



EBS Workshop on X-ray Emission Spectroscopy

**ESRF Auditorium - Grenoble, France
3, 4 & 5 December 2019**

Organisers

**Pieter Glatzel, ID26
Kristina Kvashnina, BM20
Mauro Rovezzi, BM16
Olivier Mathon, ID24/BM23
Sara Lafuerza, ID26
Marius Retegan, EMD
Claudine Roméro & Philippa Lean**

EBS workshop on X-ray Emission Spectroscopy

ESRF, Grenoble, France

ESRF auditorium

PROGRAMME

Tuesday 3rd December 2019

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|---------------|--|---|
| 11:00 - 12:00 | Registration in the ESRF Central Building entrance hall | |
| 12:00 - 13:30 | Lunch at the EPN campus restaurant | |
| 13:45 - 14:00 | Welcome/Introduction | H. Reichert <i>ESRF Director of Research</i> |
| 14:00 - 15:50 | Session 1: Instrumentation Chair: P. Glatzel | |
| 14:00 - 14:30 | Current and future possibilities of XES and XAFS in the laboratory | B. Kanngießler <i>TU Berlin, Germany</i> |
| 14:30 - 15:00 | Status of XES spectrometer at Balder beamline at MAX IV | K. Klementiev <i>Lund University, Sweden</i> |
| 15:00 - 15:30 | High resolution X-ray spectroscopy at SLAC | D. Sokaras <i>SLAC NAL Stanford, USA</i> |
| 15:30 - 15:50 | FAME-UHD: High-Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy on ultra-trace elements | O. Proux <i>CNRS St Martin d'Hères, France</i> |
| 15:50 - 16:20 | Coffee break | |
| 16:20 - 18:30 | Session 2: Instrumentation Chair: M. Rovezzi | |
| 16:20 - 16:50 | What to do with a portable von Hámos spectrometer? | C. Sternemann <i>TU Dortmund, Germany</i> |
| 16:50 - 17:20 | X-ray emission spectroscopy in the tender and hard X-ray regime at the Swiss Light Source and SwissFEL | M. Nachttegaal <i>PSI Villigen, Switzerland</i> |
| 17:20 - 17:40 | High-resolution hard X-ray spectroscopy at PETRA III beamline P64: present and future | A. Kalinko <i>Paderborn University, Germany</i> |
| 17:40 - 18:00 | PINK: tender X-ray beamline for an X-ray emission spectroscopy at BESSY II. First results | S. Peredkov <i>MPI Mülheim/Ruhr, Germany</i> |
| 18:00 - 18:30 | Sponsors: XRStech, easyXAFS, SAINT GOBAIN | |
| 18:30 - 21:00 | Poster session + Buffet dinner on the ESRF mezzanine | |

Wednesday 4th December 2019

09:00 - 10:40 Session 3: Materials Science and Coordination Chemistry Chair: S. Lafuerza

- 09:00 - 09:30 Spectroscopic studies of Intermediates in biological dinitrogen reduction **S. DeBeer**
MPI Mülheim/Ruhr, Germany
- 09:30 - 10:00 X-ray emission spectroscopy to understand photochemical reactions and mechanisms **M. Bauer**
Paderborn University, Germany
- 10:00 - 10:20 What can we learn about nanoparticle synthesis in solution from photon-in photon-out spectroscopy? **D. Koziej**
Hamburg University, Germany
- 10:20 - 10:40 Monitoring structural changes in molybdenum sulfide phase within the confinement of Zeolite-Y under sulfidation/hydrogenation conditions via HERFD-XAS and VtC-XES measured under *operando* conditions **R. Khare**
TU Munich, Germany

10:40 - 11:10 Coffee break and group picture

11:10 - 12:40 Session 4: Materials Science and Coordination Chemistry Chair: S. Butorin

- 11:10 - 11:40 Selective redox catalysis over Cu-zeolites: insights by HERFD-XANES and vtc-XES **E. Borfecchia**
Turin University, Italy
- 11:40 - 12:00 Lithium-sulfur batteries studied by tender X-ray emission spectroscopy **M. Kavcic**
Institute J. Stefan Ljubljana, Slovenia
- 12:00 - 12:20 TEXS: in-vacuum tender X-ray emission spectrometer based on eleven Johansson crystal analysers **M. Rovezzi**
CNRS FAME Grenoble, France
- 12:20 - 12:40 Local coordination of molybdenum in crystalline compounds from high-energy resolution L3-XANES: experiment and theory **A. Svyazhin**
ESRF Grenoble, France

12:40 - 14:00 Lunch at the EPN campus restaurant

14:00 - 15:50 Session 5: Actinides Chair: K. Kvashnina

- 14:00 - 14:30 HERFD in actinide research **S. Butorin**
Uppsala University, Sweden
- 14:30 - 14:50 Structural studies of actinide materials applying high resolution X-ray absorption and emission spectroscopy **T. Vitova**
Karlsruhe Institute of Technology, Germany
- 14:50 - 15:10 Uranium M-edge HERFD-XANES at MARS beamline **M. Hunault**
Synchrotron Soleil, France
- 15:10 - 15:30 HERFD-XAS studies of actinide materials **L. Zhang**
Chinese Academy of Sciences Shanghai, China
- 15:30 - 15:50 Uranium transport by Cl-bearing aqueous fluids: insights from HERFD-XAS **E. Bazarkina**
Institut Néel Grenoble, France

15:50 - 16:20 Coffee break

| | | |
|----------------------|---|---|
| 16:20 - 18:20 | Session 6: Environmental Sciences Chair: O. Mathon | |
| 16:20 - 16:50 | Structural biogeochemistry of mercury in wildlife | A. Manceau <i>CNRS Grenoble, France</i> |
| 16:50 - 17:10 | Revealing the chemical form of 'invisible' gold in natural sulfides with high energy-resolution X-ray absorption spectroscopy | M. Merkulova <i>ESRF Grenoble, France</i> |
| 17:10 - 17:40 | New scientific opportunities for high energy-resolution XAS/XES measurements at ambient and extreme conditions - the ID24-EBS project | A. Rosa <i>ESRF Grenoble, France</i> |
| 17:40 - 18:00 | Valence-to-core X-ray emission spectroscopy of germanate glasses: sensitivity with respect to coordination and network polymerization | G. Spiekermann <i>Potsdam University, Germany</i> |
| 18:00 - 18:20 | High Energy Resolution Fluorescence Detected XANES spectra of Cu complexes | M. Soldatov <i>Southern Federal University, Rostov-on-Don, Russia</i> |
| 19:30 - 22:00 | Workshop dinner at the Restaurant L'Epicurien, 1 place aux Herbes, Grenoble | |

Thursday 5th December 2019

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|----------------------|--|---|
| 09:00 - 10:30 | Session 7: Data Analysis and Theory Chair: M. Retegan | |
| 09:00 - 09:30 | <i>Ab initio</i> simulations to study valence to core XES and HERFD-XANES | Y. Joly <i>CNRS Grenoble, France</i> |
| 09:30 - 10:00 | Wavefunction based approaches in X-ray spectroscopy | D. Manganas <i>MPI Mülheim/Ruhr, Germany</i> |
| 10:00 - 10:30 | Modeling Resonant Inelastic X-ray Scattering and Resonant X-ray Emission in the LDA+DMFT framework | J. Kolorenc <i>Czech Academy of Sciences Prague, Czech Republic</i> |
| 10:30 - 11:00 | Coffee break | |
| 11:00 - 12:30 | Session 8: Data Analysis and Theory Chair: L. Amidani | |
| 11:00 - 11:30 | Chemical sensitivity of K β and K α X-ray emission spectroscopy: insights from a systematic investigation on iron compounds | S. Lafuerza Bielsa <i>ESRF Grenoble, France</i> |
| 11:30 - 11:50 | The transition metal K edge spectral shape | F. de Groot <i>Utrecht University, The Netherlands</i> |
| 11:50 - 12:10 | Development of X-ray absorption spectroscopic methodology for investigating relaxation processes in periodically driven systems | H. Singh <i>Oulu University, Finland</i> |
| 12:10 - 12:30 | Conclusions | |
| 12:30 - 13:30 | Lunch at the EPN campus restaurant | |



Speakers' Abstracts

Current and future possibilities of XES and XAFS in the laboratory

B. Kanngießler, Ch. Schlesige, R. Gnewko, S. Praet, W. Malzer

Institute for Optics and Atomic Physics, Technical University of Berlin,
birgit.kanngiesser@tu-berlin.de

X-ray Emission (XES) and Absorption Fine Structure Spectroscopy (XAFS) are well-established methods at synchrotron facilities where it is being used routinely in various kinds of research fields. In order to enlarge its availability on a day-to-day basis we developed XES and XAFS spectrometers for the laboratory. The investigations are facilitated with polychromatic radiation in contrast to most of the XES and XAFS experiments at synchrotron sources.

The first type of XES and XAFS laboratory spectrometer is dedicated to the hard X-ray regime for investigation of mainly 3d transition metals' K absorption edges. Due to the use of Highly Annealed Pyrolytic Graphite (HAPG) as the wavelength dispersive element reasonable measurement times with sufficient spectral resolving power for both methods have become possible [1], [2]. A second type of XAFS laboratory spectrometer is operating in the soft X-ray regime. With this setup NEXAFS K edge spectroscopy of the main constituents of biological samples such as C, O and N is feasible. But also the L edges of all transition metals are accessible [3]. Moreover, by using the pulsed structure of its source dynamic XAFS investigations become possible. We already carried out single shot (1 ns) NEXAFS spectroscopy at the C K- edge of Cu Chlorophyllin. This paved the way for first pump-probe experiments.



Figure 1: HAPG as the decisive material of a wavelength dispersive element in laboratory spectrometers for reasonable measurement times.

The talk will present an overview of current possibilities for lab XES and XAFS investigations as well as perspectives for the future.

References

- [1] - C. Schlesiger, L. Anklamm, H. Stiel, W. Malzer, B. Kanngießler, *J. Anal. At. Spectrom.* **30**, 1080-1085, (2015).
- [2] - W. Malzer, D. Grötzsch, R. Gnewkow, Ch. Schlesiger, F. Kowalewski, B. Van Kuiken, S. DeBeer, B. Kanngießler, *Review of Scientific Instruments* **89**, (2018)
- [3] - I. Mantouvalou, K. Witte, W. Martyanov, A. Jonas, D. Grötzsch, C. Streeck, H. Löchel, I. Rudolph, A. Erko, H. Stiel, B. Kanngießler, *Appl. Phys. Lett.* **108**, 201106 (2016).

Status of XES spectrometer at Balder beamline at MAX IV

K. Klementiev, K. Sigfridsson Clauss, J. Just

MAX IV Laboratory, Lund, Sweden, konstantin.klementiev@maxiv.lu.se

Balder is a wiggler beamline dedicated to X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) in medium and hard X-ray energy range 2.4-40 keV [1]. Our aim is to reach a high repetition rate down to 1s for full EXAFS in order to preserve the sample (reduce radiation damage) and attain redox dynamics in *in-situ* reactions. The beamline is in the user operation and under expansion of the instrumentation portfolio.

In the first part of the talk I describe the beamline and demonstrate the achieved XAS data quality. I also show the presence of undulator features in the wiggler spectrum, characteristic of low emittance storage rings.

The second part of the talk is devoted to our XES spectrometer of the 1D Johansson type [2]. I present the design, discuss major decisions, technical restrictions and the crystal technology. One of our 18 silicon crystals is shown in Figure 1.

At the time of writing this abstract we have had four days of the very first commissioning time of the spectrometer. By the time of the Workshop we will have had a few more commissioning days and hopefully some presentable spectroscopic results.

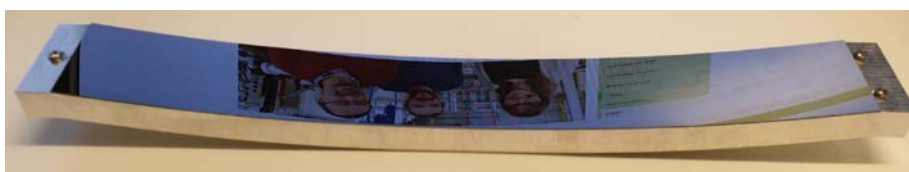


Figure 1: A ground-bent silicon crystal mounted on an aluminum support. The surface radius is 750 mm while the atomic planes are curved with a double radius. The crystal thickness is 300 μm , the working surface is 300 mm \times 38 mm.

References

- [1] - K. Klementiev, K. Norén, S. Carlson, K. Sigfridsson Clauss and I. Persson, 2016 *The BALDER Beamline at the MAX IV Laboratory*, J. Phys.: Conf. Ser. **712** 012018.
- [2] - Klementiev, I. Preda, S. Carlson, K. Sigfridsson and K. Norén, 2015 *High performance emission spectrometer at Balder/MAXIV beamline*, J. Phys.: Conf. Ser. **712** 012018.

High energy resolution X-ray spectroscopy at SLAC

D. Sokaras

SLAC National Accelerator Laboratory, Menlo Park, 94025 CA, USA, dsokaras@slac.stanford.edu

High-energy-resolution X-ray spectroscopy is an ensemble of advanced X-ray characterization tools that can provide unprecedented electronic structure insights of molecules and materials. The availability of high-photon-flux synchrotron radiation beamlines has enabled the routine application of such techniques for the characterization of metallic species and active centers in metalloproteins, heterogeneous and homogeneous catalysts, actinides, and beyond upon static and operando sample environment conditions. Moreover, the recent availability of X-ray Free Electron lasers has extended the applicability of such spectroscopy tools for the study of ultrafast dynamics such as electron transfer processes, transient molecular states, and molecular dissociation.

At SLAC National Accelerator Laboratory, we have built an extended science program based on in-house developed high-energy-resolution X-ray spectroscopic capabilities. In this presentation, we will be highlighting the developments we have been doing at SLAC in order to enable scientific studies of broad research interest. Moreover, representative examples from the ongoing spectroscopy programs of SSRL and LCLS will be discussed.

FAME-UHD: High-Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy on ultra-trace elements

A. Aguilar-Tapia¹, E. F. Bazarkina¹, W. Del Net², I. Kieffer², E. Lahera², A. Prat¹,
O. Proux², A. Ramos¹, M. Rovezzi², D. Testemale¹, J.-L. Hazemann¹

¹Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France, ²Univ. Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, proux@esrf.fr

FAME-UHD (French Absorption beamline for Material and Environmental sciences Ultra High Dilution) beamline at the ESRF is dedicated to High-Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS) and X-ray Emission Spectroscopy in the hard X-ray energy range, from 4.8 to 20 keV. The beamline is open to users operation since January 2017 and has demonstrated its performances in various scientific fields, including geosciences [1, 2], biology [3-5], bio-geochemistry [6, 7], catalysis [8], material sciences [9]... HERFD-XAS measurements on a target element down to 1ppm, and in some cases below [3, 6], are now available, as well as *in situ* or *operando* measurements [8, 9]. The study of trace and ultra-trace elements speciation by XAS offers a hard experimental challenge. How can we probe Se or Cu in biological tissues at physiological concentration, Au in arsenian pyrite...? The XAS fluorescence signal of interest is indeed very tiny compared with the signal due to the scattered beam and/or the fluorescent emission from the other elements of the sample. A solution to overcome these difficulties is to measure the fluorescence signal using a Crystal Analyzer Spectrometer, with a ≈ 1 eV energy bandwidth, in order to maximize the signal-to-background ratio [10]. The beamline is equipped with fourteen spherically bent crystal analysers arranged in the Rowland circle geometry (Fig. 1). It permits covering the fluorescence lines from 4 to 18 keV. The radius of curvature is 1 m, in order to limit the Johann's error and to have enough space available between the sample and the detector, a crucial point for *in situ* or *operando* measurements inside sophisticated cells. The two rows of seven crystals allow covering a large solid-angle (≈ 0.1 sr). This presentation will cover both FAME-UHD instrumentation and scientific goals.



Figure 1: 14-crystal Crystal Analyzer Spectrometer (left), in operation with hydrothermal cell (right)

References

- [1] - Ingrao et al., *Geochimica et Cosmochimica Acta* **265**, 182-197 (2019).
- [2] - Filimonova et al., *E3S Web of Conferences* **98**, 05007 (2019).
- [3] - De Santis et al., *Condensed Matter* **4**, 13 (2019).
- [4] - Thomas et al., *Journal of Physical Chemistry Letters* **10**, 2585-2592 (2019).
- [5] - Thomas et al., *Metallicomics* **11**, 1219-1229 (2019).
- [6] - Bissardon et al., *Analyst* **144**, 3488-3493 (2019).
- [7] - Proux et al., *Journal of Environmental Quality* **46**, 1146-1157(2017).
- [8] - Qureshi et al., *Journal of Catalysis* **109**, 545-563 (2019).
- [9] - Dantelle et al., *RSC Advances* **8**, 26857-26870 (2018).
- [10] - Llorens et al., *Review of Scientific Instruments* **83**, 063104 (2012).

What to do with a portable von Hámos spectrometer?

C. Sternemann¹, C. Albers¹, M. Elbers¹, J. Kaa^{1,2}, K. Lehninger¹, F. Otte^{1,2}, R. Sakrowski¹, G. Spiekermann³, M. Tolan¹, M. Wilke³

¹Fakultät Physik/DELTA, Technische Universität Dortmund, D-44221 Dortmund, Germany, ²European XFEL, D-22869 Schenefeld, Germany, ³Institut für Geowissenschaften Universität Potsdam, D-14476 Potsdam, Germany, christian.sternemann@tu-dortmund.de

X-ray spectrometers enabling von Hámos geometry [1] are relatively robust and easy to set up. After alignment, full emission and/or energy loss spectra with sub-eV resolution can be acquired without any moving parts and the data are self-normalizing. Consequently, such a spectrometer is well suited for pump-probe or shot-to-shot experiments [2, 3] and is ideal for portable applications [4, 5]. However, they do not reach the extraordinary signal-to-noise ratio of spectrometers in Johann geometry which complicates acquisition of weak signals.

Our portable von Hámos spectrometer utilizes an analyzer array with 4 cylindrically bent crystals having a bending radius of 500 mm together with a Pilatus 100K detector. Both, analyzer array and detector are installed on linear stages for changing the observed energy window and the whole setup can be moved around the sample position on a circular rail. Two spectrometers are available which, in principle, can be installed at any synchrotron beamline. They can be used for stand-alone (two-color) X-ray emission experiments but also in combination with other methods such as e.g. X-ray diffraction or X-ray Raman scattering. Selected examples for experiments performed with these portable spectrometers at different beamlines (P01 at PetraIII, Galaxies at Soleil, BL9 at DELTA) will be discussed.

References

- [1] - L. von Hámos, *Naturwissenschaften* **20**, 705 (1932).
- [2] - R. Alonso-Mori, J. Kern, D. Sokaras, T.-C. Weng, D. Nordlund, R. Tran, P. Montanez, J. Delor, V.K. Yachandra, J. Yano and U. Bergmann, *Rev. Sci. Instrum.* **83**, 073114 (2012).
- [3] - J. Szlachetko, M. Nachtegaal, E. de Boni, M. Williman, O. Safonova, J. Sa, G. Smolentsev, M. Szlachetko, J.A. van Bokhoven, J.-C. Dousse, J. Hoszowska, Y. Kayser, P. Jagodzinski, A. Bergamaschi, B. Schmitt, C. David and A. Lücke, *Rev. Sci. Instrum.* **83**, 103105 (2012).
- [4] - C. Weis, G. Spiekermann, C. Sternemann, M. Harder, G. Vankó, V. Cerantola, Ch.J. Sahle, Y. Forov, R. Sakrowski, I. Kuppenko, S. Petitgirard, H. Yavaş, C. Bressler, W. Gawelda, M. Tolan and M. Wilke, *J. Anal. At. Spectrom.* **34**, 384 (2019).
- [5] - G. Spiekermann, M. Harder, K. Gilmore, P. Zalden, Ch.J. Sahle, S. Petitgirard, M. Wilke, N. Biedermann, C. Weis, W. Morgenroth, J.S. Tse, E. Kulik, N. Nishiyama, H. Yavaş and C. Sternemann, *Phys. Rev. X* **9**, 011925 (2019).

X-ray emission spectroscopy in the tender and hard X-ray regime at the Swiss Light Source and SwissFEL

M. Nachtegaal, J. Szlachtko*, G. Smolentsev, U. Vogelsang, O. Safonova, A. Clark, D. Sanchez, D. Grolimund, A. Bergamaschi, R. Wetter, T. Huthwelker, J. Schneider, G. Knopp, C. Cirelli, K. Nass, C. Milne

Paul Scherrer Institute, Villigen-PSI, Switzerland, *Institute of Nuclear Physics, Polish academy of Science, Krakow, Poland, maarten.nachtegaal@psi.ch

This talk will provide an overview of the X-ray emission spectrometers and methods developed for specific applications in the tender and hard X-ray regimes at the Swiss Light Source (SLS) and SwissFEL.

At the SuperXAS beamline of the SLS both a dispersive von Hamos spectrometer (used mainly for non-resonant XES, RXES and HEROS) as well as a scanning Johann spectrometer (used mainly for valence to core XES) are available for the 4-12 keV range. For the speciation of sulphur under in situ conditions, a dedicated von Hamos setup including cell is available for operando non-resonant S K_{α} XES measurements. The von Hamos spectrometer has been introduced at the superXAS beamline already in 2012 and found application for a new technique, so-called high energy off resonant emission spectroscopy (HEROS), which allows to measure high resolution XAS like spectra in a single shot free of self-absorption and now finds application at XFELs. For non-resonant XES in the 15-26 keV range a newly develop DuMond spectrometer is available.

At the Alvra endstation at SwissFEL a multi-crystal von Hamos spectrometer is available for RXES, non-resonant XES and HEROS in the tender and hard X-ray regime.

At the microXAS beamline a von Hamos spectrometer is available with a set of segmented crystals of 25 cm diameter. Enhanced spectral resolution is combined with micro-focused beams to obtain unique spatially resolved chemical information. Scanning resonant and non-resonant XES is employed to generate two-dimensional chemical images. Furthermore, non-resonant XES is explored as promising modality for three-dimensional chemical tomography of micro-structured materials and objects.

At the PHOENIX beamline, an undulator based beamline, which operates in the tender X-ray range (0.4-8 keV), a new compact von Hamos spectrometer was installed. The spectrometer covers the energy range from 2.1 keV to about 4.8 keV, and offers an energy resolution of about 0.4 eV.

High-resolution hard X-ray spectroscopy at PETRA III beamline P64: present and future

A. Kalinko^{1,2}, W. A. Caliebe², M. Bauer¹

¹Universität Paderborn, Warburger Straße 100, 33098 Paderborn, Germany, ²DESY Photon Science, Notkestraße 85, 22603, Hamburg, Germany, aleksandr.kalinko@desy.de

PETRA III beamline P64 [1] is dedicated to advanced X-ray absorption and emission spectroscopy techniques. The beamline uses a 2m long undulator as X-ray source, providing up to 10^{13} photons/s on a sample. Beamline's optics allow beam focusing down to $150 \times 50 \mu\text{m}$ (HxV). These beamline's characteristics are the perfect basis for high energy resolution (non-)resonant hard X-ray emission (XES) spectroscopy.

In this contribution, we will present XES end station [2] at PETRA III beamline P64, which is based on a wavelength-dispersive von Hamos-type spectrometer [3]. We will demonstrate its performance and capabilities on selected scientific examples. Additionally, an overview of ongoing projects at the beamline, related to the high-resolution XES will be covered. Particularly advancement of the new focusing spectrometer implementation and a work in progress towards time-resolved pump-probe XES experiments will be discussed.

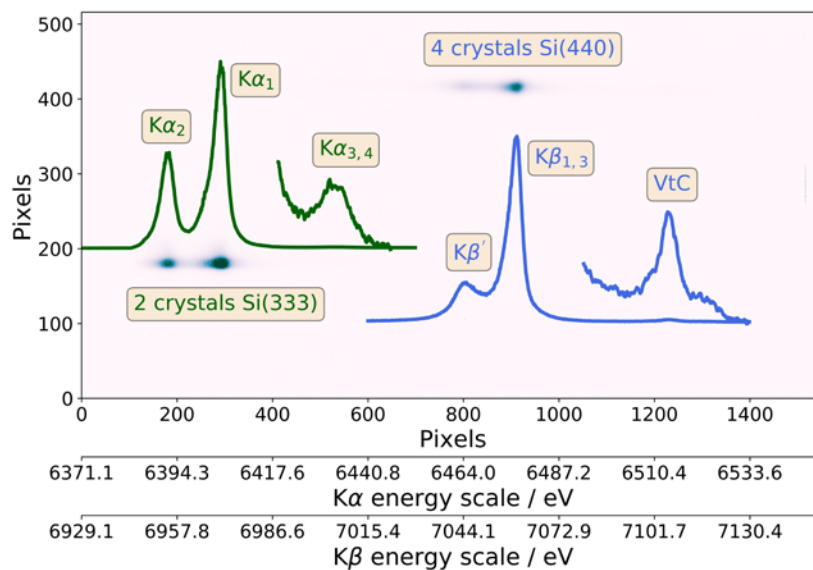


Figure 1: An example of a two-color experiment by measurement of K α and K β emission lines of Fe(BF₄)₂·6H₂O using 9300 eV excitation energy

References

- [1] - W.A. Caliebe, V. Murzin, A. Kalinko, and M. Görlitz, AIP Conf. Proc. 2054, 060031 (2019).
- [2] - A. Kalinko, W.A. Caliebe, R. Schoch, and M. Bauer, J. Synchrotron Radiat., accepted (2019).
- [3] - L.V. Hamos, Naturwiss. 20, 705, (1932).

