

**Workshop on**

**Energy Dispersive  
X-ray Absorption Spectroscopy**

**Scientific Opportunities  
and Technical Challenges**

2 - 5 February 2009

Venue: ESRF Auditorium

**Scientific Programme Committee:**

**François Baudelet** - Synchrotron SOLEIL - France  
**Dibyendu Bhattacharyya** - Bhabha Atomic Research Centre - India  
**Andy Dent** - Diamond Light Source - UK  
**Flavio Garcia** - Brazilian Synchrotron Light Laboratory - Brazil  
**Britt Hedman** - SLAC National Accelerator Laboratory - USA  
**Yasuo Nishihata** - SPring-8 - Japan

# Table of Contents

<b>List of Invited Speakers .....</b>	<b>4</b>
<b>Programme .....</b>	<b>5-8</b>
<b>Speakers' Abstracts:</b>	
<b>Early Development of Dispersive X-ray Absorption Spectrometer and Recent Extension of Dispersive Optics to Quick X-ray Reflectometry .....</b>	<b>9</b>
<u>Matsushita T.</u>	
<b>EDXAS, First Steps at LURE.....</b>	<b>10</b>
<u>Fontaine A.</u>	
<b>Steps towards understanding Catalytic Reactions .....</b>	<b>11</b>
<u>Evans J.</u>	
<b>Ultrafast Time-resolved X-ray Absorption Spectroscopy:Watching Atoms Move.....</b>	<b>12</b>
<u>Milne C.J., Pham V.-T., Gawelda W., van der Veen R.M., El Nahhas A., Lima F., Amarasinghe D., Johnson S.L., Beaud P., Ingold G., Borca C.N., Grolimund D., Abela R., Cannizzo A., Bressler Ch. and Chergui M.</u>	
<b>Measuring Strain at the Atomic-Scale with Differential X-ray Absorption Spectroscopy .....</b>	<b>13</b>
<u>Ruffoni M. P.</u>	
<b>2D micro-XAS Mapping using Energy Dispersive X-ray Absorption Spectroscopy .....</b>	<b>14</b>
<u>Muñoz M.</u>	
<b>High Pressure Studies using EDXAS .....</b>	<b>15</b>
<u>San Miguel A.</u>	
<b>Investigating the Minerals Crystal Chemistry at Very High Pressure using Tandem EDXAS and XRD Experiments .....</b>	<b>16</b>
<u>Andrault D., Muñoz M., Bolfan-Casanova N., Guignot N., Perrillat J.-P., Aquilanti G. and Pascarelli S.</u>	
<b>EDXAS and Melting in the DAC .....</b>	<b>17</b>
<u>Aquilanti G., Trapananti A., Boehler R.</u>	
<b>Magnetism at High Pressures.....</b>	<b>18</b>
<u>Haskel D.</u>	
<b>High Magnetic Field X-ray Magnetic Circular Dichroism in Valence Fluctuating Compounds .....</b>	<b>19</b>
<u>Matsuda Y.H.</u>	
<b>Field Induced Phase Transition in Ca<sub>2</sub>FeReO<sub>6</sub> Double Perovskite: an XMCD Study in 30T Pulsed Magnetic Field .....</b>	<b>20</b>
<u>Sikora M., Mathon O., van der Linden P., Michalik J.M., de Teresa J.M., Pascarelli S., Kapusta Cz.</u>	
<b>Structure-Function Studies in Heterogeneous Catalysis .....</b>	<b>21</b>
<u>Fernández-García M.</u>	

<b>In Situ Redispersion of Platinum Nanoparticles Supported on Ceria-Based Oxide for Auto-Exhaust Catalysts .....</b>	<b>22</b>
<u>Nagai Y.</u> , Dohmae K., Ikeda Y., Takagi N., Tanabe T., Hara N., Guilera G., Pascarelli S., Newton M.A., Kuno O., Hongying J., Shinjoh H., and Matsumoto S.	
<b>State of the Art Quick-EXAFS: Applications in Catalysis .....</b>	<b>23</b>
<u>Frahm R.</u> , Stötzel J., Lützenkirchen-Hecht D.	
<b>An Energy Dispersive X-ray Absorption and X-ray Diffraction Study of Photomagnetic CoFe Prussian Blue Analogues .....</b>	<b>24</b>
<u>Bleuzen A.</u> , Baudalet F., Itié J.-P.	
<b>DXAFS at the Photon Factory .....</b>	<b>25</b>
<u>Nomura M.</u> , Inada Y., and Niwa Y.	
<b>The ODE Beamline at SOLEIL: First Results on XMCD and EXAFS under Extreme Conditions and Kinetics Experiments .....</b>	<b>26</b>
<u>Congeduti A.</u> , Kong Q., Chagnot S., Monza A., Abeillé G., Delmotte A., and Baudalet F.	
<b>First Results from a Dispersive EXAFS Beamline at Indus-2 Synchrotron Source .....</b>	<b>27</b>
<u>Jha S.N.</u> , Bhattacharyya D., Poswal A.K. and Sabharwal S.C.	
<b>The LNLS Dispersive XAS (DXAS) beamline .....</b>	<b>28</b>
<u>Azevedo G.M.</u> , Carvalho E. and Garcia F.	
<b>Energy Dispersive EXAFS at Diamond Light Source .....</b>	<b>29</b>
<u>Diaz Moreno S.</u>	
<b>TE-XAS Project, Scientific Opportunities and Technical Challenges .....</b>	<b>30</b>
<u>Mathon O.</u> , Mairs T. Pascarelli S.	
<b>Ray Tracing Simulations for Optical Configurations.....</b>	<b>31</b>
<u>Sánchez del Río M.</u>	
<b>Beyond the Geometric toward a Wave Optical Approach in the Design of Curved Crystal and Multilayer Optics for EDXAS .....</b>	<b>32</b>
<u>Mocella V.</u> , Ferrero C., Morawe C., Guigay J.P.	
<b>Ray Tracing Simulations for Bendable Crystals in Bragg Geometry .....</b>	<b>33</b>
<u>Moreno T.</u> , Baudalet F., Chagnot S., Mourad I., Brochet S., Thomasset M.	
<b>XH Ge Microstrip Detector for EDXAS .....</b>	<b>34</b>
<u>Headspith J.</u> , Groves J.	
<b>Sample Environment on ID24.....</b>	<b>35</b>
<u>van der Linden P.J.E.M.</u> , Gorges B., Steinmann R.	
<b>EDXAS: a Great Technique. Why is it so Difficult? .....</b>	<b>36</b>
<u>Mairs T.R.</u> , Mathon O.	
<b>List of Posters .....</b>	<b>37-38</b>
<b>Poster Abstracts.....</b>	<b>39-54</b>
<b>List of Participants.....</b>	<b>55-62</b>

# Energy Dispersive X-ray Absorption Spectroscopy: Scientific Opportunities and Technical Challenges

## List of Speakers

**Denis Andraut** - Université Blaise Pascal, Clermont-Ferrand - France

**Giuliana Aquilanti** - ESRF, Grenoble - France

**Gustavo Azevedo** - Brazilian Synchrotron Light Laboratory, Campinas - Brazil

**Anne Bleuzen** - Université Paris Sud - France

**Alberta Congeduti** - Synchrotron SOLEIL, Gif-sur-Yvette - France

**Sofia Diaz Moreno** - Diamond Light Source Ltd, Chilton - UK

**John Evans** - University of Southampton - UK

**Marcos Fernandez Garcia** - Instituto de Catalisis y Petroleo, Madrid - Spain

**Alain Fontaine** - CNRS, Grenoble - France

**Ronald Frahm** - Bergische Universität Wuppertal - Germany

**Daniel Haskel** - Advance Photon Source, Argonne - USA

**Jon Headspith** - Daresbury Laboratory, Warrington - UK

**S.N. Jha** - Bhabha Atomic Research Center, Mumbai - India

**Trevor Mairs** - ESRF, Grenoble - France

**Olivier Mathon** - ESRF, Grenoble - France

**Yasuhiro Matsuda** - University of Tokyo - Japan

**Tadashi Matsushita** - Photon Factory, Ibaraki - Japan

**Chris Milne** - Swiss Light Source, Villigen - Switzerland

**Vito Mocella** - CNR Napoli - Italy

**Thierry Moreno** - Synchrotron Soleil, Gif-sur-Yvette - France

**Manuel Muñoz** - Université Joseph Fourier, Grenoble - France

**Yasutaka Nagai** - Toyota, Aichi - Japan

**Masaharu Nomura** - Photon Factory, Tsukuba - Japan

**Matthew Ruffoni** - ESRF, Grenoble - France

**Alfonso San Miguel** - University Lyon 1 - France

**Manolo Sanchez Del Rio** - ESRF, Grenoble - France

**Marcin Sikora** - University of Science and Technology, Krakow - Poland

**Peter van der Linden** - ESRF, Grenoble - France

# Energy Dispersive X-ray Absorption Spectroscopy: Scientific Opportunities and Technical Challenges

## Programme

Venue: ESRF Auditorium

### Monday 2<sup>nd</sup> February

11:30 - 12:30	Pre-registration	
12:30 - 14:00	<i>Lunch at the ESRF/ILL Restaurant</i>	
13:30 - 14:00	Registration	
<b>Session I: Historical Overview</b> <i>Chair: M. Hagelstein</i>		
14:00 - 14:10	Welcome by <b>H. Reichert, Research Director of the ESRF</b>	
14:10 - 14:50	Early Development of Dispersive X-ray Absorption Spectrometer and Recent Extension of Dispersive Optics to Quick X-ray Reflectometry	<b>T. Matsushita</b> Photon Factory Ibaraki, Japan
14:50 - 15:30	EDXAS, First Steps at LURE	<b>A. Fontaine</b> CNRS Grenoble, France
15:30 - 16:10	Steps towards understanding Catalytic Reactions	<b>J. Evans</b> University of Southampton, UK
16:15 - 16:45	<i>Coffee Break</i>	
<b>Session II: New Scientific Opportunities</b> <i>Chair: S. Pascarelli</i>		
16:45 - 17:15	Ultrafast Time-resolved X-ray Absorption Spectroscopy: Watching Atoms Move	<b>C. Milne</b> SLS Villigen, Switzerland
17:15 - 17:45	Measuring Strain at the Atomic-Scale with Differential X-ray Absorption Spectroscopy	<b>M. Ruffoni</b> ESRF Grenoble, France
17:45 - 18:15	2D micro-XAS Mapping using Energy Dispersive X-ray Absorption Spectroscopy	<b>M. Muñoz</b> UJF Grenoble, France

**Tuesday 3rd February**

<b>Session III: Extreme Conditions</b>		
<i>Chair: J.P. Itié</i>		
09:00 - 09:30	High Pressure Studies using EDXAS	<b>A. San Miguel</b> Université Lyon 1, France
09:30 - 10:00	Investigating the Minerals Crystal Chemistry at Very High Pressure using Tandem EDXAS and XRD Experiments	<b>D. Andrault</b> Université Blaise Pascal Clermont-Ferrand, France
10:00 - 10:30	EDXAS and Melting in the DAC	<b>G. Aquilanti</b> ESRF Grenoble, France
10:30 - 11:00	<i>Coffee Break</i>	
11:00 - 11:30	Magnetism at High Pressures	<b>D. Haskel</b> APS Argonne, USA
11:30 - 12:00	High Magnetic Field X-ray Magnetic Circular Dichroism in Valence Fluctuating Compounds	<b>Y. Matsuda</b> University of Tokyo, Japan
12:00 - 12:30	Field Induced Phase Transition in $\text{Ca}_2\text{FeReO}_6$ Double Perovskite: an XMCD Study in 30T Pulsed Magnetic Field	<b>M. Sikora</b> University of Science and Technology Krakow, Poland
12:30 - 14:00	<i>Lunch at the ESRF/ILL Restaurant</i>	
<b>Session IV: Chemistry and Catalysis (Operando)</b>		
<i>Chair: A. Dent</i>		
14:00 - 14:30	Structure-Function Studies in Heterogeneous Catalysis	<b>M. Fernandez Garcia</b> ICP CSIC Madrid, Spain
14:30 - 15:00	In Situ Redispersion of Platinum Nanoparticles Supported on Ceria-Based Oxide for Auto-Exhaust Catalysts	<b>Y. Nagai</b> Toyota Aichi, Japan
15:00 - 15:30	State of the Art Quick-EXAFS: Applications in Catalysis	<b>R. Frahm</b> Bergische Universität Wuppertal, Germany
15:30 - 16:00	An Energy Dispersive X-ray Absorption and X-ray Diffraction Study of Photomagnetic CoFe Prussian Blue Analogues	<b>A. Bleuzen</b> Université Paris Sud, France
16:00 - 16:30	<i>Coffee Break</i>	
16:30 - 18:00	<b>Visit of ID24</b>	
19:30	<i>Bus departure for the restaurant</i>	
20:00	<i>Workshop Dinner</i>	

