

Swiss-Norwegian Beam Lines
at ESRF

“SNBL – Planning for the next decade”

Swiss-Norwegian Workshop

**May 28-29, 2015
Grenoble, France**



09:00 Registration

09:30 Welcome (10 min)

Gervais Chapuis
SNX Foundation

09:40 Exploring new directions in the chemistry of hydrides

Yaroslav Filinchuk
UCL, Louvain-la-Neuve, Belgium

10:25 Combining X-ray crystallography and *in situ* single-crystal UV-Vis and Raman spectroscopy to study redox proteins

Hans-Petter Hersleth
University of Oslo, Norway

11:10 Coffee (20 min)

11:30 Flexible Metal-Organic-Frameworks : from synthesis, structural flexibility under stimuli to potential applications

Christian Serre
Institut Lavoisier, Versailles, France

12:15 Lunch (90 min)

13:45 Photocrystallography on spin-crossover compounds

Andreas Hauser
University of Geneva, Switzerland

14:30 X-ray induced variations in the depletion capacitance correlating with K-shell transitions of defect constituting impurities: testing iron in silicon

M.E.Ingebrigtsen¹, V.Venkatachalapathy¹, H.Emerich², L.Vines¹, and A.Yu.Kuznetsov¹
¹*Department of Physics and Center for Materials Science and Nanotechnology, University of Oslo, Norway;* ²*SNBL at the ESRF, Grenoble, France*

14:55 Functionalisation of porous materials

Karina Mathisen
NTNU, Trondheim, Norway

15:20 Coffee (30 min)

15:50 SNBL: Celebrating 20 years of catalyst characterisation development

Magnus Rønning
NTNU, Trondheim, Norway

16:35 Formation of natural nanoparticles and their impact on trace elements

Andreas Voegelin

Eawag, Switzerland

17:00 *In situ* and *operando* XAS-XRD studies on materials for sustainable energy

Q. Imtiaz¹, S.M. Kim¹, D. Hosseini¹, N.S. Yüzbaşı¹, A. Kierzkowska¹, P.M. Abdala¹,

W. van Beek², C. Müller¹

¹*Laboratory of Energy Science and Engineering, ETH Zurich, Switzerland*

²*SNBL at ESRF, Grenoble, France*

17:25 XAS and XRD investigations of argillaceous rock formations and cement-clay interfaces relevant to the Swiss radioactive waste disposal program

Rainer Dähn

PSI, Villigen, Switzerland

17:50 Powder Diffraction for Catalysis at SNBL

David Wragg

University of Oslo, Norway

18:15 Posters Presentations

19:30 Dinner, Château de la Baume (Seysins)

09:00 Recent developments in X-ray diffraction and scattering

Hans-Beat Bürgi
University of Zürich, Switzerland

09:45 From charge transfer to charge ordering: towards giant structural complexity in transition metal oxides

Werner Paulus
University of Montpellier, France

10:30 Coffee (20 min)

10:50 Rare-earth borohydrides – structures and thermal properties

Magnus H. Sørby, Christoph Frommen, Bjørn C. Hauback
Institute for Energy Technology, Physics Department, Kjeller, Norway

11:15 Complex metal hydrides for energy applications: borohydrides and mixed-anion closo-borane-borohydrides

Radovan Černý, Pascal Schouwink, Yolanda Sadikin, Matteo Brighi and Emilie Didelot
Laboratory of Crystallography, University of Geneva, Switzerland

11:40 Mimicking the SwissFEL X-ray Beam at SNBL

C. Dejoie^a, S. Smeets^a, C. Baerlocher^a, N. Tamura^b, P. Pattison^c, R. Abela^d, L.B. McCusker^a
^a*Laboratory of Crystallography, ETH Zurich, Switzerland*, ^b*ALS, Lawrence Berkeley National Laboratory, Berkeley CA, USA*, ^c*SNBL at ESRF, Grenoble, France*, ^d*PSI, Villigen, Switzerland*

12:05 Lunch (85 min)

13:30 Diffraction studies of partially disordered materials

Wojciech Slawinski
University of Oslo, Norway

13:55 DUBBLE (Wim Bras), MAX-IV (Katarina Noren), SLS (Nicola Casati)

14:40 The role of SNBL in the context of modern synchrotron beamlines (SNBL Committee of the Future)

Robert Cernik
University of Manchester, UK

15:10 Closing remarks

ABSTRACTS

Yaroslav Filinchuk

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In attempts to get to better hydrogen storage materials, many new compounds are synthesized in powder form, and we are facing the challenge of structure solution from powder data for compounds with unknown composition, moreover on multiphase samples! The power of powder diffraction is extended by the variable temperature diffraction, which became a standard tool at SNBL. Ramping the temperature allows to get through different decomposition steps, thus breaking the big problem into a number of smaller ones. Scanning different compositions with temperature allows getting crystal structures of all the new compounds and to characterize the decomposition reaction pathways on complex mixtures, typically obtained by mechanochemistry [1].

When hydrogen content is also varied, *in situ* diffraction experiments can yield equilibrium phase diagrams [2]. Most remarkably, for some porous systems, the thermodynamic parameters of solid-gas interaction can be extracted directly from diffraction data. Thus, the isosteric heats of adsorption vs. loading can be obtained for small-pore systems, where a guest can be reliably located and its occupancy refined as a function of gas pressure and temperature [3]. Experimental data can be collected in a form of isotherms or isobars, and the interpolation or an analytical description can be used in order to get values for the equal loadings. The enthalpies are obtained using the Clausius-Clapeyron equation. In contrast to the bulk volumetric measurements, this method allows to characterize samples having an amorphous fraction or containing more than one crystalline phase.

Another parameter that can be unfolded in the diffraction experiment is the reaction time during ball milling. A new technique, combining a reactive ball milling with a simultaneous X-ray powder diffraction, allows for in-situ monitoring the mechano-chemical reactions [4]. Our recent developments are aiming to improve the data quality to the requirements of structure solution. This is done by designing 3D-printed milling jars with geometries suitable for high resolution measurements at moderate-energy beamlines, like SNBL. With these modifications, the ball milling followed by diffraction can become a standard and informative technique.