PINK: tender X-ray beamline for an X-ray emission spectroscopy at BESSY II. First results

S. Peredkov¹, S. DeBeer¹, N. Pereira¹, D. Grötzsch², N. Levin Rojas¹, O. Rüdiger¹, Z. Mathe¹, O. McCubbin Stepanic¹

¹Max Planck Institute for Chemical Energy Conversion Mülheim an der Ruhr, Germany, ²Technical University of Berlin, Germany, sergey.peredkov@cec.mpg.de

Knowledge of the changes in the transition metal electronic structure and ligation environment are essential for any detailed mechanistic understanding, which forms the basis for rational catalysis design. XES measurements and analysis of X-ray emission lines can reveal the ligand identity, the ligand ionization potential and the metal-ligand distance, etc. [1,2].

The PINK beamline is designed to operate in the tender X-rays regime with energies ranging from 2.2 to 9.5 keV. This energy range will provide access to XES and XAS studies of transition metals ranging from Ti to Cu ($K\alpha$, $K\beta$ lines) and Zr to Ag ($L\alpha$, $L\beta$), as well as light elements P, S, Cl, K, Ca ($K\alpha$, $K\beta$).

The beamline will be operated in two modes. In the high flux mode, a multilayer monochromator ($E/\Delta E \approx 30 \div 80$) will focus beam in a $30\mu\text{m} \times 500\mu\text{m}$ (VxH) spot and provide the high photon flux (10^{15} ph/s @ 5 keV) allowing non-resonant XES measurements of very dilute substances. In order to reduce radiation damages and avoid decomposition, the samples can be maintained under cryogenic conditions.

Fluorescent X-rays will be analyzed by two in-house designed short radius von Hamos crystal spectrometers. High energy resolution of $\Delta E = 0.2\text{-}0.7$ eV will be achieved by using diced Si, Ge and quartz crystals optimized for operation at large $82^\circ\text{-}55^\circ$ bragg angles. Taking advantage of a wavelength-dispersive analyzer to record the entire spectrum simultaneously, we will be able to provide very attractive time resolved (2ms - 10s) XES measurements. Both spectrometers can be run independently, thus we will be able to record non-resonant XES spectra for two elements simultaneously, so called "two-color" experiments. XANES and XERFD techniques will be available in the second - high monochromatic mode ($E/\Delta E \approx 10000 \div 40000$) with the help of DCM monochromator.

Here we will present the PINK set-up and XES $L\beta$ spectra of Ru and P complexes recorded during the PINK beamline commissioning.

References

- [1] - M.A. Beckwith, M. Roemelt, M.-N. Collomb, C. DuBoc, T.-C. Weng U. Bergmann, P. Glatzel, F. Nesse and S. DeBeer, "Manganese $K\beta$ X-ray emission spectroscopy as a probe of metal-ligand interactions", *Inorg. Chem*, 50, 8397, (2011).
- [2] - C.J. Pollock, K. Grubel, P.H. Holland, S. DeBeer, "Experimentally quantifying small-molecule bond activation using valence-to-core X-ray emission spectroscopy", *J. of the Am. Chem. Soc.*, 135, 32, 11803 (2013).

Spectroscopic studies of intermediates in biological dinitrogen reduction

S. DeBeer

Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr,
Germany, serena.debeer@cec.mpg.de

The conversion of dinitrogen to ammonia is a challenging, energy intensive process, which is enabled biologically by the nitrogenase family of enzymes. The Mo-dependent nitrogenases contain two cofactors, the 8Fe-8S P-cluster and the Mo-7Fe-9S-C iron-molybdenum cofactor, known as “FeMoco”, which is the active site for dinitrogen reduction. FeMoco has long been, and continues to be, an enigmatic cluster. Over 8 years ago the presence of a carbide in the cluster was first revealed. However, the role of the carbide, the role of the Mo heterometal, and the changes which occur at the seven iron sites during the course of catalysis all remain open questions. Herein, we present studies of selenium incorporated FeMoco. High-energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) at the Se K-edge is utilized to obtain selective information about the electronic structure of FeMoco. These studies reveal a significant asymmetry in the electron distribution within FeMoco, suggesting a much more localized electronic structure than typically assumed for iron sulfur clusters. Further XAS studies of both natively reduced and cryoreduced MoFe protein will be presented. These studies are essential for establishing the nature of the first redox event in the catalytic cycle of nitrogenase. The beamline instrumentation advances that are needed to further our understanding of biological nitrogen reduction will be highlighted.

Financial support by the Max Planck Society and the DFG SPP-1927 is gratefully acknowledged.

X-ray emission spectroscopy to understand photochemical reactions and mechanisms

M. Bauer

University of Paderborn, Chair for Inorganic chemistry, Warburger Str. 100, 33098 Paderborn, Germany,
matthias.bauer@upb.de

The conversion of sunlight into fuels or chemicals gains lots of attention by the so-called Sun-to-X approach. The conversion of protons in water to hydrogen using sun light is the standard reaction of this type. In particular with the renaissance of fuel cells as alternative to batteries, sustainable hydrogen production becomes even more important.

Using base metals instead of noble metals increases the sustainable character of photocatalytic proton reduction. Both in photosensitizers and photocatalysts metals like iron and cobalt can be used. However, achieving competitive activity requires major efforts in photosensitizer and catalyst design. Due to the very limited knowledge about the properties and functionality of base metal compounds in this context, fundamental insights into their working principle are required.

X-ray emission based spectroscopy provides unique details about the electronic and geometric structure of iron and cobalt photosensitizers and photocatalysts [1]. This will be demonstrated with selected examples of tow-component systems, where photosensitizer and catalyst are independent compounds. One focus here will be the identification and investigation of hydride ligands, which play a dominant role in proton reduction reactions [2].

The contribution will close with the presentation of dyads (figure 1), that connect photosensitizer and catalyst in a bimetallic complex.[3] Cutting edge two-colour emission experiments at X-ray free electron lasers, that record the emission lines of both metal sites simultaneously, show unprecedented new insights into the excited state behaviour of this new compound class.

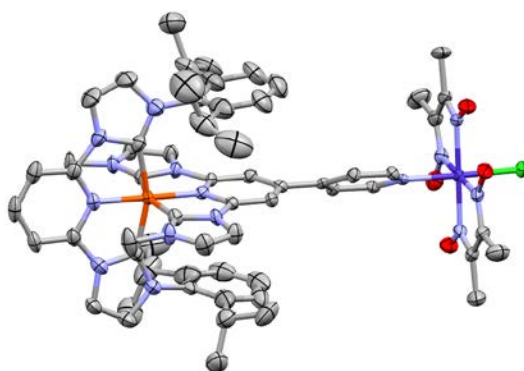


Figure 1: Example of a bimetallic dyad using iron as photosensitizer and cobalt as catalyst

References

- [1] - M. Bauer, *Phys. Chem. Chem. Phys.* **16**, 13827 (2014).
- [2] - L. Burkhardt, M. Holzwarth, B. Plietker, M. Bauer, *Inorg. Chem.* **56**, 13300 (2017).
- [3] - P. Zimmer, L. Burkhardt, R. Schepper, K. Zheng, D. Gosztola, A. Neuba, U. Flörke, C. Wölper, R. Schoch, S.E. Canton, M. Bauer, *Eur. J. Inorg. Chem.* 5203 (2018).

What can we learn about nanoparticle synthesis in solution from photon-in photon-out spectroscopy?

D. Koziej¹, M. Staniuk², C. Zito^{1,3}, L. Grotto¹, M. Sikora⁴, J. Kuciakowski⁴, K. Pitala⁴

¹Institute for Nanostructure and Solid-State Physics, University of Hamburg, Germany, ²Department of Materials, ETH Zürich, Switzerland, ³LabMatSus, São Paulo State University, Brazil, ⁴AGH University of Science and Technology, Kraków, Poland, dorota.koziej@uni-hamburg.de

Over the past few decades, material scientists have developed a wide variety of approaches to deliberately introduce chemical and structural inhomogeneities into nanoparticles, achieving for example intentional doping, concentration gradients, and multicomponent structures. This talk presents a sense of how modern hard X-ray spectroscopic methods are extending the way we study and understand such complex nanoparticles.

Particularly, the possibility to select with high resolution the incident and emission hard X-ray energies offers unprecedented site selectivity helps to uncover the complex chemical world behind the state-of-the-art synthetic methods. Today the in situ X-ray spectroscopic, complements X-ray scattering and microscopy studies and provide a new view into the genesis of heterogeneity in colloidal nanoparticles.

References

[1] - D. Koziej, Revealing Complexity of Nanoparticle Synthesis in Solution by in Situ Hard X-ray Spectroscopy-Today and Beyond, Chem. Mater. **2016** 28 (8) 2478.

Monitoring structural changes in Mo_xS_y phase within the confinement of Zeolite-Y under sulfidation/hydrogenation conditions via HERFD-XAS and VtC-XES measured under *operando* conditions

R. Khare, R. Weindl, H. Shi, A. Jentys, J.A. Lercher

Lehrstuhl II für Technische Chemie, Technische Universität München, Garching 85747 Deutschland,
rachit.khare@tum.de

Transition metal sulphides encaged in the (sub)nanometric confines of ordered porous zeolites are a class of promising catalysts for processing heavy petroleum feedstock. However, rather limited knowledge has been accumulated over the past decades regarding the dispersion, local structure, and electronic state of the Mo_xS_y phase encaged in zeolites, in its as-prepared state and under sulfidation/hydrogenation reaction conditions. We monitored the structural changes in the Mo_xS_y phase in zeolite-Y (Si/Al = 2.4) under sulfidation and hydrogenation reaction conditions at 673 K using *operando* HERFD-XANES, VtC-XES, and EXAFS measurements.

HERFD-XANES, EXAFS, and VtC-XES measurements were performed at the ID26 beamline of the ESRF at Mo K-edge (20 keV) under *operando* conditions using a capillary cell. For HERFD-XANES measurements, the energy of the monochromator was scanned between 19.95 keV and 20.2 keV while for VtC-XES, monochromator energy was fixed at 20.1 keV. Data analysis was performed using PyMCA v5.4.1 and Athena/Artemis software packages. The spectra were normalized and flattened for further analysis. *Operando* measurements were performed under sulfidation reactions conditions i.e. in $\text{H}_2\text{S}/\text{H}_2$ flow, or under hydrogenations conditions i.e. in pure H_2 , ethene/ H_2 , or toluene/ H_2 flow. DFT calculations were performed using the ORCA package version 4.1. Relativistic effects were taken into account using ZORA. All electron Karlsruhe basis sets (def2-TZVP) were used throughout. TDDFT calculations were performed using Tamm-Dancoff approximations and up to 50 roots were calculated allowing for transitions only from Mo 1s orbitals. We also performed TDDFT calculations on six different reference materials: Mo^0 -foil, $\text{Mo}^{\text{IV}}\text{S}_2$, $\text{Mo}^{\text{VI}}\text{O}_3$, $\text{K}_2\text{Mo}^{\text{VI}}\text{O}_4$, $(\text{NH}_3)_6\text{Mo}^{\text{VI}}_7\text{O}_{24}$, and $\text{Mo}^0(\text{CO})_6$, using eight different functionals: BP86, BLYP, PBE, TPSS, PBE0, B3LYP, BHLYP, and TPSSh. The performance of each functional was assessed by comparison with HERFD-XANES and VtC-XES experimental data obtained at ID26 beamline.

It was observed that the predominant Mo-species under sulfidation reaction conditions is Mo_2S_6 with Mo-Mo coordination of ~ 1 and Mo-S coordination of ~ 4 . Under hydrogenation conditions at 673 K, on the other hand, the dominant Mo-species observed was Mo_4S_8 with a Mo-Mo coordination of ~ 3 and Mo-S coordination of ~ 3 . We also observed that this process was reversible with Mo_2S_6 species forming back on re-sulfidation of the reduced catalyst. HERFD-XANES and EXAFS measurements at ID26, together with VtC-XES, and complemented with TDDFT calculations, enhanced our understanding of the structure of Mo_xS_y phase in zeolite-Y under *operando* reaction conditions. An enhanced understanding of the structure will further our knowledge of the mechanism of ethene or toluene hydrogenation on these catalysts.

Selective redox catalysis over Cu-zeolites: insights by HERFD-XANES and vtc-XES

E. Borfecchia

Dept. of Chemistry, University of Turin, Via P. Giuria 7, 10125, Turin (Italy), elisa.borfecchia@unito.it

Cu-exchanged zeolites are attracting increasing attention as platforms for high-impact selective redox chemistry, including NH₃-mediated selective catalytic reduction of harmful nitrogen oxides (NH₃-SCR) and direct selective oxidation of methane to methanol (DMTM) [1]. Quantitative determination of Cu-speciation in the zeolite framework under realistic reaction conditions and robust correlation between spectroscopic and catalytic observables are essential to keep advancing the field.

This contribution will focus on the role of HERFD-XANES and vtc-XES applied under *in situ* and *operando* conditions at the ID26 beamline of the ESRF to accomplish this task, in synergy with conventional XAS, laboratory-based multi-technique characterization, computational modelling and systematic performance evaluation.

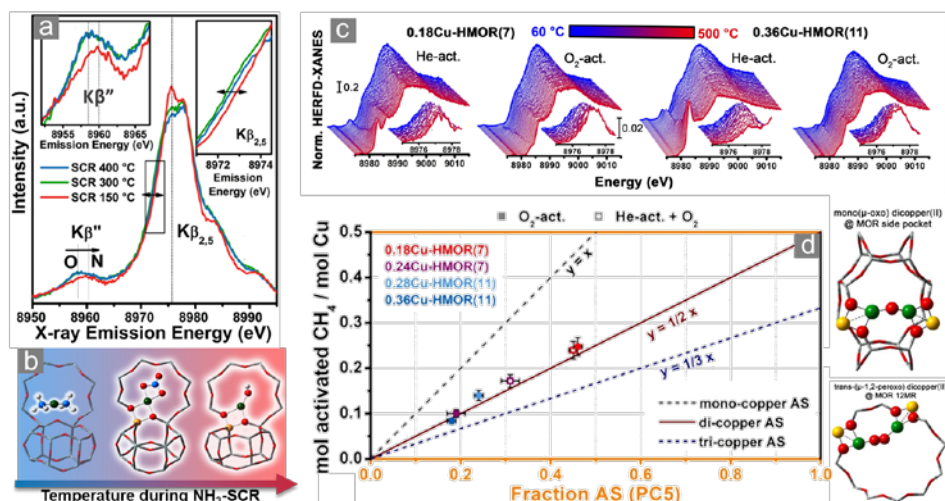


Figure 1: (a) Vtc-XES during temperature-dependent NH₃-SCR over Cu-CHA providing direct evidences for preferential N-ligation of Cu-centers at 150 °C, as illustrated in part (b). (c) Time-resolved HERFD-XANES during O₂ and He-activation of Cu-MOR zeolites with different composition. (d) Quantitative correlation between DMTM activity and Cu-speciation derived from MCR analysis of spectra in part (c), unambiguously indicating a di-copper active site, such as the mono-(μ -oxo) or the trans(μ -1,2-peroxo) dicopper(II) species.

The presented results will highlight the unique sensitivity of vtc-XES in discriminating among almost-isoelectronic ligands, such as O and N, crucial in the context of NH₃-SCR [2]. The great potential of HERFD-XANES combined with the emerging multivariate curve resolution (MCR) approach [3, 4] will be also exemplified, to resolve the finest details of Cu-speciation during the activation of Cu-CHA [4] and Cu-MOR [5]. In the latter case, quantitative correlation of MCR results with DMTM activity measurements provided, for the first time, unambiguous evidence of a di-copper (II) active site for CH₄ activation [5].

References

- [1] - E. Borfecchia et al., *Chem. Soc. Rev.* **47**, 8097 (2018).
- [2] - K. A. Lomachenko et al., *J. Am. Chem. Soc.* **138**, 12025 (2016).
- [3] - A. Martini et al., *Chem. Sci.* **8**, 6836 (2017).
- [4] - A. Martini et al., *Top. Catal.* **61**, 1396 (2018).
- [5] - D. K. Pappas et al., *J. Am. Chem. Soc.* **140**, 15270 (2018).

Lithium-sulfur batteries studied by tender X-ray emission spectroscopy

M. Kavčič¹, M. Petric¹, A. Rajh², A. Vizintin³, S. Drvarič³, R. Dominko³

¹J. Stefan Institute, Jamova 39, SI-1000, Ljubljana, Slovenia, ²Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia, ³National Institute of Chemistry, Hajdrihova 19, SI-1000, Ljubljana, Slovenia, matjaz.kavcic@ijs.si

Sulfur-metal batteries are one of the most promising options in powering applications requiring high energy density. Compared to more conventional lithium-ion systems, sulfur-based batteries have significantly larger theoretical gravimetric capacity. In addition, the elemental sulfur is highly abundant and relatively inexpensive, which reduces the cost factor. A detailed understanding of complex electrochemical reactions during battery cycling is required to improve the battery performance. For that purpose, numerous analytical techniques being capable to probe different sulfur species under realistic conditions within a working battery cell have been applied to address the electrochemistry mechanism [1]. In our previous work operando RIXS and XAS spectroscopy in the tender X-ray range around the sulfur K absorption edge have been successfully applied to study Li-S [2] and Mg-S batteries [3].

Currently, we are trying to explore also laboratory based X-ray analytical techniques which could be used to perform analytical laboratory testing. While laboratory XAS setups developed recently [4,5] are restricted to transmission measurements in hard X-ray energy range, tender XES spectrometer [6] can be used to perform laboratory study of S-based battery systems. In this work we have applied XES spectroscopy to examine the local electronic structure of sulfur in three different phases, which appear in the Li-S battery. Sulfur $K\alpha$ and $K\beta$ PIXE spectra of pure S, Li_2S and the lithium polysulfides (Li_2S_x) standards prepared by a chemical reaction between metallic lithium and sulfur were measured. Next, we have recorded also $K\alpha$ and $K\beta$ spectra from several battery cathodes stopped at different stages during the discharge. Finally, operando XES measurements on the working battery cell have been performed to study reduction of sulfur within the battery during the discharge.

References

- [1] - E. Zhao et al., *Adv. Funct. Mater.* 28 (2018) 1707543.
- [2] - M. Kavčič et al., *Phys. Chem. C* 120 (43), (2016), 24568-24576.
- [3] - A. Robba et al., *Chem. Mater.* 29, (2017) 9555-9564.
- [4] - G. T. Seidler et al., *Review of Scientific Instruments* 85 (11) (2014) 113906.
- [5] - C. Schlesiger et al., *J. Anal. At. Spectrom.* 30 (2015) 1080-1085.
- [6] - M. Kavčič et al., *Rev. Sci. Instrum.* 83 (3) (2012) 03311.

TEXS: in-vacuum tender X-ray emission spectrometer based on eleven Johansson crystal analysers

M. Rovezzi^{1,2}, B. Detlefs², T. Bohdan², A. Sviazhin², D. Degler², C. Lapras², R. Verbeni², M. Kocsis², A. Manceau³, P. Glatzel²

¹Univ. Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ²European Synchrotron Radiation Facility, 38000 Grenoble, France, ³Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, ISTERRE, 38000 Grenoble, France, mauro.rovezzi@esrf.fr

We present a high-efficiency in-vacuum X-ray emission spectrometer (TEXS) [1]. The optimised energy range is from 1.5 to 5.5 keV, the so-called “tender X-ray range”. It covers the K-fluorescence of light elements, such as aluminum, sulphur and chlorine, the L-lines of 4*d* transition metals and the M-lines of 5*d* elements and actinides.

TEXS is based on an array of eleven cylindrically bent Johansson crystal analysers of 25×80 mm² (flat side × bent side) size, working within a Bragg angular range from 85° down to 35°. It mounts crystal analysers with a bending radius from 1000 mm down to 500 mm, reaching an effective solid angle up to 90 msr. A two-axis crystal analyser table and a three-axis detector arm, encased in a ≈4 m³ high vacuum (< 10⁻⁵ mbar) vessel, perform the Rowland circle tracking (energy scan). The array of analysers is sagittally focused dynamically via an innovative mechanical slider on a flat plate. The detector is a sixteen-wire gas flow proportional counter of 40 × 50 mm² active area and 1 MHz maximum count rate with spatial resolution. The sample environment consists of a windowless liquid helium cryostat coupled with a load-lock system for quick sample exchange. *In situ* and *operando* catalysis reactors are available.

The spectrometer is installed on beamline ID26 of the ESRF. The commissioning phase has validated the concept and mechanical design, with a measured energy resolution ($\Delta E/E$) below 10⁻³.

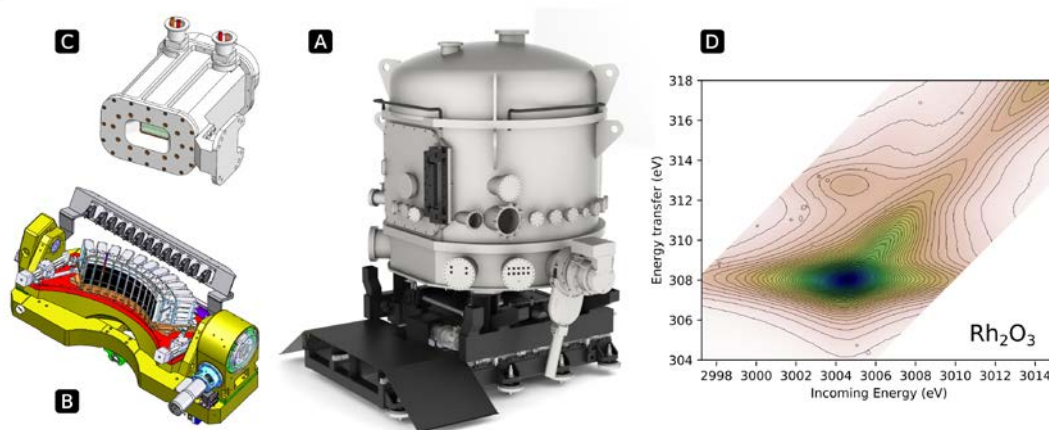


Figure 1: Layout of the spectrometer (A), analysers cradle (B) and detector (C). Example of RIXS data (D).

References

[1] - <http://bit.ly/2OQS051>

Local coordination of molybdenum in crystalline compounds from high-energy resolution L₃-XANES: experiment and theory

A. Svyazhin¹, V. Nalbandyan², R. Baran¹, A. Chumakova¹, B. Detlefs¹, A. Guda³,
M. Rovezzi⁴, A. Santambrogio¹, A. Manceau⁵, P. Glatzel¹

¹European Synchrotron Radiation Facility, 38000 Grenoble, France, ²Faculty of Chemistry, Southern Federal University, 7 ul. Zorge, 344090 Rostov-on-Don, Russia, ³The Smart Materials Research Institute, Southern Federal University, 344090 Rostov-on-Don, Russia, ⁴Univ. Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ⁵Univ. Grenoble Alpes, CNRS, ISTERre, CS 40700, 38058 Grenoble, France, art.svyazhin@gmail.com

Molybdenum-based compounds find broad applications in many branches of applied science. X-ray absorption spectroscopy (XAS) at the L₃-edge of Mo is widely used to characterize symmetry of local environment around the absorbing atom as the tetrahedral and octahedral environments reveal significantly different splitting of unoccupied 4d states. In this work we demonstrate the advantages of application of high-energy resolution fluorescence-detected (HERFD) XAS – a method of x-ray absorption spectra acquisition with the resulting energy resolution below the core hole lifetime [1-3] – to the Mo L₃-edge.

With the example of several reference compounds we show that application of HERFD-XAS allows for experimental observation of crystal field-split unoccupied 4d states (Figure 1). We also demonstrate that a qualitative analysis of the spectral features of the spectra permits one to estimate the deviations of local environment from the regular T_d/O_h one, to separate the contributions from Mo-ligand bond lengths and Mo-ligand-Mo angles to the asymmetry of the white lines, and to estimate Mo-ligand bond lengths.

The experimental spectra were simulated using Wien2k and FDMNES packages. On the basis of comparison of the experimental and the calculated spectra, the influence of the core hole potential and multiplet effects on the L₃-edge absorption spectra of Mo are discussed.

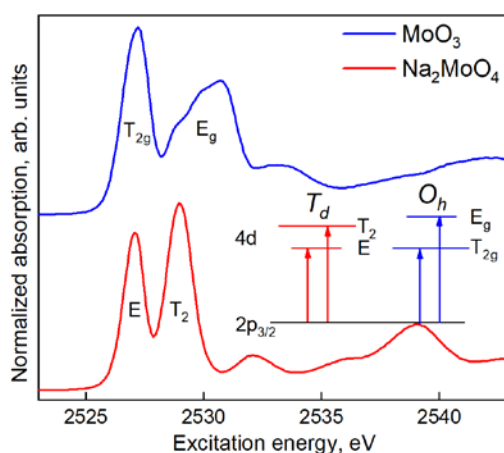


Figure 1: L₃-edge HERFD-XAS spectra of Mo in the tetrahedral and octahedral environments.