## Wednesday 4th February

<b>Session V: News from Facilities</b> <i>Chair: T. Matsushita</i>		
14:00 - 14:30	DXAFS at the Photon Factory	<b>M. Nomura</b> Photon Factory Tsukuba, Japan
14:30 - 15:00	The ODE Beamline at SOLEIL: First Results on XMCD and EXAFS under Extreme Conditions and Kinetics Experiments	<b>A. Congeduti</b> Synchrotron Soleil Gif-sur- Yvette, France
15:00 - 15:30	First Results from a Dispersive EXAFS Beamline at Indus-2 Synchrotron Source	<b>S.N. Jha</b> Bhabha Atomic Research Center Mumbai, India
15:30 - 16:00	The LNLS Dispersive XAS (DXAS) beamline	<b>G. Azevedo</b> LNLS Campinas, Brazil
16:15 - 16:45	<i>Coffee Break</i>	
16:45 - 17:15	Energy Dispersive EXAFS at Diamond Light Source	<b>S. Diaz Moreno</b> Diamond Light Source Ltd Chilton, UK
17:15 - 17:45	TE-XAS Project, Scientific Opportunities and Technical Challenges	<b>O. Mathon</b> ESRF Grenoble, France
17:45 - 18:30	<b>Discussion</b>	
18:30 - 19:50	<i>Poster Session and Cocktail</i>	
20:00 - 22:30	<i>Users' Meeting Dinner at the ESRF/ILL Restaurant</i>	

**Thursday 5th February**

<b>Session VI: Technical Challenges</b> <i>Chair: F. Baudelet</i>		
09:00 - 09:30	Ray Tracing Simulations for Optical Configurations	<b>M. Sanchez del Rio</b> ESRF Grenoble, France
09:30 - 10:00	Beyond the Geometric toward the Wave Optical Approach in the Design of Curved Crystal and Multilayer Optics for EDXAS	<b>V. Mocella</b> CNR Napoli, Italy
10:00 - 10:30	Ray Tracing Simulations for Bendable Crystals in Bragg Geometry	<b>T. Moreno</b> Synchrotron Soleil Gif-sur-Yvette, France
10:30 - 11:00	<i>Coffee Break</i>	
11:00 - 11:30	XH Ge Microstrip Detector for EDXAS	<b>J. Headspith</b> Daresbury Laboratory Warrington, UK
11:30 - 12:00	Sample Environment on ID24	<b>P. van der Linden</b> ESRF Grenoble, France
12:00 - 12:30	EDXAS: a Great Technique. Why is it so Difficult?	<b>T. Mairs</b> ESRF Grenoble, France
<b>Conclusions</b>		
12:30 - 12:45	Final Remarks	<b>S. Pascarelli and</b> <b>O. Mathon</b> ESRF Grenoble, France
12:45 - 14:00	<i>Lunch at the ESRF/ILL Restaurant</i>	



# Speakers' Abstracts

# Early Development of Dispersive X-ray Absorption Spectrometer and Recent Extension of Dispersive Optics to Quick X-ray Reflectometry

Matsushita T.

Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Oho 1-1, Tsukuba, Ibaraki, 305-0801 Japan; [tadashi.matsushita@kek.jp](mailto:tadashi.matsushita@kek.jp)

The very first idea of the dispersive XAS was born in 1978 on an occasion that Matsushita attended one small workshop at Osaka for discussing EXAFS spectrometer to be installed at the Photon Factory and occasionally heard someone's comment for the necessity of a quick EXAFS spectrometer to carry out time-resolved EXAFS studies on reacting objects. In the conference room it suddenly occurred to him that a whole EXAFS spectrum could be measured at once with a geometry in which a specimen is placed at the focus position of the convergent beam having a one-to-one relationship between the energy and the direction. The usefulness of this scheme was experimentally demonstrated using a laboratory X-ray source and a Laue-case flat crystal polychromator [1]. During his stay at Stanford in 1979-1980, Matsushita wanted to extend this method to the case of synchrotron radiation. With a help of a graphical method [2] using a space-momentum-wavelength space to describe properties of X-ray optics, he noticed that a convergent beam having a one-to-one relationship between its energy and direction is just realized by a curved crystal when an X-ray source is placed very far way from the point on the Rowland circle and that the X-ray beam is focused to a point inside the Rowland circle [3, 4]. In this talk, early development of the dispersive XAS will be retrospectively discussed.

In the second part of the talk, a new extension of the dispersive X-ray optics to quick X-ray reflectometry [5 - 7] will be briefly discussed. Using a Laue-case bent crystal (Si 111, R = 100mm, 72  $\mu\text{m}$  thick), a convergent X-ray beam is produced where the energy changes continuously from 8 keV to 40 keV as a function of the horizontal ray direction. The X-ray beam is specularly reflected in the vertical direction by a specimen placed at the focus. The horizontal intensity distribution measured downstream of the focus represents the specular X-ray reflectivity curve as a function of the X-ray energy. Specular reflectivity curves were measured with exposure times of a second or less. Some examples of static and dynamic measurements of specular reflectivity will be described.

## References

- [1] - U. Kaminaga, T. Matsushita and K. Kohra, *Jpn. J. Appl. Phys.* **20** L355-L358 (1981).
- [2] - T. Matsushita and U. Kaminaga, *J. Appl. Cryst.* **13** 465-471 (1980), *ibid* **13**, 472-478 (1980).
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- [4] - T. Matsushita and R. P. Phyzackerley, *Jpn. J. Appl. Phys.* **20**, 2223-2228 (1981).
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- [7] - T. Matsushita, E. Arakawa, Y. Niwa, Y. Inada, T. Hatano, T. Harada, Y. Higashi, K. Hirano, K. Sakurai, M. Ishii and M. Nomura, *Eur. Phys. J. Special Topics* **168**, 113 (2009).

# EDXAS, First Steps at LURE

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Following the Matsushita San enlighting work, the EDXAS development at Lure came from the start of the 80's. The crucial point which made the breakthrough, was the implementation of a reliable photo-diode array-based-linear detector. This device came available at that period, following the emergence of the CCD. We learnt from the ability of the astrophysics community, but used the nitrogen-cooled array for high flux, fast and numerical reading when astrophysicists were essentially concerned by the low electronic noise. The first studies which helped to boost the implementation of EDXAS took a full benefit of the two main features of the spectrometer, the "highly focused" X-ray beam and the fast and parallel data acquisition. Hence high pressure studies (GeO<sub>2</sub>,...) and time resolved experiments were performed with different materials (redox of conducting polymers, oxygen uptake of the new YBCO high T<sub>c</sub> superconductors,...). And then came the use of circular polarised X-ray, to carry out XMCD investigations of magnetic materials.

# Steps towards understanding Catalytic Reactions

Evans J.

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The important presentations at the XAFS3 conference in Stanford in 1984 on energy dispersive XAFS inspired the UK community to establish an Energy Dispersive EXAFS (EDE) or Dynamic EXAFS (DEXAFS) facility primarily to serve the chemical community. The initial test facility was created on a bending magnet station at station 7.4 of the SRS at the Daresbury Laboratory with low flux. Both the optical and detector properties made it a difficult base for studying catalytic reactions, particularly on solid compounds. In the early 1990s the Materials Science beamline, Station 9.3 utilising a 5T wavelength shifter, was developed for twin use with scanning and dispersive as alternative uses. Investigations into homogeneous catalysts were initiated there to probe the active sites in the dimerisation of alkenes as catalysed by nickel complexes.[1] Throughout this period different photodiode array detectors were developed to improve sensitivity, linearity and durability, and this provided sub second time resolution appropriate to stopped flow mixing.[2] Also our first experiments were carried out on ID24 (1996) and this provided an excellent comparison point for instrumentation development. Notably, the 3-point bend was then replaced at Station 9.3 by a 4-point one. The improved focus allowed heterogeneous samples to be investigated successfully and this provided the platform for the first in situ microreactor studies at the Pt L(III) edge,[3] and this was subsequently extended to the simultaneous study of two elements by spanning the Pt L(III) and Ge K edges.[4] Only once beam stability and optical purity was addressed on ID24 could that beamline compete successfully with Station 9.3.[5]

Subsequent developments have concentrated on the combination of time resolved IR and XAFS, the enhanced time resolution from a silicon microstrip detector [6,7] and most recently of a germanium analogue which promises single bunch capability. [8] Most reactions studied so far have involved multiple chemical steps. This last development offers the chance of monitoring the structural changes of primary chemical events.

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- [1] - D. Bogg, M. Conyngham, J.M. Corker, A.J. Dent, J. Evans, R.C. Farrow, V.L. Kambhampati, A.F. Masters, D.N. McLeod, C.A. Ramsdale and G. Salvini, *J. Chem. Soc., Chem. Commun.*, 1996, 647-648.
- [2] - M. B. B. Abdul Rahman, P. R. Bolton, J. Evans, A.J. Dent, I. Harvey, and S. Diaz-Moreno, *Disc. Faraday Soc.*, 2003, **122**, 211 - 222.
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# Ultrafast Time-resolved X-ray Absorption Spectroscopy: Watching Atoms Move

Milne C.J.<sup>1,2</sup>, Pham V.-T.<sup>1</sup>, Gawelda W.<sup>3</sup>, van der Veen R.M.<sup>1,2</sup>, El Nahhas A.<sup>1</sup>,  
Lima F.<sup>2,1</sup>, Amarasinghe D.<sup>1,2</sup>, Johnson S.L.<sup>2</sup>, Beaud P.<sup>2</sup>, Ingold G.<sup>2</sup>, Borca C.N.<sup>2</sup>,  
Grolimund D.<sup>2</sup>, Abela R.<sup>2</sup>, Cannizzo A.<sup>1</sup>, Bressler Ch. and Chergui M.<sup>1</sup>

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X-ray absorption spectroscopy has the ability to achieve structural resolution down to the sub-Å level in the condensed phase. By using XAS to probe laser-excited samples we can obtain excited-state structural and electronic dynamical information not available through other techniques [1]. Recent advances in femtosecond hard X-ray generation [2] have allowed us to extend our ultrafast XAS techniques into the sub-picosecond time domain which is the fundamental time scale of molecular motion. By combining ultrafast laser spectroscopic techniques [3] with picoseconds [4] and femtosecond [5] XAS measurements we have completely resolved the photocycle of an Fe(II)-based molecular spin-crossover system in solution. The future of these measurements at next-generation X-FELs will also be discussed, with particular attention paid to dispersive spectroscopic techniques.

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# Measuring Strain at the Atomic-Scale with Differential X-ray Absorption Spectroscopy

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The structural changes exhibited by materials in response to their surroundings are of fundamental importance across countless disciplines in science and engineering. In the particular field of transducer technologies, strain-inducing phenomena – such as magnetostriction, electrostriction, and piezoelectricity – are utilised in their own right, and form the physical foundation for sensor and actuator devices. Knowledge of the origin and mechanics of such phenomena, and how they manifest themselves in different materials, underpins the development of new transducers and the optimisation of existing technologies. As such, considerable research is undertaken each year to develop an understanding of the physical processes at work. Yet this is not without its limitations.

Theoretical work may study the fundamental properties of a given material, and develop models for its behaviour at an atomic scale. However, experimental observation of strain on a similarly microscopic scale, and thus verification of such models, has presented some serious technical challenges. This has essentially been due to the difficulty in detecting and quantifying atomic motion with sufficient precision. In the case of magnetostriction, inter-atomic displacements in response to an external magnetic field typically saturate at a few femtometres. Here, even commonly employed local probes, such as X-ray Absorption Spectroscopy (XAS), lack the resolution to observe this motion by some two orders of magnitude. As a result, work to date has almost exclusively dealt with magnetostriction in a scaled-up form. Common experiments employ strain gauges on large, macroscopic samples, where the strain is easier to detect, but where atomic information is lost.

However, by exploiting the intrinsic stability and time resolution of the dispersive XAS set-up, the recent development of Differential XAS (DiffXAS) on ID24 at the ESRF has made such direct, atomic-scale measurements possible [1].

This talk will introduce the Differential XAS technique, and chart its development through some of the most significant results obtained to date. These include the first DiffXAS measurements, which demonstrated the technique's sensitivity to femtometre scale motion [1]; studies of the technologically important  $\text{Fe}_{(1-x)}\text{Ga}_x$  system, where the development of DiffXAS data analysis procedures allowed chemically-selective, atomic magnetostriction coefficients to be quantified [2][3]; studies of the magneto-elastic coupling of FeCo through measurements under applied hydrostatic pressure [4]; and studies of structural changes as a function of temperature with Thermal DiffXAS [5].

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# 2D micro-XAS Mapping using Energy Dispersive X-ray Absorption Spectroscopy

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Originally developed for time-resolved X-ray absorption spectroscopy (XAS), Energy-Dispersive X-ray Absorption Spectroscopy (EDXAS) offers new opportunities for applications such as fluorescence detection and microbeams, thanks to recent developments in both instrumentation and optics [1]. In this context, we illustrate the first examples of chemical and speciation mapping recorded at ID24. Using a  $5 \times 5 \mu\text{m}^2$  focal spot combined to the acquisition speed, we have performed 2-dimensional micro-XAS mapping of complex and heterogeneous samples, where each of the thousands of pixels composing the image provides full XAS information.