The above examples show that *in situ* diffraction has become instrumental in materials chemistry, but it requires the use of know-how and good skills in crystallography. The knowledge transfer should be improved on the interface between the interested communities and the large facilities. This should ensure an easy insertion of new students / users into the existing teams, and the continuity of developments.

[1] Ravnsbæk D.B., Sørensen L.H., Filinchuk Y., Besenbacher F., Jensen T.R. *Angew. Chem. Int. Ed.* (2012) 51, 3582.

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Combining X-ray crystallography and *in situ* single-crystal UV-Vis and Raman spectroscopy to study redox proteins

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X-ray crystallography is the central methods for studying the structure-function relation of redox proteins, however the crystal structures are missing key information. This includes oxidation state, protonation and spin state, which are essential for understanding the reaction mechanisms of these redox protein systems. Therefore, a combination of crystallographic and spectroscopic methods is vital for a more fully characterisation. Additionally, the redox sites are very labile for X-ray induced radiation damage and reduction during crystallographic data collection at synchrotrons. Therefore combining X-ray crystallography with *in situ* UV-Vis and Raman spectroscopy is important for both characterisation and radiation damage monitoring. There are now a few beamlines around the world that have this possibility, with the Swiss-Norwegian Beamlines being one of them. The lecture will focus on why this combined setup is important for the study of redox proteins, and how they can be used to give complementary and additional information, as well as guiding the crystallographic data collection.

**Flexible Metal-Organic-Frameworks :
from synthesis, structural flexibility under stimuli to potential applications**

Christian Serre

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Versailles, France*

Metal Organic frameworks (MOFs) are ordered micro- or meso-porous hybrid solids of interest for a wide range applications, owing to their tunable chemical and structural features [1], including drug delivery [2], or purification, separation or storage of gases [3-4]. Among them, highly flexible MOFs can be considered as stimuli-responsive materials due to their large changes in pore opening as a function of the nature of the guests, or the impact of the temperature or mechanical pressure. [5] Series of highly flexible metal(III or IV) polycarboxylates materials (M=Cr, Fe, V...), exhibiting various building units, pore sizes and shapes have been reported since early 2000's. Their flexible character and properties were tuned through the nature of the organic linker bearing either different spacers or exhibiting polar or apolar functional groups. [6-8]

Here, we report a review of our contribution in this field from the synthesis, structural analysis of these highly flexible MOFs, their *ex situ* and *in situ* Synchrotron or Neutron structural analysis as well as their most significant potential applications.

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[8] E. Alvarez, N. Guillou, C. Martineau, B. Bueken, B. Van de Voorde, C. Le Guillouzer, P. Fabry, F. Nouar, F. Taulelle, D. de Vos, J.-S. Chang, K. Ho Cho, N. Ramsahye, T. Devic, Marco Daturi, G. Maurin, C. Serre, *Angew Chem Int Ed* 2015, 54(12), 3664–3668

Photocrystallographie on spin-crossover compounds

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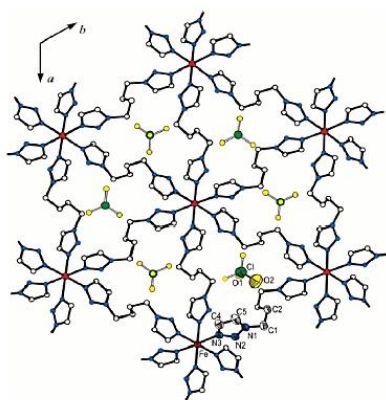
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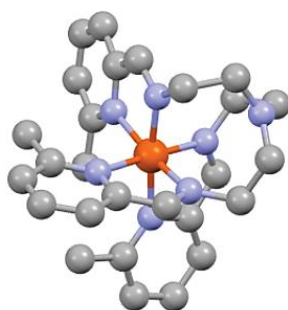
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Spin crossover in transition metal complexes is associated with large structural changes. For instance, the metal-ligand bond length difference in iron(II) complexes is typically around 0.2 Å and creates elastic interactions between the centers. These result in cooperative effects, which may lead to a hysteresis in the thermal spin transition, and which influence the relaxation processes following light-induced spin transitions. In our contribution we will discuss three examples of how synchrotron X-Ray diffraction serves to elucidate the structural changes of light-induced spin states in iron(II) complexes at low temperatures and to shed light on the ensuing relaxation processes.

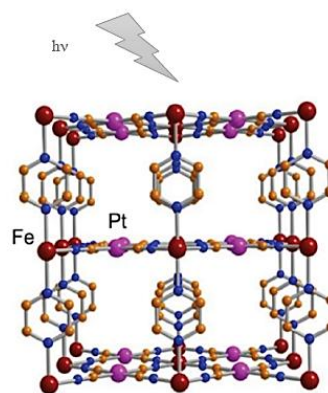
These comprise (i) the determination of the crystal structure in the light-induced low-spin state of $[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2$,^[1] which under normal conditions remains in the high-spin state at all temperatures, (ii) the determination of the crystal structure of the spin-crossover compound $[\text{Fe}(6\text{-mepy})_3\text{tren}](\text{PF}_6)_2$ in the light-induced high-spin state,^[2] which has a lifetime of only a few seconds at 10 K, and (iii) the determination of the crystal structure of $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ in the light-induced high-spin state and evidence for nucleation and growth processes during the subsequent high-spin \rightarrow low-spin relaxation.^[3]



$[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2$



$[\text{Fe}(6\text{-mepy})_3\text{tren}](\text{PF}_6)_2$



$[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4] \cdot x\text{H}_2\text{O}$

[1] P. Chakraborty, R. Bronisz, C. Besnard, L. Guénée, P. Pattison, A. Hauser, *J. Am. Chem. Soc.* 134 (2012) 4049, "Persistent bidirectional optical switching in the 2D high-spin polymer $[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2$ ".

