



# **EBS Workshop on X-ray Raman Scattering spectroscopy**

**ESRF Auditorium – Grenoble, France  
3, 4 & 5 April 2019**

- **Programme**
- **Abstracts**
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# EBS workshop on X-ray Raman Scattering spectroscopy

ESRF, Grenoble, France

ESRF auditorium

## Day 1 - Wednesday 3<sup>rd</sup> April 2019

**11:00 - 12:00** Registration in the ESRF Central Building entrance hall with welcome coffee

**12:00 - 13:30** Lunch at the EPN campus restaurant

**13:30 - 13:45** Welcome/Introduction **H. Reichert**  
*ESRF Director of Research*

**13:45 - 15:00** Session Instrumentation  
Chair: C. Sternemann

13:45 - 14:15 Considerations on the capabilities of ID20 X-ray Raman spectrometer **S. Huotari**  
*University of Helsinki (Finland)*

14:15 - 14:45 XRS at the GALAXIES beamline, SOLEIL Synchrotron **J.-P. Rueff**  
*Synchrotron SOLEIL (France)*

14:45 - 15:00 Inelastic X-ray scattering at P01, DESY **M. Sundermann**  
*University of Cologne (Germany)*

**15:00 - 15:30** Coffee

**15:30 - 16:40** Session Instrumentation  
Chair: C. Sternemann

15:30 - 16:00 X-ray Raman Spectroscopy using the LERIX facility at the APS **M. Balasubramanian**  
*ANL - APS (USA)*

16:00 - 16:20 High energy resolution fourteen-crystal spectrometer for high quality fluorescence and absorption measurements on an X-ray Absorption Spectroscopy beamline **O. Proux**  
*ESRF (France)*

16:20 - 16:40 Discussions on Instruments

**16:40 - 17:20** Session Imaging  
Chair: S. Huotari

16:40 - 17:20 Carbon speciation in ancient and historical systems using X-ray Raman spectroscopy and imaging **L. Bertrand**  
*IPANEMA - CNRS Paris (France)*

**17:20 - 18:20** Visit ID20

**19:00 - 21:00** Dinner onsite

## Day 2 - Thursday 4<sup>th</sup> April 2019

<b>09:00 - 10:30</b>	<b>Session Theory</b> Chair: G. van der Laan	
09:00 - 09:20	Modeling X-ray Raman scattering with XSpectra	<b>G. Radtke</b> <i>Sorbonne University (France)</i>
09:20 - 09:50	X-ray Raman scattering calculations with the OCEAN code	<b>K. Gilmore</b> <i>BNL (USA)</i>
09:50 - 10:10	Momentum transfer dependence in X-ray Raman scattering	<b>Y. Joly</b> <i>CNRS Grenoble (France)</i>
10:10 - 10:30	Discussions on Calculs	
<b>10:30 - 11:00</b>	<b>Coffee</b>	
<b>11:00 - 12:30</b>	<b>Session Liquids</b> Chair: G. Lelong	
11:00 - 11:30	Statistical view on core-level spectra of liquids	<b>J. Niskanen</b> <i>University of Turku (Finland)</i>
11:30 - 11:50	X-ray Raman scattering study of hydrothermal fluids: The case of aqueous sodium chloride solutions	<b>M. Elbers</b> <i>TU Dortmund (Germany)</i>
11:50 - 12:10	X-ray Raman scattering for the study of hydrothermal carbon materials	<b>L. Higgins</b> <i>University of Leeds (UK)</i>
12:10 - 10:30	Discussions on Liquids	
<b>12:30 - 14:00</b>	<b>Lunch at the EPN campus restaurant</b>	
<b>14:00 - 15:45</b>	<b>Session Correlated Electron Systems</b> Chair: K. Gilmore	
14:00 - 15:00	Core-level non-resonant inelastic X-ray scattering (NIXS): Beyond the dipole limit	<b>H. Tjeng, A. Severing, A. Amorese, M. Sundermann</b> <i>MPI Dresden / University of Cologne (Germany)</i>
15:00 - 15:30	Electronic excitations and momentum densities in oxides studied by inelastic X-ray scattering	<b>K. Ruotsalainen</b> <i>HZB Berlin (Germany)</i>
15:30 - 15:45	Discussions on Correlated Electron Systems	
<b>15:45 - 16:15</b>	<b>Coffee</b>	
<b>16:15 - 18:00</b>	<b>Session High Pressure</b> Chair: M. Wilke	
16:15 - 16:45	Polyamorphism in oxide glasses	<b>G. Lelong</b> <i>IMPMC Paris (France)</i>
16:45 - 17:15	Magma properties at deep earth's conditions from electronic structure of silica measured using X-ray Raman Spectroscopy	<b>S. Petitgirard</b> <i>University of Bayreuth (Germany)</i>
17:15 - 17:35	Pressure-driven changes in XRS spectra of compressed amorphous MgSiO <sub>3</sub> glass	<b>G. Spiekermann</b> <i>University of Potsdam (Germany)</i>
17:35 - 17:50	Discussions on High Pressure	
<b>20:00 - 22:00</b>	<b>Workshop dinner at the Restaurant L'Epicurien</b>	