We illustrate the potential of this method using two examples. The first is dedicated to a fluorescence detected XAS study of a natural metamorphic rock including different types of minerals [2,3]. In such systems, the challenge is to date back to P and T conditions of the formation of rocks that have been subducted to great depth. This would provide key information to help in understanding the formation of mountain belts and the geodynamics of convergent zones at the lithospheric scale. Estimates of these so-called P-T maps have never been successfully achieved because they critically rely on the quantitative knowledge of redox and speciation within the crust, at least in two dimensions. The analysis of  $\sim 3000$  XANES spectra allows to produce maps of iron content, oxidation state, and speciation, with a  $5 \mu\text{m}$  spatial resolution.

The second example is devoted to an energy dispersive XAS study to investigate the behavior of iron during the decomposition of (Mg,Fe)-ringwoodite into perovskite and ferropicriase at conditions relevant to Earth upper/lower mantle boundary [4,5]. The analysis of 1600 Fe K-edge XANES spectra collected in the laser-heated Diamond Anvil Cell allows to the reconstruction of maps based on iron-speciation, but it also drives to iron-concentration maps in a complex mixture of three crystalline phases. This analytical procedure opens the way to *in situ* studies at extreme conditions of pressure and temperature for the geosciences, physics and chemistry communities

EDXAS fulfills now the conditions for an evolution towards a microanalysis technique for practical use in fields such as geology, archeology, environmental sciences, cultural heritage, geophysics, and many more.

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# High Pressure Studies using EDXAS

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High pressure studies take profit of the main characteristics of the energy dispersive XAS technique, which is especially well adapted for the combination with the diamond anvil cell apparatus. The small focus provided by the elliptical polychromator focusing optics[1] allows for obvious benefits when combined with the mechanical stability inherent to the technique: higher pressures can be reached allowing for over Megabar experiments. Time resolution is also fundamental in high pressure experiments using single-crystal anvils as in the diamond anvil cell. In fact, the abundant diffraction glitches produced by the anvils rapidly limit the exploitable energy span around the absorption edge. The on line capacity of anvil orientation given by the millisecond order of magnitude time resolution of the technique allows for a relatively easy alignment.

I will provide a number of examples of the applications of EDXAS on high pressure investigations including the first determination of a high pressure structure with the help of EDXAFS[2], the study of the anisotropy of the compressibility in lamellar systems[3], polarization dependent single-crystal energy dispersive EXAFS at high pressure[4] or Megabar studies in molecular systems [5,6].

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# Investigating the Minerals Crystal Chemistry at Very High Pressure using Tandem EDXAS and XRD Experiments

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The Al-bearing (Mg,Fe) silicates are dominant phases in the Earth's interior. In particular, the Al-(Mg,Fe)SiO<sub>3</sub> perovskite is from far the major lower mantle phase and thus the most abundant mineral on Earth. A very important property of this phase is a great affinity between Al<sup>3+</sup> and Fe<sup>3+</sup> in the MgSiO<sub>3</sub>-based structure. This affects largely (a) the crystal chemistry of this phase, including presence of various types of point defects, (b) the Fe<sup>3+</sup>/ΣFe content and thus the lower mantle redox state, and (c) the mineralogy of all types of geological materials found in the lower mantle. The perovskite phase (Pv) transforms to a post-perovskite (PPv) CaIrO<sub>3</sub>-type structure at about 300 km above the core-mantle boundary. This phase transition could explain the very peculiar seismic observations reported for this region. This PPv phase has motivated several studies in the past few years.

In order to constraint better the mechanism of the Pv to PPv phase transformation for geophysically relevant Al-bearing (Mg,Fe)SiO<sub>3</sub> composition, we coupled performances of laser heated diamond anvil cell experiments with tandem analyses of both structure using X-ray diffraction (XRD) at ID27 and crystal chemistry using Fe K-edge μ-XANES at the ID24 beamline. Because two (or three) minerals coexist in a same sample, the Rietveld analyses provide quantitative information on the minerals fraction, while the μ-XANES results yield to both Fe-speciation (Fe<sup>3+</sup>/Fe<sup>2+</sup>/Fe<sup>0</sup> contents) and Fe-fraction in each minerals. Thus, the use of tandem XRD and XANES analyses makes it possible determination of the Fe partitioning coefficient between the different minerals, and it also informs on the sample redox state.

In the case of the Al-bearing (Mg,Fe)SiO<sub>3</sub> system, we show that both Pv and PPv phases coexist between 110 and 170 GPa and that the PPv-phase is largely depleted in Fe compared to the Pv.

# EDXAS and Melting in the DAC

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Science at extreme pressure conditions in diamond anvil cells (DAC) historically represents one of the main applications of EDXAS and is well documented in the literature. However, applying pressure is not sufficient for studying chemical properties of matter or to have access to its different states: solid and liquid.

Laser-heating in the diamond anvil cell has shown to be applicable for many fields of research ranging from mineral physics, to material synthesis through the study of basic physical and chemical properties in the high P-T regime.

In this contribution we show the first melting XAS data in a laser heated DAC recorded at the beamline ID24 of the ESRF. The specific advantages of EDXAS for melting in the DAC using the laser heating techniques will be highlighted.

Two examples will be shown: molten iron and germanium above 50 GPa.

# Magnetism at High Pressures

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The interactions between electrons in a solid, particularly those affecting its magnetic properties, are intimately related to the overlap of their electronic wavefunctions. Altering this overlap by the application of pressure modifies these interactions and provides a powerful playground for studies of magnetic materials. Coupled with the element- and orbital-selectivity of X-ray magnetic circular dichroism (XMCD), high-pressure studies of magnetism with synchrotron radiation in the diamond anvil cell (DAC) are bound to improve our understanding of magnetic interactions in complex magnetic systems. We describe the recent development of a high-pressure XMCD capability at the Advanced Photon Source for low-temperature (10 K), high-field (0.7 Tesla) experiments in a DAC featuring perforated diamond anvils (25 GPa) [1-3]. These measurements can currently be performed in the 6-13 keV energy range allowing studies of transition metal ( $3d$ ), rare-earth ( $4f$ ) and ( $5d$ ) magnetic systems. We illustrate this capability with examples from recent experiments on giant magneto-caloric material  $Gd_5(Si_xGe_{1-x})_4$ , and  $EuX$  ( $X=O, S, Se, Te$ ) magnetic semiconductors.

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# High Magnetic Field X-ray Magnetic Circular Dichroism in Valence Fluctuating Compounds

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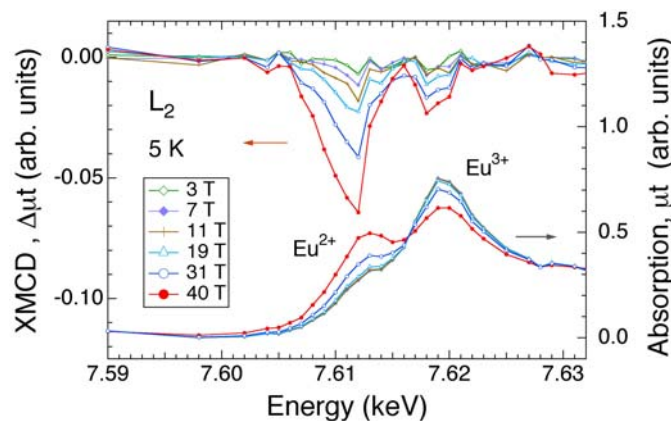
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Valence fluctuating compounds  $\text{EuNi}_2(\text{Si}_{0.18}\text{Ge}_{0.82})_2$ ,  $\text{EuNi}_2\text{P}_2$  and  $\text{YbInCu}_4$  have been studied by X-ray magnetic circular dichroism (XMCD) in pulsed high magnetic fields up to 40 T. The experiments were made at SPring-8 BL39XU. A miniature solenoid type magnet (inner dia. 3 mm) and a small capacitor bank (2.4 kJ) were used for generation of pulsed magnetic fields [1]; the duration time of the field is around 1 ms.

The observed Eu  $L_{2(3)}$ -edge XMCD spectra of the Eu-based compounds show the double peak structure due to the fluctuating two valence states ( $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ ). Figure 1 shows the XMCD spectra of  $\text{EuNi}_2(\text{Si}_{0.18}\text{Ge}_{0.82})_2$  at several magnetic fields. The absorption spectra are also shown; a significant field variation of the absorption spectrum shape suggests the valence change by magnetic fields [2]. Since the ground state of  $\text{Eu}^{2+}$  is magnetic ( $f^7$ ,  $S=7/2$ ,  $L=0$ ,  $J=7/2$ ), it is reasonable that the significant XMCD signal was observed. However, the ground state of  $\text{Eu}^{3+}$  is expected to be nonmagnetic ( $f^6$ ,  $S=3$ ,  $L=3$ ,  $J=0$ ). Hence, it was not obvious whether we should have a finite XMCD signal for  $\text{Eu}^{3+}$  state. In the talk, a possible explanation for the double peak of XMCD is discussed in terms of the strong hybridization between the conduction and 4f electrons.

In contrast to the Eu-based compounds, the Yb  $L_{2(3)}$ -edge XMCD spectra show a single peak structure. Although we have no clear explanation for the different feature of the XMCD spectra found between the Eu- and Yb-based compounds, the hybridization strength can be a key parameter as a recent theoretical paper suggests [3].



**Figure 1:** XMCD and absorption spectra of  $\text{EuNi}_2(\text{Si}_{0.18}\text{Ge}_{0.82})_2$  in several magnetic fields

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# Field Induced Phase Transition in $\text{Ca}_2\text{FeReO}_6$ Double Perovskite: an XMCD Study in 30T Pulsed Magnetic Field

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Spin and orbital contributions to the magnetic moment of Rhenium have been studied in  $\text{Ca}_2\text{FeReO}_6$  double perovskite employing X-ray Magnetic Circular Dichroism at the Re  $L_{2,3}$  edges. Temperature dependent measurements, performed at ID24, energy dispersive X-ray spectroscopy beamline at ESRF, were carried out under pulsed magnetic field varying from 6.8 to 30 T in the temperature range from 10 to 250 K. [1,2] They revealed that the two structural phases reported in this half-metallic compound [3] are characterized by a different spin-orbit coupling. At  $T = 10$  K the average orbital-to-spin moment ratio of the Re sublattice decreases upon application of 30 T magnetic field by  $\sim 5\%$ , while at  $T = 250$  K it is field independent and amounts to  $m_L/m_S = -0.362(6)$ , see figure 1.

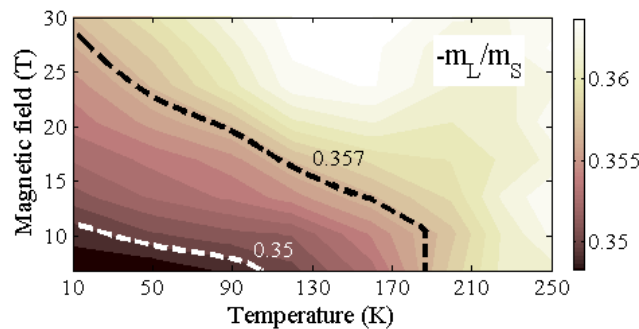


Figure 1: Evolution of the  $m_L/m_S$  ratio of Rhenium measured at 64 points of the  $B$ - $T$  space

A comparison of the field and temperature dependences of the rhenium XMCD and bulk magnetization shows that the Re sublattice is magnetically softer and more sensitive to the temperature increase at  $T < 150$  K. The results are explained within a scenario of field induced phase coexistence and transition between two monoclinic phases of diverse magnetocrystalline coupling, which plausibly explains the colossal magnetoresistance observed in the compound studied. [4] We demonstrate that XMCD spectroscopy can successfully be combined with pulsed magnetic field generation providing an element selective technique for systematic study of the spin and orbital behavior under extreme magnetic fields

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# Structure-Function Studies in Heterogeneous Catalysis

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X-ray absorption spectroscopy (XAS) is a well-established materials characterization technique with many uses in homogeneous/heterogeneous catalysis research. This element-specific, local-order sensitive spectroscopy has a number of unique features to carry out catalytic studies. Namely, it does not perturb the catalyst and the reaction, can be used at variable pressure and temperature and, in most cases, in presence of gases or liquids, making it ideal for *in-situ* studies. Time-resolved and, particularly, energy-dispersive XAS corresponds to an experimental approach with a characteristic absence of movement of the optics, having significant advantages with respect to conventional approaches related to a constant energy scale, a stable focal spot, and a significantly enhanced temporal resolution, down to the millisecond with current technology.

In this presentation we will review recent investigations which exploit the above mentioned main advantages of novel XAS spectroscopies/methodologies and provide a route to new electronic and geometric information, encompassing oxidation-state, coordination symmetry and number, and interatomic distances, in the context of spatial- and time-resolved and/or *in-situ* studies of catalytic processes. Both near-edge structure (XANES) and extended fine structure (EXAFS) data will be examined with topics including two and three-dimensional spatial/chemical mapping of solid catalysts, the measurement of femtometre-scale atomic displacements under external perturbations, and the characterization of heterogeneous catalysts evolution under real, *operando* conditions. *In-situ, operando* investigations described here in detail concern the synchronous XAS/UV-visible/Infrared/Raman/Mass-spectrometry analysis of; *i*) the temporal evolution of complex, multicomponent solid catalysts having a considerable number of “active” chemical species, e.g. four or more [1]. Also, *ii*) bimetallic catalysts for hydrocarbon activation reactions [1,2]; *iii*) redox-type multicomponent-oxide catalysts for CO and small molecules activation [3]; and, *iv*) heterogeneous three way catalysts used as automobile gas exhaust cleaning systems under strong gas-phase/temperature (the so-called lambda/temperature oscillations) dynamic conditions [4].