References

- [1] - K. Hämmäläinen et al., Physical Review Letters **67**, 2850 (1991).
- [2] - F.M.F. de Groot, M.H. Krisch, and J. Vogel, Physical Review B **66**, 195112 (2002).
- [3] - P. Glatzel et al., JESRP **188**, 17 (2013).

HERFD in actinide research

S. M. Butorin

Department of Physics and Astronomy, Uppsala University, Sweden, sergei.butorin@physics.uu.se

Among various methods of gaining the knowledge about the properties of actinide materials, X-ray spectroscopy plays the most important role. Better understanding of the electronic structure and fundamental properties of the actinide systems contributes to the knowledge relevant for the technological performance of actinide materials under study. In case of actinides, only techniques, such as XAS and EXAFS, can provide accurate information about the chemical state, homogeneity of compounds, (non)stoichiometry, oxygen/metal (O/M) ratio, local symmetry and environment and charge distribution.

I have been involved in recent development of the advanced technique, such as high energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) applied both at the actinide L_3 ($2p_{3/2}$ -6d transition) and $M_{4,5}$ (3d-5f transition) edges (the hard and tender X-ray range, respectively). In particular, the application of this technique at the $M_{4,5}$ edges has led to a tremendous improvement in the experimental resolution (up to 8 times higher) due to reduced core-hole lifetime broadening and revealed additional structures in the XAS spectra, not measurable before.

In my talk, I will present a few examples of studies of actinide materials using this advanced technique at the L and M edges, in particular at ESRF, where the best quality data to date were measured. I will discuss how the development of this technique and its application to actinides help to resolve long standing and debated questions. The interpretation of the data is supported by calculations in framework of the Anderson impurity model using the modified TT-MULTIPLETS package and by DFT+ U calculations using the OCEAN program.

In the end, I will discuss an extension of a similar technique, based on a selective detection of X-ray emission, to the soft X-ray range and shallow $O_{4,5}$ (5d-5f transition) edges of actinides which increases the sensitivity of XAS to the chemical state of dilute species.

Structural studies of actinide materials applying high resolution X-ray absorption and emission spectroscopy

T. Vitova¹, A. Beck¹, B. Schacherl¹, J. Galanzew¹, T. Prüßmann¹, S. Bahl¹, I. Pidchenko¹, P. Bagus², Y. Joly^{3,4}, P.M. Kowalski⁵, K. Dardenne¹, J. Rothe¹, H. Geckeis¹

¹Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Germany, ²Department of Chemistry, University of North Texas, Denton, Texas 76203-5017, USA, ³University Grenoble Alpes, Inst NEEL, F-38042 Grenoble, France, ⁴CNRS, Inst NEEL, F-38042 Grenoble, France, ⁵Institute of Energy and Climate Research, IEK-6, Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Strasse, 52428 Jülich, Germany, **Tonya.Vitova@kit.edu**

The actinide (An) M_{4,5} and L₃ edge high energy resolution X-ray absorption near edge structure (HR-XANES) and core-to-core 3d4f resonant inelastic X-ray scattering (3d4f RIXS) are becoming increasingly important for electronic structure and speciation studies of actinide materials. Recent results for uranium (U), neptunium (Np) and plutonium (Pu) containing materials will be discussed [1.4]. The experiments were performed at the INE- and CAT-ACT beamlines at the KIT light source, which operates the Karlsruhe Research Accelerator (KARA), Karlsruhe Germany [5].

The HR-XANES spectra measure relative energies within An 5f (M_{4,5}) and 6d (L₃) as well as in some cases between An 5f and 6d (L₃ edge) unoccupied valence states [1.4]. This information can help to benchmark and drive improvement in theoretical approaches for calculations of An electronic structures. Experimental spectra will be compared with computed spectra applying FDMNES [1], FEFF9 [3], DFT+U [2], TD-DFT and multiplet calculations[1]. It will be shown that the enhanced resolution allows using the An L₃ and M_{4,5} HR-XANES spectra for the estimation of An(V)/An(VI)-Oax bond lengths for actinyl cations. This can be a valuable tool for studies of systems with An concentrations below the limit for extended X-ray absorption fine structure (EXAFS) measurements [2.3].

We will also discuss the role of the 5f valence orbitals of U, Np and Pu in the chemical bonding. The level of localization and participation of the actinide (An) 5f valence orbitals in covalent bonds across the actinide series is one of the long-standing debates in actinide chemistry. An M_{4,5} HR-XANES and 3d4f RIXS results reveal that the 5f orbitals are active in the chemical bonding for U and Np, shown by significant variations in the level of their localization evident in the spectra. In contrast, the 5f orbitals of Pu appear localized and less sensitive to different bonding environments. It will be shown that the An M_{4,5} absorption edge HR-XANES and 3d4f RIXS can help to distinguish between the classical notion of overlap-driven covalency and energy-driven covalency [1.4].

Acknowledgements: This work is a joint effort from many scientists (cf. references). The authors acknowledge the Helmholtz Association of German Research Centers for the Helmholtz Young Investigators Group (VH-NG-734). We thank the Institute for Beam Physics and Technology (IBPT), KIT for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).

References

- [1] - T. Vitova, I. Pidchenko, D. Fellhauer, P.S. Bagus, Y. Joly, T. Pruessmann, S. Bahl, E. Gonzalez-Robles, J. Rothe, M. Altmaier, M.A. Denecke, H. Geckeis, **2017**, *8*, 16053.
- [2] - T. Vitova, I. Pidchenko, S. Biswas, G. Beridze, P.W. Dunne, D. Schild, Z.M. Wang, P. Kowalski, R.J. Baker, *Inorganic Chemistry* **2018**, *57*, 1735-1743.
- [3] - T. Vitova, I. Pidchenko, D. Fellhauer, T. Pruessmann, S. Bahl, K. Dardenne, T. Yokosawa, B. Schimmelpfennig, M. Altmaier, M. Denecke, J. Rothe, H. Geckeis, *Chem Commun* **2018**, *54*, 12824-12827.
- [4] - M. Zegke, X. Zhang, I. Pidchenko, J.A. Hlina, R.M. Lord, J. Purkis, G.S. Nichol, N. Magnani, G. Schreckenbach, T. Vitova, J.B. Love, P.L. Arnold, *Chem Sci* **2019**.
- [5] - A. Zimina, K. Dardenne, M.A. Denecke, D.E. Doronkin, E. Huttel, H. Lichtenberg, S. Mangold, T. Pruessmann, J. Rothe, T. Spangenberg, R. Steininger, T. Vitova, H. Geckeis, J.D. Grunwaldt, *Rev Sci Instrum* **2017**, *88*, 113113.

Uranium HERFD-XANES at MARS beamline

M.O.J.Y. Hunault, P.-L. Solari, D. Menut, H. Hermange

Synchrotron SOLEIL, L'Orme des merisiers, Saint-Aubin, 91192 Gif-sur-Yvette,
myrtille.hunault@synchrotron-soleil.fr

The use of an emission spectrometer to detect the actinide X-ray fluorescence and measure high-energy resolved fluorescence detected-XANES (HERFD-XANES) has opened new perspectives in the investigation of actinide electronic structure with X-ray spectroscopy. In particular, M-edge HERFD-XANES probes the actinide 5f empty states and allows investigating the 5f electronic localisation in light of the atomic structure.

The MARS (Multi-Analysis on Radioactive Samples) beamline at the SOLEIL synchrotron (France) is dedicated to the study of radioactive samples [1] with a specific radioprotection safety design that fulfills the French ASN (Autorité de Sûreté Nucléaire) requirements. Today, the maximum total equivalent activity present at the same time, including the storage on the beamline, is 185 GBq with a maximum of 18.5 GBq (0.5 Ci) per sample. The bending magnet source of the beamline offers an energy range from 3keV to 35keV. The recent development of an air-free set-up allowed us to reach the lower limit of this energy range and to measure the HERFD-XANES of uranium and plutonium M₄-edges.

Hexavalent uranium can form highly covalent UO₂²⁺ trans-dioxo linear species called uranyl. The chemical reactivity of these species is crucial in a number of applications including nuclear and medical domains, geochemistry and environmental sciences. The covalency of the uranyl and hence its reactivity in the equatorial coordination shell, is governed by the localization of the 5f electrons and strongly depends on the nature of the equatorial ligands. I will present the study of the influence of the uranyl equatorial coordination on the 5f electronic states with the example of amorphous and crystalline alkali-borate uranyl compounds.[2]

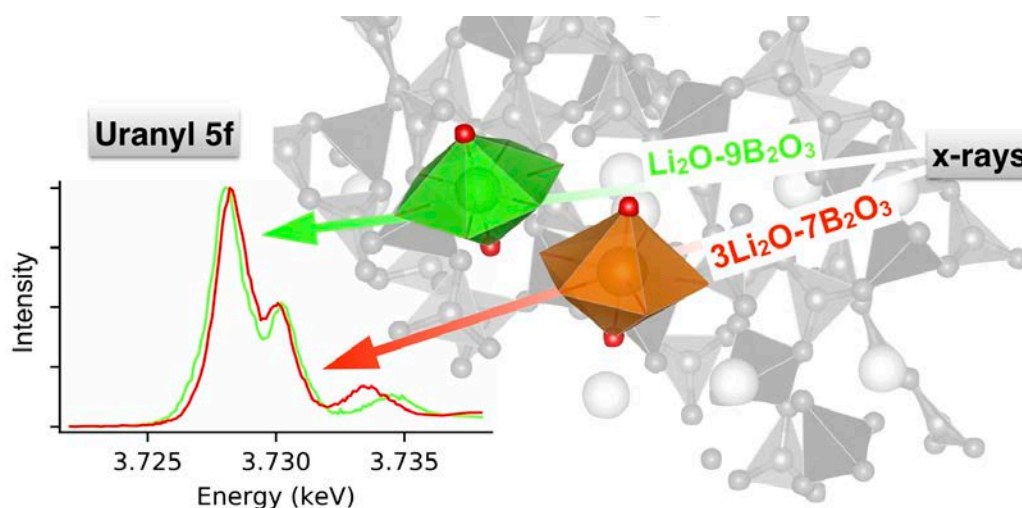


Figure 1: Influence of the uranyl equatorial coordination number on U M₄-edge HERFD-XANES.

References

- [1] - B. Sitaud, P.L. Solari, S. Schlutig, I. Llorens & H. Hermange, *J. Nucl. Mat.* **425**, 238-243 (2012).
- [2] - M.O.J.Y. Hunault *et al.*, *Inorg. Chem.* **58**, 6858-6865 (2019).

HERFD-XAS studies of actinide materials

L. Zhang, H. Yu, H. Bao, J.-Q. Wang

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China,
zhanglinjuan@sinap.ac.cn

Actinide elements as important nuclear fuel components, are hot topic in the field of environmental radiochemistry and nuclear energy materials. Actinide run through the whole industrial chain of nuclear energy, including the uranium extraction, spent fuel reprocessing, disposal solidification and other environmental phenomena. However, compared to the transition metals and lanthanides, the understanding of actinides is only the tip of the iceberg. Due to the high radioactivity and complex structure, the researches of actinide are relatively rare. The coordination environment, valence distribution and redox behaviour of actinide elements are far more complex than other elements. The key lies in the unique of actinide 5f electron. For example, the uranium 5f and 6d orbitals coupling and the interaction with the ligand 2p orbitals determine the structural stability of uranium species [1-3], further to affect the extraction, separation and solidification technology. However, due to weak crystal field in actinide compounds, the splitting of 5f electronic configurations are not easy to distinguished, which puts forward higher demand on experimental technology.

X-ray absorption fine structure spectroscopy has been widely confirmed as an element-selective and atomic level probe, which can unveil the chemical environment and bonding information in the actinide chemistry. However, due to heavy atomic number of actinides, short core-hole lifetime induces broader spectral pattern and cannot further to extract fine information of 5f electronic orbitals. High-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) with reduced spectral broadening can be obtained by employing an X-ray emission spectrometer, which is necessary for the actinide elements researches. The HERFD-XAS spectra at different edges, such as U L₃ and M_{4,5} edge have different widths of the spectral features. The HERFD-XAS spectra at the Th or U L₃ edge are generally recorded by monitoring the maximum of the L_{α1} (3d_{5/2}-2p_{3/2}) emission line, which has the highest transition probability compared with other emission lines. The spectral broadening can be further reduced if the L₃ edge XANES spectrum is collected at the L_{β5} (5d_{5/2}-2p_{3/2}) emission line. Recently, increasing works about actinide materials have been reported using HERFD-XANES technology [4-6]. Based on the Shanghai Synchrotron Radiation Facility, we also performed some HERFD-XAS experiments on beamline BL14W1 to exploring the charge transfer and covalency effects about the uranium and thorium oxides. In future, we wish make extensive use of HERFD-XAS studies of actinide chemistry and further tackle the problems in the structural evolution processes for actinide species from environmental radiochemistry and nuclear energy materials.

References

- [1] - R.G.Denning et al., J. Chem. Phys., 2002. **117**(17), 8008-8020.
- [2] - J., Su et al., Inorg. Chem., 2011. **50**(6), 2082-2093.
- [3] - S.O. Odoh and G. Schreckenbach, Inorg. Chem., 2013. **52**(9), 5590-5602.
- [4] - K. Kvashnina et al., Anal. Chem. 2015, **87**, 8772-8780.
- [5] - K. Kvashnina et al., Phys. Rev. Lett., 2013, **111**, 253002
- [6] - T. Vitova T. et al., Nat. Commun., 2017, **8**, 16053.
- [7] - H. Bao H. et al., Inorg.Chem., 2018, **57**, 11404-11413.

Uranium transport by Cl-bearing aqueous fluids: insights from HERFD-XAS

E.F. Bazarkina¹, W. Del Net², E. Lahera², M. Dargent³, J. Dubessy³, L. Truche⁴, O. Proux², M. Rovezzi², D. Testemale¹, J.-L. Hazemann¹

¹Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France, ²Univ. Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ³Univ. Lorraine, GeoRessources, Nancy, France, ⁴Univ. Grenoble Alpes, CNRS, ISTERre, 38000 Grenoble, France, elena.bazarkina@esrf.fr

The knowledge of aqueous chemistry of uranium at elevated temperature and pressure (*T-P*) has primary importance in hydrothermal ore deposit geochemistry. The unconformity type related U ore deposits display a major strategic importance with exceptional U concentration and tonnage [1]. Aqueous fluids circulating in the Earth's crust and associated with these deposits consist of Cl-rich evaporitic brines and can transport high concentration of dissolved uranium. [2] However, existing experimental studies on uranium hydrothermal transport are fragmentary and generally ignore the role of Cl complexes. Our recent in situ Raman spectroscopy measurements [3, 4] provided original results: 1) at 25-350°C the uranyl ions form stable chloride complexes; 2) at 250-350°C and high Cl concentration a new type of uranyl species appears; 3) the speciation of uranium controls the redox chemistry of uranyl and UO₂ precipitation. In order to identify this new uranyl species and the relationship between redox and speciation, we performed HERFD-XAS (High Energy Resolution Fluorescence Detection) measurements conducted at the French CRG beamline FAME-UHD at ESRF [5].

Conventional XAS data contain only limited XANES information. In contrast, the HERFD-XAS technique provides a better spectral resolution, more distinct XANES features, and thus allows better identification of the uranyl speciation changes. In particular, the energy-resolved spectra unveil the pre-edge feature around ~17171 eV, which corresponds to the quadrupole 2p_{3/2}-5f transition as described in other uranium compounds [6]. We have found that this pre-edge feature is the most pronounced for UO₂(H₂O)₆²⁺, but when Cl atoms replace H₂O molecules in this structure (with increasing Cl concentration or increasing *T*), this feature disappears progressively. This is the case of the unknown species we were chasing: according to the corresponding EXAFS modelling, this new uranium species contains 2 O atoms in axial plane and 3 Cl atoms in equatorial plane and displays an unusual trigonal bipyramidal structure. Such structure is unexpected for uranyl and could hardly be identified with conventional XAS data. In the presence of reducing agents, uranyl is reduced and precipitated (most commonly) as UO₂. However, the conditions when only the new trigonal bipyramidal complex is predominant are exceptional. In this case, all dissolved uranium (0.01*m*) can be reduced from UO₂Cl₃⁻ to UCl₆²⁻. The high total amount of dissolved reduced uranium has never been observed before. This finding opens new perspectives for hydrothermal transport of uranium in Cl-rich brines at reduced conditions and high *T*, and may have strong consequences for the understanding and modelling of uranium cycling in the Earth' crust.

References

- [1] - Richard et al., *Terra Nova* **22**, 303-308 (2010).
- [2] - Richard et al., *Nature Geoscience* **5**, 142-146 (2012).
- [3] - Dargent et al., *Eur. J. Miner.* **25**, 765-775 (2013).
- [4] - Dargent et al., *Geochim. Cosmochim. Acta* **167**, 11-26 (2015).
- [5] - Proux et al., *Journal of Environmental Quality* **46**, 1146-1157 (2017).
- [6] - Vitova et al., *Phys. Rev. B* **82**, 235118 (2010).

Structural biogeochemistry of mercury in wildlife

A. Manceau¹, B.A. Poulin², P. Bustamante³, Y. Cherel⁴, J.P. Bourdineaud⁵, A.C Gaillot⁶,
P. Glatzel⁷, K.L. Nagy⁸

¹ISTerre, Univ. Grenoble Alpes and CNRS, France (manceau@univ-grenoble-alpes.fr), ²U.S. Geological Survey, Boulder, USA (bpoulin@usgs.gov), ³LIENSs, CNRS-La Rochelle Univ., France (paco.bustamante@univ-lr.fr), ⁴CEBC, CNRS-La Rochelle Univ., France (cherel@cebc.cnrs.fr), ⁵IECB, Univ. Bordeaux and CNRS, France (jean-paul.bourdineaud@u-bordeaux.fr), ⁶IMN, Univ. Nantes and CNRS, France (anne-claire.gaillot@cnrs-immn.fr), ⁷ESRF, Grenoble, France (glatzel@esrf.fr), ⁸Univ. of Illinois at Chicago, USA (klnagy@uic.edu)

Mercury, a global pollutant widely distributed in aquatic and terrestrial ecosystems, is highly toxic to life. It hinders the biological function of proteins by binding to cysteine and selenocysteine residues, bioaccumulating and biomagnifying in food webs as predators eat other organisms. The chemical forms of mercury are usually determined by chemical analysis, and the sources and cycling of mercury in environmental systems can be traced by stable isotope geochemistry. As powerful as these methods are, chemical analysis only differentiates “inorganic” (divalent mercury, Hg(II)) from “organic” (methylmercury, MeHg) mercury, and isotopy does not provide information on the underlying molecular mechanisms that control the fractionation of mercury isotopes (e.g., $\delta^{202}\text{Hg}$). Precise knowledge of the molecular forms and transformation reactions of mercury in its biogeochemical cycle is key for understanding how it is bioaccumulated and detoxified, which is essential for protecting wildlife and designing treatment against mercury poisoning. The speciation of metals in environmental matter is obtained usually by X-ray absorption spectroscopy (EXAFS and XANES) and chemical reactions are modeled most often by the density functional theory (DFT). However, these two approaches have limited applications in the case of mercury for the following reasons: (1) the detection limit of standard EXAFS is at best 30-40 ng/mg (ppm), at least one order of magnitude too high to study the large majority of environmental samples, (2) L₃-edge XANES spectra are featureless because the width of the Hg(2p_{3/2}) level is 5.8 eV and, (3) Hg is a 5d element with strong relativistic effects not well accounted for by DFT.

The two first limitations have been overcome by development of a high-luminosity multi-crystal analyzer on beamline ID26 through the EcoX Equipex project. The third limitation has been addressed by modeling reaction pathways at a high level of molecular orbital theory (post-Hartree-Fock).

We will demonstrate how this new instrumentation laid the foundation for identifying two new mercury species in three animal phyla (birds, fishes, and earthworms). One is a dicysteinylyl Hg complex stabilized through interactions with secondary N/O electron donors, such as amine and amide nitrogen and carboxyl and carbonyl oxygen. This complex can transform into nanoparticulate metacinnabar ($\beta\text{-HgS}$). The second species is a tetraselenolate complex resulting from the demethylation of methylmercury. It is stable in waterbirds and transforms into tiemannite (HgSe) in seabirds. Calculations of the free and activation energies of the chemical reactions at the ccscd(t) level show that Hg is more selenophilic than thiophilic. Although HgSe is a detoxification product of methylmercury, its formation depletes the cell in Se, an essential element for selenoprotein synthesis and activity. The Hg-Se antagonism and Hg/Se toxicity threshold will be discussed.

Acknowledgement. The EcoX Equipex project is supported by the French National Research Agency (ANR) under Grant ANR-10-EQPX-27-01.

Revealing the chemical form of “invisible” gold in natural sulfides with high energy-resolution X-ray absorption spectroscopy

M. Merkulova^{1§}, O. Mathon¹, P. Glatzel¹, M. Rovezzi^{1,2}, A. Manceau³

¹European Synchrotron Radiation Facility (ESRF), 38000 Grenoble, France, ²Univ. Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ³Univ. Grenoble Alpes, CNRS, ISTERre, 38058 Grenoble, France, margarit.merkulova@gmail.com

Arsenian pyrite (FeS₂) and arsenopyrite (FeAsS) are the main auriferous minerals in refractory gold ores, such as Carlin-type gold deposits, in which gold is usually referred to as “invisible” gold. Despite the economic importance of gold its structural chemistry in arsenian pyrite and arsenopyrite is as yet unknown. The co-occurrence of Au and As in natural sulfides poses a challenge for measuring the Au L₃-edge X-ray absorption spectra because the Au L α emission line is partly (pyrite) to totally (arsenopyrite) obscured by the intense As K α line. A new five-crystal analyser spectrometer [1] developed on the EXAFS beamline BM23 of the ESRF allowed separating the Au L α and As K α lines. When combined with a micro-focused beam, the new spectrometer provided direct insight into the geochemistry and crystal chemistry of Au in natural heterogeneous ore samples (Fig. 1) [2]. High energy-resolution XANES (HR-XANES) shows that gold has a formal oxidation state of 1+ in the two sulfides, but a different bonding environment. In arsenian pyrite Au occupies the Fe site and is bonded to six S atoms at 2.41 Å, as determined by HR-EXAFS. In contrast, in arsenopyrite octahedrally coordinated Au is bonded only to As atoms at 2.52 Å. The results reveal the atomic-scale structure of gold and its intricate geochemical association with arsenic in auriferous Fe sulfides. This work demonstrates that high energy-resolution X-ray absorption spectroscopy on synchrotron X-ray microprobes can illuminate the structural chemistry of trace elements in chemically complex Earth and planetary materials.

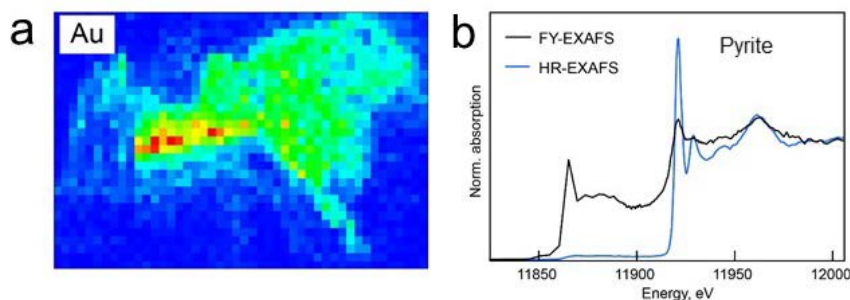


Figure 1: a. HR-SXRF map of Au distribution in arsenian pyrite, map dimension: $290 \times 150 \mu\text{m}^2$, pixel size: $5 \times 5 \mu\text{m}^2$; b. Fluorescence-yield XANES and HR-XANES of pyrite

§Present address: Department of Geology, University of Liege, B-4000 Liege, Belgium

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References

- [1] - M. Rovezzi et al., *Rev. Sci. Instrum.* **88**(1):013108 (2017).
- [2] - M. Merkulova et al., *ACS Earth Space Chem.* **3**, 1905 (2019).