# Day 3 - Friday 5<sup>th</sup> April 2019

<b>09:00 - 10:10</b>	<b>Session Energy Materials</b> <b>Chair:</b> J.-P. Rueff	
09:00 - 09:30	Fingerprinting reaction pathways of lightweight compounds by X-ray Raman scattering Spectroscopy: Application to hydrogen storage materials	<b>C. Sternemann</b> <i>TU Dortmund (Germany)</i>
09:30 - 09:50	The effect of Ni doping on the performance and electronic structure of LSCF cathodes used for IT-SOFCs	<b>A. Longo</b> <i>ESRF (France)</i>
09:50 - 10:10	Bulk sensitive soft X-ray edges probing in electrodes for battery application	<b>M. Fehse</b> <i>Delft University of Technology (The Netherlands)</i>
<b>10:10 - 10:40</b>	<b>Coffee</b>	
<b>10:40 - 12:15</b>	<b>Session Energy Materials</b> <b>Chair:</b> M. Balasubramanian	
10:40 - 11:00	XRS study of medium range order in crystalline alkali borates	<b>E. de Clermont</b> <i>IMPMC Paris (France)</i>
11:00 - 11:20	X-ray Raman scattering study of Li-based compounds at high temperature	<b>M.R. Cicconi</b> <i>CNRS - IPG Paris (France)</i>
11:20 - 11:40	XRS study of metal hydride nanocomposites for energy storage applications	<b>P. Ngene</b> <i>Utrecht University (The Netherlands)</i>
11:40 - 12:00	X-ray Raman scattering of photocharged BiVO <sub>4</sub> reveals beneficial effect on the space charge region	<b>N. Firet</b> <i>Delft University of Technology (The Netherlands)</i>
12:00 - 12:15	Discussions on Energy Materials	
<b>12:15 - 12:35</b>	<b>Future of XRS / XRS workshop 2</b>	<b>Organisers</b>
<b>12:35 - 14:00</b>	<b>Lunch at the EPN campus restaurant</b>	
<b>14:00</b>	End of workshop	



# Abstracts

# Considerations on the capabilities of ID20 X-ray Raman spectrometer

S. Huotari<sup>1</sup>, Ch. Sahle<sup>2</sup>, A.-P. Honkanen<sup>1</sup>, G. Monaco<sup>3</sup>

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We describe selected specific aspects of the ID20 X-ray Raman spectrometer [1] starting from its design goals and current capabilities. The spectrometer has 72 spherically bent analyzer crystals arranged in six modular groups of 12 analyzer crystals each for a combined maximum flexibility and large solid angle of detection. Each of the six analyzer modules houses one pixelated area detector allowing for X-ray Raman scattering based imaging (“direct tomography”) [2] and efficient separation of the desired signal from the sample and spurious scattering from the often used complicated sample environments.