[2] P. Chakraborty, A. Tissot, L. Peterhans, L. Guénée, C. Besnard, P. Pattison, A. Hauser, *Phys. Rev. B* 87 (2013) 214306, "Determination of the molecular structure of the short-lived light-induced high-spin state in the spin-crossover compound $[\text{Fe}(6\text{-mepy})_3\text{tren}](\text{PF}_6)_2$ ".

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X-ray induced variations in the depletion capacitance correlating with K-shell transitions of defect constituting impurities: testing iron in silicon

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Microscopic identification of defects responsible for the device performance is one of the mainstays for many well-established methodologies clearly prioritizing in-situ observations providing unambiguous arguments. Concurrently, there is a significant progress reached in applications of various types of capacitance spectroscopy to reveal characteristics of localized levels in semiconductors [1]. However, assigning a particular defect to a particular carrier trap is always a challenge for capacitance spectroscopies and requires additional assumptions as well as ex-situ measurements. Consequently, it would be very helpful to develop an in-situ methodology that may bridge electrical and structural characteristics of defects in semiconductors. Accordingly, Ishii et al. reported the use of x-rays for changing the depletion capacitance and correlating it with the properties of DX centers in AlGaAs:Se [2, 3]. The idea was followed by Fujioka et al. using Al/AlN/Si Schottky diodes discriminating the chemical content of two characteristic traps as a function of the x-ray excitation energy [4]. Upon that, to the best of our knowledge, there was no further development of this interesting methodology as reported in literature. One reason for no further interest may be due to relative complexity of the samples used in [2-4], challenging the credibility of the interpretations. Thus, we decided to revisit the measurements using a well-established test system of iron in silicon. Indeed, accounting for the critical impact of Fe on the minority carrier lifetime in p-type Si, this system has been extensively studied [5] and owing to the presence of several Fe related deep levels this system is well suited for our purposes. In particular, the capacitance was measured as a function of time while the samples were sequentially illuminated with x-rays having energies below and above the K-shell absorption edge of Fe at 7.1 keV. The measurements were made at the SNBL/ESRF and, as a result,

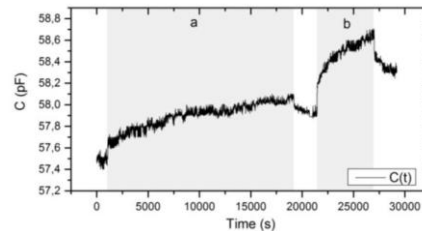


Fig.1. Depletion capacitance as a function of time under x-ray illumination in Fe doped Si.

Fig.1 plots the data using either (a) 6 keV or (b) 7.3 keV excitations at 90K, resolving a significantly higher capacitance response for photons capable to knock-out Fe K-shell electrons. This additional electron emission is indeed “element sensitive” and can be used for correlating the electronic and structural properties of the defect. In conclusion, our observations support the ideas reported in Ref.2-4 previously and the method combining x-ray and capacitance spectroscopy may be promising to investigate further.

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- [2] M. Ishii et al., *Applied Physics Letters*, **74** 2672(1999).
- [3] M. Ishii et al., *Journal of Applied Physics*, **88** 3962(2000).
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- [5] A.A.Istratov et al., *Applied Physics A*, **70** 489(2000).

Functionalisation of porous materials

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The specific research area dealing with composite systems made up of nanoparticulates formed and stabilized in 3D-carriers with high surface area and molecular sieving properties is currently expanding. Growth limitations of metallic nanoparticles formed in microporous zeolites materials from ionic precursors has been known for several decades, and utilizing 3D supports to obtain single site heterogeneous catalyst is highly relevant today.^{1,2} The areas of application for these systems are currently emerging, leading to new and interesting areas where the bi-functionality of these systems can be utilised.^{1,3} The established selection of 3D supports in the micro-range is wide and a range of systems are currently available both commercially, or via synthesis. Even if the selection of supports in the micro-range is versatile, controlled functionalization to obtain hydrothermally stable framework single sites can be challenging. Nanoparticulate species can further be formed from precursor cations during reducing atmospheres. The added function of the shape selective carrier will ensure high dispersion and distribution of metal ionic precursors, and also add growth limitations to the metallic species present inside the pores.⁴ Understanding the formation, stability and structure of metallic mono and bi-metallic nanoparticles is an important aspect in many areas today.⁵

- (1) Somorjai, G.; Park, J. *Top Catal* 2008, 49, 126.
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SNBL: Celebrating 20 years of catalyst characterisation development

Magnus Rønning

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Formation of natural nanoparticles and their impact on trace elements

Andreas Voegelin

Eawag, Switzerland

Natural nanoparticles formed in terrestrial and aquatic systems may act as immobilizing sorbents or colloidal carriers for co-transformed major and trace elements and thereby profoundly affect their fate as essential nutrients or toxic contaminants. Two key examples are presented, which also allow to point out some of the specific needs for the use of XAS in environmental sciences.

(i) Flooding of contaminated wetland soils may lead to the release of trace metals into surface or groundwater resources. In microcosm experiments, we found that contaminated soil flooding not only led to a decrease of dissolved metal concentrations, but concomitantly also to a substantial mobilization of colloidal Cu, Hg, Pb and Cd into soil porewater [1-4]. XAS in combination with TEM showed that colloid release was initially due to bacterially-mediated formation of Cu(0) nanoparticles with some Hg-for-Cu substitution. Microbial sulfate reduction subsequently led to Cu(0) sulfidation and the formation of Cu-rich metal sulfide nanoparticles that also contained Cd, Pb and Hg. Formation of metallic and metal sulfide nanoparticles may thus drive the colloidal mobilization of chalcophile trace metals from flooded soils. To characterize the redox-sensitive dilute to ultra-dilute samples from this project by XAS, perfectly anoxic sample handling, a cryogenic sample environment, and sensitive fluorescence detectors were essential.