New scientific opportunities for high energy-resolution XAS/XES measurements at ambient and extreme conditions - the ID24-EBS project

A.D. Rosa¹, O. Mathon¹, G. Spiekermann², M. Wilke², C. Sahle¹, M. Merkulova^{1,3},
M. Rovezzi^{1,4}, P. Glatzel¹ and A. Manceau⁵

¹ESRF, 71 Avenue des Martyrs, 38000 Grenoble, France, ²Institut für Geowissenschaften, Universität Potsdam, 14476 Potsdam, Germany, ³Department of Geology, University of Liege, B-4000 Liege, Belgium, ⁴UGA, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ⁵UGA, CNRS, ISTERre, 38058 Grenoble, France, angelika.rosa@esrf.fr

The new Extremely Brilliant Source (EBS) will feature an important increase in brilliance (10^{13} ph/s) combined with focusing capabilities down to 1 μm FW between 4 and 35 keV at ID24-DCM. It will open up new possibilities for the application of HP-HT spectroscopy and micro-spectroscopy of inhomogeneous materials at ambient and extreme conditions. This will allow studying trace elements embedded in chemically and structurally complex and highly absorbing matrices at higher dilution levels than before (down to few ppm), and with higher spatial resolution [1]. The EBS upgrade will also allow extending the reachable P/T domain at ID24-DCM to the conditions prevailing in the Earth's core (T up to 6000 K and P>150 GPa), and therefore studying heterogeneous samples and trace elements at such extreme conditions.

To fully exploit the capabilities of the new source, the recently developed and commissioned five crystal analyser spectrometer [2] will be installed on the ID24-DCM microspectrometer. The five crystal analyser permits to perform high energy resolution fluorescence detected (HERFD) measurements, which are used in different techniques, such as SXRF, XAS, XES and RIXS. Complementary to the spherically bent crystal analyser spectrometer, we plan to install 1-4 cylindrically bent analyser crystals at 90 degree scattering angle in the von-Hamos geometry. The crystals will be combined with a two-dimensional detector, which makes this setup ideally suited for time-resolved XES in high pressure and temperature sample environments (*i.e.*, laser-heated diamond anvil cell) [3].

I will provide information about the planned crystal-analyser setup at ID24-DCM that will reap the benefits of the EBS and present our plans for the extreme conditions XES programme at ID24-DCM/BM23.

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References

- [1] - M. Merkulova *et al.*, ACS Earth Space Chem. **3**, 1905 (2019).
- [2] - M. Rovezzi *et al.*, Rev. Sci. Instrum. **88**(1):013108 (2017).
- [3] - G. Spiekermann *et al.* Rev. Sci. Instrum. (in review).

Valence-to-core X-ray emission spectroscopy of germanate glasses: sensitivity with respect to coordination and network polymerization

G. Spiekermann¹, S. Petitgirard², K. Gilmore³, C. Sahle⁴, G. Henderson⁵, C. Sternemann⁶,
M. Wilke¹

¹University of Potsdam, ²ETH Zurich, ³BNL Brookhaven, ⁴ESRF Grenoble, ⁵University of Toronto, ⁶University of Dortmund, geospiek@uni-potsdam.de

Two important structural parameters in amorphous GeO₂ and in complex germanate glasses like those in the systems GeO₂-Na₂O and GeO₂-SiO₂, at ambient and at high pressure, are the degree of tetrahedral polymerization and the germanium coordination.

With this work, we aim at exploring the extent to which valence-to-core X-ray emission spectroscopy (vtc-XES) can provide this first- and second-coordination-shell information from amorphous germanium oxides.

We measured the vtc-XES spectra of germanium oxides at ambient and high pressure. The Kβ'' emission line, part of the vtc-XES spectra, is sensitive to coordination and oxygen-germanium bond distance as first coordination shell effects. Furthermore, it reflects the different binding energies of bridging and non-bridging oxygen atoms. The Kβ'' emission line may thus allow for tracking the coordination and the state of polymerization of a germanium oxide glass under pressure in diamond anvil cells or in other confining environments.

Reference for coordination sensitivity of Kβ'':

Spiekermann et al. (2019) Persistent octahedral coordination in amorphous GeO₂ up to 100 GPa revealed by Kβ'' X-ray emission spectroscopy, *Physical Review X*, 9, 011025.

High Energy Resolution Fluorescence Detected XANES spectra of Cu complexes

M.A. Soldatov, M.A. Kremennaya, C. Hureau¹, B. Lassalle², F. Collin¹

Southern Federal University, ¹LCC, CNRS and University of Toulouse, ²SOLEIL synchrotron,
mikhail.soldatov@gmail.com

Cu coordination and electronic structures in metalloenzymes or metalloproteins defines their function. X-ray absorption (XAS) and emission (XES) spectroscopies have been successfully applied to study local atomic and electronic structures of Cu binding site in Amyloid beta peptides [1-5]. Combination of high-energy resolution X-ray absorption and emission spectroscopy resulting in HERFD spectra is even more sensitive to local coordination and is capable of giving new information on the spin-state and oxidation state [6]. Moreover, XAS and XES could be used in physiological conditions - in aqueous solutions and give complementary information to protein crystallography. However, X-ray spectroscopy analysis is complicated by complex proteins structure and vast variety of different species and conformations in the liquid sample. Thus the optimization of combined theoretical and experimental analysis of HERFD XAS spectra on such simple biologically relevant molecules as Cu porphyrin, corrole and phthalocyanine could shed light on the local atomic and electronic structure of Cu proteins such as amyloid beta, superoxide dismutases, plastocyanin, etc.

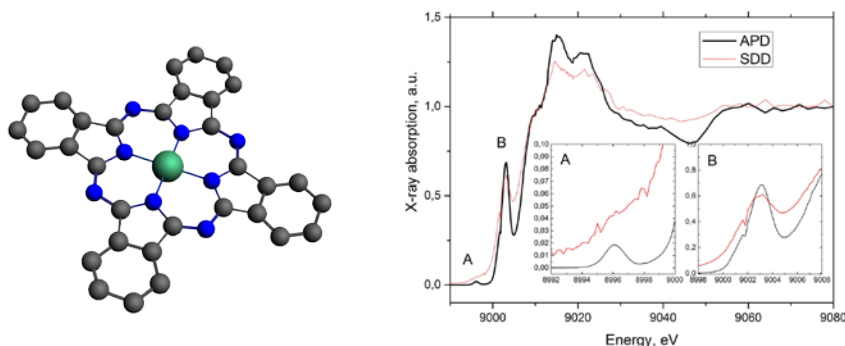


Figure 1: The structure of Cu phthalocyanine (left), comparison of HERFD (APD) and ordinary XANES (SDD) spectra measured for Cu phthalocyanine.

Experimental HERFD XANES spectra of Cu porphyrin, corrole and phthalocyanine in aqueous solution measured at Galaxies beamline of Synchrotron SOLEIL was analyzed by means of advanced theoretical methods. This could be a step forward in understanding the electronic structure of Cu complexes used for photodynamic therapy.

This work is supported by the Russian Science Foundation under grant №19-15-00305.

References

- [1] - C. Hureau, V. Balland, Y. Coppel et al, *J Biol Inorg Chem.* 14 (2009) 995.
- [2] - J. Shearer and V.A. Szalai, *J. Am. Chem. Soc.*, 130 (2008) 17826.
- [3] - V.A. Streltsov, S.J. Titmuss, V.C. Epa et al. *Biophys J.* 95 (2008) 3447.
- [4] - V.A. Streltsov and J.N. Varghese, *Chem. Commun.* (2008) 3169.
- [5] - A. Chaynikov, M. Soldatov, V. Streltsov et al *Journal of Physics: Conference Series* 430(2013) 012042.
- [6] F. M. F. de Groot, *AIP Conf. Proc.* 882 (2007) 37

***Ab initio* simulations to study valence to core XES and HERFD-XANES**

Y. Joly¹, M. Diaz-Lopez²

¹Institut Néel, CNRS, Grenoble, France ²Diamond Light Source and ISIS facility, Didcot, UK,
yves.joly@neel.cnrs.fr

Materials for catalysis and batteries have the complexity of their atomistic structure in common. Moreover, *operando*, the correlated atomic disorder can influence the chemical properties. Its understanding is crucial and X-ray spectroscopies are very good candidates for this purpose.

After a brief introduction to show how these spectroscopies are calculated in the *fdmnes* code, we present two cases where *ab initio* simulations help to solve the electronic and geometric structures of such materials. The first one concerns nanoparticles of Pt and PtSn adsorbed on alumina. We show that thanks to XANES recorded in High-resolution Fluorescence Detection mode, the *ab initio* determination of their structure and the confrontation to the calculated spectra, it is possible to find the general structure of the particles, with the number of Hydrogen atoms bonded to them. The second one deals with characterization of nano-Li₂MnO₃ where both HERFD-XANES and XES were used to observe the local geometry and some aspects of the associated electronic structure.

Wavefunction based approaches in X-ray spectroscopy

D. Maganas

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany,
dimitrios.maganas@kofo.mpg.de

With the aim to uniquely correlate spectroscopic properties to electronic structure and geometric properties of target materials, we employ in house developed wavefunction based methods in an effort to evaluate unique spectroscopic signatures of transition metal complexes and materials in both equilibrium and under operando conditions. This requires to use methods that do not belong in the standard arsenal of quantum chemistry. Over the last years we have developed and employed the restricted open shell configuration interaction singles methods (ROCIS and PNO-ROCIS) and their parameterized versions, (ROCIS/DFT and PNO-ROCIS/DFT)[1,2] to compute a large variety of XAS and valence to core resonance X-ray emission spectra (VtC-RXES) of classes of chemical systems ranging between molecules to ‘real-life’ molecular and solid systems [2,3]. Recently even more accurate computational protocols based on the complete active space configuration interaction in conjunction with N-electron valence second order perturbation theory (CASCI/NEVPT2)[4] as well as multireference configuration interaction (MRCI) and multireference equation of motion coupled cluster (MREOM-CC)[5] methods have been employed to compute challenging metal L-edge XAS spectra of medium sized molecules with high predictive accuracy. The talk will provide an overview of all the above methods and will explore their abilities in representative examples.

References

- [1] - M. Roemelt, D. Maganas, S. DeBeer and F. Neese, *J. Chem. Phys.*, **138**, 204101 (2013).
- [2] - D. Maganas, S. DeBeer, F. Neese, *J. Phys. Chem. A*, **122**, 1215 (2018).
- [3] - D. Maganas, S. DeBeer, F. Neese, *Inorg. Chem.* **56**, 11819 (2017).
- [4] - A. Chantzis, J. K. Kowalska, D. Maganas, S. DeBeer, F. Neese, *J. Chem. Theo. Comp.* **14**, 3686 (2018).
- [5] - D. Maganas, J. K. Kowalska, M. Nooijen, S. DeBeer, F. Neese, *J. Chem. Phys.* **150**, 104106 (2019).

Modeling Resonant Inelastic X-ray Scattering and Resonant X-ray Emission in the LDA+DMFT framework

J. Kolorenč

Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 182 21 Praha, Czech Republic,
kolorenc@fzu.cz

I will introduce a theoretical description of photon-in/photon-out resonant X-ray spectroscopies, which is based on the Anderson impurity model. The parameters of the model are determined with the aid of the material-specific LDA+DMFT electronic-structure calculations and the spectra themselves are evaluated using a combination of the Krylov subspace methods [1].

As an application, I will discuss the valence-to-core resonant inelastic X-ray scattering (RIXS) at the europium L_3 edge in the ferromagnetic semiconductor EuS. In this setup, the main signal comes from the direct RIXS: an Eu 2p core electron is excited to an empty Eu 5d band above the Fermi level, and then another electron from an Eu 5d state hybridized with the S 3p bands (located below the Fermi level and hence occupied) fills back the Eu 2p core hole. I will analyze if one can expect to detect also indirect RIXS processes where additional excitations are induced by the Coulomb potential of the 2p core hole.

In the EuS example, the multiplet coupling between the deep Eu 2p core hole and the open Eu 4f shell in the intermediate state of the RIXS process is negligible. The same, however, is not true for resonant X-ray emission (RXES) when a shallower core hole (3d or 4d) is present in the final state. I will illustrate these core-hole effects, relate them to effects seen in the core-level photoemission [2,3], and discuss them also in the context of the high-resolution fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS).

References

- [1] - J. Kolorenč, *Physica B* **536**, 695 (2018).
- [2] - C. Caspers, M. Müller, A. X. Gray, A. M. Kaiser, A. Gloskovskii, C. S. Fadley, W. Drube, and C. M. Schneider, *Phys. Rev. B* **84**, 205217 (2011).
- [3] - P. S. Bagus, C. J. Nelin, C. R. Brundle, S. A. Chambers, *J. Phys. Chem. C* **123**, 7705 (2019).

Chemical sensitivity of $K\beta$ and $K\alpha$ X-ray emission spectroscopy: insights from a systematic investigation on iron compounds

S. Lafuerza¹, A. Carlantuono², M. Retegan¹, P. Glatzel¹

¹ESRF - The European Synchrotron, CS40220, F-38043 Grenoble Cedex 9, France, ²Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy, sara.lafuerza@esrf.fr

K fluorescence X-ray emission spectroscopy (XES) is increasingly used in all branches of natural sciences to investigate the spin moment in $3d$ transition metal compounds. Unlike the valence-to-core emission lines, the core-to-core transitions in $K\beta$ ($3p$ to $1s$) and $K\alpha$ ($2p$ to $1s$) do not probe the valence shell directly and the chemical sensitivity is thus indirect. In $K\beta$ and $K\alpha$ emission the chemical sensitivity arises from intra-atomic electron-electron interactions. In particular, the local spin sensitivity stems from the exchange interaction between the $3p$ ($K\beta$) or $2p$ ($K\alpha$) core-hole and the $3d$ valence shell spin of the transition metal ion, which is larger for $K\beta$ than $K\alpha$ [1]. The magnitude of the exchange interaction depends for a given element on the valence shell spin, which, within an ionic picture, is defined by the metal atom oxidation and spin state. This is a very crude description of the electronic structure and the influence of covalence in $K\beta$ has been pointed out by several authors [1,2].

Herein, we present a thorough investigation of $K\beta$ and $K\alpha$ XES spectra measured on a wide range of Fe compounds with the aim to get further insights into the spectral sensitivity beyond an ionic model. More than 30 samples with different oxidation state (+2, +3, +4 and mixed-valence), spin (high spin, low spin and mixed-spin), ligands (fluorides, oxides, sulfides, etc.) or local coordination (octahedral, tetrahedral) were measured at beamline ID26 of the ESRF. We analysed the experimental spectra in terms of commonly used quantitative parameters ($K\beta_{1,3}$ -first moment, $K\alpha_1$ -full width half maximum, and integrated absolute difference –IAD- [3]) and we examined the fine structure in the difference spectra. Semi-empirical multiplet calculations were also performed to interpret the experimental trends.

Our results provide evidence that covalency strongly influences both $K\beta$ and $K\alpha$ lines. We establish a reliable local spin sensitivity of $K\beta$ XES as it is dominated by the exchange interaction whose variations can be quantified by either $K\beta_{1,3}$ -first moment or $K\beta$ -IAD and result in a systematic difference signal lineshape. For $K\alpha$ XES, the smaller exchange interaction together with the influence of other electron-electron interactions make it difficult to extract a quantity that directly relates to the spin.

References

- [1] - P. Glatzel and U. Bergmann, *Coord. Chem. Rev.* **249**, 65 (2005).
- [2] - C.J. Pollock, M.U. Delgado-Jaime, M. Atanasov, F. Neese and S. DeBeer, *J. Am. Chem. Soc.* **136**, 9453 (2014).
- [3] - G. Vankó, T. Neisius, G. Molnár, F. Renz, S. Kárpáti, A. Shukla, and F.M.F. de Groot, *J. Phys. Chem. B* **110**, 11647 (2006).

The transition metal K edge spectral shape

F. de Groot

Inorganic Chemistry and Catalysis, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, Netherlands,
f.m.f.degroot@uu.nl

The 1s X-ray absorption spectra (XAS) of 3d transition metal systems will be discussed, also based on the analysis of 1s2p resonant X-ray emission (XES) and 1s X-ray photoemission (XPS) spectra.

The 1s XAS spectrum can be divided in the pre-edge involving transitions into the 3d-band and the edge involving transition into the higher-energy metal p-character bands. Recently we measured a series of 1s XPS spectra of transition metal oxides, which show multiple peaks/features [1]. This observation implies that with the excitation at one photon energy above the X-ray absorption edge a series of states with different binding energies is reached. In other words, a series of electrons with different kinetic energies is created and a 1s XAS spectrum cannot be interpreted from the electron scattering of an electron with a single kinetic energy. This implies that the usual interpretation of the 1s XAS spectrum as excitations to the empty metal p-projected density of states breaks down. It is a better approach to convolute the calculated DOS with the 1s XPS spectral shape.

The pre-edge of the 1s XAS spectrum contains the 1s3d quadrupole excitations. These excitations involve the transition from the $3d^N$ ground state to the $1s^1 3d^{N+1}$ final state. These excitations are self-screened and the pre-edge can be calculated with the multiplet interpretation. Tetrahedral coordination complexes have more intense pre-edge structures due to the local mixing of 3d and 4p states, implying a combination of 1s 3d quadrupole and 1s 4p dipole transitions, where this local dipole-quadrupole mixing that can be included into the multiplet calculations.

In general, divalent transition metal oxides can be described similar to coordination complexes, but for oxides with a higher valency, additional structures are visible in the pre-edge region due to non-local dipole transitions [2]. The non-local dipole transitions involve a 1s4p local transition, where the 4p-states of the metal ion has overlap with the 3d-states of a nearby transition metal ion, mediated via the bridging oxygen. The non-local peak is not pulled down by the core hole potential as much as the local transitions, creating an energy difference of approximately 3 eV in the 1s XAS spectra. The non-local peaks can also be observed for mixed-metal oxides; for example the iron 1s XAS spectrum of FeTiO_3 contains a non-local peak due to the iron p-states mixed with the 3d states of the nearby titanium atoms [3].

References

- [1] - M. Ghiasi, A. Hariki, M. Winder, J. Kuneš, A. Regoutz, T.L. Lee, Y. Hu, J.-P. Rueff, F.M.F. de Groot, Charge-transfer effect in hard X-ray 1s and 2p XPS spectra, *Phys. Rev. B.* 100, 075146 (2019).
- [2] - F.M.F de Groot, G. Vanko and P. Glatzel, The 1s X-ray absorption pre-edge structures in transition metal oxides, *J. Phys.: Condens. Matter* 21, 104207 (2009).
- [3] - M. Hunault, W. Khan, J. Minár, T. Kroll, D. Sokaras, P. Zimmermann, M.U. Delgado-Jaime, F.M.F. de Groot, Local vs Nonlocal States in FeTiO_3 Probed with 1s2pRIXS, *Inorg. Chem.* 56, 10882 (2017).

Development of X-ray absorption spectroscopic methodology for investigating relaxation processes in periodically driven systems

H. Singh^{1,2}, D. Donetski³, J. Liu³, K. Attenkofer⁴, B. Cheng¹, J.R. Trelewicz¹,
I. Lubomirsky⁵, E. Stavitski⁴, A.I. Frenkel¹

¹Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, USA, ²Nano and Molecular Systems Research Unit, University of Oulu, FIN-90014, Finland, ³Department of Electrical and Computer Engineering, Stony Brook University, Stony Brook, New York 11794, USA, ⁴National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, USA, ⁵Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel, singh85harish@gmail.com

Rationing advanced nanoscale functional materials such as catalysts and electrocatalysts, electromechanical actuators, battery and energy materials for improved performances and greater versatility are the key drivers of innovation. This is also because they exhibit new functionalities due to the changes in their local structures and electronic properties that occur within a range of a few interatomic distances. There is a paucity of either available experimental methods or a dedicated research infrastructure in the case of materials in which the response to the external stimulation is weak [1]. Through this work, we present the development, testing and demonstration of a setup for modulation excitation spectroscopy experiments recently developed at the Inner Shell Spectroscopy (ISS) beamline of NSLS-II [2]. A computer algorithm and dedicated software were developed for asynchronous data processing and analysis. The setup and the software will be applicable to a broad range of functional materials which exhibit structural and/or electronic responses to the external stimulation, such as catalysts, energy and battery materials and electromechanical devices. The external simulation under which materials exhibit dynamic response can be electric or magnetic field, temperature, pressure, gas composition, electromagnetic radiation (e.g. UV or visible light), etc. In one class, such as classical electro- or magnetostrictors or piezoelectrics the structural or electronic response to the external excitation is uniform but weak. In the other class, such as nanocatalysts or some electromechanical materials, only a small subset of the material responds to the external stimulation. Coupled with high flux and dedicated data acquisition software that enables synchronization of the external stimulation and X-ray spectra the setup enables a broad range of experiments with periodic external stimulation, aimed at investigation of functional materials with weak structural and electronic responses. We have also investigated measurements regimes in terms of the signal quality (energy resolution and signal to noise ratio), in order to provide guidance to future applications of this setup. The method can be applied to a broad range of problems, from studying novel electromechanical properties in thin films to nanoscale catalysts to battery and solar cell materials. Together, these capabilities cover a broad range of systems that exhibit novel functionalities due to their local structural effects and will enable modulation excitation spectroscopy research by synchrotron X-ray absorption methods.

References

- [1] - P.Müller, I. Hermans, *Ind. & Eng. Chem. Res.* **56**, 1123 (2017).
- [2] - H. Singh, D. Donetskiy, J. Liu, K. Attenkofer, B. Cheng, J.R.Trelewicz, I. Lubomirsky, A. Stavitski, A.I. Frenkel, *Rev. Sci. Instrum.* **89**, 045111 (2018).



Poster Abstracts



EBS workshop on X-ray Emission Spectroscopy
3, 4 & 5 December 2019
ESRF Grenoble

List of Posters

- L. Amidani** Simulations of HERFD XANES of actinide systems
- C. Bacellar** Ultrafast electronic and structural dynamics of heme proteins unveiled by time-resolved X-ray spectroscopy at XFELs
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- R. Gnewkow** Potential of highly annealed graphite crystal analyzers for von Hamos spectrometers
- N. Hyatt** Developing laboratory based X-ray Absorption Spectroscopy for nuclear waste management
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- M. Irar** X-ray absorption spectroscopy study of aqueous electrolyte solution critical properties
- N. Kawamura** X-ray Emission Spectrometer at BL39XU of SPring-8
- I. Kieffer** SSHADE, the European solid spectroscopy database infrastructure
- A. Longo** Observation of electronic metal support interaction: investigation of Au/Ceria catalysts by HERFD-XANES
- S. Malyshev** Novel Nd_{2-y}CayCo_{1-x}NixO₄-driven nanocomposite POM catalysts: synthesis, catalytic performance and chemical transformations
- A. Malysheva** Chiral BINAM-containing macrocycles for enantioselective fluorescent detection

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| O. Mathon | ID24-EBS project: a hard X-ray crystal analyser combined with a micro-focused beam for XAS/XES measurements |
| V. Mazalova | Time-resolved XES studies on photosystem II and manganese model compounds |
| F. Otte | Determining the footprints of organic ligands in X-ray Raman spectroscopy during spin-transition in transition metal complexes |
| C. Pollock | Development of a 'barrel' von Hamos XES spectrometer and its application to catalytically-relevant platinum compounds |
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| G. Subias Peruga | Probing atom off-centering displacements in epitaxial strained Sr _{1-x} BaxMnO ₃ thin films by HERFD-XANES |
| P. Tack | Development of a laboratory based quick X-ray absorption and emission spectrometer in a Von Hamos geometry |
| F. Tavani | Investigating Cu(II) solvation through Resonant Valence-to-core X-ray Emission Spectroscopy |
| A. Trigub | In-, Au-, and Cu-bearing sphalerites studied by X-ray absorption spectroscopy |
| N. Trofimov | The state of copper, silver and indium in sphalerite studied by X-ray spectroscopy of synthetic crystals and natural minerals |
| W. van Beek | SNBL BM31: towards multi probe operando XRD + XAS + PDF |
| R. Verbeni | Crystal Analyser Laboratory at the ESRF |
| H. Yu | Uranium-induced changes in crystal-field and covalency effects of Th ⁴⁺ in Th _{1-x} U _x O ₂ mixed oxides probed by high energy resolution fluorescence detected X-ray absorption spectroscopy |

Simulations of HERFD XANES of actinide systems

L. Amidani and K. Kvashnina

Institute of Resource Ecology, Helmholtz Zentrum Dresden-Rossendorf, Dresden, Germany, The Rossendorf Beamline at ESRF, The European Synchrotron, Grenoble, France, lucia.amidani@esrf.fr

X-ray Absorption Near-Edge Structure (XANES) is an invaluable tool in material science, allowing to probe the oxidation state and the local electronic structure of a selected atomic species. The theory behind XANES is complex and extracting information from data is not straightforward. Nowadays the availability of *ab initio* codes specifically written for XANES analysis boosted the interpretation of XANES. Moreover, the use of High Energy Resolution Fluorescence Detected (HERFD) XANES, giving better-resolved spectral features, increases the information that can be extracted. HERFD XANES is particularly advantageous to study actinide systems since the gain in resolution is big.

We present two examples where we systematically used the *ab initio* code FDMNES [1] to reproduce the HERFD XANES L_3 edge and obtained valuable information on the local structure of the systems studied: ThO_2 nanoparticles and U adsorbed on graphene oxide. The analysis of ThO_2 small nanoparticles revealed that a post-feature of the Th L_3 edge is very sensitivity to the more exposed cations at the surface [2].

The simulations of U adsorbed in different local geometries onto graphene oxide reveals that it preferentially occupies holes in the graphene sheet, pointing out to the importance of the defect density in the perspective of maximizing the adsorption capabilities of graphene oxide [3].