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# In Situ Redispersion of Platinum Nanoparticles Supported on Ceria-Based Oxide for Auto-Exhaust Catalysts

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Platinum (Pt) in particular is found at the core of catalysts used for the cleaning up of motor vehicle exhaust emissions. When the exhaust catalyst is exposed to high temperatures (800°C and above), the highly-dispersed Pt nanoparticles agglomerate and sinter, decreasing the active surface area (i.e. degradation). Exhaust gases exiting from petrol engines fluctuate quickly between oxidative and reductive compositions during vehicle operation. Therefore, in-situ dynamic observation on the sintering and redispersion phenomena of the precious metal in the automotive catalysts is very important indeed. Real-time observation of the sintering/redispersion behaviour

of Pt on ceria-based oxide was made possible by the fluorescence yield variant (Turbo-XAS) of DXAFS [1, 2]. Fig. 1 shows the variation of the white line peak height of the normalised Pt L<sub>III</sub> edge XANES for the Pt particles supported on Ce-Zr-Y mixed oxide (CZY) under cyclical redox condition at 400 ~ 800°C [3].  $\Delta I$  denotes the difference between the white-line peak height of the oxidized and reduced samples. From a previous experiment, we found that the  $\Delta I$  increased with the decreasing particle size of Pt. Using the correlation between the Pt particle size and  $\Delta I$ , we observed that the Pt particle size

got bigger and smaller according to the temperatures. Especially, it is interesting to note that the sintering and redispersion phenomena are caused reversibly in a simulated flowing exhaust by controlling temperature. This kind of Pt redispersion on CZY is reasonably attributed to the strong Pt-ceria support interaction. In the workshop, in-situ TEM observation on redispersion will be presented.

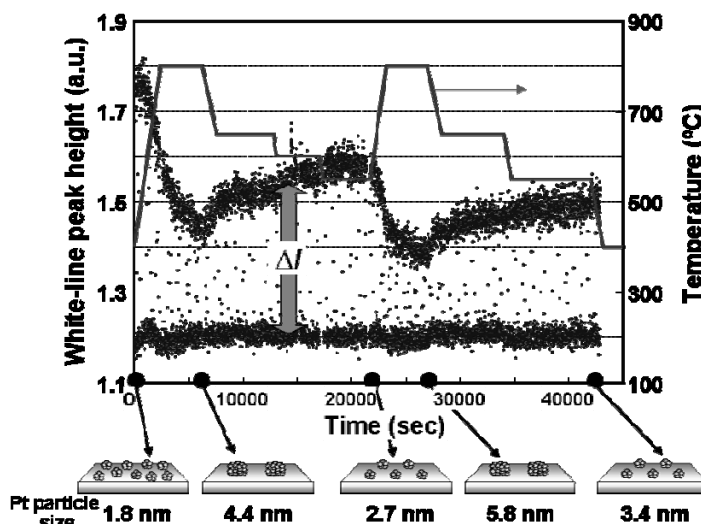


Figure 1: Temporal dependence of the white line peak height of the Pt L<sub>III</sub> edge XANES for the fresh 2 wt% Pt/CZY catalysts under oxidizing/reducing atmosphere at 400~800 °C and the schematic representation of the sintering/redispersion. 4 or 20% O<sub>2</sub>/He gas and 3% H<sub>2</sub>/He gas were alternately introduced into the cell every 60 seconds.

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# State of the Art Quick-EXAFS: Applications in Catalysis

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Time resolved XAFS experiments can be performed in the so-called Quick-EXAFS (QEXAFS) mode, where the spectrum is collected “on-the-fly” within only a couple of seconds using a stable double-crystal monochromator [1]. This technique is well suited for in situ investigations of catalytic reactions [2]. Piezo driven tilt tables oscillating the monochromator crystals allow the continuous recording of XANES scans with repetition rates of about 100 Hz, depending on photon flux and sample quality [3]. Latest experiments even enable the acquisition of full EXAFS spectra with a scan range of typically 1 keV - up to about 2.5 keV - at a repetition rate of 10 Hz, i.e. 50 ms/spectrum. The optimized monochromator design used for such experiments employs a channel cut crystal, a cam driven tilt table for rapid angular oscillations [4] and a fast readout system for the Bragg angle [5]. Using cryogenic cooling, the silicon crystal can cope with the full heat load from third generation undulator sources, e.g. at the APS, and excellent data quality can be obtained [6]. Since a fast sequential energy scanning technique is used the detection of fluorescence radiation or surface sensitive techniques can be directly applied, which is important for dilute samples like catalysts. Additionally, a reference sample can be monitored simultaneously with each measurement to detect even minor edge shifts reliably. Even XANES micro tomography on active catalysts becomes feasible using the fast scanning monochromator with refractive X-ray lenses for beam focusing [7].

The technical developments of the QEXAFS technique, its current state and the most challenging results are presented. QEXAFS has become very attractive for the investigation of catalysts, and several dedicated facilities are in operation or planned worldwide. Recent scientific investigations - especially from SOLEIL and the new, dedicated QEXAFS monochromator at the SLS [8,9] - demonstrate the state of the art.

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# An Energy Dispersive X-ray Absorption and X-ray Diffraction Study of Photomagnetic CoFe Prussian Blue Analogues

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Recent years have seen the discovery of unusual electronic properties in Prussian blue analogues and derivatives. Thus, some CoFe Prussian blue analogues exhibit a photomagnetic effect due to the photo-induced  $\text{Co}^{\text{III}}(\text{Low Spin})\text{-Fe}^{\text{II}} \rightarrow \text{Co}^{\text{II}}(\text{High Spin})\text{-Fe}^{\text{III}}$  electron transfer accompanied by the spin change of the Co ion and a significant bond lengthening of the Co to ligand bond. Such systems undergoing a reversible and controlled change of their physical properties under external stimuli offer promising perspectives for the realization of nano-scale electronic devices provided that their properties fulfill the conditions of application (working temperature, switching speed). To achieve this goal in a rational way, it is necessary to understand the origin of the phenomenon. We are therefore engaged in the study of the switching properties of those compounds for several years.

Energy Dispersive X-ray Absorption, X-ray magnetic circular dichroism and X-ray Diffraction were used to study the switching properties of CoFe Prussian blue analogs and these techniques turned out to be particularly fruitful. The photo-induced electron transfer, the appearance of antiferromagnetic exchange interaction between the transition metal ions in the  $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$  metastable state at low temperature[1] as well as local and long range structural changes accompanying the photo-induced electronic event were thus evidenced.[2] More recently, a variable pressure Energy Dispersive X-ray Absorption and X-ray Diffraction study of a pressure-induced  $\text{Co}^{\text{II}}(\text{High Spin})\text{-Fe}^{\text{III}} \rightarrow \text{Co}^{\text{III}}(\text{Low Spin})\text{-Fe}^{\text{II}}$  electron transfer has shown interplay between structural and electronic events and a structural distortion of the  $\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$  ground state, which probably plays an essential role in the switching properties of the compounds.[3]

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# DXAFS at the Photon Factory

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Time-resolved XAFS studies using DXAFS techniques has restarted at a dipole beamline BL-9C in 1999 after a long blank after the early pioneering DXAFS works by Prof. Matsushita and Dr. Oyanagi. The time-resolution was limited owing to the limited flux from the dipole magnet.

A beamline NW2A with a tapered undulator source was constructed at PF-AR in 2004 [1]. The performance of the DXAFS system at NW2A is reported by Inada [2]. Comparison of some detectors such as photodiode array with/without some phosphors, CCD and PAD will be summarized. Also the effect of scattering from catalyst substrates will be shown.

PF-AR is a unique storage ring that is always operated as single-bunch, *ca.* 100ps long pulse comes every 1.26 $\mu$ s. The rather large emittance of 293 nrad enables the high current, 60mA, and gives fairly flat  $I_0$  within a DXAFS spectrum energy region. Trials to get a DXAFS spectrum with single shot exposure are made with various kinds of detectors such as CCD and PAD. Single pulse expose DXAFS spectrum of nickel foil is taken with a specially modified XSTRIP detector [3]. Although the signal-to-noise is limited, it suggests the possibilities of DXAFS experiments in ps time-scale in near future.

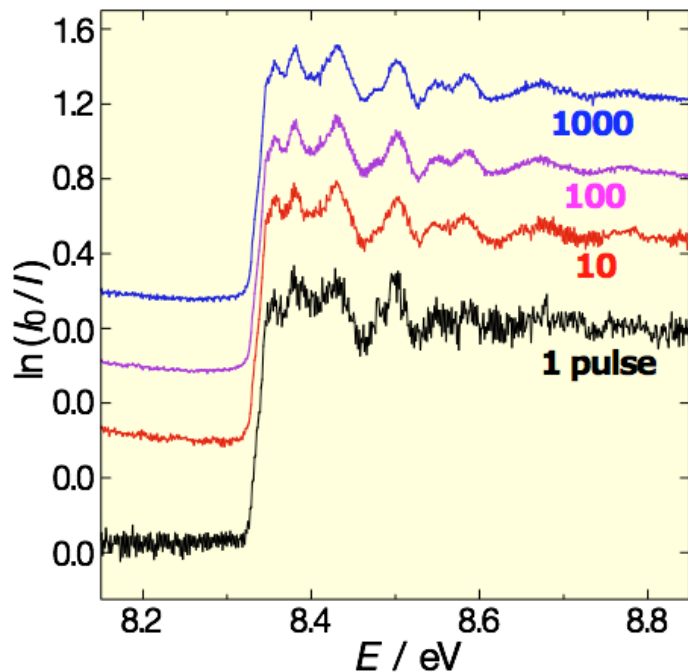


Figure 1: Ni K-edge DXAFS spectra with single to 1000 shots

DXAFS activities in SPring-8 will be also reported.

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# The ODE Beamline at SOLEIL: First Results on XMCD and EXAFS under Extreme Conditions and Kinetics Experiments

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The new dispersive absorption beam line ODE, recently built at the Synchrotron SOLEIL, will be presented.

In the "dispersive mode" the use of a bent monochromator eliminates the need for a stepwise scanning of the X-ray energy (Figure1). The suppression of any mechanical movement combined with the strongly focusing optics allows short acquisition times, small spot size and a greatly improved stability during the measurements. These features are particularly suitable for high-pressure experiments, X-ray Magnetic Circular Dichroism (XMCD) and kinetics measurements.

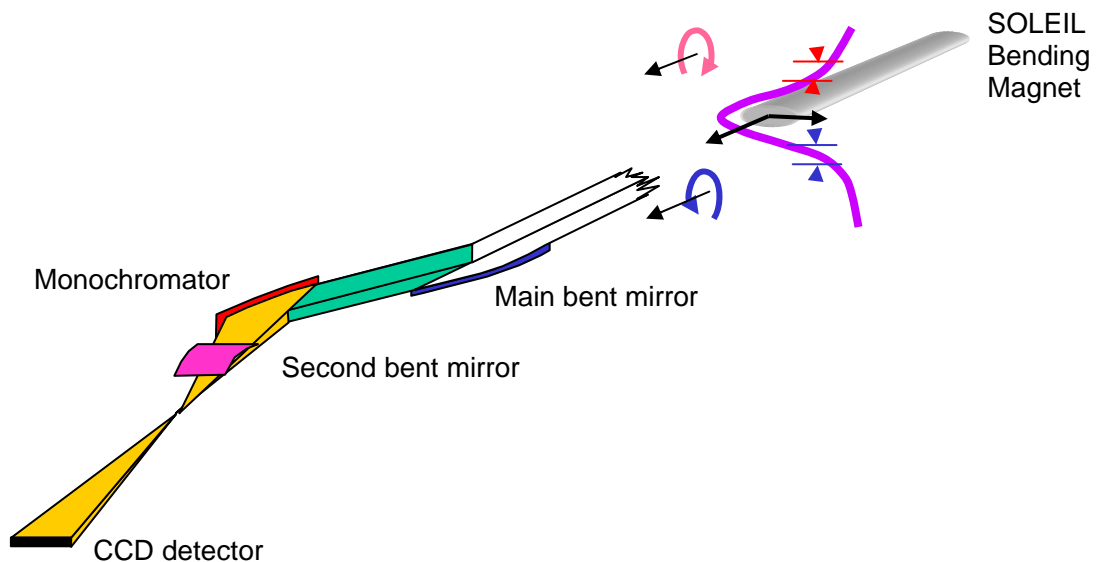


Figure 1: Dispersive XAFS set-up installed on the ODE beamline

The ODE beamline, opened to external users since the beginning of 2008, allows absorption measurements in the 3.5 – 23 keV energy range with, at present, a minimum spot size of  $20 \times 35 \mu\text{m}$  FWHM. The choices taken for the optics and the other constitutive elements of the beamline will be discussed, as well as the technical problems encountered during the beamline set-up and the solutions adopted. Further improvements of the optical performances, already planned, will be examined as well.