(ii) Oxidation of dissolved Fe(II) by O₂ at anoxic/oxic boundaries induces the precipitation of nanoparticulate Fe(III)-precipitates with a high capacity for cation and anion uptake. Related to studies on As removal from anoxic Fe(II)-containing groundwater in Asia, we study how phosphate, silicate and Ca affect the formation, structure and As uptake of Fe(III)-precipitates [5-8]. The structure of Fe(III)-precipitates formed over a wide range of conditions) was characterized by Fe K-edge XAS (200-300 samples to date). Analysis of the XAS results by principal component analysis and linear combination fitting revealed gradual shifts in precipitate structure as a function of water chemistry between several structural end-members, most importantly lepidocrocite, ferrihydrite and amorphous Fe(III)-phosphate. The extensive XAS-derived structural data provides a quantitative basis for the assessment of various aspects of precipitate reactivity, including precipitate aging over time and uptake of trace elements like As.

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2. Hofacker et al., *Environ. Sci. Technol.* **2013**, 47, 7739-7746.
3. Weber et al., *Geochim. Cosmochim. Acta* **2009**, 73, 5513-5527.
4. Weber et al., *Nature Geoscience* **2009**, 2, 267-271.
5. Senn et al., *Geochim. Cosmochim. Acta* **2015**, in press.
6. Voegelin et al., *Geochim. Cosmochim. Acta* **2013**, 117, 216-231.
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8. Kaegi et al., *Geochim. Cosmochim. Acta* **2010**, 74, 5798-5816.

In situ and operando XAS-XRD studies on materials for sustainable energy

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²*SNBL at ESRF, Grenoble, France*

Global warming is a major concern due to serious global implications such as droughts, rising sea levels and food scarcity. According to the IPCC global warming is mostly likely linked to the increased anthropogenic greenhouse gas emissions, in particular CO₂ from fossil-fuel fired power stations and transportation. A more efficient use of fuels and the implementation of CO₂ capture technologies are potential solutions to mitigate climate change. In this context, our research group is highly active in the development of novel materials for sustainable energy, such as transition metal-based oxygen carriers for chemical looping combustion (CLC) based CO₂ capture or catalysts for the dry reforming of methane. For example, the dry (CO₂) reforming of methane (DRM) produces a synthesis gas from two major greenhouse gases. On the other hand, CLC is a promising CO₂ capture technology that could substantially reduce the costs associated with the capture of CO₂ when compared to the currently available technology (*i.e.* amine scrubbing). In CLC, lattice oxygen of an oxygen carrier, typically of a transition metal oxide is used to combust a hydrocarbon fuel.

Application of XAS and XRD to study energy related materials under relevant conditions can help us to understand better structure – property relationships and, in turn allows us to rationally improve further these materials. In this presentation we will present results of two recent XAS/XRD studies investigating Ni-based dry reforming catalysts and Cu-based oxygen carriers, performed at SNBL facilities.

As the first example, a combined XAS and XRD study on monometallic Ni and bimetallic Ni-Fe supported on a Mg_xAl_yO_z-matrix (derived via a hydrotalcite-like precursor) for the dry reforming of methane (DRM) is presented. Before reaction a pre-reduction treatment was applied allowing us to follow the formation of Ni and bimetallic Ni-Fe nanoparticles. Using bimetallic catalysts for DRM XANES revealed the formation of FeO_x species while XRD confirmed that de-alloying occurred simultaneously. On the other hand, mono-metallic Ni catalyst showed the formation of crystalline graphite during DRM. For both mono- and bimetallic catalysts Ni remained in its metallic form. These results, in combination with catalytic tests and Raman spectroscopy experiments indicate that the FeO_x species play a significant role in the reduction of carbon formation and the stability of the catalysts.

The second example presents studies concerning the phase stability and reduction pathways of Na⁺-doped and Al₂O₃-supported CuO based oxygen carriers synthesized using a sol-gel technique for chemical looping-based CO₂ capture. Using XRD and XAS we could conclude that Na⁺ inhibits the formation of the CuAl₂O₄ spinel. Moreover, in-situ XANES data collected during pulsed H₂ redox experiments showed that Na⁺-doping facilitates the reduction of CuO.

XAS and XRD investigations of argillaceous rock formations and cement-clay interfaces relevant to the Swiss radioactive waste disposal program

Rainer Dähn

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Argillaceous rocks and cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of radioactive wastes in deep geological repositories. An approximately 180 million year old marine clay-rich sediment (Opalinus Clay, OPA) has been identified and selected as the first-priority host-rock for the disposal of high-level radioactive waste in Switzerland. One of the main aspects for evaluating the safety case of a potential radioactive waste repository in a deep geological formation is to understand and quantify the geochemical and physical processes that influence the mobility of the radionuclides in the geochemical environment imposed by the host rock and technical barriers such as cement. This information is needed to make reliable predictions of the long-term retardation behaviour of radionuclides. Synchrotron-based micro X-ray fluorescence (microXRF), micro X-ray absorption spectroscopy (microXAS) and micro X-ray diffraction (microXRD) combined with bulk-XAS measurements play an important role in the investigations of retention processes in such heterogeneous systems.

Exemplarily the investigations of metal uptake by argillaceous rocks (OPA and the Hungarian BODA rock) and the formation of newly formed phases at cement-clay interfaces will be presented. In the latter study samples from a natural analogue (Maqarin, Jordan) and samples from a long-term Cement/OPA-Interaction experiment ("CI-project") in the Mont Terri Rock Laboratory (St-Ursanne, Switzerland) were investigated. The results of these studies can be an essential step in further constraining and, consequently, improving reactive transport models, which are currently being used for long-term predictions of the evolution of the interfaces between cement and OPA and the release of radionuclides from a deep geological radioactive waste repository into the environment.

Powder Diffraction for Catalysis at SNBL

David Wragg
University of Oslo, Norway

Catalysts are vital to many of the processes we take for granted in everyday life. In industry, catalysts are used in all kinds of processes but often their activity is poorly understood. *In Situ* powder diffraction has recently proved itself as an extremely valuable technique in our attempts to understand how catalysts work. SNBL has been a key part of this and I will present some of our work in the field. Linking the structural behaviour of catalysts gives us a new insight into the activity of materials such as zeolites under real working conditions.