The cases presented illustrate that HERFD XANES supported by *ab initio* simulations have great potential for the investigation of actinide-based materials.

References

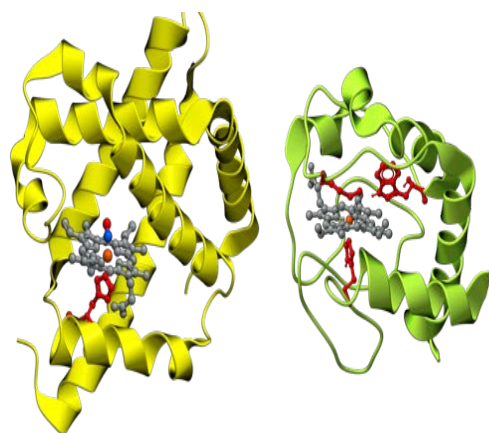
- [1] - O. Bunau and Y. Joly, J. Phys.: Condens. Matter **21**, 345501 (2009).
- [2] - L. Amidani et al., Phys. Chem. Chem. Phys. **21**, 10635 (2019).
- [3] - A.S. Kuzenkova et al., Carbon, *in press*.

Ultrafast electronic and structural dynamics of heme proteins unveiled by time-resolved X-ray spectroscopy at XFELs

C. Bacellar^{1,2}, D. Kinschel^{1,2}, R. Ingle², G.F. Mancini^{1,2}, J. Rouxel^{1,2}, O. Canelli¹, B. Sorokin¹, J. Budarz¹, C. Cirelli², G. Knopp², P. Johnson², S. Menzi², G. Pamfilidis², J. Szlachetko³, F.A. Lima⁴, W. Gawelda⁴, D. Khakhulin⁴, C. Bressler⁴, T. Katayama⁵, Y. Obara⁶, J. Nishitani⁷, H. Ito⁶, T. Ito⁶, N. Kurahashi⁸, C. Higashimura⁷, S. Kudo⁷, T. Suzuki⁷, K. Misawa⁵, C. Milne² and M. Chergui¹

¹LSU, Ecole Polytechnique Fédérale de Lausanne, Switzerland, ²SwissFEL, Paul Scherrer Institute, Switzerland, ³Institute of Physics, Jan Kochanowski University in Kielce, Poland, ⁴European XFEL, Germany, ⁵XFEL Division, Japan Synchrotron Radiation Research Institute, Japan, ⁶Tokyo University of Agriculture and Technology, Japan, ⁷Kyoto University, Japan, ⁸Sophia University, Japan,
camila.bacellar@epfl.ch

Metalloproteins correspond to almost half of all known proteins. In these proteins, the metal-binding center is paramount to protein function and iron containing heme proteins are amongst the most important ones. Myoglobin was the first three-dimensional structure ever resolved by x-ray crystallography, and since then much effort has been dedicated to the study of the structure, function and dynamics of these subgroup of proteins. Time-resolved X-ray spectroscopy, and particularly X-ray Emission (XES), is a particularly well-suited tool to investigate these systems. The element specificity provides a direct and sensitive probe of the protein dynamics from the metal-binding center point of view. This work focuses in the investigation of light induced ultrafast electronic and structural dynamics of two important heme proteins, Nitrosyl Myoglobin (MbNO) and Cytochrome C (CytC), by femtosecond time-resolved x-ray absorption (fs-XAS) and x-ray emission (fs-XES) spectroscopies.



The structures of Myoglobin (left) and Cytochrome C (right).

Upon visible photoexcitation of the heme group (530 nm) MbNO undergoes dissociation of the ligand (NO) which is accompanied by a spin change and a structural reconfiguration of the porphyrin ring. Part of the excited population undergoes recombination in multiple timescales through an intermediate state that is presumed to be a high spin domed ligated form of MbNO. We carried out a combined time-resolved non-resonant XES and Fe K-edge XAS experiment in physiological media. The results offer new insight on the dissociation-recombination dynamics and capture the signature of the proposed hexacoordinated intermediate state.

Meanwhile, in CytC we focused on the investigation of the nature of the relaxation process following excitation of the heme at 350-400 nm. Ferrous heme proteins such as the MbNO example above are known for undergoing dissociation of the axial ligand, however this is not observed in their ferric counterparts. This has led to a long discussion of the relaxation pathway involved in these types of systems, which for the most part was believed to be entirely via vibrational cooling back to the ground state. We recently performed fs-XAS and fs-XES experiments that challenge this interpretation evidencing the presence of heme doming and de-excitation via high spin states.

PyXES: the all-in-one beamline control and data analysis tool for HERFD/XES/RIXS

S. Bauters^{1,2}, V. Dyadkin³, A. Scheinost^{1,2}, K. Kvashnina^{1,2}

¹Rossendorf Beamline at ESRF - The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France, ²Helmholtz Zentrum Dresden-Rossendorf, Institute of Resource Ecology, PO Box 510119, 01314, Dresden, Germany, ³ESRF - The European Synchrotron, Swiss Norwegian Beamlines, Grenoble, France, stephen.bauters@esrf.fr

With the rise of High Energy Resolution Fluorescence Detected (HERFD) X-ray Absorption Near-Edge Structure (XANES) and the increasing presence of multi-crystal spectrometers at beamlines all around the world, the need for straight-forward user-friendly tools to perform data acquisition and analysis has also risen^[1,2].

PyXES is a newly developed program capable of controlling all necessary equipment involved with HERFD, X-ray Emission Spectroscopy (XES) and Resonant Inelastic X-ray Scattering (RIXS) experiments; monochromator movement, defining scan parameters, multi-crystal alignment and movement are all possible with or without SPEC. The online data visualisation tools combined with the easy to use macro builder allow for a completely Graphical User Interface (GUI) based control, if preferred. Also several tools for off-line data treatment and analysis are available, creating an all-in-one user experience from start to finish.

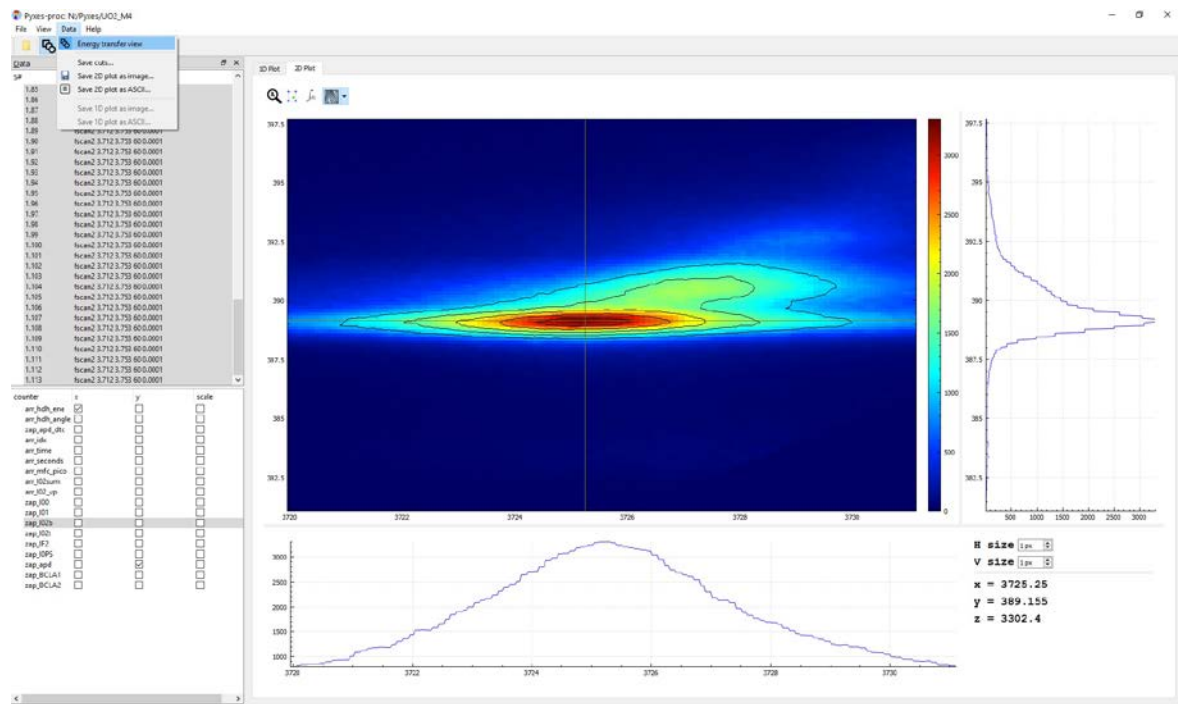


Figure 1: Example of the data analysis module displaying UO₂ M4 RIXS data with energy transfer y-axis

References

- [1] - K. Hämäläinen, D.P. Siddons, J.B. Hastings and L.E. Berman, Phys. Rev. Lett., 1991, 67, 2850-2853.
- [2] - P. Glatzel, T.-C. Weng, K. Kvashnina, J. Swarbrick, M. Sikora, E. Gallo, N. Smolentsev and R.A. Mori, J. Electron Spectros. Relat. Phenomena, 2013, 188, 17-25.

SNBL BM31: towards multi probe operando XRD + XAS + PDF

H. Emerich, G. Wiker, D. Chernyshov, V. Dyadkin and W. van Beek

Swiss Norwegian Beamlines at ESRF, 71, Avenue des Martyrs, Grenoble, France, wouter@esrf.fr

The availability of experimental methods that probe a material's structure, often complex and dynamic, at different length and time scales is key to obtain fundamental insight in technologically relevant materials and environmental geochemistry. Indeed, progress in sustainable technologies relies on the development of innovative materials utilizing an in-depth understanding of the interplay between a material's structure and its macroscopic properties. To this end, there is a need for advancing current X-ray based facilities allowing the study of materials with multiple techniques at their working state (i.e., operando methods).

The BM31 station of the Swiss Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF), offers the possibility to combine X-ray absorption spectroscopy (XAS) and X-ray powder diffraction (XRD) in an alternating fashion, quasi-simultaneously, in the same experimental setup. SNBL aims at extending these capabilities, by upgrading the current setup with a new CdTe area detector and focusing capabilities. This equipment will allow to i) implement pair distribution function analysis (PDF) of total scattering data, enabling combined XRD-PDF-XAS experiments and ii) enhance appreciably both the temporal (~ 1 s for XAS, ~ 100 ms for XRD-PDF) and spatial resolution (utilizing a beam size of $\sim 100 \times 100 \mu\text{m}^2$) of the experiments. The upgraded BM31 optics and endstation will also be compatible with the implementation of a XES von Hamos spectrometer, foreseen at a later stage.

The combined XRD-PDF-XAS measurements will allow the acquisition of complementary information of a material under the relevant working conditions: covering the length-scale from short to mid-range atomic arrangements viz. $\sim 1 \text{ \AA}$ to several nm by PDF, the average structure by XRD, as well as the electronic state, and geometry around the element of interest by XAS. All these data can be acquired in a temporal and spatially resolved manner in a single experiment. This will constitute a unique tool allowing the detailed study of materials for a wide range of applications, for instance: heterogeneous and electrocatalysis, CO_2 capture, gas separation, batteries and trace element reactions in environmental studies.

The state of Au and As in pyrite studied by X-ray absorption spectroscopy of natural minerals and synthetic phases

O.N. Filimonova¹, A.L. Trigub², M.S. Nickolsky¹, E.V. Kovalchuk¹, V.D. Abramova¹,
M. Rovezzi³, E. Belogub⁴, I.V. Vikentyev¹ and B.R. Tagirov¹

¹Institute of Geology of Ore Deposits (IGEM RAS), 35, Staromonetny per., 119017 Moscow, Russia, ²NRC “Kurchatov Institute”, Moscow, Russia, ³Université Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ⁴Institute of Mineralogy, Urals Branch of RAS, Chelyabinsk District, 456317 Miass, Russia, oliel@list.ru

Arsenian pyrite FeS₂ of hydrothermal origin can contain considerable amount of “invisible” (or refractory) Au. The Au and As contents in pyrite are often directly correlated. In the present work the oxidation states and the local atomic environments of Au and As were determined using X-ray absorption spectroscopy (XAS). The samples of natural (from Au-sulfide and Carlin type deposits) and synthetic (450 °C/ 1 kbar, 300 °C/ P_{sat}) arsenian and As-free pyrites were studied. The Au L_3 -edge and As K -edge XAS spectra were recorded at BM16 FAME-UHD beamline of ESRF (Grenoble) and STM beamline of KSRS (Moscow, Russia, only As spectra). The High Energy Resolution Fluorescence Detection mode (HERFD) was applied to record the Au spectra. The As K -edge spectra were obtained simultaneously with the Au L_3 -edge ones. The XAS data processing was performed using IFEFFIT package. The analyses of Au L_3 -edge XAS data showed that Au in pyrites is present in two forms: Au¹⁺ in the solid solution state where Au substitutes for Fe and is surrounded by 6 S atoms, and Au in Au¹⁺₂S-like clusters where Au is surrounded by 2 S atoms. Significant fraction of Au¹⁺₂S-like clusters results in decrease of the average Au-S bond length and coordination number observed by means of the EXAFS spectra fitting. The admixture of As has no effect on the Au oxidation state and local atomic environment (Fig.1), except one synthetic sample which contains a minor amount of FeAsS or FeAs₂. The presence of these phases is consistent with results of SEM/EDS and EPMA analyses. The analyses of As K -edge absorption spectra showed that As mostly presents in the solid solution state substituting S atoms in the pyrite matrix ($\text{S}^{1-} \leftrightarrow \text{As}^{1-}$). Our data demonstrate that natural pyrites of hydrothermal origin can host economic concentrations of “invisible” Au in solid solution state independently of As content.

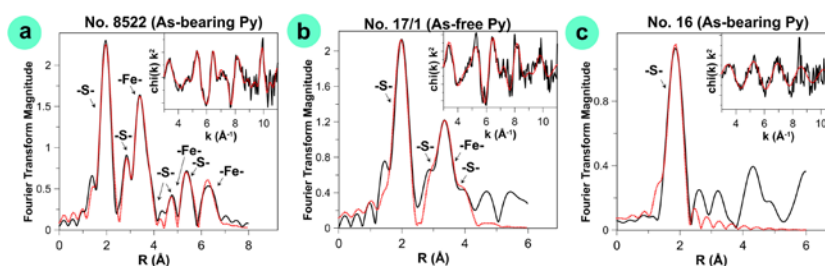


Figure 1: The k^2 -weighted background-subtracted Au L_3 -edge EXAFS spectra and their Fourier transforms (FT, not corrected for phase shift). (a) - natural; (b, c) - synthetic pyrites. The spectra of natural arsenian (a) and synthetic As-free (b) pyrites are similar; As is absent in the nearest coordination shells of Au in natural (a) and synthetic (c) arsenian pyrites.

An expanding view on plutonium oxide nanoparticles

E. Gerber^{1,2,3}, A. Yu. Romanchuk³, I. Pidchenko^{1,2}, L. Amidani^{1,2}, A. Rossberg^{1,2},
C. Hennig^{1,2}, G. Vaughan⁴, A. Trigub⁵, T. Egorova³, S. Bauters^{1,2}, T. Plakhova³,
M O.J.Y. Hunault⁶, S. Weiss², S.M. Butorin⁷, A.C. Scheinost^{1,2}, S.N. Kalmykov^{3,5} and
K.O. Kvashnina^{1,2}

¹Rossendorf Beamline at ESRF – The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France, ²Helmholtz Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, PO Box 510119, 01314, Dresden, ³Lomonosov Moscow State University, Department of Chemistry, 119991 Moscow, Russia, ⁴ESRF – The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France, ⁵National Research Centre “Kurchatov Institute”, 123182 Moscow, Russia, ⁶Synchrotron SOLEIL, L’Orme des Merisiers, Saint Aubin BP 48, 91192 Gif-sur-Yvette, France, ⁷Molecular and Condensed Matter Physics, Department of Physics and Astronomy, Uppsala University, P.O. Box 516, Uppsala, Sweden, evgeny.gerber@esrf.fr

The nanoscience field often produces results more mystifying than any other discipline. It has been argued that changes of the plutonium dioxide (PuO₂) particle size from bulk to nano can have a drastic effect on PuO₂ properties [1-2]. Here we report a full characterization of PuO₂ nanoparticles (NPs) at the atomic level and probe their local and electronic structure. The particles were synthesized from precursors with different oxidation states (Pu III, IV and V) under various environmentally and waste storage relevant conditions (pH 8 and pH 12). Synthesized PuO₂ nanoparticles were studied by complementary methods: X-ray diffraction (XRD), atomic pair distribution function analysis (PDF), high energy resolution fluorescence detection (HERFD) X-ray absorption spectroscopy at the Pu L₃ and M₄-edges [3] and extended X-ray absorption fine structure (EXAFS) spectroscopy. This approach - the application of multifold synchrotron methods - is crucial to confirm results, obtained with individual methods. By combinations of these techniques it was found that small (2 nm) nanoparticles are formed from the Pu(III), Pu(IV), Pu(V) aqueous solutions at pH 8 and 12, with the crystal structure close to PuO₂, without any other Pu-O contributions or oxidation states of Pu except Pu(IV) [4].

References

- [1] - A.P. Novikov, S.N. Kalmykov, S. Utsunomiya, R.C. Ewing, F. Horreard, A. Merkulov, S.B. Clark, V.V. Tkachev, B.F. Myasoedov, *Science* **314**, 638 (2006).
- [2] - A. Yu. Romanchuk, T.V. Plakhova, A.V. Egorov, T. B. Egorova, P.V. Dorovatovskii, Ya.V. Zubavichus, A.A. Shiryaev, S.N. Kalmykov, *Dalton Trans.* **47**, 11239 (2018).
- [3] - K.O. Kvashnina, A. Romanchuk, I. Pidchenko, L. Amidani, E. Gerber, A. Trigub, A. Rossberg, S. Weiss, K. Popa, O. Walter, R. Caciuffo, A. Scheinost, S. Butorin, S. Kalmykov, *Angewandte Chemie*, doi.org/10.1002/anie.201911637 (2019).
- [4] - E. Gerber A. Romanchuk, I. Pidchenko, L. Amidani, A. Rossberg, C. Hennig, G. Vaughan, A. Trigub, T. Egorova, S. Bauters, T. Plakhova, M. Hunault, S. Weiss, S. Butorin, A. Scheinost, S. Kalmykov, K. Kvashnina, submitted, (2019).

Potential of highly annealed graphite crystal analyzers for von Hamos spectrometers

R. Gnewkow, C. Schlesiger, W. Malzer and B. Kanngießer

Institute for Optics and Atomic Physics, Technische Universität Berlin, Sekr. EW 3-1,
Hardenbergstraße 36, 10623 Berlin, Germany, richard.gnewkow@gmail.com

Currently perfect crystals in the form of silicon or germanium are almost exclusively used as wavelength dispersive optics in synchrotron facilities. Efficient collection is realized by using Johann, Johansson or von Hamos geometries. The advantage of the energy dispersive von Hamos geometry is the simultaneous collection of the entire spectrum without scanning but with the disadvantage of a reduced effective solid angle compared to the point-to-point focusing geometries. Here highly annealed pyrolytic graphite crystals (HAPG) with their higher integral reflectivity could help to offset the reduced solid angle making the von Hamos geometry as efficient as the Johann or Johansson geometries.

The HAPG crystal can be described as a composition of small perfect crystal blocks called crystallites with an angular orientation distribution of 0.1° . Small means that the mosaic crystal model assumes negligible multiple scattering inside a single crystallite and is therefore within the kinematical approximation compared to perfect crystals. As a result of the crystallite distribution the resolving power is decreased but the integrated intensity of a mosaic crystal is at least one order of magnitude higher compared to a perfect crystal.

In this presentation the use of HAPG crystal analyzers in synchrotron applications is explored. A comparison to established perfect crystal analyzers is done with the focus on efficiency, resolving power and alignment procedures.

Developing laboratory based X-ray Absorption Spectroscopy for nuclear waste management

L.M. Mottram, M.C. Dixon Edwards, L.R. Blackburn, T. Oulton, M.C. Stennett, S.K. Sun, C.L. Corkhill, and N.C. Hyatt*

Immobilisation Science Laboratory, University of Sheffield, Department of Materials Science and Engineering, Sir Robert Hadfield Building, Mappin Street, S13JD, UK. l.m.mottram@sheffield.ac.uk

X-ray absorption spectroscopy (XAS) provides a unique and sensitive probe of element speciation and local environment in materials relevant to the nuclear fuel cycle and security. Hitherto, this technique has primarily required access to a synchrotron radiation facility as a broadband X-ray source of high brilliance, which has limited application for routine and high throughput studies. This of particular challenge for the field of nuclear materials where scientific opportunity may be constrained by the absence of an accessible synchrotron source or sample containment requirements and inventory limits. Here, we report our exploitation of a newly available commercial XAS spectrometer, based on the design of Seidler *et al* [1-4], utilising spherically bent crystal analysers to acquire XAS data in the range 5 - 18 keV resolution from actinide, nuclear and radiological materials. We show that XAS data may be acquired in a few hours, or less in favourable circumstances, from moderately dilute to concentrated absorbers to address routine questions of element speciation and co-ordination of particular relevance to radioactive waste immobilisation. These data and analyses are compared with counterpart synchrotron studies, on an identical sample suite, to highlight both the potential opportunities and limitations of laboratory XAS, and feasibility of routine application.

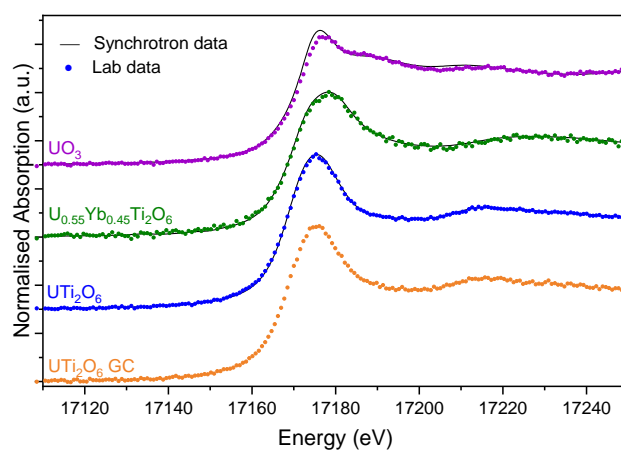


Figure 1: Comparison of laboratory (points) and synchrotron (black solid line) U L₃ XANES data from reference compounds incorporating U⁴⁺ - UTi₂O₆, U⁵⁺ - U_{0.55}Yb_{0.45}Ti₂O₆, U⁶⁺ - UO₃, and a brannerite glass ceramic with unknown U oxidation state; note: laboratory data were corrected for “leakage effects”; GC - glass ceramic.

References

- [1] - G.T. Seidler, D.R. Mortensen, A.J. Remesnik, J.I. Pacold, N.A. Ball, N. Barry, M. Styczinski, O.R. Hoidn, *Rev. Sci. Instr.*, 85, 113906 (2014).
- [2] - D.R. Mortensen, G.T. Seidler, A.S. Ditter, P. Glatzel, *J. Phys. Conf. Ser.*, 712, 012036 (2016).
- [3] - G.T. Seidler, A.S. Ditter, N.A. Ball, A.J. Remesnik, *J. Phys. Conf. Ser.*, 712, 012015 (2016).
- [4] - E.P. Jahrman, W.M. Holden, A.S. Ditter, D.R. Mortensen, G.T. Seidler, T.T. Fister, S.A. Kozimor, L.F.J. Piper, J. Rana, N.C. Hyatt, M.C. Stennett, *Rev. Sci. Instr.*, 90, 024106 (2019).

Carbon K-edge X-ray emission of gas phase ethylenic systems

R.A. Ingle¹, C. Bacellar¹, T.R. Barillot¹, L. Longetti¹, P. Miotti², L. Poletto², M. Coreno³, M. de Simone⁴, F. Zuccaro³, M. Odelius⁵, A. Röder⁶, M. Schuurman^{6,7}, A. Stolow^{6,7}, M. Chergui¹

¹Laboratoire de spectroscopie ultrarapide, Ecole polytechnique fédérale de Lausanne, ISIC, FSB-BSP, CH-1015 Lausanne, Switzerland, ²School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK, ³CNR - Istituto di struttura della materia (ISM), Basovizza Area Science Park, 34149 Trieste, Italy, ⁴CNR - Istituto officina dei materiali (IOM), Laboratorio TASC, 34149 Trieste, Italy, ⁵Department of Physics, AlbaNova University Center, Stockholm University, 106 91 Stockholm, Sweden, ⁶Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, K1N 6N5, Canada, ⁷National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada, rebecca.ingle@epfl.ch

X-ray emission (XES) is a powerful tool for investigating the electronic structure of molecules, probing not just the energetic separation of occupied electronic states but also determining the symmetries of the occupied orbitals.¹ The combination of element-selectivity and the sensitivity of the X-ray signal to changes in the local environment also mean such techniques are ideally suited to resolving structural dynamics.² However, in the soft X-ray regime, where the K-edge transitions for most of the light elements like carbon, nitrogen and oxygen are located, the quantum yield for X-ray fluorescence is significantly lower.³ The result of this is, while soft X-ray XES has become a routine technique for characterisation of solids, only very limited studies have been carried out on low-density samples^{4,5}, particularly at the carbon K-edge where the ‘carbon hole’ results in significantly reduced X-ray flux.