The specific set-ups for extreme conditions, XMCD and kinetic measurements allow carrying out measurement in the 0-100 GPa quasi-hydrostatic pressure range (or higher pressure in non-hydrostatic conditions), in the 2.5 – 1100 K temperature range and for a 2 Tesla magnetic field (7 Tesla in the near future). The short acquisition times allow to follow chemical reactions in the tenth of second range. A survey of some scientific results obtained so far will illustrate the performances achieved.

# First Results from a Dispersive EXAFS Beamline at Indus-2 Synchrotron Source

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A dispersive EXAFS beamline has been developed at BL-8 bending magnet port of the 2.5 GeV Synchrotron source (Indus-2) at Raja Ramanna Centre for Advanced Technology, Indore, India. The beamline employs a bent crystal polychromator which is used to bend a profiled Si(111) crystal in the shape of an elliptical cylinder such that the source and the sample positions fall at the two foci of an ellipse. The bent crystal, selects a band of energy from the white synchrotron light, disperses and focuses it horizontally at the sample position to enable simultaneous measurement of X-ray absorption spectra in the energy band of 5-20 keV. A mirror is appropriately placed before the crystal to cut off the higher energy part of the radiation and to vertically focus the beam at the sample position. With the arrangement a 200 $\mu\text{m}$ (H) x 150 $\mu\text{m}$ (V) focus spot is obtained at the sample position for the synchrotron beam having 1.5 mrad horizontal and 0.2 mrad vertical divergences. The beam upon transmission through the sample gets defocused and fills the entire sensitive area of the position sensitive CCD detector, which enables simultaneous recording of the whole absorption spectrum in a very short period of time.

The X-ray absorption spectra of Mo and Nb foils were measured at 20000 eV setting and from the known values of the K absorption edges of Mo and Nb, the CCD channels were calibrated in terms of energy. An energy resolution of  $\sim 2$  eV per channel obtained corresponded to the designed value. The absorption spectra of pure MoO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> powders were also studied to measure shifts in the absorption edges of these elements on oxidation. The results were found to agree well with the reported values in literature. The EXAFS spectrum of Bi<sub>2</sub>O<sub>3</sub> powder was recorded around 13000 eV to obtain radial distribution function. By fitting the first shell of the radial distribution with the theoretically generated spectrum assuming a monoclinic crystal structure, the Bi-O nearest neighbour distance was found to be 2.23 $\text{\AA}$ . This result agrees well with the reported value in literature. In conclusion, the first results from newly developed EXAFS beamline at Indus-2 are found to be in excellent agreement with those reported in literature which implies the excellent performance of the beamline

# The LNLS Dispersive XAS (DXAS) beamline

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The Brazilian synchrotron light laboratory (LNLS) located in Campinas, Brazil, is a National Laboratory that encompasses a number of open facilities, including a second generation 1.37 GeV synchrotron light source, an electron microscopy center and a structural biology center. The light source has been in operation since 1997 and currently 14 beamlines are available for external users. Seven beamlines are dedicated to scattering and diffraction techniques and the other seven are dedicated to X-ray absorption spectroscopies, covering photon energies from a few eV up to 25 keV.

The DXAS beam line is mounted on a bending magnet port, covering the 5-14 keV energy range. The number of submitted proposals is continuously increasing since the beamline opening for users in 2004. Every year, around 25 proposals are executed involving experiments in such diverse areas as time-resolved analysis of catalysts, electrochemistry, XMCD/XMRS and materials under high pressure and high magnetic field conditions.

In this talk, we will present the current status of the LNLS DXAS beamline, including its optics, some operational parameters and the instrumentation available for users. Highlights of recent results will be utilized to demonstrate the beamline capabilities. Finally we will present some perspectives and planned upgrades.

# Energy Dispersive EXAFS at Diamond Light Source

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The Versatile Spectroscopy beamline at Diamond Light Source, I20, is currently being designed and built, and aims to begin operation in late 2009 and early 2010. The beamline consists of two independent experimental end-stations operating from a pair of canted wigglers located in a 5m diamond straight section. One branch of the beamline will deliver monochromatic x-ray radiation of high spectral purity to one of the experimental hutches, whilst the other branch will constitute an energy dispersive spectrometer. The design of the beamline allows both branches to operate simultaneously.

The energy dispersive spectrometer will take its radiation from a 750mm multipole wiggler that will deliver a divergence fan of x-rays in the energy range from 6keV to 26keV. The design of the beamline is optimized to deliver a spectral bandpass of 10% across the entire operating energy range from a Bragg geometry polychromator. Two crystal cuts will be used: Si(111) and Si(311).

The dispersive branch is principally optimized for time resolved experiments, and will take advantage of two state of the art micro strip detectors, one silicon based and optimized for low energies and one germanium based to be used for high energies. To maximize the utility of the end-station the experimental area will be equipped with a suite of sample environment equipment to facilitate multi technique time resolved measurements. The aim is to combine Energy Dispersive EXAFS with techniques including mass spectrometry and IR and UV-Visible optical spectroscopy.

# TE-XAS Project, Scientific Opportunities and Technical Challenges

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After 12 years of operation and constant evolution, the ID24 beamline has clearly demonstrated the unique potential of the EDXAS technique coupled with insertion devices on 3<sup>rd</sup> generation synchrotron sources. The high flux, the decrease of focal spot size and the fast time resolution has opened new scientific opportunities like hyperspectral mapping or studies under extreme P, H, T conditions. The full exploitation of these scientific opportunities requires a new beamline design based on new stability standards, optimized optics and new generation of EDXAS detectors.

This project named TE-XAS (Time resolved and Extrême condition XAS) is part of the upgrade programme of the ESRF. It foresees the construction of a double branch EDXAS beamline on the ID24 port and of the renovation of the standard ESRF EXAFS beamline BM29. In this presentation, starting from the present performance and drawbacks of ID24, we will describe the goals and the rationale of the TE-XAS project.



Figure 1: General view of the TE-XAS project.

# Ray Tracing Simulations for Optical Configurations

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One of the main goals of the ESRF Upgrade Programme is to characterize materials at nanoscale. For that, it is essential to focus the x-ray beam down to sub-micrometer, or better, nanometer spots. As the ESRF source size (10-400  $\mu\text{m}$  RMS) will not be significantly reduced, the only way to reduce the spot size is to use optical systems with high demagnification. From the engineering point of view it is desirable to use a minimum of elements to minimize figure errors, vibration stability and absorption. The use of long beamlines will allow for large demagnification values using a single element. In such configuration of constant source size and constant beamline length, the spot size is limited by the diffraction limit and the demagnification factor. However, even assuming perfect optical surfaces (Cartesian), the demagnification factor is limited because perfect imaging cannot be accomplished with a single optical element (the Abbé sinus law cannot be fulfilled). I discuss here the spot sizes that can be produced using ESRF x-ray beams, and their limits in terms of maximum demagnification and figure errors (approximated surfaces). The particular case of a polychromator (Bragg or Laue) will be analysed and the effects of crystal shape and thickness will be treated in connection to the minimum spot that can be produced.



# Beyond the Geometric toward a Wave Optical Approach in the Design of Curved Crystal and Multilayer Optics for EDXAS

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The performance optimization of the optical components in an EDXAS set-up is fundamental, in view of a further improvement of the technique.

In particular the polychromator plays an essential role in the achievement of a stable (in position and size) sub-micrometer spot that is one of the main improvements expected in the optics for EDXAS.

Together with the technological limitation in the optics manufacture - such as surface roughness or the homogeneity of the practically achievable bending, optical performances are also limited when the design is based on a purely geometrical approach.

In this study we will analyze the main intrinsic limitations of a geometrical approach, indicating how to overcome such limitations and how to use wave-optical effects to improve the optics performance.

In transmission geometry the focusing properties are mainly affected by the spreading over the Borrmann triangle. However, using typical dynamical diffraction effects, focusing of the beam can be obtained even without any bending, using the curvature of the dispersion surfaces [1]. This effect is counterintuitive, when using a geometrical approach, but can be combined with the usual geometrical focus of a bent polychromator, thus widely improving the focusing performances [2].

Apart from the technological considerations related to surface and interface roughness, the focusing performances in reflection geometry are typically limited by the penetration length of the wave. Indeed, both using Bragg curved crystals or elliptically shaped multilayers, the beam penetration cannot be easily neglected, in particular on a sub-micrometer scale [3]. Analytical derivations of the caustic shape, using a simplified model combining refraction and penetration, put a lower limit on the focal spot size obtained using a purely geometrical approach.

A combination of refraction and diffraction effects can be anticipated as a further step for reducing the focal size while optimizing the intensity, both in Laue and Bragg geometry [4]. The requirement of the full integration of a wave-optical approach in the polychromator design, including also dynamical diffraction theory appears then a necessary task, if one wants to achieve a significant improvement of the optics quality.

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# Ray Tracing Simulations for Bendable Crystals in Bragg Geometry

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ODE beamline uses dispersive XAFS to analyze local environment in material science. The advantages of this technique are the short acquisition time and the great stability during the measurement but require a focused beam without angular striations. From Hook's law, we review the main parameters of the bending crystal involved in the focalization: thickness, triangular or torpedo shape and their effect on the beam degradation. Experimental and simulated results are compared and analyzed for several energies using a ray tracing.

# XH Ge Microstrip Detector for EDXAS

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XSTRIP for High Energies (XH) is a new detector system developed between Daresbury Laboratory (DL) and Lawrence Berkeley National Laboratory (LBNL) specifically for EDXAS at 3rd generation synchrotrons.

XH has derived from a long history of strip detector developments at DL starting with the Si photodiode array based systems in the 1990's then moving on to the Si XSTRIP detector implementation early in 2001. Limitations of these Si based systems for EDXAS lead to the commissioning of the XH detector to enable experiments up to energies of 40keV with high efficiency, good spatial performance, long system lifetime and excellent frame rates.

This paper will briefly discuss the early DL developed systems and their limitations. It will then look at the detailed specification of the XH detector and its performance. We will then look at the near term enhancements of this detector followed by the longer term future direction for development in this area.

# Sample Environment on ID24

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A number of sample environment applications currently in use on ID24 have been developed by the ESRF Sample Environment Support Service. These include cryostats providing temperatures down to 3 Kelvin and furnaces to above 1000 °C; pressures up to 1Mbar are available and pulsed magnetic fields up to 30 Tesla. Few beamlines can present this wide range of extreme conditions. This contribution describes the constraints and the advantages of working in dispersive mode which lead to this success. Some examples of equipment will be presented.

# **EDXAS: a Great Technique. Why is it so Difficult?**

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In principle the EDXAS technique is simple. Once the beamline optics and the sample have been aligned there are no moving parts during data acquisition. This methodology should produce data of high quality and high reproducibility. However, experience has shown that the quality of the data obtained is highly sensitive to alignment issues, mechanical (in)stabilities, source instabilities, material choices and surface degradations of optical components.

Over several years the quality of data has been improving at ID24. The measures that have been taken to achieve these improvements are described together with possible improvements that could be envisaged in the future.