By extracting real crystallographic information from the powder diffraction data we have linked changes in the structure of SAPO-34 during the methanol to olefin conversion process to the deactivation of the catalyst, as well as creating a model of coke distribution in the particles based on high resolution powder diffraction, Raman and adsorption data. Recently we have used the Pilatus@SNBL setup to carry out time and space resolved studies on the methanol to gasoline catalyst ZSM-22. These have revealed very different structural behaviour in the catalyst depending on how it has been treated prior to use. I will attempt to explain how this behaviour can be related to the catalyst structure thanks to new *in situ* XRD results.

Recent developments in X-ray diffraction and scattering

Hans-Beat Bürgi

Universities of Bern and Zürich, Switzerland

The presentation will be a potpourri of recent developments in which I have participated or which I find particularly interesting and promising.

- Hirshfeld Atom Refinement (HAR) is a relatively new method for obtaining quite accurate hydrogen atom positions and anisotropic ADPs from X-ray diffraction data. It is based on tailor-made *ab initio*, non-spherical atomic form factors and has become possible thanks to the ever increasing computing resources.

- The low frequency molecular vibrations, both frequencies and Eigenvectors, can be obtained from the temperature dependence of ADPs with a mean molecular field, Einstein type model. The low frequencies from the diffraction data combined with the high frequencies of molecular deformations calculated *ab initio* give access to specific heat curves of crystalline solids. Based on such curves the relative stabilities of α -, β - and γ -glycine are discussed.

-Of the 750'000 structures in the CSD 20% show disorder. With state of the art instrumentation and computing resources the associated diffuse scattering can be measured relatively accurately with both X-rays and neutrons. With the programs ZODS (Zürich-Oak Ridge Disorder Simulation), YELL (3D-PDF analysis, T. Weber, A. Simonov, ETHZ) and parallel computing resources disordered structures can be simulated and analyzed. The scattering of the resulting structural models approaches quantitative agreement with the experimental data.

- In conclusion it is suggested that studies of the type described here (and in other presentations during this meeting) could help to move the image of 'crystallography' from that of a crystal structure service tool back towards an autonomous scientific discipline, one that studies crystals in the broadest sense.

From charge transfer to charge ordering: towards giant structural complexity in transition metal oxides

Werner Paulus

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Rare-earth borohydrides – structures and thermal properties

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Metal borohydrides have been extensively investigated over the last few years for energy storage application due to high volumetric and gravimetric hydrogen capacities and in some cases high Li-ion conductivities.

An overview of our structural work on rare-earth borohydrides is given, highlighting the complementarity of neutron and X-ray diffraction. Both the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, and the high-resolution neutron powder diffractometer PUS, located at the JEEP II reactor in Kjeller, have been invaluable tools for the structure determination of a large number of compounds. Whereas synchrotron radiation powder X-ray diffraction (SR-PXD) gives lattice parameters and positions of heavy atoms with high accuracy, powder neutron diffraction (PND) excels when it comes to the accurate determination of light-weight elements, especially hydrogen, in close proximity to heavy scatters, which would otherwise be (almost) invisible to X-rays.

Mixtures of $RECl_3$ and $LiBH_4$ have been synthesized by ball milling with $RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb$ and Lu [1-3]. The formed compounds show a large structural variety with: (i) anion substitution; (ii) polymorphism; (iii) different coordination numbers; and (iv) multiple oxidation states of the RE . An overall trend is that: (i) the early RE : La, Ce, Pr, Nd, Sm and Gd form $LiRE(BH_4)_3Cl$ in space group $I-43m$; the later RE : Sm, Gd, Tb, Dy, Er, Tm and Yb form $\alpha-RE(BH_4)_3$ in $Pa-3$, while for Sm, Er and Yb a second polymorph named $\beta-RE(BH_4)_3$ is formed in the higher-symmetry space group $Pm-3m/Fm-3c$; (iii) the smallest RE : Yb and Lu form $LiRE(BH_4)_4$, space group $P-42c$; (iv) upon heating $Sm(BH_4)_2$ and $Eu(BH_4)_2$ (space group $Pbcn$) and two modifications of $Yb(BH_4)_{2-x}Cl_x$ ($P-4$ and $Pbca$) are observed.

The thermal decomposition of the mixtures has been investigated by *in situ* synchrotron radiation powder X-ray diffraction, thermogravimetric analysis/differential scanning calorimetry and temperature programmed desorption. Furthermore we have studied the effect of different ratios between $RECl_3$ and $LiBH_4$ and how different experimental conditions e.g. decomposition against backpressure or vacuum and the addition of LiH influence the reaction paths.

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Complex metal hydrides for energy applications: borohydrides and mixed-anion *closo*-borane-borohydrides

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The significant interest in novel metal borohydrides was initially driven by the extreme hydrogen densities and the potential to develop efficient on-board hydrogen storage. A deeper understanding of their underlying building principles in the past years has provided means of going beyond hydrogen storage and making use of further properties specific to the borohydride anion. With our contribution we wish to present new developments in the field of borohydride perovskites,¹ targeting energy-related applications such as hydrogen-storage, solid state lighting or magnetic refrigeration.² Heteropolar di-hydrogen contacts are exploited to facilitate H₂ elimination while homopolar contacts and structural dynamics give rise to exotic mechanisms able of stabilizing lattice instabilities at high temperatures in the perovskite lattice, thus breaking down the intuitive temperature behaviour of the lattice type. First results will also be discussed on the magnetocaloric effect of Gd³⁺-containing borohydrides, being potentially useful materials that are paramagnetic down to very low temperatures.

