs, as of today's knowledge about their transport, possible transformations, final fate and concentration in the ecosystems is scarce [3]. Even more alarming is the lack of comprehensive knowledge/understanding of the nature and mechanisms of the effects of MNPs on their possible host ecosystems and the associated living organisms such as algae, plants, and fungi, which are expected to be affected by an exposure to MNPs [4]. Particularly, research related to the effect of MNPs on soil was reported to be virtually absent as of 2008 [4], even though for MNP classes with antibacterial activity (e.g., Ag and ZnO nanoparticles) negative effects could definitely be expected to occur [4]. At the same time, deliberate exposure of ecosystems to selected nanoparticles may also turn out to be advantageous. Iron-containing MNPs, for example, can be potentially beneficial to ecosystems involving plants, given that iron is among the most important transition metal plant nutrients, and its deficiency is a most limiting factor of plant biomass production [5].

In the frame of the present work we set out to explore the effects of iron-based nanoparticles on plants. Reliable knowledge concerning these effects can only be gained if the nanoparticle agent being subject of the study is properly characterized for its relevant physico-chemical attributes. Consequently, the application of a wide range of experimental techniques from the fields of physics, chemistry and biology is required in order to perform the preparation of nanoparticle samples, to carry out their morphological, structural and magnetic characterization, as well as to assess their effects on plants via controlled plant-growth experiments under laboratory conditions. One of the most adequate methods for the characterization of the chemical forms of iron in nanoparticle agents as well as in plant tissues is <sup>57</sup>Fe Mössbauer spectroscopy [6,7].

In this contribution we present recent results obtained in connection with iron-containing nano-particle agents and their effects on the growth and physiological activity of cucumber (*Cucumis sativus*) plant.

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- [1] A. Bour, F. Mouchet, J. Silvestre, L. Gauthier, E. Pinelli, *Journal of Hazardous Materials* 283 (2015) 764.
- [2] F. Piccinno, F. Gottschalk, S. Seeger, B. Nowack, *J. Nanopart. Res.* 14 (2012) 1109.
- [3] J.D. Posner, *Nano Today* 4 (2009) 114.
- [4] E. Navarro, A. Baun, R. Behra, N.B. Hartmann, J. Filser, A. Miao, A. Quigg, P.H. Santschi, L. Sigg, *Ecotoxicology* 17 (2008) 372.
- [5] J. Abadía, S. Vázquez, R. Rellán-Álvarez, H. El-Jendoubi, A. Abadía, A. Álvarez-Fernández, A.F. López-Millán, *Plant. Phys. Biochem.* 49 (2011) 471.
- [6] K. Kovács, E. Kuzmann, E. Tatár, A. Vértes, F. Fodor, *Planta* 229 (2009) 271.
- [7] K. Kovács, J. Pechoušek, L. Machala, R. Zbořil, Z. Klencsár, Á. Solti, B. Tóth, B. Müller, H.D. Pham, Z. Kristóf, F. Fodor, *Planta* (2016) DOI:10.1007/s00425-016-2502-x



## P-17. Topic 11: Metals and Alloys

### MÖSSBAUER AND XRD STUDY OF HOT DIP GALVANIZED ALLOY

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The hot dip galvanizing (HDG) process is carried out on many steel components such as sculptures, railings, children's play parks, structural beams and automotive frames, creating corrosion protection both in the form of barrier protection and cathodic protection. HDG has been used as a process for over 150 years and is still an important process for corrosion protection of steel. Powder coating is added to galvanized steel for two main purposes; to improve aesthetic characteristics and to provide greater corrosion protection through the addition of a second barrier coating, which reduces the rate at which the zinc galvanized coating is consumed.

Pinholing and outgassing type surface defects have been reported on powder coating since the introduction of powder coatings in the early 1970s, with these surface defects being particularly prominent when the substrate is HDG steel. These surface defects can result in a reduction in aesthetic quality and a reduction in the corrosion performance of the duplex coating, and are clearly undesirable in the final product, weakening performance in the working environments and causing increased costs in the manufacturing process.

A study into the causes of pinhole defects on powder coatings on HDG steel identified many factors which can contribute. One of the most significant factors identified is the alloy nature of the steel. The presence of silicon within steel has a significant impact on the nature of the zinc-iron alloys that are formed within the HDG coating, this phenomenon is known as the Sandlin effect. Where silicon is present at levels of greater than 0.20% HDG coatings are non-uniform and abnormally thick. These thick HDG coatings are observed to provide problematic substrates for further processing, and are considered to contribute to pinholing and outgassing defects in powder coating.

Mössbauer spectroscopy has been used to investigate the nature of the Zinc-Iron alloys present within the HDG layers of steel with a silicon content of 0.35%. The investigation also studied the impact of the powder coating pretreatment on the nature of the alloy layers. The acid etching process within the pretreatment process in particular would be expected to have a significant impact on the HDG layer. This study utilized <sup>57</sup>Fe Mössbauer spectroscopy to examine identically processed samples prior to and post pretreatment.

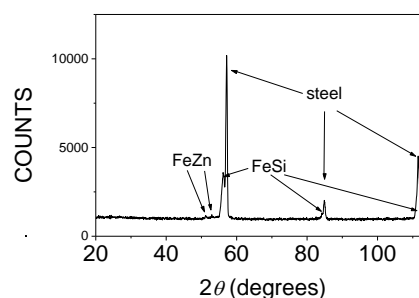


Fig. 1 XRD of a hot galvanized sample

XRD and <sup>57</sup>Fe CEMS measurements were performed on hot galvanized S355J2+N samples with sandwiched structure when the X-ray and  $\gamma$ -ray was applied parallel to the galvanized layers. Both XRD and CEMS (Figs 1 and 2) reveal the presence of dominant steel phase in accordance with its estimated occurrence on the surface of the sandwiched samples. Minor  $\Gamma$ -Fe<sub>3</sub>Zn<sub>10</sub>,  $\zeta$ -FeZn<sub>15</sub> and solid solution Fe-Zn as well as minor Fe-Si phases could also be identified.

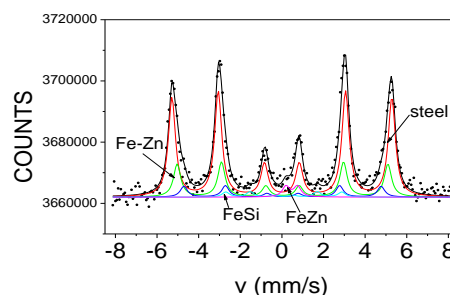


Fig. 2. <sup>57</sup>Fe CEMS of a hot galvanized sample

## **P-17. Topic 4: Magnetic Materials and Superconductive materials**

### **Synthesis and characterisation of 2- and 6-line ferrihydrite nanoparticles**

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#### **Abstract**

Powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, Mössbauer spectroscopy (MS) and magnetic measurements (MM) on 2-line, 2-line deposited onto SiO<sub>2</sub> and 6-line ferrihydrite nanoparticles are reported. Disordered 2LFh and 2LFh/SiO<sub>2</sub> present poor crystallinity while 6LFh has a relatively better crystallinity. TEM micrographs feature globular nanoclusters with average crystallite sizes of 4.0, 3.5 and 6.0 nm for 2LFh, 2LFh/SiO<sub>2</sub> and 6LFh, respectively. The morphology of the nanoparticles and their relatively small crystallite sizes determine the magnetic properties. They result in a superparamagnetic behaviour and high anisotropy constants arising mainly from high surface anisotropy caused by an increase of the fraction of surface atoms and surface energies.