# Poster Abstracts

# List of Posters

	Poster number	Page
<b>XRMR Determination of the Magnetic Contribution to the Dispersive Part of Susceptibility by Shifts of Kiessig.....</b>	<b>C1</b>	39
<u>Andreeva M.A.</u> , Odintsova E.E., Dufour C., Dumesnil K., Rogalev A., Smekhova A., Wilhelm F.		
<b>Dynamical Focussing by Elliptical Laue Bender at ID-24 Dispersive EDXAS Beamline of ESRF .....</b>	<b>C2</b>	40
<u>Bhattacharyya D.</u> , Mathon O. and Pascarelli S.		
<b>EDXAS: Improvement in Bragg Crystal Bender Design for Polychromator.....</b>	<b>C3</b>	41
<u>Borrel J.</u> , Mathon O., Mairs T.R.		
<b>The Magnetostriction of Amorphous FeCoB Alloys studied at Atomic Level by Differential EXAFS.....</b>	<b>C4</b>	42
<u>Díaz J.</u> , Quirós C., Alvarez-Prado L.M., Aroca C., Ruffoni M., Pascarelli S.		
<b>Do you really need EDXAS to perform High Pressure Experiments? .....</b>	<b>C5</b>	43
<u>Itié J.P.</u> , Polian A.		
<b>Energy-Dispersive XAFS Station for Wide-Energy Range at BL28B2, SPring-8.....</b>	<b>C6</b>	44
<u>Kato K.</u> , Uruga T., Tanida H., Teramura K., Imai H., Imai Y., Irie T.		
<b>Dynamic Structural Change of Pd-Perovskite Automotive Catalyst Studied by Dispersive XAFS at SPring-8 BL14B1 .....</b>	<b>C7</b>	45
<u>Matsumura D.</u> , Okajima Y., Nishihata Y., Mizuki J., Taniguchi M., Uenishi M., Tanaka H.		
<b>Measurement of Individual Bond Magnetostrictive Strain in a-TbFe<sub>2</sub>.....</b>	<b>C8</b>	46
<u>Pascarelli S.</u> , Ruffoni M.P., Trapananti A., Mathon O., Pasquale M., Magni A., Sasso C.P., Celegato F., Olivetti E.		
<b>EXAFS Measurements on Sorption of Uranyl Ions onto Alumina and Kaolinite at INDUS-2, RRCAT, Indore .....</b>	<b>C9</b>	47
<u>Poswal A.K.</u> , Jha S.N., Bhattacharyya D., Kumar S., Jain A., Tomar B.S., Manchanda V.K. and Sabharwal S.C.		
<b>EXAFS Measurements on Crystalline Pb<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub>.....</b>	<b>C10</b>	48
<u>Poswal A.K.</u> , Bhattacharyya D., Sangeeta, Jha S.N. and Sabharwal S.C.		
<b>Strong Correlated Systems under Pressure using X-ray Absorption Spectroscopy .....</b>	<b>C11</b>	49
<u>Ramos A.Y.</u> , Souza-Neto N.M., Piamonteze C., Tolentino H.C.N., Itié J.-P., Flank A.-M., Lagarde P., Morales L., Canero A.		
<b>Performance Degradation in Direct Methanol Fuel Cells by Ru Dissolution and CO Poisoning.....</b>	<b>C12</b>	50
<u>Schökel A.</u> , Roth C.		
<b>The Originality of MARS: Dispersive and Standard XAS in One Beamline .....</b>	<b>C13</b>	51
<u>Sitaud B.</u> , <u>Solari P.L.</u> , Lequien S., Schlutig S. and Moreno T.		
<b>Decomposition of FeTiO<sub>3</sub> Perovskite to (Fe<sub>1-δ</sub>,Ti<sub>δ</sub>)O and Fe<sub>1+δ</sub>Ti<sub>2-δ</sub>O<sub>5</sub>.....</b>	<b>C14</b>	52
Wu X., Steinle-Neumann G., Narygina O., Kantor I., McCammon C., Prakapenka V., Swamy V., and <u>Dubrovinsky L.</u>		

<b>Characterization of the Lithium Battery Materials during their Functioning.....C15</b>	<b>53</b>
Ouvrard G., <u>Zerrouki M.</u> , Soudan P., Morcrette M., Masquelier C., Shu J., Belin S., Leriche J. B., Baudelet F.	
<b>Combined In Situ XAS and EDXRD Study of the Hydrothermal Formation of Nanostructured Transition Metal Oxides.....C16</b>	<b>54</b>
<u>Zhou Y.</u> , Pienack N., Bensch W., Grunwaldt J.-D., Patzke G. R.	



# XRMR Determination of the Magnetic Contribution to the Dispersive Part of Susceptibility by Shifts of Kiessig Oscillations

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Magneto-Optical constant determination for X-rays in vicinity of the absorption edges remains one of the important experimental challenges in materials science. XMCD measurements give only the imaginary part of the refractive index (after proper but not reliable normalization). In soft X-ray region Faraday rotation and the shift of the Bragg peaks are successfully used for the absolute determination of the refractive part of this term. Here we have used the shift of the Kiessig oscillations on the reflectivity curves measured for the right and left circular polarized radiation in L-MOKE geometry for the direct determination of the refractive index in the hard X-ray range. The physics behind this effect is obviously the different phase shifts for the multiple reflected right and left circularly polarized waves in a magnetized thin film.

The sample Nb(4 nm)/YFe<sub>2</sub>(40 nm <110>)/Fe(1.5 nm)/Nb(50 nm) has been epitaxially grown on a sapphire substrate at the LPM, University of Nancy. YFe<sub>2</sub> is known to be a soft ferrimagnet [1], in which Y atoms carry a magnetic moment of *ca.* 0.4  $\mu_B$ . The X-ray reflectivity curves and corresponding asymmetry ratio have been measured at different energies near the Y L<sub>2,3</sub> edges (L<sub>3</sub>: 2071 – 2095 eV, L<sub>2</sub>: 2145 – 2185 eV). Results for the L<sub>3</sub> are reproduced in Fig.1. For data analysis we have used a modified version of the software package ASYM [2] that is based on the general theory of reflectivity.

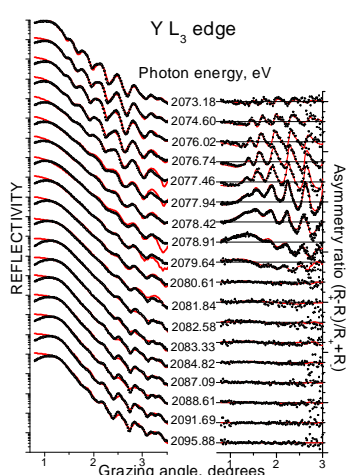


Fig. 1

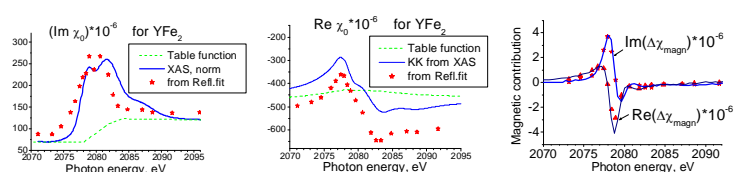


Fig. 2

Fit of the data provides us with the exact structure of our film and the complex susceptibility  $\chi_0$  and  $\Delta\chi_{\text{magn}}$  in YFe<sub>2</sub> layer as a function of energy (symbols in Fig. 2). These dependences are compared with properly normalized XAS, XMCD spectra and their Kramers-Kronig transforms (blue lines in Fig. 2). Excellent agreement of the results is observed though there is a difference of the absolute values for  $\text{Re}\chi$ .

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## Dynamical Focussing by Elliptical Laue Bender at ID-24 Dispersive EXAFS Beamline of ESRF

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Bent crystals in transmission/Laue configuration are generally used as dispersive-cum-focussing elements in energy dispersive set up for X-ray absorption and scattering experiments since the reflectivity profile of Laue crystals remain symmetric over a large energy range leading to better energy resolution. The energy dispersive EXAFS beamline ID-24 at ESRF employs an inter-changeable Bragg-Laue polychromator set up to cover a wide energy range for carrying out a variety of X-ray absorption experiments. However, in the transmission geometry, the spreading of the wavefields inside the so called “Borrmann fan” effectively increases the divergence of the beam at the exit surface of the crystal. The beam carries the footprint of the Borrmann fan along with its geometrical path and this causes significant broadening of the geometrical focus spot. However, it had been found that with a particular choice of crystal thickness and detector distance, the Borrmann fan can be focussed on an image plate due to a combined effect of interference of the different wave fields inside the Borrmann fan and Fresnel’s diffraction in air. Motivation of the present paper is to investigate the focalisation of the Borrmann fan by the bent Laue crystal of the ID-24 beamline of ESRF to achieve a reasonably small geometrical focal spot.

Measurements of geometrical focal spots at various distances from the crystal have been carried out with Si (111) crystal used in Laue geometry at two representative energies of 8 keV and 22 keV at the ID-24 Dispersive EXAFS beamline. The experiment has been carried out separately with crystals having thickness of 200  $\mu\text{m}$  and 300  $\mu\text{m}$  for each of the energies mentioned above. In all the cases it has been observed that the size of the geometrical focal spot increases on average as the focal distance increases. However, due to the dynamical focusing of the Borrmann fan along with the geometrical focusing, the size of the focal spot is found to be smaller than the expected value at a particular focal distance depending on the energy and thickness of the crystal, where the dynamical focal distance and the geometrical focal distance coincide. The theoretical focalisation distances of the Borrmann fan have been estimated using the existing theory for an incident spherical wave at the entrance surface of a flat crystal and theoretical results have been compared with the experimentally observed values which are found to agree well. The small difference observed between the experimental values and theoretically predicted values may be attributed to the fact that the theoretical estimation presented above has been carried out assuming a perfectly cylindrically bent crystal whereas in the actual experiment the crystal is bent to an elliptical or hyperbolic profile to reduce spherical aberration. To investigate the focusing of Borrmann fan further, an experiment has also been carried out with flat (without any intentional bending) crystal and compared with the corresponding theoretical value. The horizontal FWHM of the focal spots have been obtained experimentally at the positions where the dynamical focusing and geometrical focusing coincide and the corresponding theoretical values for the FWHM of the focal spots have been estimated for the 8 keV case where the absorption coefficient of the crystal is significant. It has been observed that the FWHM values agree well with each other at this photon energy for both the thickness of the crystal.

## EDXAS: Improvement in Bragg Crystal Bender Design for Polychromator

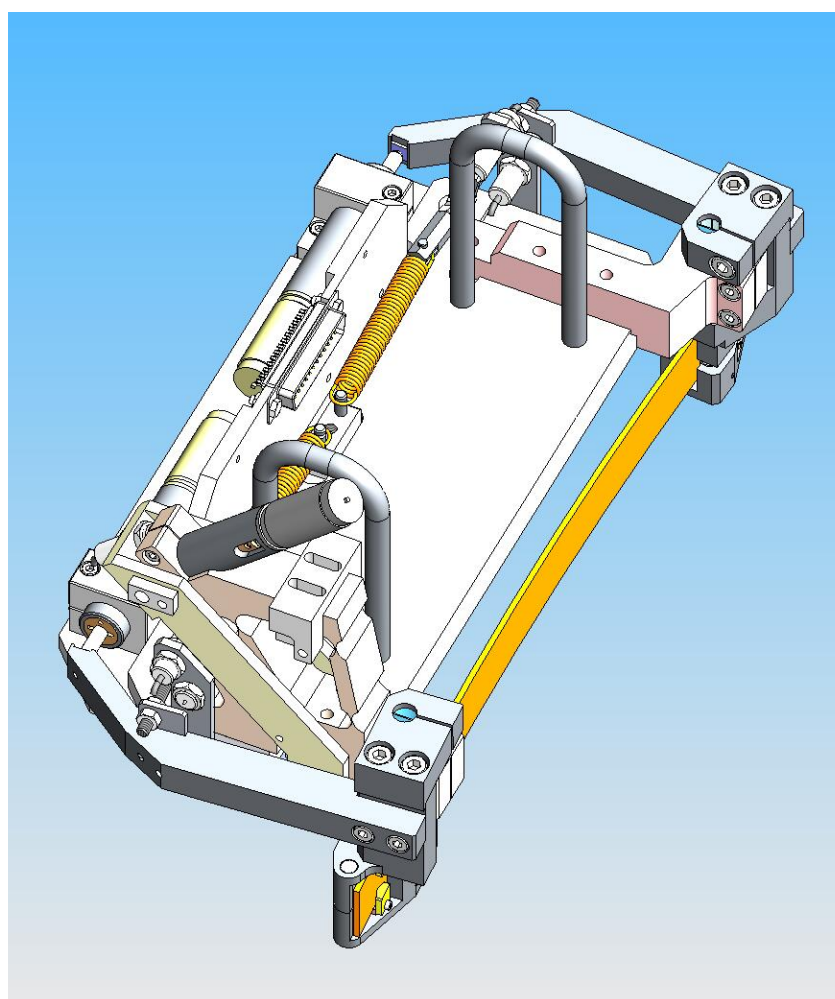
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The precision and stability of the curvature of the Bragg crystal in the Polychromator is critical for the quality of experimental data. The adjustment of the focal spot onto the sample at each change of energy has been very time consuming for scientists coming to ESRF for only few shifts.

Repeatability and possible automation were the goals we wanted to meet when it was decided to upgrade the Polychromator of the ID24 beam line at ESRF.

The new design and the improvement in the operation will be described. It shows that improvements in stability repeatability of the shape of the bent crystal has been achieved leading to reduced time finding the best focal spot.



## The Magnetostriction of Amorphous FeCoB Alloys studied at Atomic Level by Differential EXAFS

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The Fe and Co atomic environments that caused the magnetostrictive properties of FeCoB amorphous alloys were identified by Differential EXAFS [1]. The alloys were prepared in the form of thin films by magnetron sputtering with different relative concentrations of Fe, Co and B, with this last element introduced to amorphize the alloys. The magnetostriction constant  $\lambda$  was isotropic in all the films, and ranged from 30 ppm ((Fe<sub>80</sub>Co<sub>20</sub>)B<sub>20</sub>) to -20 ppm ((Fe<sub>10</sub>Co<sub>90</sub>)B<sub>20</sub>) [2]. EXAFS characterization showed disordered bcc environments for Fe and Co, and a stronger affinity of Fe to be bonded to B than Co. Differential EXAFS detected significant variations in the Fe environments with applied magnetic fields. They were not observed in the Co environments, showing that only the Fe environment determined the magnetostrictive properties of the FeCoB alloys. Moreover, the Fe environments that modified their bond length with the applied magnetic fields resulted to be different from those detected by EXAFS. This indicates that only certain Fe environments participated in the magnetostriction of the alloys. Changes in the Co environments with applied magnetic fields were measured only in the alloy with the highest Co concentration, and they were of a negative sign, as expected from its macroscopic  $\lambda$ . This is an example of how much chemically selective this technique is to identify the causes of magnetostriction in complex materials and compounds.