In this work, we present the feasibility of X-ray emission at the carbon K-edge on three ethylenic, gaseous molecules, ethylene, propa-1,2-diene (allene) and *trans*-1,3-butadiene. Non-resonant X-ray emission spectra of ethylene show good agreement with previous high-resolution electronic impact experiments.^{6,7} The resonant emission spectra for all three ethylenic systems show significant change from the non-resonant case and allow, in combination with *ab initio* calculations, us to probe the behaviour of different excited, intermediate states. This work was carried out at the GasPhase beamline at the Elettra synchrotron and is a key development for future gas-phase time-resolved experiments with XES.

References

- [1] - F. de Groot, *Chem. Rev.*, **101**, 1779-1808, (2011).
- [2] - M. Chergui and E. Collet, *Chem. Rev.*, **117**, 11025-11065, (2017).
- [3] - J. Nordgren and J.E. Rubensson, *J. Electron Spectros. Relat. Phenomena*, **188**, 3-9, (2013).
- [4] - P. Skytt *et al.*, *Phys. Rev. A - At. Mol. Opt. Phys.*, **55**, 146-154, (1997).
- [5] - M. Oura *et al.*, *J. Phys. Conf. Ser.*, **235**, 012016, (2010).
- [6] - R. Brammer *et al.*, *Chem. Phys. Lett.*, **106**, 425-427, (1984).
- [7] - R.A. Mattson and R.C. Ehlert, *J. Chem. Phys.*, **48**, 5465-5470, (1968).

X-ray absorption spectroscopy study of aqueous electrolyte solution critical properties

M. Irar¹, E. Bazarkina^{1,2}, D. Testemale¹, O. Proux³, A. Aguilar-Tapia¹, I. Kieffer³,
W. Del Net³, E. Lahera³, M. Rovezzi¹, and J.L. Hazemann^{1*}

¹Inst. Néel, UPR 2940 CNRS - UGA, F-38000 Grenoble, France, ²IGEM RAS, 119017 Moscow, Russia

³OSUG, UMS 832 CNRS - UGA, F-38041 Grenoble, France, mohammed.irar88@gmail.com

The goal of this study is to quantify the properties of electrolytes at near-critical conditions using X-ray Absorption Spectroscopy (XAS) techniques on BM30b FAME beamline at ESRF (Grenoble, France) using hydrothermal spectroscopy cell and high-pressure autoclave [1]. Two types of measurements were performed: transmission XAS density measurements and High Energy Resolution Fluorescence Detection (HERFD) XAS measurements via crystal analyzers [2].

With heating from 25 to 500°C at constant pressure (280, 300, 345 and 400bar), the absorption coefficients of chloride and bromide solutions decrease slowly until ~373°C (similarly with pure water), but then increase up to ~380°C, and finally decrease to gas-like values at higher temperatures. These absorption measurements reflect the anomalous density behavior at near-critical T-P-x region. At the same electrolyte concentration 0.3 mol/kg of H₂O, the relative density increase in this critical zone is more pronounced in order Li < Na < K < Rb < Cs for both bromides and chlorides. Complementary HERFD XAS measurements at Br K-edge in bromide solutions at similar T-P-x indicate that this density phenomenon is probably accompanied by structural changes (ion-pairing). Our new data complement previous synchrotron small angle X-ray scattering measurements [3] and open new perspectives for studies on electrolyte aqueous fluid properties in near-critical state.

References

- [1] - D. Testemale et al., *Rev. Sci. Instrum.* **76**, 43905 (2005).
- [2] - O. Proux et al., *J. Environ. Quality* (in press) (2017).
- [3] - Da Silva Cadoux et al., *J. Chem. Phys.* **136**, 044515 (2012).

X-ray emission spectrometer at BL39XU of SPring-8

N. Kawamura

Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan,
naochan@spring8.or.jp

X-ray emission spectrometer with high efficiency are now developing at BL39XU of SPring-8 to investigate electronic states for functional materials at a viewpoint of basic aspects and their applications. Target materials are mainly bulk/single crystals in strongly correlated electron systems, nanoclusters and thin films in reactive catalyst, and so on. The spectrometer with the scattering plane on a horizontal plane has three towers which can mount a set of five analyser crystals each. The initial operation was started with five analyzer crystals mounted on a tower. An acrylic chamber filled with helium gas is placed on the X-ray paths of sample-to-analyzer and analyzer-to-detector to avoid a decrease of X-ray emission intensity. In near future, a dedicated vacuum chamber will be installed to put the towers and the analyser goniometers into the vacuum instead of the acrylic chamber.

Incident photon energy of 4.92-23 keV with variable polarization (horizontal/vertical linear and circular) is available by a diamond X-ray phase retarder. Emitted photon energy of 4.66-15.87 keV is covered by using Si, Ge, and InSb crystals. Wide energy range can provide us information of electronic states for many intended elements using the X-ray emission spectroscopy.

Recently, study on valence states and chemical states in $3d/5d$ transition metal, $4f$ rare-earth, and uranium compounds using high-energy resolution XAFS measurements in High-Energy Resolution Fluorescence Detection (HERFD) method [1] have been actively investigated by using the spectrometer [2-7]. Polarization/configuration dependence of XES and HERFD-XAFS measurements have been also performed in the spinel-type ferrites, the single crystals of Ce, Pr, Tm, and Yb compounds, and TiO₂ nanosheets [8-11]. In this workshop, recent activities using the spectrometer are presented.

References

- [1] - K. Hämäläinen, D.P. Siddons, J.B. Hastings, and L.E. Berman, *Phys. Rev. Lett.* **67**, 2850 (1991).
- [2] - N. Kawamura, N. Kanai, H. Hayashi, Y.H. Matsuda, M. Mizumaki, K. Kuga, S. Nakatsuji, and S. Watanabe, *J. Phys. Soc. Jpn.* **86**, 014711 (2017).
- [3] - H. Asakura, N. Kawamura, M. Mizumaki, K. Nitta, K. Ishii, S. Hosokawa, K. Teramura, and T. Tanaka, *J. Anal. At. Spectrom.* **33**, 84 (2018).
- [4] - Y. Hirose, Y. Suzuki, F. Honda, R. Kulkarni, A. Thamizhavel, N. Kawamura, M. Mizumaki, R. Shimokasa, K. Mimura, H. Doto, and R. Settai, *AIP Advances* **8**, 115017 (2018).
- [5] - H. Sato, T. Nagasaki, K. Suekuni, H.I. Tanaka, A. Rousuli, S. Nakamura, N. Kawamura, X. Zheng, T. Fujii, and T. Takabatake, *Rad. Phys. Chem.*, *in press*.
- [6] - R. Shimokasa, N. Kawamura, T. Matsumoto, K. Kawakami, T. Kawabata, G. Isumi, T. Uozumi, A. Mitsuda, H. Wada, M. Mizumaki, and K. Mimura, *Rad. Phys. Chem.*, *in press*.
- [7] - N. Kawamura, Y. Hirose, F. Honda, R. Shimokasa, N. Ishimatsu, M. Mizumaki, S. Kawaguchi, N. Hirao, and K. Mimura, *submitted to JPS Conf. Ser.*
- [8] - N. Kawamura, E. Ikenaga, M. Mizumaki, N. Hiraoka, H. Yanagihara, and H. Maruyama, *J. Electr. Spectrosc. Relat. Phenom.* **220**, 81 (2017).
- [9] - N. Kawamura, *in preparation for publication*.
- [10] - M. Liu, Y. Ishida, Y. Ebina, T. Sasaki, T. Hikima, M. Takata, and T. Aida, *Nature* **517**, 68 (2018).
- [11] - Y. Ishida, *unpublished*.

SSHADE, the European solid spectroscopy database infrastructure

**I. Kieffer¹, D. Testemale², Ph. Bollard³, A. Garenne³, D. Albert³, L. Bonal³, O. Poch³
and B. Schmitt³**

¹OSUG, FAME, Univ. Grenoble Alpes/CNRS/IRD/Irstea/Météo France, Grenoble, France, ²Institut Néel, Univ. Grenoble Alpes/CNRS/Grenoble INP, Grenoble, France, ³Institut de Planétologie et Astrophysique de Grenoble (IPAG), Univ. Grenoble Alpes/CNRS, Grenoble, France, **isabelle.kieffer@esrf.fr - denis.testemale@neel.cnrs.fr**

The SSHADE database infrastructure (<http://www.sshade.eu>) hosts spectral data from many different types of materials: minerals, meteorites, organic matters, ..., as well as calculated spectra, covering the whole electromagnetic spectra from gamma rays to radio wavelengths. Its searching / viewing / downloading interface is operational and open to users since February 2018. The SSHADE consortium currently gathers 21 laboratories from 11 different countries.

In this context, the ESRF FAME et FAME-UHD beamlines have joined SSHADE by creating the SSHADE/FAME database. Two main goals motivated this initiative:

- filling the lack of XAS databases. Indeed, few databases exist in the domain and they generally provide too few details in the sample descriptions, so that it is difficult to use the spectra for data analysis. The consequences are a multiplication of measurements on identical samples across the different beamlines, and a lack of global complementarity between beamlines, generating a global waste of beam time.
- anticipating the current political trend which requires to render all the data publicly available, but also making these data effectively accessible, reusable, indexed and containing enough details to build a repository that could be used in the future for simulation codes (e.g. based on artificial intelligence).

Being part of SSHADE, the SSHADE/FAME database is a durable solution (its has been labeled by the CNRS/INSU as a National Observation Service). It is based on an elaborate data model which enables a very precise description of all the elements (from the sample to the measurement) and an efficient and user-friendly search strategy. Moreover, by attributing a DOI (Digital Object Identifier) to each data set, it offers the possibility to diffuse the spectra in a robust way and accordingly to the current publication recommendations. The database already contains more than 200 XAS spectra (and more than 1800 spectra in total).

The poster will present the database, its goals, its specificities and its use, from both the spectra user and provider points of view.

Observation of electronic metal support interaction: investigation of Au/Ceria catalysts by HERFD-XANES

A. Longo^{1,2}, M. Rovezzi³, M.P. Casaletto², P. Glatzel⁴, A. Martorana⁵ and L. Vince¹

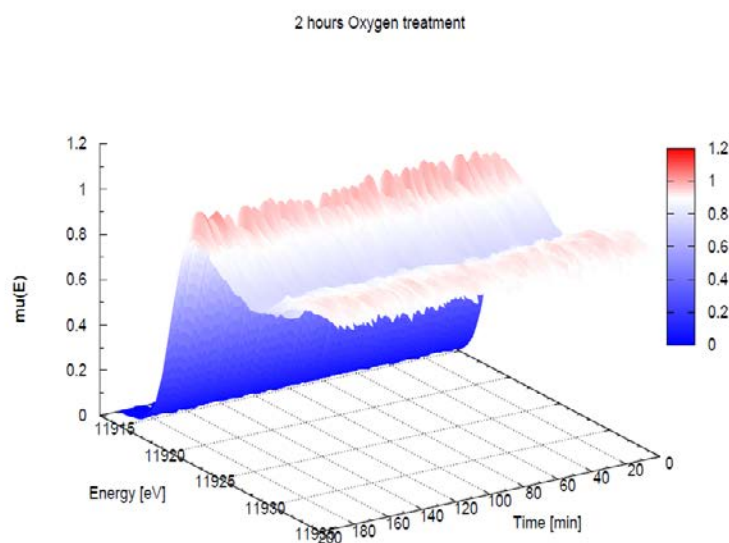
¹XMI, Department of Chemistry, Ghent University, Krijgslaan 281 S12, Ghent, East Flanders 9000, Belgium,

²Istituto per lo Studio dei Materiali Nanostrutturati (ISMN)-CNR, UOS Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy, ³Univ. Grenoble Alpes, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ⁴European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS 40220, 38043 Grenoble, France, ⁵Dipartimento di Fisica e Chimica, Università di Palermo, Viale delle Scienze Ed. 17, 90128 Palermo, Italy, alessandro.longo@esrf.fr

CO oxidation on a supported gold nanocatalyst has been a paradigmatic and pivotal problem in catalysis in the last two decades¹. The scientific debate is focused on the relevance of particle size, valence state of gold and interaction with the support, however, despite the huge amount of experimental data and model simulations reported in the literature, an ultimate analysis of the key-factors determining the impressive low-temperature activity of nanosized gold towards CO oxidation is still lacking. Actually, these factors are difficult to isolate because they are closely intertwined.¹ However, the beneficial effect of the metal support interaction remains one of more accredited phenomenon able to explain the high catalytic performance of gold based metal catalysts. To address this crucial issue, a detailed investigation, by both experimental and computational approach, of the metal-support interface was undertaken.

According to theoretical prediction, the most important information arises from the interface Au atoms, which determine band modification both for the metal cluster and the support.

In this paper we report the results of a recent in situ HERFD-XANES at RT experiment carried out at the ID26 beam line of ESRF. It is evidence that a cyclic modification occurs and this is reversible during the redox treatments. Interestingly, Au cluster mediates the oxygen uptake in the ceria support (see fig below).



Novel $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ -driven nanocomposite POM catalysts: synthesis, catalytic performance and chemical transformations

S.A. Malyshev, O.A. Shlyakhtin

Lomonosov Moscow State University, Department of Chemistry, 119991, Moscow, Leninskie Gory, 1-3, Russia, malyshev.sergey.a@gmail.com

At present, the problem of catalytic methane conversion into syngas - the mixture of CO and H_2 - is very acute. Catalytic partial methane oxidation ($\text{CH}_4 + 0.5\text{O}_2 = \text{CO} + \text{H}_2$) seems to be one of the most perspective methods which allows obtaining syngas under milder conditions. However, its practical application is complicated by the lack of systematic structural investigations of existing and newly discovered POM catalysts and different reaction pathways on their surface [1]. According to our considerations, metal-oxide nanocomposites produced by the reductive decomposition of perovskite-like oxides can be regarded as the perspective precursors for the POM catalysts [2].

Our studies deal with the synthesis of POM catalysts using the reductive decomposition of newly obtained complex oxides $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ with perovskite-like K_2NiF_4 structure. For these compounds the crystal structure and compositional boundaries are determined for the first time. According to the Rietveld refinement of the XRD data, the gradual distortion of the K_2NiF_4 structure was indicated with increasing Ni content. H_2 -TPR measurement showed that all $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ solid solutions were reduced completely at 700 °C producing fine Ni^0 and Co^0 metal nanoparticles incorporated into Nd_2O_3 and CaO oxide matrix. $\text{Nd}_{1.5}\text{Ca}_{0.5}\text{NiO}_4$ -derived catalyst demonstrated the highest POM conversion and selectivity among all the $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ derivatives (Figure 1). However, metal nanoparticles were found to reoxidize in the course of POM reaction. Such oxide particles participated in the solid state reaction regenerating the initial perovskites-like structure which was indicated by the ex situ XRD measurements.

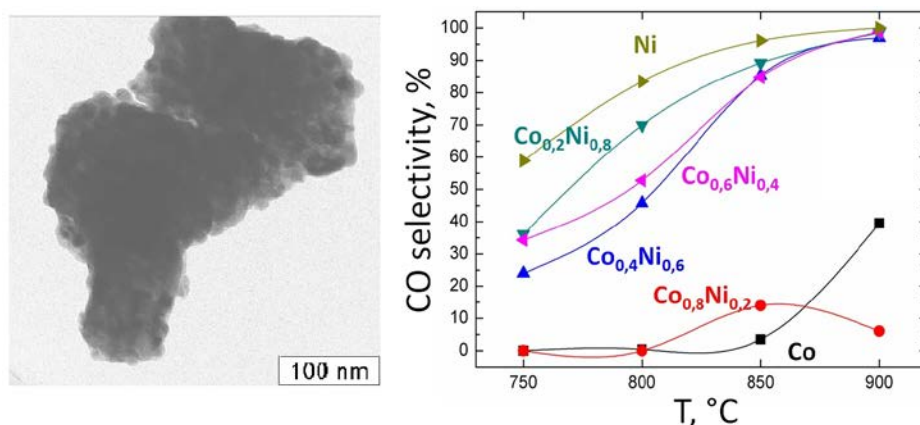


Figure 1: TEM image of the $\text{Nd}_{1.3}\text{Ca}_{0.7}\text{Co}_{0.4}\text{Ni}_{0.6}\text{O}_4$ reduction product after POM test (left) and the dependence of CO selectivity vs temperature for $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ -based catalysts with various Co/Ni ratio (right).

References

- [1] - B.C. Enger, R. Lødeng, A. Holmen, Appl. Catal. A **346**, 1-27 (2008).
- [2] - A.G. Dedov, A.S. Loktev, D.A. Komissarenko et al, Fuel Proc. Technol. **148**, 128-137 (2016).

Chiral BINAM-containing macrocycles for enantioselective fluorescent detection

A.S. Malysheva, A.D. Averin

Lomonosov Moscow State University, Department of Chemistry, 119991, Moscow, Leninskie Gory, 1-3, Russia, annette9513@gmail.com

Nowadays the identification of individual enantiomers of the bio- and catalytically active compounds is of great significance for both fundamental and applied chemistry. One of the most promising approaches for the enantiomers detection is fluorescence spectroscopy due to its high selectivity and sensitivity as well as the ability to perform an express analysis. The essential feature of this method is the interaction of the analyte molecule with the optically active fluorescent compound, *i.e.* chemosensor; the spectrum of fluorescence of the chemosensor should selectively change in respect with a chiral analyte. However, the nature of such analyte-chemosensor interaction is still unclear in most cases.

Recently we have begun successful investigation of the chiral macrocyclic compounds with endocyclic (*S*)-2,2'-diamino-1,1'-binaphthalene (BINAM) fragment as chemosensors for the selective fluorescent detection of model chiral amino alcohols [1-3].

In this work a novel series of BINAM-containing macrocycles has been synthesized. Macrocycles differ by the nature of the aromatic spacer (phenylene, naphthalene), the length of the polyoxadiazine chain, the presence of the exocyclic fluorophore groups (dansyl, coumarin, quinoline) and additional chiral substituents with nitrogen and oxygen atoms increasing the number of coordination sites of the molecules. Thus synthesized macrocycles were investigated as enantioselective fluorescent detectors of seven pairs of chiral amino alcohols, the possibility of the use of selective quenching or enhancement of the emission by one of enantiomers for detection was demonstrated. Also macrocycles were studied as fluorescent detectors for a series of 21 metal cations.

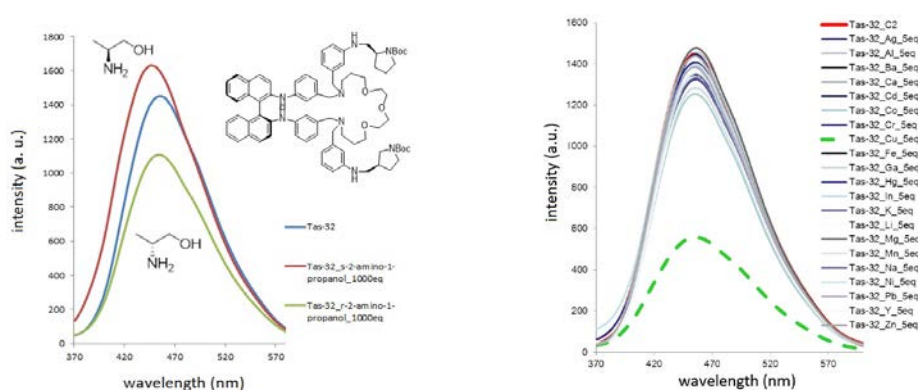


Figure 1: The changes in the spectra of fluorescence of the BINAM-containing macrocycle in the presence of the enantiomers of 2-amino-1-propanol (a) and various metal cations (b).

References

- [1] - O.K. Grigorova, A.D. Averin, O.A. Maloshitskaya and I.P. Beletskaya, *Macrocyclic Chemistry* **9**, 425 (2016).
- [2] - O.K. Grigorova, A.D. Averin, O.A. Maloshitskaya and I.P. Beletskaya, *Macrocyclic Chemistry* **10**, 446 (2017).
- [3] - O.K. Grigorova, D.I. Gusev, A.D. Averin, O.A. Maloshitskaya, I.P. Beletskaya, *Russ. Chem. Bull.* **68**, 848 (2019).

ID24-EBS project: a hard X-ray crystal analyser combined with a micro-focused beam for XAS/XES measurements

M. Merkulova^{1,2}, O. Mathon¹, M. Rovezzi^{1,3}, P. Glatzel¹ and A. Manceau⁴

¹ESRF, 71 avenue des Martyrs, 38000 Grenoble, France, ²Department of Geology, University of Liege, B-4000 Liege, Belgium, ³UGA, CNRS, IRD, Irstea, Météo France, OSUG, FAME, 38000 Grenoble, France, ⁴UGA, CNRS, ISTERre, 38058 Grenoble, France, mathon@esrf.fr

We have developed and commissioned a five crystal analysers spectrometer for high energy resolution X-ray emission detection on the ESRF EXAFS beamline BM23. The spectrometer is combined with the BM23 microXAS station, leading to a unique coupling between an X-ray micro beam ($4 \times 4 \mu\text{m}^2$) with five spherically bent single crystals of 100 mm diameter, arranged in a 0.5 m Rowland geometry [1]. It covers Bragg angles ranging from 65° to 89° and operates from 5 to 25 keV, with an energy resolution varying from 0.5 to 5 eV.

The five crystal analysers spectrometer allows performing high energy resolution fluorescence mapping, high energy resolution fluorescence detected (HERFD), X-ray Emission Spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS). The spectrometer has been used to study the structural chemistry of gold in natural arsenian pyrite (FeS_2) and arsenopyrite (FeAsS) [2]. In these minerals, the systematic co-occurrence of Au and As poses a challenge for measuring the Au L_3 -edge X-ray absorption spectra because the Au $L\alpha$ emission line is partly (pyrite) to totally (arsenopyrite) obscured by the intense As $K\alpha$ line.

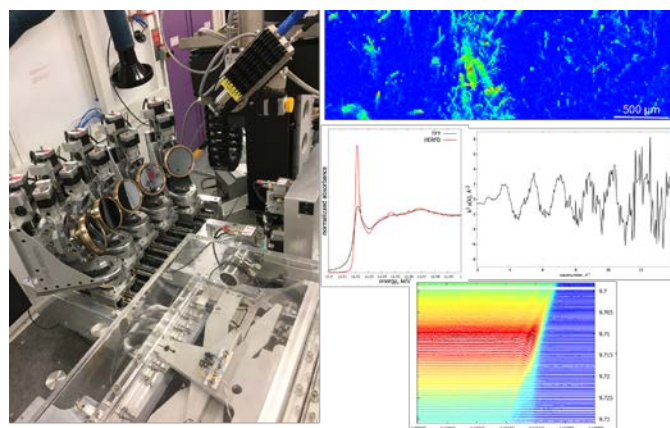


Figure 1 : The five crystal analysers spectrometer combined with the BM23 microXAS station

The new instrument will be fully operational and available for users after the ESRF - Extremely Brilliant Source (EBS) upgrade. The spectrometer will be installed on the new XAS beamline ID24-DCM. The beamline will provide a tailored flux up to 10^{13} photons s^{-1} and a spatial resolution down to $1 \mu\text{m}$ full width. In combination with the new crystal analyser spectrometer the beamline will allow users to study extremely diluted and heterogeneous samples. This work was supported by the French National Research Agency (ANR) under Grant ANR-10-EQPX-27-01 (EcoX Equipex).

References

- [1] - M. Rovezzi *et al.*, Rev. Sci. Instrum. **88**(1):013108 (2017).
- [2] - M. Merkulova *et al.*, ACS Earth Space Chem. **3**, 1905 (2019).

Time-resolved XES studies on photosystem II and manganese model compounds

V. Mazalova¹, G. Subramanian², P. Schwander³, A. Ourmazd³, P. Fromme^{4,5}

¹Center for Free Electron Laser Science CFEL, DESY, Hamburg, Germany, ²Department of Physics, Arizona State University, Tempe, USA, ³Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, USA, ⁴Biodesign Center for Applied Structural Discovery, Arizona State University, Tempe, USA, ⁵School of Molecular Sciences, Arizona State University, Tempe, USA, victoria.mazalova@desy.de

X-ray Free Electron Lasers (XFELs) have opened a new chapter in the study of the dynamics of biomolecules, as time-resolved structural snapshots of biomolecular reactions can be captured from crystals at room temperature in native aqueous environment using ultra-bright femtosecond X-ray pulses. The aim is for diffraction snapshots to be recorded before molecules are destroyed by the process of photoionization leading to a coulomb explosion in the time range of femtoseconds. However, the reports on the pulse length where damage-free data can be collected vary from the sub fs range to 50fs [1-3]. It is also clear that alteration of the electronic structure of molecules precedes photoionization and the final destruction of the molecules and the crystals in the process of coulomb explosion. The time required for photoionization and Auger decay also depends on the chemical element, with metals being most easily photoionized.