The tetrahydroborate anion is prone to vivid structural dynamics which have recently been made use of in the development of solid state electrolytes based on complex hydrides. Very recently, the focus has extended to compounds based on higher boranes, such as B₁₂H₁₂²⁻ or B₁₀H₁₀²⁻. We have extended this concept to mixed-anion compounds and will present the ionic conductivity results supported by topostructural analyses revealing migration paths in Na₃BH₄B₁₂H₁₂.³ Its ionic conductivity was measured using electrical impedance spectroscopy and is close to of 10⁻³ S/cm at room temperature, with an activation energy of 0.34 eV, evidencing high mobility of Na⁺. We will show how the research on energy related materials is strongly supported by the crystallographic and crystal chemistry analysis which would not be possible without a top level source of powder diffraction data such as provided by the SNBL. High time resolution and high data statistics of 2D diffraction data provided by Pilatus detector in combination with in-situ Raman and mass spectroscopies and with the use of temperature and gas sample cell allows to map many physical properties while exploring the composition-temperature phase diagrams and discovering novel thermodynamically stable and meta-stable phases which are designed according to the predicting power of the borohydride-oxide analogy.⁴

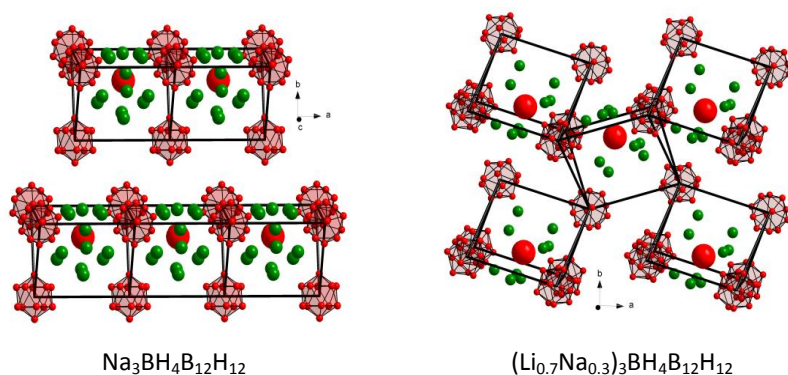


Figure 1

Connectivity and stacking of basic building units, trigonal prisms of *closo*-boranes, in two novel mixed anion borohydrides-*closo*-boranes. The borohydrides are shown as large red and cations like green spheres. Hydrogen atoms are omitted for clarity.

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Mimicking the SwissFEL X-ray Beam at SNBL

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With the development of X-ray free-electron laser (X-FEL) sources that create ultrafast X-ray pulses of unprecedented brilliance, a new option for the structural characterization of microcrystalline inorganic materials is arising [1]. Any crystal placed in an X-FEL beam will be destroyed, but not before a diffraction pattern is generated. To get a full data set, therefore, many randomly oriented stationary crystals have to be measured. The SwissFEL facility [2], which is scheduled to come online in 2017, will have a unique feature: the bandpass of the X-ray beam will be adjustable to give as much as a 4% energy spread. To evaluate the possibility of exploiting this option for microcrystal diffraction of crystals with relatively small unit cells ($\leq 25000 \text{ \AA}^3$), we simulated data for typical inorganic structures and found that with the 4%-energy-bandpass mode, not only can more reflections be recorded per shot, but the intensities can also be measured more reliably [3].

To test the viability of these simulations experimentally, we took advantage of the flexibility of the single-crystal diffractometer on SNBL to mimic the SwissFEL setup. The broad bandpass mode was simulated by collecting a diffraction pattern while the monochromator was scanned over a 4% energy range. Three relatively large test crystals with unit cells typical of small-molecule and inorganic structures were measured: the zeolite ZSM-5, a hydrated cesium cyanoplatinate, and the mineral sanidine.

In order to index the resulting, relatively sparse, single-shot patterns of randomly oriented crystals, we developed two indexing algorithms, one using Laue diffraction concepts and the other starting with a monochromatic approximation [4]. Both algorithms worked well with the experimental data, so they were further optimized to deal with multicrystal patterns, in which several crystal orientations are present in a single exposure. We could show that the individual patterns of up to 10 crystals measured simultaneously can be indexed, and the intensities extracted reliably for structure analysis. This means that even with a single shot (a single pulse at SwissFEL), at least a partial analysis of the crystal structure will be possible, and this offers tantalizing possibilities for time-resolved studies. While our algorithms were developed with SwissFEL in mind, they can be applied to any diffraction data collected in single snapshot mode with a broad bandpass beam.

Having access to a flexible diffractometer on SNBL has allowed us to perform some critical tests that help us to plan SwissFEL experiments with a better chance of success.

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Diffraction studies of partially disordered materials

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Since the discovery of X-Ray diffraction by W.C. Roentgen in 1895 and the observation of X-Ray diffraction on crystalline materials by P.P. Ewald and M. von Laue in 1912, this technique has been widely used to study single crystal and polycrystalline materials. Probably the most well-known *Bragg's law*, discovered in 1912-1913, is still the foundation of crystal structure studies. A key point is that it cannot be fully used to describe partially disordered materials. X-Ray powder diffraction data provide information based on the position of Bragg reflections as well as their shape, width and anisotropic broadening and asymmetry (hkl-dependent), in addition to diffuse scattering between Bragg reflections. Such aspects were already shown by Warren in 1941 on disordered layers of carbon [1].

We have studied several different partially disordered materials by X-Ray powder diffraction. The disorder can be caused by 1D stacking fault disorder of fully crystalline 2D layers as in zeolite intergrowth framework SAPO-18/34 [2]. To model this kind of disordered structure it is necessary to integrate scattered intensity inbetween Bragg reflections. Even small chemical substitutions cause significant structural changes. These are proven by complementary NMR studies. In nanoscale materials is also likely to obtain crystalline disordered structures. A promising anode material for Li-batteries MoO_3 in forms of nanobelts (with strongly anisotropic crystallite size) revealed nearly random distribution of layers [3] as confirmed by transmission electron microscopy and selected area electron diffraction – in strong contrast with ordered stackings in crystalline bulk materials. This causes the interpretation of X-Ray diffraction data challenging but were currently done using the *DISCUS* package [4].