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## Do you really need EDXAS to perform High Pressure Experiments?

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Until recently, high pressure X-ray Absorption Spectroscopy (XAS) was performed using energy dispersive set-up, mainly because this technique was well-suited to overcome the specific drawbacks due to the use of diamond anvil cells. In this presentation we will show that now with highly focused classical XAS beamlines operating in third generation synchrotron, the majority of these drawbacks can be avoided. Therefore the choice between scanning or energy dispersive set-ups will strongly depend on the specificity of the planned experiments: energy of the edge, measurements at one or more edges, time resolved requirement, diluted sample or not, .... The advantages and limitations of the two possible set-ups will be discussed and illustrated.

## Energy-Dispersive XAFS Station for Wide-Energy Range at BL28B2, SPring-8

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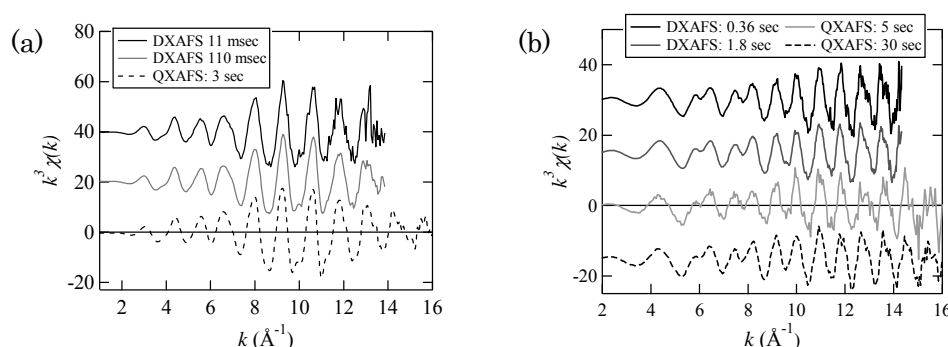
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Energy-dispersive XAFS (DXAFS) station has been constructed at the bending magnet beamline BL28B2 at SPring-8 to study local structural changes of materials during chemical reactions or functional processes[1]. The bending magnet source at SPring-8 has a high photon flux at energy range higher than 50 keV. The purpose of this station is to measure DXAFS spectra in the wide energy range from 7 to 50 keV covering K-edges of lanthanides. Main components of the station are a mirror to reject higher harmonics, a polychromator with a bent silicon crystal, and a position-sensitive detector (PSD). The crystal is used in Bragg geometry in the energy region from 7 to 12 keV. The polychromator crystal is a symmetrically cut Si (111). At the higher energy region, the polychromator is switched to Laue configuration with (hkk) net plane, such as (422) and (311). The PSD used is CCD (spatial resolution, 9.9 micrometer; time resolution, 6 msec) coupled with a fluorescent screen and a lens system. The fluorescent materials and their thickness were optimized for measurement in the x-ray range.

Figure 1 (a) shows  $k^3\chi(k)$  DXAFS spectra for Pd foil at Pd K-edge (24.3 keV) together with a Quick-XAFS(QXAFS) spectrum measured at the conventional XAFS beamline BL01B1. Good quality spectra can be obtained with exposure time of about 10 msec for standard samples. Figure 1 (b) shows  $k^3\chi(k)$  DXAFS spectra for a CeO<sub>2</sub> pellet at Ce K-edge (40.5 keV). The DXAFS method provided good quality spectra of the signal to noise ratio at 40 keV with time resolution of about 0.36sec for standard samples.



**Figure 1:**  $k^3\chi(k)$  DXAFS spectra for Pd foil at Pd K-edge (24.3 keV) (a) and  $k^3\chi(k)$  DXAFS spectra for CeO<sub>2</sub> pellet at Ce K-edge (40.5 keV) (b) together with QXAFS spectrum measured at XAFS beamline BL01B1.

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# Dynamic Structural Change of Pd-Perovskite Automotive Catalyst Studied by Dispersive XAFS at SPring-8 BL14B1

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The beamline BL14B1 of SPring-8 was established by Japan Atomic Energy Agency for study of materials science with white and monochromatic x-rays from a bending magnet source. We started to attach a dispersive XAFS system to BL14B1 in 2004 and the system has been supplied as a general use since 2006 for the real time observation and the precise structural analysis [1].

Here, the study of structural transformation of  $\text{LaFe}_{0.9}\text{Pd}_{0.1}\text{O}_3$  automotive catalyst is described.  $\text{Pd}/\text{LaFeO}_3$  is known to keep the metal particle size small after the long time redox process because Pd atoms make solid solution with  $\text{LaFeO}_3$  perovskite-type crystal under the oxidative atmosphere [2]. The local structure of Pd atom is investigated by dispersive XAFS system from the viewpoint of dynamics of movement of Pd under particular atmosphere to reveal how different from the conventional supported catalyst  $\text{Pd}(4 \text{ wt } \%) / \text{Al}_2\text{O}_3$ .

Pd K-edge XAFS spectra was observed at BL14B1 of SPring-8. Laue configuration with (422) reflection plane was adopted. The transmitted x-rays were observed by CCD camera (640 x 480, 12 bits) with  $\text{Gd}_2\text{O}_2\text{S}(\text{Tb})$  phosphor at 20-50 Hz.

Figure 1 shows the local structural transformation around Pd atoms on  $\text{LaFeO}_3$  and  $\text{Al}_2\text{O}_3$  under reductive (50%  $\text{H}_2$  in He) and oxidative (50%  $\text{O}_2$  in He) atmosphere at 300 °C. It is recognized that, under the reductive atmosphere, Pd atoms show similar speed of movement from oxide to metal state. However, under the oxidative atmosphere, Pd atoms in  $\text{LaFeO}_3$  show faster movement from metal to oxide state with single reaction step than those on  $\text{Al}_2\text{O}_3$  with two step oxidation mechanism. Oxidation of Pd metal particle is regarded to segregate Pd particles to atomic level configuration. The faster oxidative reaction speed is the key of preventing sintering of Pd atoms on  $\text{LaFeO}_3$ .

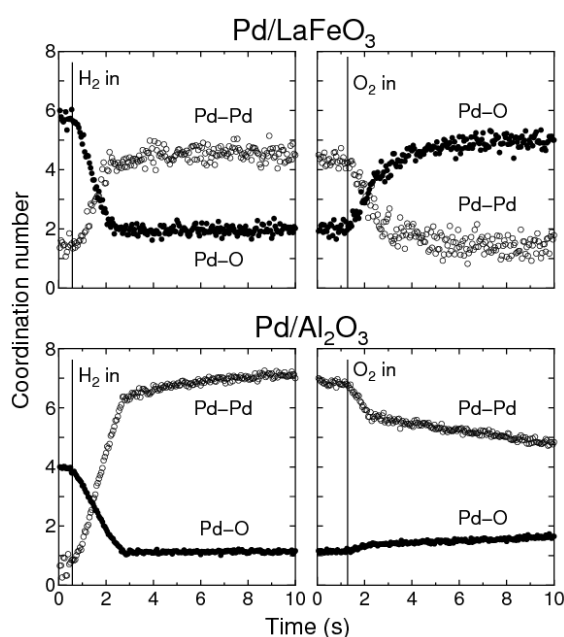


Figure 1: Coordination numbers of Pd-O and Pd-Pd shells for  $\text{Pd}/\text{LaFeO}_3$  and  $\text{Pd}/\text{Al}_2\text{O}_3$ . The spectra were taken under reductive and oxidative atmosphere.

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## Measurement of Individual Bond Magnetostrictive Strain in a-TbFe<sub>2</sub>

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We have succeeded in measuring the magnetostrictive strain of Fe-Fe and Fe-Tb bonds in an amorphous film of TbFe<sub>2</sub>. This has been made possible thanks to recent developments in the field of synchrotron radiation based methods, which have enabled the measurement of femtometer atomic displacements [1]. Using linearly polarized synchrotron radiation and the energy dispersive X-ray Absorption Spectroscopy beamline ID24 [2] we have performed Differential EXAFS (DiffXAS) at the Fe K-edge on a 6 μm thick a-Tb<sub>28</sub>Fe<sub>72</sub> film. We have observed a clear X-ray Magnetic Linear Dichroism signal that extends over ~ 300 eV above the edge. A preliminary analysis yields an increase of 0.0006 Å and of 0.001 Å in the Fe-Fe and Fe-Tb bonds respectively when the electric field E of the synchrotron radiation is perpendicular to the direction of the applied magnetic field B compared with the case when E is parallel to B. This work represents one of the first applications of these new methods to the investigation of amorphous matter. Previous work on polycrystalline matter may be found in references [1, 3, 4].

These results have been obtained in the framework of an EXAFS study at the Fe K and rare earth (RE) L<sub>3</sub> absorption edges on amorphous RE-Fe<sub>2</sub> films such as TbFe<sub>2</sub>, DyFe<sub>2</sub> and TbDyFe<sub>2</sub> in the attempt to identify and eventually quantify magnetostrictive atomic displacements in these compounds. Such studies are aimed at elucidating the atomic origin of the giant magnetostriction observed in RE- transition metal compounds. It is well known for example that in RE-Fe<sub>2</sub> compounds, the huge anisotropy of the 4f electron cloud, the high moment, and the high Curie temperature, lead to large magnetostriction at room temperature [5]. In these systems, when the orientation of the magnetic moment of the 4f shell is rotated with respect to the crystallographic axes by an external magnetic field, it is assumed that the anisotropic 4f charge density is rigidly co-rotated and atomic displacements from the equilibrium positions are expected to occur. Internal distortions in c-TbFe<sub>2</sub> were predicted 40 years ago [6] but to date have not yet been detected.

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## EXAFS Measurements on Sorption of Uranyl Ions onto Alumina and Kaolinite at INDUS-2, RRCAT, Indore

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An extended X-ray absorption fine structure (EXAFS) beam-line for X-ray absorption studies using energy dispersive geometry and position sensitive detector has recently been set up at the BL-8 port of INDUS-II synchrotron source at RRCAT, Indore, INDIA. This beamline has been built based on the working principle that a single crystal bent in the shape of an ellipse by a crystal bender, would act as a dispersing as well as focusing element. The crystal bender which has been designed on the basis of the principle of four-point bending has been fabricated indigenously. The crystal bender is capable of producing pre-defined elliptical curvature on a crystal surface by applying different torques at the two-ends of the crystal which has variable width along its length. A Rh coated cylindrical pre-mirror is used in the beamline for vertical focussing and higher harmonic rejection. The beam-line has been successfully commissioned and after carrying out several calibration experiments with standard metal foils, EXAFS studies have been carried out on few samples of current scientific and technological importance.

In the present paper, we report the results of the EXAFS experiments on the actinide speciation, wherein the sorption of uranyl ions on the alumina and kaolinite colloids was studied. EXAFS provides the most direct information about the structure of the sorbed species, e.g., the coordination number of the metal ion and the distance of the near neighbours of the metal ion and this technique has earlier been used to characterize the uranyl species sorbed onto silicic acid [1] and montmorillonite [2]. Sorption of U(VI) by alumina and kaolinite at varying pH has been carried out in the present study. Kaolinite is a clay mineral containing aluminol and silanol surface sites for sorption of metal ions, and is also considered as a backfill material in the deep geological repository. U(VI) is chosen as the analogue of the hexavalent actinides, e.g., Np(VI), Pu(VI), so as to study their migration behavior in the near field of a deep geological repository. The absorption intensity was found to increase with increasing pH of the suspension. In uranium samples, near neighbor distances of oxygen atoms were calculated by fitting the EXAFS data using the various codes within the IFEFFIT package [3]. The EXAFS data is being used to infer about the mechanism of sorption (viz., inner sphere or outer sphere complex formation with the surface sites of the colloids/ backfill material).

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## EXAFS Measurements on Crystalline $\text{Pb}_5\text{Ge}_3\text{O}_{11}$

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Lead germanate ( $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ ) is a technologically important pyroelectric crystal. Its single crystal growth and characterization were investigated in literature during early seventies. Detailed structure analysis of  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  (LGO) was carried out by Iwata et al. using X-ray and neutron diffraction techniques and the atomic coordination in the unit cell was obtained by X-ray Patterson maps [1]. Newnham et al. also carried out refinement of X-ray single crystal diffraction data and suggested a prototype structure of  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  from which metal oxygen bond lengths were estimated [2]. However, these results have not been corroborated by EXAFS measurement, which is a more direct technique for determination of local structure.

For present investigation, the single crystal growth of LGO was carried out by Czochralski technique, using an automatic diameter controlled crystal puller. The starting charge for growth was prepared from 4N pure PbO and  $\text{GeO}_2$  constituent oxides taken in stoichiometric ratio and rapidly raising the mixture to the melting temperature. The crystals of 20mm diameter and upto 50mm length were grown using 40mm diameter crucible under normal ambient. The EXAFS measurements were performed using recently commissioned extended X-ray absorption fine structure (EXAFS) beamline at the BL-8 bending magnet port of 2.5 GeV synchrotron source (INDUS-2) at RRCAT, Indore, India. The X-ray absorption data obtained for LGO samples was used to obtain radial distribution  $\chi(r)$  versus  $r$  plots and the best-fit theoretical simulation plot was obtained using IFEEIT code. The theoretical analysis was carried out assuming trigonal structure for LGO [1]. Two Pb-O bond lengths of 2.40Å and 2.71Å and the lowest Pb-Ge bond length of 3.74Å are obtained for LGO. The average Pb-O bond length obtained here is found to agree well with the bond lengths estimated by Newnham et al. [2].