The main focus of this work was an XES study of the changes in Mn oxidation states during the water splitting cycle and the damage threshold of the Mn cluster in its different oxidation states. As a first step we aimed to systematically study the X-ray radiation damage of the Mn model compounds as a function of the X-ray energy above the Mn absorption edge, the photon flux and the pulse duration.

The results provided clear evidence that there is a very strong correlation between the X-ray induced photoreduction of the Mn compounds and the pulse duration as well as the beam energy. Data collected at two energies (9.5 and 7.25 keV) showed significant differences, with significant more changes in the electronic states observed at the lower energy, even below 10fs pulse duration, while the data at higher energy indicated that the OEC electronic structure might be intact at pulse durations below 15fs.

References

- [1] - I. Inoue, Y. Inubushi, T. Sato, K. Tono, T. Katayama, T. Kameshima et al. Proc Natl Acad Sci USA **113**(6), 1492-7 (2016).
- [2] - A. Barty, C. Caleman, A. Aquila, N. Timneanu, L. Lomb, T.A White et al. Nat Photonics **6**, 35-40, (2012).
- [3] - L. Lomb, T.R. Barends, S. Kassemeyer, A. Aquila, S.W. Epp, B. Erk et al. Phys Rev B Condens Matter Mater Phys. **84**(21), 214111 (2011).

Temperature-induced changes in the charge and spin density of valence tautomers probed by X-ray emission and K β -detected absorption spectroscopy

F. Otte^{1,2}, F.A. Lima¹, J. Rogalinski¹, J. Latarius², S. Jannuzzi³, M. Riberio⁴,
C. Sternemann², C. Bressler¹

¹European XFEL Facility, FXE instrument, Schenefeld, Germany, ²Technische Universität Dortmund, Fakultät Physik / DELTA, Dortmund, Germany, ³MPI for Chemical Energy Conversion, Mülheim, Germany, ⁴Universidade Federal do Espírito Santo, Vitória, Brazil, florian.otte@xfel.eu

Valence tautomeric transitions (VT) are characterized by stimulated intramolecular charge transfer and single-site spin crossover [1,2]. Similar to spin-crossover and charge transfer induced spin transitions, valence tautomers have been studied extensively as candidates for electronically-labile molecular systems, which can be essentially “flipped” between two electronic states by relatively small changes in temperature, pressure or by laser excitation [1-8]. Cobalt-based organometallic compounds with redox-active *o*-dioxolene ligands are of special importance in this field, as their metal- and ligand frontier orbitals tend to be of similar energy, thus fulfilling an important prerequisite for VT to occur [1,2]. The nature of the charge transfer and the metal-ligand magnetic exchange interaction is still an open question and has been addressed by density functional theory (DFT) calculations, and speculated based on Co K β X-ray Emission Spectroscopy (XES) measurements [8,9].

Here we present a series of temperature-dependent K β and valence-to-core (VtC) XES data as a means to further elucidate the nature of the magnetic exchange interaction and ancillary ligand contribution in cobalt valence tautomers from the *o*-dioxolene family. Exploratory Co K β resonant XES are also being explored and will provide further insight into the mechanisms of VT transitions in those systems.

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References

- [1] - D.A. Shultz, in *Magnetism: Molecules to Materials II* 281-306 (Wiley-VCH Verlag GmbH & Co. KGaA, 2003).
- [2] - D.N. Hendrickson & C.G. Pierpont, in 1, 63-95 (2004).
- [3] - C. Boskovic, in *Spin-Crossover Materials* 203-224 (John Wiley & Sons Ltd, 2013).
- [4] - O. Sato, A. Cui, R. Matsuda, J. Tao & S. Hayami, *Acc. Chem. Res.* 40, 361-369 (2007).
- [5] - O. Sato, J. Tao & Y.-Z. Zhang, *Angew. Chem. Int. Ed. Engl.* 46, 2152-87 (2007).
- [6] - A. Dei, D. Gatteschi, C. Sangregorio & L. Sorace, doi:10.1021/AR0200706 (2004).
- [7] - E. Evangelio & D. Ruiz-Molina, *Comptes Rendus Chim.* 11, 1137-1154 (2008).
- [8] - R.D. Schmidt, D.A. Shultz & J.D. Martin, *Inorg. Chem.* 49, 3162-3168 (2010).
- [9] - H.W. Liang et al., *Inorg. Chem.* 56, 737-747 (2017).

Development of a "barrel" von Hamos XES spectrometer and its application to catalytically-relevant platinum compounds

C.J. Pollock, L.M. Debeve, K.D. Finkelstein

Cornell High Energy Synchrotron Source, Wilson Laboratory, Cornell University, Ithaca, NY 14853, US,
cjp227@cornell.edu

X-ray emission spectroscopy has developed into a powerful technique for investigating the geometric and electronic structures of inorganic species, finding applications in fields as diverse as heterogeneous catalysis and bioinorganic chemistry. Increasingly, it is of interest to apply x-ray emission methods to time-resolved studies so that chemical reactions under *operando* conditions can be investigated using the rich information content of these spectra. Dispersive von Hamos type spectrometers based on cylindrically-bent crystal analyzers allow for the simultaneous collection of an entire XES spectra at once, enabling such time resolution. Unfortunately, these spectrometers typically intercept only a small solid angle per energy, limiting their applications to samples with low concentrations of emitting element. To overcome this limitation, herein we present the development of a "barrel" type von Hamos spectrometer, which employs cylindrically-bent Si analyzers arranged in a 360° ring. The small 125 mm radius and 360° of collection allow this spectrometer to intercept a large solid angle, and detection is possible using either 1D (e.g. Mythen) or 2D (e.g. Pilatus) detectors. This work demonstrates the functionality of this spectrometer and details its application to studying the $L\beta_{2,15}$ and $L\gamma$ emission lines of platinum complexes.

Development of X-ray crystal analyzers

J.Q. Qian

XRS TECH LLC, New Jersey, USA, qqian@xrstech.com

X-ray crystal analyzers are the key for success in application of XIS and XES, as well as XAFS with laboratory X-ray sources. In the last 16 years, we developed most analyzers to cover such applications, which include spherically bent analyzers, cylindrically bent analyzers, both with diced, striped and stand free type, and also few Johansson type of cylindrical and spherical curvature. The energy resolution can be down from meV of stand free type to few eV for very short radius analyzers.

Our patented spherically striped-bent crystal analyzers open a door to very short curvature radius analyzers, both in silicon and germanium. Our anodic bonding stand free flat-diced analyzers is also proved its value in very high energy resolution for XIS, XES and XAFS.

References:

- [1] - J.-P. Rueff, SOLEIL, private communication, 2017-2018.
- [2] - G.T. Seidler, et al, Review of Scientific Instruments **85**, 113906 (2014).
- [3] - Q. Qian, US patent, US9761340 B2, Sep. 12, 2017.
- [4] - A.H. Said et al, J. Synchrotron Rad. 18, 492-496 (2011).
- [5] - T. Gog, D.M. Casa, A.H. Said et al, J. Synchrotron Rad. 20, 74-79 (2013).

Instrumentation for X-ray emission spectroscopy at the KIT-INE radionuclide beamline stations at KARA

A. Beck, K. Dardenne, J. Galanzev, K. Hardock, V. Krepper, J. Rothe, B. Schacherl, T. Vitova, and H. Geckeis

Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, D-76021 Karlsruhe, Germany, rothe@kit.edu

KIT-INE operates two experimental stations dedicated to the investigation of radionuclide materials by X-ray based methods at the Karlsruhe research accelerator KARA (former ANKA synchrotron light source) - the INE-Beamline at a bending magnet port (fully operational since 2005) and the ACT laboratory at the CAT-ACT wiggler beamline (commissioned in 2016) [1,2]. Both experimental hutches are equipped and licensed for handling radioisotopes up to $1\text{E}+6$ times their exemption limits and are operated as temporary controlled areas, enabling the investigation of ‘hot’ materials including genuine nuclear waste forms as well as in situ investigations (e.g., high p / high T) of radionuclide containing samples. While the focus at both beamlines was originally on XAFS-based speciation investigations in the context of the nuclear waste disposal safety case (encompassing processes during interim storage of spent nuclear fuel or nuclear waste glass and final deep geological disposal), another emphasis has been recently placed on fundamental studies employing the emerging high-resolution X-ray emission spectroscopy (HRXES) techniques.

The Johann-type X-ray emission spectrometer at the ACT laboratory is routinely applied for high-resolution/HERFD-XANES and RIXS experiments in a broad energy range encompassing the actinide M- and L-edges. In the tender X-ray region, scattering and absorption of X-rays is efficiently minimized by enclosing all beam paths - i.e., the impinging beam, the sample stage, five analyser crystals and the detector stage in Rowland circle geometry - in a He atmosphere. A new rigid He-flushed glove box with a flexible bag enclosing the spherical analyser crystals has been designed and will be permanently installed on the ACT experiment table at the beginning of 2020. The box is equipped with a spacious load lock for inserting sample cells (e.g., for in situ or combined UV-Vis/XES experiments) and various instrumentation feedthroughs (encompassing a LN_2 cryostat) and will allow for faster changes between standard transmission/fluorescence detection XAFS and HRXES experiments.

The capabilities for soft X-ray absorption and total yield fluorescence detection XAFS studies at INE-Beamline down to 2.1 keV - profiting from naturally narrow line widths - have been recently significantly improved by designing an advanced window-less ‘He flow chamber’. The new setup has meanwhile allowed for recording the world’s first Tc L_3 -edge XANES (~ 2.68 keV) spectra of Tc species in aqueous solution.

References

- [1] - A. Zimina, K. Dardenne, M.A. Denecke, D.E. Doronkin, E. Huttel, H. Lichtenberg, S. Mangold, T. Pruessmann, J. Rothe, T. Spangenberg, R. Steininger, T. Vitova, H. Geckeis, J.-D. Grunwaldt, *Rev. Sci. Instrum.* **88**, 113113 (2017).
- [2] - J. Rothe, M. Altmaier, R. Dagan, K. Dardenne, D. Fellhauer, X. Gaona, E. González-Robles Corrales, M. Herm, K.O. Kvashnina, V. Metz, I. Pidchenko, D. Schild, T. Vitova, H. Geckeis, *Geosciences* **9**, 91 (2019).

Fe/N/C - catalysts: probing the spin state of iron using X-ray Emission Spectroscopy

V.A. Saveleva¹, K. Ebner¹, L. Ni², A. Zitolo³, J. Li⁴, G. Smolentsev¹, O.V. Safonova¹,
M. Nachttegaal¹, E. Marelli¹, M. Medarde¹, D. Klose⁵, U.I. Kramm², F. Jaouen⁴,
T.J. Schmidt^{1,5} and J. Herranz¹

¹Paul Scherrer Institut, ²Technische Universität Darmstadt, ³Synchrotron SOLEIL, ⁴Université Montpellier, ⁵ETH Zürich, viktoriia.saveleva@psi.ch, kathrin.ebner@psi.ch

The needed improvements for a successful implementation of non-noble metal catalysts of the Fe/N/C-type in polymer electrolyte fuel cells require a fundamental understanding of their active site structure, which is currently still lacking. Specifically, the spin state and local configuration of the N-coordinated, atomically dispersed Fe-ions that are believed to constitute the active sites in these materials remain under vivid debate [1, 2]. With this motivation, non-resonant X-ray emission spectra of several catalysts prepared with a variety of synthesis methods were acquired using the von Hamos X-ray emission spectrometer at the SuperXAS beamline (Swiss Light Source) (see Fig. 1a), and their corresponding, average spin number was quantified with the help of reference compounds with a similar N-coordination environment and a well-known spin state (cf. Fig. 1b). Complemented with other spin-sensitive techniques including Mössbauer spectroscopy, these results provide unprecedented insights into the spin state of the active sites in these Fe/N/C-type catalysts both under *ex* and *in situ* conditions, as well as on the relation between these sites' electronic configuration and their contribution to the catalysts' O₂-reduction activity.

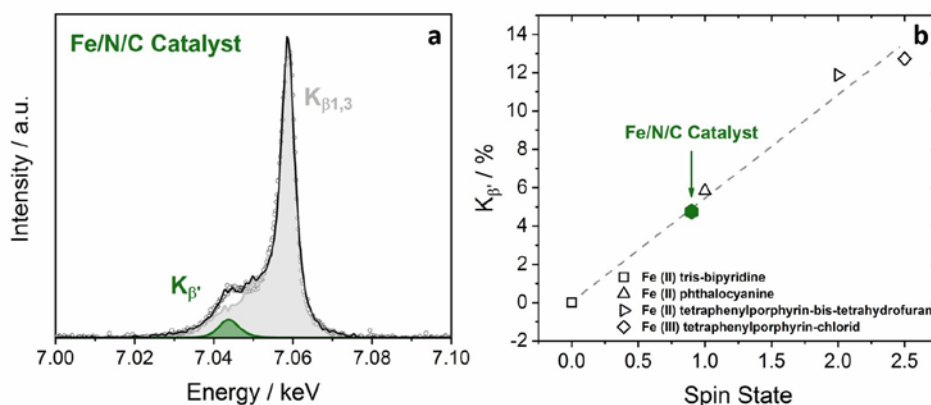


Figure 1: a) exemplary K_{β} -XE spectrum of an Fe/N/C catalyst fitted with two components ($K_{\beta 1,3}$ and K_{β}); b) correlation between the K_{β} -contribution derived from the fitted XE spectra and the spin state of Fe in various reference compounds (empty symbols), alongside the interpolation for an Fe/N/C catalyst from which an average spin number of 0.9 is estimated.

References

- [1] - A. Zitolo, V. Goellner, V. Armel, M.-T. Sougrati, T. Mineva, L. Stievano, E. Fonda, F. Jaouen, Nat. Mater. **14**, 937 (2015).
- [2] - U.I. Kramm, J. Herranz, N. Larouche, T.M. Arruda, M. Lefèvre, F. Jaouen, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, S. Mukerjee, J.P. Dodelet, Phys. Chem. Chem. Phys. **14**, 11673 (2012).

Np M₅-edge HR-XANES and L₃-edge EXAFS spectroscopy on illite samples with 20 - 140 ppm Np

B. Schacherl, C. Joseph, P. Lavrova, A. Beck, A. Schnurr, F. Rieder, K. Dardenne, D. Fellhauer, T. Kupcik, J. Rothe, H. Geckeis, T. Vitova

Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe, Germany, bianca.schacherl@kit.edu

A deep geological disposal with a multi-barrier system is proposed, to safely isolate the high-level radioactive waste from the biosphere. Clays are considered as potential host rock and as potential backfill material. This study is focused on understanding the interaction between illite, a clay mineral present in several clay host rocks, and Np-237, a radionuclide presenting a considerable fraction in high-level waste. Np is a redox-sensitive element with pentavalent Np being stable in oxidizing to redox-neutral environment and tetravalent Np prevailing under reducing conditions. To understand the mechanism of Np retention, it is necessary to understand the sorption but also the migration behaviour.

This investigation probes the redox-species and the atomic environment of Np sorbed onto illite for samples from batch sorption and diffusion experiments applying different spectroscopic and microscopic techniques (Np M₅-edge high-energy resolution X-ray absorption near edge structure (HR-XANES) [1], Np L₃-edge extended X-ray absorption fine structure (EXAFS), Fe K-edge XANES, and Mössbauer spectroscopy as well as scanning electron (SEM), transmission electron (TEM), and fluorescence microscopy).[2]

This is the first Np M₅-edge HR-XANES study where it was possible to record conclusively spectra at very low Np loadings of (18 ± 6) ppm due to an optimised set-up and sample preparation. It was conducted at the CAT-ACT beamline for catalysis and actinide science at the Karlsruhe research accelerator (KARA) at KIT, Karlsruhe [3]. Np L₃-edge XANES and Np M₅-edge HR-XANES spectra strongly suggest the presence of Np(IV) and Np(V) in both the dispersed illite sorption samples kept under anaerobic conditions but also in segments taken from the diffusion experiments carried out under an aerobic atmosphere. These results are corroborated by the results of solvent extraction according to the method of Bertrand and Chopin (1982) [4]. EXAFS analyses of illite sorption samples prepared at pH 9 confirm the presence of solely sorbed mononuclear Np species and a Np-O-Fe coordination at (3.44 ± 0.02) Å. Fe K-edge XANES and Mössbauer spectroscopy found Fe(III) and Fe(II) in the structure of illite. Results obtained by SEM, TEM, and fluorescence microscopy studies exclude the presence of amorphous Fe phases and microorganisms as possible reductants. The observation of a partial reduction of Np(V) and the finding that Np is coordinated to Fe-OH groups points to a partial reduction through electron transfer from structural Fe(II) in the illite.

The present study demonstrates that by the complementary application of advanced spectroscopic methods, mechanistic insight into complex geochemical actinide reactions can be achieved at even low concentrations.

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References

- [1] - T. Vitova, I. Pidchenko, D. Fellhauer et al., Nat. Commun. 8, (2017).
- [2] - R. Marsac, N. Banik, J. Lützenkirchen et al., Geochim. Cosmochim. Acta 152, 39 (2015).
- [3] - A. Zimina, K. Dardenne, M.A. Denecke et al., Rev. Sci. Instrum. 88, 1 (2017).
- [4] - P.A. Bertrand and G.R. Choppin, Radiochim. Acta 31, 135 (1982).

XRF with chemometric data processing for analysis of iron oxidation state

V.G. Semenov^{1,2}, V.V. Panchuk^{1,2}

¹Department of Chemistry of St Petersburg State University, 198504, Universitetskii pr. 26, St. Petersburg, Russia, ²Institute for Analytical Instrumentation, 190103, Rizhskii pr. 26, St. Petersburg, Russia, val_sem@mail.ru

XRF (X-ray fluorescence) analysis is a widely employed spectroscopic method for elemental analysis which allows for determination of quantitative content for elements from beryllium to uranium. Iron is involved in many geological formations (hematite, magnetite, hydrogoethite etc.) and it is important for various construction materials. It is not only quantitative content which is important when analyzing such objects, but also the oxidation state of iron. To solve the last problem one can use the phase analysis methods. On the other hand the energy (or wavelength) of some X-ray fluorescence lines depends on the energy of the atom valence levels. X-ray fluorescence lines shift can be used to determine oxidation state and this was shown in numerous studies. However, the practical implementation of this approach is associated with certain difficulties mainly due to insufficient energy resolution of spectrometers and uncertain interpretation of results. The purpose of this work is to determine oxidation states of the iron atoms from X-ray fluorescence lines shifts using logistic regression, PCA and PLS-DA.

Solid samples containing iron with different oxidation states were analyzed: α -Fe, Fe₂O₃, K₃[Fe(CN)₆], K₄[Fe(CN)₆]*3H₂O, FeCl₂*4H₂O, FeCl₃*6H₂O. The L - series lines of iron (FeL _{α 1-2}, FeL _{β 1-3}) were employed as analytical signals for determination of the iron atoms oxidation states. The reason for this choice is the energy of these lines which mostly depends on the energy of 3d electron levels involved in formation of chemical bonds.

Spectra of the samples were measured by wavelength dispersive X-ray fluorescence spectrometer with high resolution (Shimadzu XRF-1800). Measurement conditions were: TAP crystal with first order of reflection; X-ray tube with Rh anode, voltage 90 kV and current 45 mA. These conditions allowed for the largest changes in X-ray lines, good reproducibility and reasonable accumulation time.

The spectra were decomposed into single lines followed by logistic regression, PCA and PLS-DA. It was shown that all three methods can solve the task of oxidation state analysis.

Probing atom off-centering displacements in epitaxial strained $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$ thin films by HERFD-XANES

G. Subías^{1,2}, J. Blasco^{1,2}, S. Lafuerza³, P.A. Algarabel^{1,2}, C. Magén^{1,2,4}, J. A. Pardo^{1,4,5,6}

¹Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain, ²Depto de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain, ³ESRF-The European Synchrotron, 71 Avenue des Martyrs, Grenoble, France, ⁴Laboratorio de Microscopías Avanzadas, Universidad de Zaragoza, 50018 Zaragoza, Spain, ⁵Instituto de Nanociencia de Aragón, Universidad de Zaragoza, 50018 Zaragoza, Spain, ⁶Depto de Ciencia y Tecnología de Materiales y Fluidos, Universidad de Zaragoza, 50018 Zaragoza, Spain, gloria@unizar.es

$\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$ (SBMO) perovskites are promising multiferroic materials due to the expected strong coupling between polar instability and spin order since both are driven by the Mn cation. Epitaxial SBMO films are then ideal candidates for tailoring the magnetoelectric properties since much larger tetragonal distortions can be imposed than in bulk samples by combining epitaxial strain with chemical doping (replacing Sr with Ba).

We have selected SBMO films with $x=0.2$ and 0.4 grown on (001)-oriented LSAT substrate. The thickness of the films was limited to 10 nm. A change in the tetragonality from $c/a < 1$ (tensile strain 1.24% for $x=0.2$) to $c/a > 1$ (compressive strain -0.36% for $x=0.4$) is induced with increasing the Ba content [1]. Strain-induced polar order was experimentally confirmed in epitaxial SrMnO_3 (SMO) films with 1.7% tensile strain [2] but it shows G-type antiferromagnetic (AF) order [3]. Despite the strains in SBMO films are still below the critical value ($\sim 3.5\%$) to induce ferromagnetism, a strong spin-phonon coupling has been demonstrated at the onset of the AF order in $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{MnO}_3/\text{LSAT}$, which may lead to magnetoelectric coupling [4].

With the aim to probe the polar character of the SBMO/LSAT films, we performed Mn K-edge polarized HERFD-XANES measurements (in-plane and out-of-plane with \mathbf{E} perpendicular and parallel to the c axis, respectively) acquired at the Mn $K\alpha_1$ emission line at ID26 beamline. The local off-centering of the Mn atom in its octahedral environment was investigated from the intensity variations in the pre-edge features, much better resolved in HERFD detection mode. The magnitude of the local displacements was quantified by comparison of the experimental linear dichroism spectra ($\text{XANES}_{\text{out-of-plane}} - \text{XANES}_{\text{in-plane}}$) with theoretical FDMNES calculations [5]. We have determined a significant off-centering of the O atoms in the equatorial plane of the octahedron of about 0.05 Å along the in-plane $\langle 110 \rangle$ direction for tensile $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{MnO}_3/\text{LSAT}$, similar to the behaviour found in polar SMO/LSAT [2] and $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{MnO}_3/\text{TSO}$ films [6] by scanning transmission electron microscopy (STEM). For compressive $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{MnO}_3/\text{LSAT}$, out-of-plane polarization is expected but hard to be detected by STEM or second-harmonic generation (SHG) techniques. A significant off-centering of both Mn and equatorial O atoms of about 0.12 Å along the out-of-plane $\langle 001 \rangle$ direction is revealed by HERFD-XANES with Mn and O oppositely shifted along the c axis.

References

- [1] - L. Maurel et al., APL Mater. **7**, 041117 (2019).
- [2] - C. Becher et al., Nat. Nanotechnol. **10**, 661 (2015); R. Guzmán et al., Nano Lett. **16**, 2221 (2016).
- [3] - L. Maurel et al., Phys. Rev. B **92**, 024419 (2015).
- [4] - V. Goian et al., Phys. Rev. B **95**, 075126 (2017).
- [5] - Y. Joly, Phys. Rev. B **63**, 125120 (2001).
- [6] - E. Langenberg et al., Adv. Mater. Interfaces **4**, 1601040 (2017)

Development of a laboratory based quick X-ray absorption and emission spectrometer in a Von Hamos geometry

P. Tack, L. Vincze

X-ray Micro-spectroscopy and Imaging group, Ghent University, Krijgslaan 281 S12, 9000 Ghent, Belgium,
Pieter.Tack@UGent.be

Currently, the application of X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) is mainly reserved for synchrotron radiation facilities due to the need for an intense, energy tuneable, narrow bandwidth X-ray beam. However, due to the high demand for measurement time at these facilities and their limited accessibility, experiments are usually granted through a highly competitive peer-reviewed proposal process, and are usually limited to a few days of available 'beam time' per year.

The development of a laboratory based XAS/XES spectrometer will provide an alternative for experiments that do not necessarily require e.g. highly focussed X-ray beams or very fast acquisition speeds. In addition, the laboratory based spectrometer can improve experiments that are currently performed at synchrotron radiation facilities by performing initial tests, pre-characterization and identification of samples of interest, resulting in more streamlined and efficient synchrotron experiments.

One typical drawback of laboratory based XAS/XES spectrometers is the significantly reduced photon flux with respect to synchrotron radiation facilities, and thus reduced data statistics and increased measurement times[1]. The proposed device will resolve these matters in several ways: i) the spectrometer makes use of a 80 W X-ray tube, providing an integrated photon flux in the order of 10^{10} ph/s. The absorbed or emitted X-rays are detected by a position sensitive energy dispersive CCD detector (SLcam, Colour X-ray Camera)[2] in a quick-XAS/XES geometry, which allows for the detection of a full XANES/XES spectrum without the need for scanning by the monochromator crystal. ii) Additionally, the SLcam's energy dispersive properties will result in an improved signal-to-background ratio as a X-ray photon energy region of interest can be monitored selectively, without interference of other fluorescent, scattered or higher order diffracted radiation. In XAS, this approach has also been shown to partially improve the spectral energy resolution[3].