Finally, an intriguing sequence of structural transformations of metastable layered double hydroxide (LDH) was studied by using both X-Ray powder diffraction and also X-Ray based pair distribution function (PDF) analysis. By combining those two different approaches of powder diffraction data analysis we were able to describe long range order inside the LDH layer together with the interlayer random stacking disorder (causing Warren type Bragg reflections) [5]. On the other hand we used Reversed Monte Carlo method [6] to study the local atomic arrangement and cation distribution inside the LDH layer.

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The Balder Beamline at the MAX IV Laboratory

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The Balder beamline, dedicated to X-ray absorption spectroscopy, is one of the phase one beamlines under construction on the 3 GeV ring at the MAX IV Laboratory. The design of the beamline has focused on a high flux of photons in a wide energy range, 2.4-40 keV, and an experimental set-up allowing several kinds of measurements to be performed simultaneously. The reason for this choice is manifold. A further development of several research areas, especially biogeochemistry and catalysis, require very low element concentrations. Experiments conducted at naturally occurring in water and soil, and used in catalytic driven processes are increasingly important. At the same time, a too high brilliance may cause radiation damage to several kinds of samples, this apply especially to biological samples and organic compounds. The broad spectrum of users, with very different scientific projects, demands a beamline with photon flux internationally competitive in the energy range 2.4-40 keV, where the K edge is covered for the elements from S to La. Most importantly, high-quality EXAFS spectroscopy measurements require exceptional beam stability over a long time period. In order to meet these criteria a wiggler has been chosen as insertion device. The monochromator is designed to collect standard step scans as well as quick-XAS. The overall design of the beamline will allow large flexibility in energy range, beam size and data collection time. The other focus at the design of this beamline is the possibility to perform multi-technique analyses of the sample. The environment around the sample holder is designed in such a way that auxiliary methods as Fourier transform infrared (FTIR), UV-Raman spectroscopy, X-ray diffraction and/or mass spectrometry can be performed simultaneously as the XAS study. It will be a flexible system where different instruments can be plugged in and out depending on the needs for the particular investigation.

POSTERS

The long-term stability of cement investigated by X-Ray Absorption Spectroscopy

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Cement is worldwide the most successful construction material for buildings and structures, which have service lives of 50 to 100 years or even more. Therefore, there is a need to demonstrate performance of the cementitious materials over long time scales, which requires a thorough understanding of the physical and chemical processes affecting the performance of materials at the macroscopic level, including strength development, setting behaviour, etc. ¹. Knowledge of cement hydration and of the cement phases formed during the hydration process is essential to the understanding of formation and property development of cementitious materials ².

Current developments in cement chemistry increasingly rely on predictive thermodynamic modelling of the phase composition in cementitious composites with the aim of linking the performance of the material with the phase composition of the material. This approach requires identification of the cement phases that form in hydrating cementitious materials. The major constituents of an Ordinary Portland Cement (OPC) are Si and Ca oxides, alite (Ca_3SiO_5) and belite (Ca_2SiO_4); the minor phases include calcium aluminates ($\text{Ca}_3\text{Al}_2\text{O}_6$), calcium ferrites ($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$), calcite (CaCO_3) and calcium sulphate (CaSO_4). This mix consisting of high temperature oxide phases as well as calcite and calcium sulphate is highly reactive upon contact with water, releasing Ca, Si, Al, Fe, hydroxide and sulphate. The main secondary phases that form in large quantity are Ca-Si-hydrates (C-S-H), portlandite ($\text{Ca}(\text{OH})_2$), calcium-alumina-ferric hydroxide tri-sulphate (AFt), of which the most common is ettringite ($(\text{Ca}_6[(\text{Al}_{1-x}\text{Fe}_x)(\text{OH})_6]_2\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$), and calcium-alumina-ferric hydroxide mono-sulfate phases (AFm), $([\text{Ca}_4(\text{Al,Fe})_2(\text{OH})_{12}]) \cdot \text{X} \cdot n\text{H}_2\text{O}$, X = e.g., SO_4^{2-} or CO_3^{2-}). In addition, other Al- and Fe-containing phases such as hydrotalcite or hydrogarnet can form during the hydration of OPC ³.

In this study two ordinary Portland cements, with different chemical compositions and subject to different hydration times (~10, ~50 years), were investigated aiming at identifying the most stable Fe-containing cement phases in the cement pastes by EXAFS. The data analysis indicates the formation of a mixed Fe-Al siliceous hydrogarnet as the major Fe-containing phase. Therefore, the formation of mixed Fe-Al siliceous hydrogarnet solid solution has to be taken into consideration as the major Fe-containing phase when predicting the mineral composition of aged cement pastes.

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Structural quality of homo-epitaxial ZnO on hydrothermal ZnO by RF-magnetron sputtering

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ZnO is a II-VI semiconductor and its features include good transparency, high electron mobility, and wide bandgap (3.36 eV) with excitonic binding energy of 60 meV. Its applications as transparent conducting oxides (TCO), thin film transistors (TFT) and light emitting diodes (LED) have been extensively studied [1]. For applications, an epitaxially grown ZnO is required and it is important to characterize how the films are grown on the substrate by determining its major orientation and checking if there are any other minor orientations. The combination of the in-plane and out-of-plane techniques is useful for the study of epitaxial film orientations. Those two techniques provide orientation information in two directions which are perpendicular and parallel to the surface, respectively. For example, ZnO grown with its *c*-axis parallel to the sapphire *c*-axis has its *a*-axis rotated 30° from the sapphire *a*-axis [2]. The new detector PILATUS 2M facility for single crystal at ESRF-SNBL beam line could provide both Asymmetric Reciprocal space mapping (RSM) and in-plane RSM of ZnO thin films [3]. Homo-epitaxial ZnO films were grown by RF-sputtering on hydrothermally grown ZnO wafer by varying the sputtering power and growth temperature. The influence on sputtering power on the quality of the ZnO films is