In conclusion, the EXAFS measurements on crystalline  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  have been performed for the first time in literature and the average Pb-O bond length obtained from these measurements is found to agree well with the theoretically estimated value.

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## Strong Correlated Systems under Pressure using X-ray Absorption Spectroscopy

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The physics leading to the remarkable properties of strong correlated metal oxides is rich and complex. The actual path followed by a given system towards ferromagnetism and/or metallization, through chemical substitution, thermal treatment or pressure involves modifications of a delicate balance between delocalization and carriers trapping. X-ray absorption spectroscopy (XAS) is a well-suited technique to reveal tiny structural modifications and external pressure is a clean and straightforward way to follow the effect of structural changes on the electronic and magnetic properties. We will present here two different systems. The samples have been studied by XAS in transmission mode using the Energy Dispersive spectrometer and in fluorescence mode using the step-by-step set up. The local structure has been investigated from the XANES features and from EXAFS analysis, while information about the electronic properties has been trailed from the modification of the pre-edge structures. Our first study aims to describe the local process accompanying the pressure-induced abrupt changes in the resistivity in the Jahn-Teller distorted  $\text{LaMnO}_3$  compound.  $\text{LaMnO}_3$  is the parent compound of manganites which show colossal magneto-resistance (CMR). We explored the interplay between electronic and structural properties across the pressure-induced insulator to metal transition (IMT), reported to occur at 32 GPa in  $\text{LaMnO}_3$  [1], and in their electron doped alloys,  $\text{LaMnO}_{3,03}$  and  $\text{La}_{0.94}\text{Sr}_{0.06}\text{MnO}_3$ . Different regimes of compression were distinguished, well illustrated by the shift of the Mn K-edge [2]. The total energy shift, of about 1.4 eV, is lower than the expected value if the JT distortion were completely suppressed. A hysteretic behavior of all changes was observed, pointing to a coexistence of two phases in a large pressure range. The second study deals with the evolution under pressure of the short-range environment of formally trivalent Ni ions in  $\text{YNiO}_3$  up to 21 GPa. This compound displays a charge ordered insulating state associated to a monoclinic distortion. The insulating state, as well as the antiferromagnetic order at low temperatures, is consistent with the existence of the two non-equivalent Ni sites. Under pressure, a lattice evolution and a phonon screening consistent with a monoclinic (insulating) to orthorhombic (metallic) transition has been observed [3] around 14 GPa. A clear energy shift at Ni K-edge is observed. The energy shift/pressure is 54 meV/GPa up to 13 GPa and then decreases to 33 meV/GPa above that critical pressure. This result shows that orthorhombic and monoclinic phases have different compressibility and is consistent with the regime change from insulator to metallic.

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## Performance Degradation in Direct Methanol Fuel Cells by Ru Dissolution and CO Poisoning

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In direct methanol fuel cells (DMFC), ruthenium is needed at the anode to increase the CO tolerance of the standard Pt catalyst. Ruthenium is able to provide oxygen-containing adsorbates at lower potentials than Pt, which in turn can reduce CO adsorbates at Pt sites (so-called bifunctional mechanism). CO poisoning is an important issue, which leads to a performance loss in fuel cells. The CO adsorbates at Pt block the catalyst and prevent any other reactions to take place.

Linked to the application of ruthenium in the harsh conditions at the DMFC anode, another major degradation process of the well established PtRu catalyst system is the dissolution of the less-noble Ru. Investigations by Liang et al. [1] have shown that the co-deposition of Au nanoparticles can increase the oxidation potential of Ru and therefor stabilize it against its dissolution. Also other elements beside Au may show the ability to stabilize Ru. Theoretical models help to predict such candidates, and promising elements will be further investigated in model and prototype systems.

Research by Tada et al. [2] suggests that using time-resolved measurement methods like quick X-ray absorption fine structure (QXAFS), time-gated quick XAFS (TG-QXAFS) or energy-dispersive X-ray absorption (EDXAS) can provide valuable information about the dynamic surface reaction on fuel cell catalysts. EDXAS yields an even higher time resolution than QXAFS, but significant limitations were reported in [2]. We are interested in the potential application of EDXAS in the context of Ru dissolution under varying electrical potentials and CO poisoning and regeneration of PtRu in order to get a better insight into these processes.

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## The Originality of MARS: Dispersive and Standard XAS in One Beamline

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MARS (Multi Analyses on Radioactive Samples) is the hard X-ray beamline of SOLEIL synchrotron dedicated to the study of radionuclides or more generally radioactive samples presenting a significant hazard in terms of irradiation and/or contamination. The MARS beamline will be the fourth beamline in Europe for studying radionuclides, after the ROBL beamline at ESRF, the INE beamline at ANKA and the  $\mu$ XAS beamline at SLS. The aim is clearly to get an extension of the possibilities of analyses on radioactive samples toward high activities [1]. Hence, the infrastructure and the optics of the MARS beamline has been optimized for performing analyses with different experimental techniques particularly XAS. Characterizations can be carried out on a large variety of radioactive samples inside an innovative environment taking into account the national safety regulations [2].

Keeping in mind that most of the studies will be done on used fuels implying the presence of fission products, the bending magnet beamline has been designed to provide X-rays in the energy range of 3.5 keV to 35 keV. We then encompass the M and L absorption edges of actinides, as well as the K edges of transition metals up to heavy halogens, rare gases and alkalis. From an original optical concept, three complementary experimental end-stations which will be used alternatively, have been defined inside the same hut: a high resolution powder diffraction station, a standard XAS station and finally an EDXAS end station.

We will present the scheme and the mechanical design of the EDXAS station, its foreseen capabilities and x-ray tracing calculations which have been performed to estimate flux, sizes and divergences of the beam at the sample position. The XAS experimental station, using the monochromatic branch of the beamline, will be operational during the second semester of 2009 while the EDXAS one is expected to be installed in 2010. During the commissioning, a selection of radioactive samples with an activity below the exemption limit will be studied prior to radionuclides with higher activities.

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## Decomposition of FeTiO<sub>3</sub> Perovskite to (Fe<sub>1-δ</sub>,Ti<sub>δ</sub>)O and Fe<sub>1+δ</sub>Ti<sub>2-δ</sub>O<sub>5</sub>

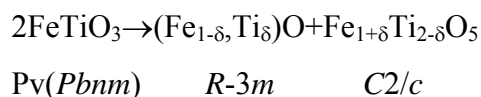
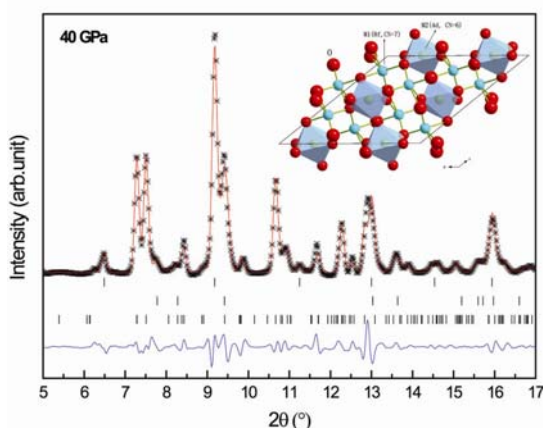
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The high pressure behavior of FeTiO<sub>3</sub> is explored up to 53 GPa. In addition to the known phase transition to the orthorhombic perovskite structure, we observed *in situ* the decomposition of FeTiO<sub>3</sub> into Ti-bearing wüstite and a high-pressure form of Fe<sub>1+δ</sub>Ti<sub>2-δ</sub>O<sub>5</sub> at 53 GPa and 2000 K. The high-pressure high-temperature Fe<sub>1+δ</sub>Ti<sub>2-δ</sub>O<sub>5</sub> phase becomes amorphous below 9 GPa on decompression. Our study demonstrates that perovskite-structured materials at high pressures could not only transform to denser polymorphs or decompose on simple oxides, but also undergo chemical changes and form complex oxides with new structures.



**Figure:** An example of full profile treated X-ray diffraction pattern from a mixture of rock salt (top ticks), wüstite (middle ticks), and post-ferropseubrookite (bottom ticks) at 40 GPa. Here the lattice parameters of wüstite (*R-3m*, *Z* = 3) are *a* = 2.8210(6) Å and *c* = 7.386(3) Å, that of NaCl (*Pm3m*, *Z* = 1) is *a* = 2.9544(2) Å. The structural parameters of high-pressure form of post-ferropseubrookite (*C2/c*, *Z* = 4) are *a* = 10.135(3) Å, *b* = 4.305(1) Å, *c* = 10.023(4) Å, *β* = 141.48(9)°, and M1(0.109, 0.694, 0.175), M2(0.25, 0.25, 0.5), O1(0.201, 0.479, 0.124), O2(0.113, 0.028, 0.514), O3(0, 0.501, 0.25). The corresponding crystal structural model of ferropseubrookite is presented in the inset.

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## Characterization of the Lithium Battery Materials during their Functioning

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We aim to characterize the lithium battery materials during their functioning (in operando mode). We address several questions about the lithium diffusion, electron mobility, phase change, charge transfer [1]. We will characterize the structure and electronic state of the electrode material, in using the time and spatial resolutions provided by various synchrotron beamlines at SOLEIL: ODE, CRISTAL, SAMBA and LUCIA. We are especially interested by the dispersive XAS beamline ODE.

For the general purpose, a new in-situ cell has been designed for synchrotron XAS and X-ray diffraction during electrochemical cycling of battery materials and operating in transmission and reflection collecting modes. This new cell allows fast data acquisition, provides hermetic sealing, high quality data collection and is easy to assemble. Its technical development, along with a discussion of its serviceability to combine electrochemical measurements with X-ray diffraction and absorption experiments (XAS), is hereby presented.

The interest of such a technique has already been proved on the positive electrode material “ $\text{Li}_{1.1}\text{V}_3\text{O}_8$ ” [2]. The results will be recalled in this poster. In this study, XAS experiments were carried out in-situ during the battery cycling in using a dispersive XAS set-up. A plastic battery has been designed for this purpose and connected to an automated battery cycling system. Decomposition of the XANES part of the spectra in few simple mathematical functions allowed us to describe some phenomena occurring during Li insertion/extraction in  $\text{Li}_x\text{V}_3\text{O}_8$ .

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## Combined In Situ XAS and EDXRD Study of the Hydrothermal Formation of Nanostructured Transition Metal Oxides

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The hydrothermal process is well known for its unique control facilities regarding the particle size of functional materials. Therefore, this method finds widespread application in the synthesis of nanostructured oxides as essential tools for a future nanotechnology [1]. Compared to the large number of studies on the synthesis and characterization of nanostructured oxides, only few contributions are focused on the investigation of the formation mechanisms and/or kinetics of these materials under hydrothermal conditions [2]. However, kinetic and mechanistic information about hydrothermal processes is requested to fully explore their synthetic potential for large-scale production processes that can be planned and predicted. Therefore, we have assigned the hydrothermal growth mechanisms of MoO<sub>3</sub> rods, nanostructured alkali tungstates and mixed nanostructured W/Mo-oxide materials with in situ EDXRD/XAS approaches using synchrotron radiation. Whereas molybdenum oxide fibers grow within a few minutes via a dissolution-precipitation sequence [3], alkali tungstates are formed through an hour-scale nucleation controlled mechanism [4]. Consequently, the kinetics of mixed W/Mo-oxide formation displays an intermediate reaction rate, following a nucleation controlled process [5] (shown in Figure 1). Very recently, we investigated the hydrothermal formation mechanism of Bi<sub>2</sub>O<sub>3</sub> nanowires. Whereas the majority of hydrothermal oxide syntheses proceeds either via dissolution-precipitation or nucleation-based mechanisms and many non-aqueous routes involve intermediate products, the growth of Bi<sub>2</sub>O<sub>3</sub> nanowires follows a different pathway. We propose that Bi<sub>2</sub>O<sub>3</sub> fibres are formed by water and additive-assisted solid-solid transformation [6].

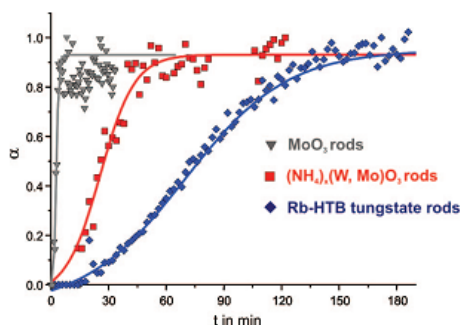


Figure 1: Extent of reaction  $\alpha$  versus time for the hydrothermal growth of MoO<sub>3</sub> rods, (NH<sub>4</sub>)<sub>x</sub>(W,Mo)O<sub>3</sub> rods and nanostructured Rb-hexagonal tungsten bronzes (HTBs).

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# Notes