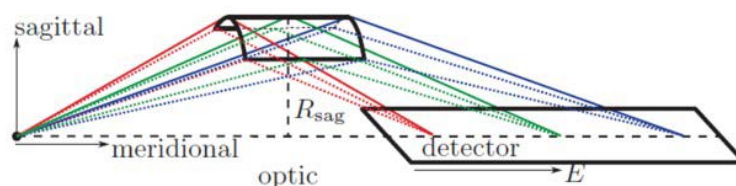


Figure 1: Schematic overview of the Von Hamos geometry for a XAS/XES spectrometer. Figure adapted from Anklamm et al.^[1b]

References

- [1] - G.T. Seidler, D.R. Mortensen, A.J. Remesnik, J.I. Pacold, N.A. Ball, N. Barry, M. Styczinski, O.R. Hoidn, *Rev. Sci. Instrum.* **2014**, 85, 113906; bL. Anklamm, C. Schlesiger, W. Malzer, D. Grotzsch, M. Neitzel, B. Kanngiesser, *Rev. Sci. Instrum.* **2014**, 85, 053110.
- [2] - I. Ordavo, S. Ihle, V. Arkadiev, O. Scharf, *Nuclear Instruments and Methods in Physics Research A* **2010**, doi:10.1016/j.nima.2011.05.080.
- [3] - P. Glatzel, T.-C. Weng, K. Kvashnina, J. Swarbrick, M. Sikora, E. Gallo, N. Smolentsev, R.A. Mori, J. *Electron. Spectrosc. Relat. Phenom.* **2013**, 188, 17-25.

Investigating Cu(II) solvation through resonant Valence-to-core X-ray Emission Spectroscopy

F. Tavani¹, P. Glatzel², P. D'Angelo¹

¹Department of Chemistry, University of Rome "Sapienza", Rome, Italy, ²European Synchrotron Radiation Facility (ESRF), Grenoble, France, tavani.1639022@studenti.uniroma1.it

Ionic hydration is one of the most attractive subjects to chemists, especially to those who are interested in reactions occurring in aqueous solutions. The structure of transition metal aqua ions has been the universal benchmark against which all other transition metal sites are referenced. Cu(II) ions are present in many biological systems and play a fundamental role in different vital processes, but, surprisingly, the structure of the simplest complex, that of Cu(II) in an aqueous solution, is a matter of ongoing debate. It has long been described as a Jahn-Teller distorted six-coordinated Cu–O octahedron. However, although there is a general agreement concerning the stable presence of four equatorial water ligands, which exhibit a uniform Cu–O distance of about 1.96 Å, there are several difficulties in detecting the number and even presence of the axial water ligands. In particular, neither X-ray or neutron diffraction nor X-ray absorption spectroscopy have provided an unambiguous probe of the loosely bound axial water molecules. In a first investigation, it has been proposed that the Cu(II) aqua ion adopts a fivefold coordination fluctuating between both a regular square pyramid and a regular trigonal bipyramid configuration, while a recent XANES study points out two equally populated 6- and 5-fold hydration conformations [1-2].

In the last decade, X-ray Emission Spectroscopy has been successfully applied to study ionic hydration. For instance, non-resonant Valence-to-core X-ray Emission Spectroscopy (Vtc-XES) was employed to determine the character of chemical bonding and to identify ligands for the solvated Mn(II) ion in water and for a series of Mn coordination complexes [3]. On the other hand, Resonant Vtc-XES experiments have been performed mostly in the solid phase, to investigate inorganic compounds such as transition-metal oxides, magnetoresistance manganites, Fe compounds and proteins [4].

In this work, Resonant Vtc-XES spectra were recorded at the Cu K-edge for water, methanol and acetonitrile solutions containing Cu(II) salts.

In order to gain insights on the local Cu(II) solvation geometry, a series of selected model geometries were then used to theoretically calculate the associated Resonant Vtc-XES spectra using the density-functional theory approach implemented in the OCEAN package [5]. The combination of Resonant Vtc-XES with theoretical tools will allow to carefully evaluate and describe the hydration geometry of Cu(II).

References

- [1] - A. Pasquarello, I. Petri, P.S. Salmon, O. Parisel, R. Car, E. Tòth, D.H. Powell, H.E. Fischer, L. Helm, A.E. Merbach, *Science* **291**, 856 (2001).
- [2] - G. Chillemi, E. Pace, M. D'Abramo and M. Benfatto, *J. Phys. Chem. A* **120**, 3958 (2016).
- [3] - G. Smolentsev, A.V. Soldatov, J. Messinger, K. Merz, T. Weyhermuller, U. Bergmann, Y. Pushkar, J. Yano, V. K. Yachandra and P. Glatzel, *J. Am. Chem. Soc.* **131**, 13161 (2009).
- [4] - T. Kroll, R. G. Hadt, S.A. Wilson, M. Lundberg, J.J. Yan, T.-C. Weng, D. Sokaras, R. Alonso-Mori, D. Casa, M.H. Upton, B. Hedman, K.O. Hodgson and E.I. Solomon, *J. Am. Chem. Soc.* **136**, 18087 (2014).
- [5] - J. Vinson, J.J. Rehr, J.J. Kas and E.L. Shirley, *Phys. Rev. B* **83**, 115106 (2011).

In-, Au-, and Cu-bearing sphalerites studied by X-ray absorption spectroscopy

A.L. Trigub^{1,2}, O.N. Filimonova², D.E. Tonkacheev², M.S. Nickolsky^{2,3}, K.O. Kvashnina^{4,5},
D.A. Chareev^{6,7}, I.V. Chaplygin², E.V. Kovalchuk², S. Lafuerza⁴, B.R. Tagirov²

¹National Research Centre 'Kurchatov Institute', 1 Akademika Kurchatova pl., Moscow, Russian Federation,

²Institute of Geology of Ore Deposits (IGEM RAS), Moscow, Russian Federation, ³Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russian Federation, ⁴ESRF-EFiguropian Synchrotron Radiation Facility, Grenoble, France, ⁵Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, Dresden, Germany, ⁶Institute of Experimental Mineralogy (IEM RAS), Chernogolovka, Moscow Region, Russian Federation, ⁷Institute of Physics and Technology, Ural Federal University, Ekaterinburg, Russian Federation, alexander.trigub@gmail.com

Sphalerite is the main source of In- A 'critical' metal widely used in high-tech electronics. In this mineral the concentration of In is commonly correlated directly with Cu content. Here we use X-ray absorption spectroscopy of synthetic compounds and natural crystals in order to investigate the substitution mechanisms in sphalerites where In is present, together with the group 11 metals. All the admixtures (Au, Cu, In) are distributed homogeneously within the sphalerite matrix, but their structural and chemical states are different. Sphalerite with In, Au and Cu admixtures was studied by XANES/EXAFS spectroscopy techniques and by means of DFT calculations. Results of our work showed that in all the samples investigated In³⁺ replaces Zn in the structure of sphalerite. Gold in synthetic sphalerites is coordinated with sulfur. Our EXAFS data suggest that at high Au concentrations (0.03-0.5 wt.%) the Au₂S clusters predominate, with a small admixture of the Au⁺ solid solution with an Au-S distance of 2.5 Å. In contrast to Au, the presence of Cu⁺ with In exists only in the solid-solution state, where it is tetrahedrally coordinated with S atoms at a distance of 2.30 ± 0.03 Å. The distant coordination shells of Cu are disordered. These results demonstrate that the group 11 metals (Cu, Ag and Au) can exist in sphalerite in the metastable solid-solution state. The solid solution forms at high temperature via the charge compensation scheme 2Zn²⁺ Me⁺+Me³⁺. The final state of the trace elements at ambient temperature is governed by the difference in ionic radii with the main component (Zn), and concentration of admixtures. This study was supported by the Russian Science Foundation grant No. 18-77-00078.

The state of copper, silver and indium in sphalerite studied by X-ray spectroscopy of synthetic crystals and natural minerals

N.D. Trofimov¹, O.N. Filimonova¹, M.S. Nickolsky¹, V.D. Abramova¹, P.V. Evstigneeva¹, K.O.Kvashnina², A.L. Trigub³, D.A. Chareev⁴ and B.R. Tagirov¹

¹Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, ²European Synchrotron Radiation Facility, ³NRC “Kurchatov Institute”, ⁴Institute of Experimental Mineralogy, Russian Academy of Science, trofim-kol@mail.ru

Sphalerite (Zn, Fe)S is a host mineral for a wide range of minor and trace elements including Ag and In. The concentration of Ag strongly correlates with the amount of In in the ore. In most samples of natural sphalerites In concentrations show a positive correlation with Cu which implies the coupled substitution mechanism $2\text{Zn}^{2+} \leftrightarrow \text{Cu}^+ + \text{In}^{3+}$. Based on similar chemical properties of Ag and Cu it can be suggested that the formation of a solid solution in Ag-In-bearing sphalerite corresponds to the scheme $2\text{Zn}^{2+} \leftrightarrow \text{Ag}^+ + \text{In}^{3+}$. X-ray absorption spectroscopy (XAS) was applied to determine the local atomic environment and the valence state of the admixtures of Cu, Ag, and In in synthetic and natural sphalerites.

Sphalerite crystals were synthesized using three methods: gas transport (In-Ag-bearing sphalerites, In-bearing sphalerite), salt-flux method (In-Cu-bearing sphalerites), and dry synthesis (In-Ag-bearing sphalerite). Natural samples were collected from La Florida mine, Spain (PE-6 and PE-8) and Picos de Europa deposit, Spain (CL-1). The phase compositions of sphalerite samples were confirmed by X-ray diffraction (XRD). The morphology of the crystals was studied by means of scanning electron microscopy (SEM/EDS). Chemical composition was determined via electron probe microanalysis (EPMA) and laser ablation inductively coupled mass spectrometry (LA-ICP-MS).

In accordance with XANES spectroscopy the studied elements are present in sphalerite in +3 (In), +2 (Cu), +1 (Ag, Cu), and 0 (Ag) “formal” oxidation states.

Results of the EXAFS spectroscopy study of synthetic crystals demonstrate that when Ag is the only admixture in sphalerite it occurs in the form of metal Ag^0 . In the presence of In the solid solution Ag^+ predominates over Ag^0 , In exists in the solid solution state as well. When sphalerite contains only Cu without any other admixtures, Cu occurs in the form of covellite (CuS) microinclusions. In Cu-In-bearing sphalerites both Cu and In are present in the solid solution state. Contrast to Ag and Cu, In alone forms the solid solution with sphalerite, according to the scheme: $3\text{Zn}^{2+} \leftrightarrow 2\text{In}^{3+} + \text{Y}$, where Y is a vacancy at cation position. In the samples of natural sphalerites the local atomic environment in the 1st coordination shell corresponds to tenorite (CuO).

In addition, X-ray emission spectra (XES) of Cu in covellite and some other Cu-bearing sulfides are presented and discussed.

Our data demonstrate that In, Cu and Ag present in sphalerite in the solid solution state, which is stabilized by charge compensation scheme $2\text{Zn}^{2+} \leftrightarrow \text{Me}^+ + \text{Me}^{3+}$.

SNBL BM31: towards multi probe operando XRD + XAS + PDF

H. Emerich, G. Wiker, D. Chernyshov, V. Dyadkin and W. van Beek

Swiss Norwegian Beamlines at ESRF, 71, Avenue des Martyrs, Grenoble, France, wouter@esrf.fr

The availability of experimental methods that probe a material's structure, often complex and dynamic, at different length and time scales is key to obtain fundamental insight in technologically relevant materials and environmental geochemistry. Indeed, progress in sustainable technologies relies on the development of innovative materials utilizing an in-depth understanding of the interplay between a material's structure and its macroscopic properties. To this end, there is a need for advancing current X-ray based facilities allowing the study of materials with multiple techniques at their working state (i.e., operando methods).

The BM31 station of the Swiss Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF), offers the possibility to combine X-ray absorption spectroscopy (XAS) and X-ray powder diffraction (XRD) in an alternating fashion, quasi-simultaneously, in the same experimental setup. SNBL aims at extending these capabilities, by upgrading the current setup with a new CdTe area detector and focusing capabilities. This equipment will allow to i) implement pair distribution function analysis (PDF) of total scattering data, enabling combined XRD-PDF-XAS experiments and ii) enhance appreciably both the temporal (~ 1 s for XAS, ~ 100 ms for XRD-PDF) and spatial resolution (utilizing a beam size of $\sim 100 \times 100 \mu\text{m}^2$) of the experiments. The upgraded BM31 optics and endstation will also be compatible with the implementation of a XES von Hamos spectrometer, foreseen at a later stage.

The combined XRD-PDF-XAS measurements will allow the acquisition of complementary information of a material under the relevant working conditions: covering the length-scale from short to mid-range atomic arrangements viz. $\sim 1 \text{ \AA}$ to several nm by PDF, the average structure by XRD, as well as the electronic state, and geometry around the element of interest by XAS. All these data can be acquired in a temporal and spatially resolved manner in a single experiment. This will constitute a unique tool allowing the detailed study of materials for a wide range of applications, for instance: heterogeneous and electro-catalysis, CO₂ capture, gas separation, batteries and trace element reactions in environmental studies.

Crystal Analyser Laboratory at the ESRF

R. Verbeni, C. Lapras, R. Barrett, C. Henriquet

European Synchrotron Radiation Facility, Grenoble, France, verbeni@esrf.fr

The ESRF Crystal Analyser Laboratory (CAL), a laboratory completely dedicated to the development of spherically (cylindrically) bent analyser crystals for spectroscopic studies, has been operational since 2015. The CAL covers an area of roughly 120 m² including a “clean room” of 60 m² where the main processing tools are installed. At the moment the CAL is developing analyser crystals for 9 multi-analyser spectrometers at the ESRF but also provides optics to other X-ray light sources around the world. The domain of applications for such analyser crystals is quite wide including chemistry (energy storage materials, batteries), physics (correlated electron systems, liquid and glass dynamics), earth science, environmental science, catalysis, materials science and biology.

The laboratory is equipped with a combination of commercial instruments (wafer grinder, wafer dicing saw) as well as in-house designed fabrication and characterisation systems (for anodic bonding, cylindrical surface polishing, glue dispersion and inspection). The CAL manufactures essentially 3 types of analyser crystals (bent, bent-striped [1] and diced) mainly using Si, with the different types satisfying the various experimental conditions required by our scientists in terms of energy resolution, intensity and collected solid angle.

This poste will give an overview of the different technologies used for crystal analyser manufacture, describe the different processing capabilities of the CAL and describe the main development activities which are currently in progress. In particular, the latest improvements for the production of Von Hamos cylindrical analysers with radius $R = 0.5$ and 0.25 m will be shown and for the fabrication of both “single side” and “double side” machining of Johansson cylindrical analysers with radius $R = 1$ m.

A new system of vacuum-clamped analyser devices developed at the ESRF will also be presented. The system is intended primarily to host Ge bent and bent striped analysers and is similar to that presented by Jahrman [2] but much more compact in order to install many chambers in one line or in array. The preliminary results on Ge bent analysers indicate good performance and we intend to install this system in many ESRF multi-analyser spectrometers.

References

- [1] - M. Rovezzi et al., Rev. Sci. Instrum. **88**, 013108 (2017).
- [2] - E.P. Jahrman et al. , Rev. Sci. Instrum. **90**, 013106 (2019).

Uranium-induced changes in crystal-field and covalency effects of Th⁴⁺ in Th_{1-x}U_xO₂ mixed oxides probed by high energy resolution fluorescence detected X-ray absorption spectroscopy

H. Yu, L. Zhang, H. Bao, J.Q. Wang

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China,
yuhaiheng@sinap.ac.cn

Synchrotron radiation X-ray absorption spectrum (XAS) and X-ray emission spectrum (XES) are important spectroscopy techniques based on the synchrotron radiation light source to research the material structure information, which could be used to acquire the valence state and electronic state of the goal atom, the species, numbers of the atoms around the selected atoms and the information about the local structure. The broadening of XAS and XES are decided by the lifetime of the core hole. The shorter lifetime of the core hole results in the increased broadening of the XAS and XES. Because of the short lifetime of the inner core hole, the conventional XAS and XES have large broadening which results in some information will be covered. Based on the conventional XAS and XES, the high energy resolution fluorescence detected XAS have the high energy resolution, which are the advanced spectroscopy techniques for Actinide elements local structural analysis [1-3].

Understanding of the local structure of thorium is a prerequisite for a better understanding of the physicochemical properties of the thorium-based mixed oxides involved in the Th-based nuclear fuel cycle. The crystalline electric field (CEF) splitting of the 6d shell in Th_{1-x}U_xO₂ solid solution was probed by the Th L₃ edge high-energy-resolution fluorescence-detected (HERFD) X-ray absorption near-edge spectroscopy (XANES) collected at the Lβ₅ emission line at 14W1 beamline of SSRF, which cannot be obtained by conventional X-ray absorption methods [4-6]. Because the split peaks of the white line corresponding to the crystal-field splitting of the unoccupied 6d states were resolved in the HERFD-XANES spectra, the analysis of these split peaks combined with first-principles calculations revealed that an increase of the U content involves the distortion of the Th-O₈ cubes in the Th_{1-x}U_xO₂ mixed oxides. The lower symmetry of the Th-O₈ cube induced by the incorporated U tends to reduce the local crystal-field around Th⁴⁺ as well as the hybridization of Th 6t_{2g}-O 2p which is mainly responsible for the covalent property of the Th-O bond.

References

- [1] - S.M. Butorin et al., *Chemistry*, 22, 9693, (2016).
- [2] - S.M. Butorin et al., *Proceedings of the National Academy of Sciences of the United States of America*, 113, 8093 (2016).
- [3] - R. Bes et al., *Inorganic Chemistry* 55, 4260(2016).
- [4] - H.S. Yu et al., *Nuclear science and techniques*, 26,050102 (2015).
- [5] - P.Q. Duan et al., *X-ray Spectrometry*, 46, 12 (2017).
- [6] - H. Bao et al., *Inorg.Chem.*, 57, 11404 (2018).

XES workshop
List of participants

| Name | Laboratory |
|-----------------------|--|
| Antonio AGUILAR | CNRS Grenoble, France |
| Frederico ALVES LIMA | European XFEL Schenefeld, Germany |
| Lucia AMIDANI | Helmholtz-Zentrum Dresden, Germany |
| Camila BACELLAR | EPFL - ISIC Lausanne, Switzerland |
| Matthias BAUER | University of Paderborn, Germany |
| Stephen BAUTERS | ROBL-CRG ESRF Grenoble, France |
| Elena BAZARKINA | IGEM (RAS) Moscow, Russia |
| Elisa BORFECCHIA | University of Turin, Italy |
| Sergei BUTORIN | University of Uppsala, Sweden |
| Maria CHRYSINA | MPI Mülheim/Ruhr, Germany |
| Marine COTTE | ESRF Grenoble, France |
| Francesco D ACAPITO | LISA/BM08 CRG ESRF Grenoble, France |
| Paola D'ANGELO | University of Rome La Sapienza, Italy |
| Frank DE GROOT | University of Utrecht, The Netherlands |
| Serena DEBEER | MPI Mülheim/Ruhr, Germany |
| Philippe DEROUINEAU | Saint-Gobain St-Pierre-lès-Nemours, France |
| Blanka DETLEFS | ESRF Grenoble, France |
| Kathrin EBNER | Paul Scherrer Institute Villigen, Switzerland |
| Hermann EMERICH | SNBL-CRG ESRF Grenoble, France |
| Olga FILIMONOVA | IGEM (RAS) Moscow, Russia |
| Lorena FRITSCH | University of Paderborn, Germany |
| Kalotina GERAKI | Diamond Light Source Ltd Didcot, UK |
| Evgeny GERBER | Lomonosov Moscow State University, Russia |
| Jan Pieter GLATZEL | ESRF Grenoble, France |
| Richard GNEWKOW | TU Berlin, Germany |
| Jean Louis HAZEMANN | CNRS Grenoble, France |
| Myrtille HUNAUT | Synchrotron Soleil Saint-Aubin, France |
| Simo Jooseppi HUOTARI | University of Helsinki, Finland |
| Neil HYATT | University of Sheffield, UK |
| Rebecca INGLE | EPFL - ISIC Lausanne, Switzerland |
| Mohammed IRAR | SESAME Synchrotron Amman, Jordan |
| Yves JOLY | CNRS Grenoble, France |
| Amélie JUHIN | CNRS Paris, France |
| Justus JUST | University of Lund, Sweden |
| Aleksandr KALINKO | University of Paderborn, Germany |
| Birgit KANNGIESSER | TU Berlin, Germany |
| Matjaz KAVCIC | Institute Jozef Stefan Ljubljana, Slovenia |
| Naomi KAWAMURA | JASRI SPRing-8 Sayo, Japan |
| Rachit KHARE | TU Munich, Germany |
| Isabelle KIEFFER | ISterre University of Grenoble Alpes, France |
| Konstantin KLEMENTIEV | University of Lund, Sweden |
| Jindrich KOLERENC | Czech Academy of Science Praha, Czech Republic |
| Kristina KVASHNINA | ESRF Grenoble, France |
| Sara LAFUERZA BIELSA | ESRF Grenoble, France |
| Philippa LEAN | ESRF Grenoble, France |
| Mathieu LIATOUD | Saint-Gobain Gières, France |
| Kirill LOMACHENKO | ESRF Grenoble, France |
| Alessandro LONGO | CNR ISMN Palermo, Italy |
| Sergei MALYSHEV | Lomonosov Moscow State University, Russia |
| Anna MALYSHEVA | Lomonosov Moscow State University, Russia |

XES workshop
List of participants

| Name | Laboratory |
|----------------------------|---|
| Alain MANCEAU | ISTerre University of Grenoble Alpes, France |
| Dimitrios MANGANAS | MPI Mülheim/Ruhr, Germany |
| Olivier MATHON | ESRF Grenoble, France |
| Victoria MAZALOVA | CFEL - DESY Hamburg, Germany |
| Margarita MERKULOVA | ESRF Grenoble, France |
| Frederick MOSSELMANS | Diamond Light Source Ltd Didcot, UK |
| Maarten NACHTEGAAL | Paul Scherrer Institute Villigen, Switzerland |
| Michal NOWAKOWSKI | University of Paderborn, Germany |
| Danilo OLIVEIRA DE SOUZA | Elettra Sincrotrone Trieste, Italy |
| Florian OTTE | DELTA Dortmund, Germany |
| Sergey PEREDKOV | MPI Mülheim/Ruhr, Germany |
| Chris POLLOCK | Cornell University Ithaca, USA |
| Olivier PROUX | CNRS Saint-Martin-d'Hères, France |
| Qing QIAN | XRS TECH LLC Freehold, USA |
| Aline RAMOS | CNRS Grenoble, France |
| Ekta RANI | University of Oulu, Finland |
| Harald REICHERT | ESRF Grenoble, France |
| Marius RETEGAN | ESRF Grenoble, France |
| Brunilda RICA | Argetest Cevher Zenginlestirme Ankara, Turkey |
| Andrei ROGALEV | ESRF Grenoble, France |
| Claudine ROMERO | ESRF Grenoble, France |
| Angelika ROSA | ESRF Grenoble, France |
| Jörg ROTHE | Karlsruhe Institute of Technology, Germany |
| Mauro ROVEZZI | CNRS Saint-Martin-d'Hères, France |
| Viktoriiia SAVELEVA | Paul Scherrer Institute Villigen, Switzerland |
| Bianca SCHACHERL | Karlsruhe Institute of Technology, Germany |
| Andreas SCHEINOST | ROBL-CRG ESRF Grenoble, France |
| Roland SCHOCH | University of Paderborn, Germany |
| Valentin G. SEMENOV | St Petersburg State University, Russia |
| Francesco SETTE | ESRF Grenoble, France |
| Kajsa SIGFRIDSSON CLAUSS | University of Lund, Sweden |
| Harishchandra SINGH | University of Oulu, Finland |
| Dimosthenis SOKARAS | SLAC NAL Stanford, USA |
| Mikhail SOLDATOV | Southern Federal Univ. Rostov-on-Don, Russia |
| Georg SPIEKERMANN | University of Potsdam, Germany |
| Christian STERNEMANN | TU Dortmund, Germany |
| Maria Gloria SUBIAS-PERUGA | University of Zaragoza - CSIC, Spain |
| Jean SUSINI | ESRF Grenoble, France |
| Artem SVIAZHIN | ESRF Grenoble, France |
| Pieter TACK | University of Ghent, Belgium |
| Francesco TAVANI | University of Rome La Sapienza, Italy |
| Alexander TRIGUB | NRC Kurchatov Institute Moscow, Russia |
| Nikolay TROFIMOV | IGEM (RAS) Moscow, Russia |
| Wouter VAN BEEK | SNBL-CRG ESRF Grenoble, France |
| Roberto VERBENI | ESRF Grenoble, France |
| Tonya VITOVA | Karlsruhe Institute of Technology, Germany |
| Sven WENDHOLT | University of Paderborn, Germany |
| Haisheng YU | Shanghai Institute of Applied Physics, China |
| Linjuan ZHANG | Shanghai Institute of Applied Physics, China |