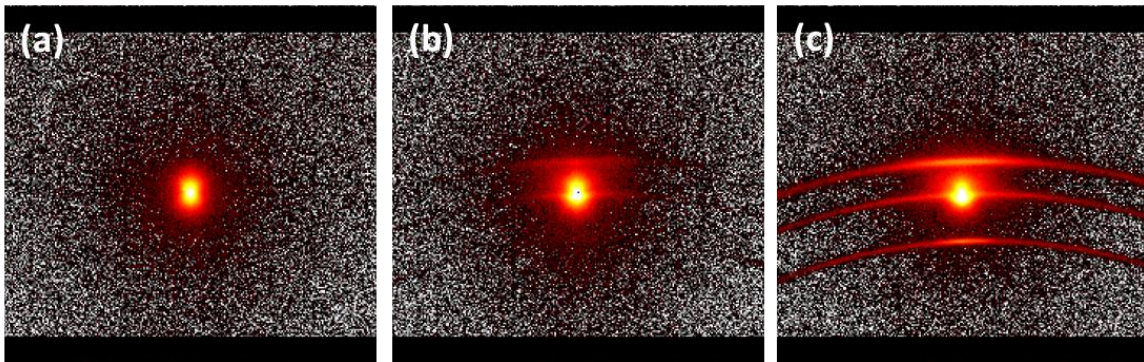


Figure 1: Reciprocal space mapping of epitaxial ZnO (0002) film sputtered on ZnO wafer at different sputtering power (a) 10 W (b) 40 W and (c) 110 W.

shown in Fig.1. Increasing the sputtering power increases both in-plane rotation and polycrystalline nature in the as-grown ZnO film, which is not-evident in conventional X-ray diffractometer. Observed optical properties (photoluminescence) of these films will be discussed in the context of the structural quality. Structural and optical properties of hetero-epitaxial ZnO thin films on sapphire substrates will also be presented for comparison.

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In-operando studies of the Prussian Blue Analogue $\text{Na}_{1.35}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.83} \cdot z\text{H}_2\text{O}$ as promising cathode material for sodium ion batteries

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Energy storage will play a pivotal role in the implementation of intermittent renewable energy sources to the electrical grid. The rechargeable battery technology offers good opportunities to balance electricity supply and demand. Unlike lithium, sodium is relatively cheap and readily available worldwide. It follows, that there is a huge incentive to develop rechargeable, low-cost sodium ion batteries (SIBs) of reasonable energy density with high discharge/charge rate and long service life time¹. The fundamental understanding of the intercalation processes (single phase vs. two-phase), structural stability and voltage-composition profiles is pivotal for optimization of electrode materials. For this reason we developed a fully operational set-up electrochemical cells, sample changer and interfacing software) for in operando quasi-simultaneous powder X-ray diffraction (XRD) and X-ray absorption spectroscopy (XANES, EXAFS) studies in transmission geometry at the European Synchrotron Radiation Facility (ESRF) on BM01B (Swiss Norwegian Beamlines, SNBL). Taking advantage of the newly developed equipment, we investigated the prussian blue analogue (PBA) $\text{Na}_x\text{Mn}[\text{Fe}(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$ as a promising low cost, high rate and high capacity cathode material for SIB technology². PBA of formula $\text{Na}_x\text{Mn}[\text{Fe}(\text{CN})_6]_y$ can be stabilized in both cubic ($Fm\bar{3}m$) and monoclinic ($P21/n$) ordering scheme depending on the amount of guest species (Na and water). In both structures the $\text{Mn}^{2+/3+}$ and $\text{Fe}^{2+/3+}$ reside on alternate corners of a cube of corner-shared octahedra linked by $(\text{C}\equiv\text{N})^-$ bridges. The rigid open PB crystal and the comparatively weak interaction of Na^+ and $(\text{C}\equiv\text{N})^-$ ligands during diffusion along the vast 3D pathways give rise to the promising properties of this family of cathode materials. We have characterized electrochemically and structurally both modifications of $\text{Na}_{1.35}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.83} \cdot z\text{H}_2\text{O}$ ($z = 2.2$ and 3.0 , respectively). We have observed a series of reversible structural phase transitions which can be clearly linked to the galvanostatic charge/discharge profiles and are further supported by XANES data. The influence of the water content and structural changes will be discussed.

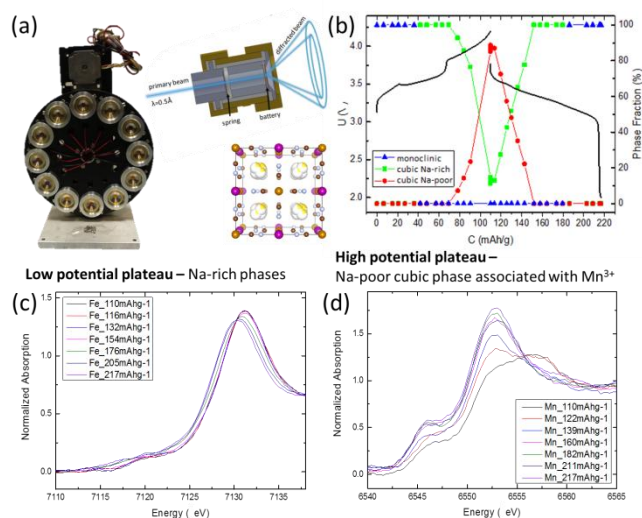


Figure 1: The figure shows (a) the X-ray path through the electrochemical cell, the automated sample changer wheel with cells, the structure of $\text{Na}_x\text{Mn}[\text{Fe}(\text{CN})_6]_y$ (b) the phase fractions of monoclinic and cubic phases of $\text{Na}_x\text{Mn}[\text{Fe}(\text{CN})_6]_{0.83} \cdot 3.0 \text{H}_2\text{O}$ compared to galvanostatic charge ($C < 110\text{mAh/g}$) and discharge ($C > 110\text{mAh/g}$) curves, and the normalized absorption signal at the Fe- (c) and Mn-edge (d) at various points throughout the first discharge ($C > 110\text{mAh/g}$).

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