Numerous optimisations were done in obtain the geometry of the ID20 spectrometer. The spectrometer design was a development from the previous design with 9 crystal analyzers [3]. The development included the optimization of the versatility of scattering angles, imaging [2], luminosity as well as resolution [4]. The large number of the analyzers was an ambitious goal but the modular design made it feasible. Several steps were made in order, e.g., to improve the crystal quality [5] and to improve the spatial resolution in direct tomography [6]. A few selected applications will be presented.



Figure 1: ID20 XRS spectrometer at the front page of Journal of Synchrotron Radiation (March 2017 issue)

## References

- [1] - S. Huotari, Ch. Sahle, C. Henriquet, A. Al-Zein, K. Martel, L. Simonelli, R. Verbeni, H. Gonzalez, M.-C. Lagier, C. Ponchut, M. Moretti Sala, M.I. Krisch, G. Monaco: A large-solid-angle X-ray Raman scattering spectrometer at ID20 of the European Synchrotron Radiation Facility, *J. Synchrotron Radiat.* 24, 521 (2017).
- [2] - S. Huotari, T. Pylkkänen, R. Verbeni, G. Monaco, K. Hämäläinen, *Nature Materials* 10, 489 (2011).
- [3] - R. Verbeni, T. Pylkkänen, S. Huotari, L. Simonelli, G. Vanko, K. Martel, C. Henriquet, G. Monaco: Multiple-element spectrometer for non-resonant inelastic X-ray spectroscopy of electronic excitations, *J. Synchrotron Radiat.* 16, 469 (2009).
- [4] - A.-P. Honkanen, G. Monaco, S. Huotari, A computationally efficient method to solve the Takagi-Taupin equations for a large deformed crystal, *J. Appl. Cryst.* 49, 1284 (2016).
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- [6] - Ch. Sahle, A. Mirone, T. Vincent, A.-P. Kallonen, S. Huotari: Improving the spatial and statistical accuracy in X-ray Raman scattering based direct tomography, *J. Synchrotron Radiat.* 24,476 (2017).

# XRS at the GALAXIES beamline, SOLEIL Synchrotron

J.-P. Rueff<sup>1</sup>, J.M. Ablett<sup>1</sup>, R. Georgiou<sup>1,2</sup> and L. Bertrand<sup>2</sup>

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The GALAXIES beamline is dedicated to IXS / RIXS and HAXPES spectroscopies in the tender x-ray range at SOLEIL Synchrotron [1]. We will review some of our recent activities in the field of X-ray Raman scattering and hyperspectral imaging [2]. Prospective for XRS at GALAXIES in the view of the SOLEIL upgrade will be discussed.

## References

- [1] - J.-P. Rueff, J.M. Ablett, D. Céolin, D. Prieur, Th. Moreno, V. Balédent, B. Lassalle, J.E. Rault, M. Simon and A. Shukla, *J. Synchrotron Rad.* **22**, 175 (2015).
- [2] - P. Gueriau, J.-P. Rueff, S. Bernard, J.A. Kaddissy, S. Goler, Ch.J. Sahle, D. Sokaras, R.A. Wogelius, P.L. Manning, U. Bergmann and L. Bertrand, *Analytical Chemistry* **89**, 10819 (2017).

## Inelastic X-ray scattering at P01, DESY

H. Gretarsson<sup>1,2,3</sup>, M. Sundermann<sup>2,3,4</sup>, H. Yavas<sup>1,2,3\*</sup>, B. Keimer<sup>1</sup>, L.H. Tjeng<sup>2</sup>

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P01 at Petra III DESY is a beamline dedicated to novel x-ray spectroscopy techniques. It is equipped with two 5m undulators, providing an ample flux of photons in the energy range of 2.5-80 keV. The beamline is equally split between two fields of physics, nuclear resonant scattering (NRS), requiring timing mode, and inelastic x-ray scattering (IXS), using multi bunch mode. The IXS branch of P01 is dedicated to two experimental techniques: resonant inelastic x-ray scattering (RIXS) and x-ray Raman scattering (XRS). While our RIXS endstation is still under commissioning, the XRS has been open to users since 2013. It is equipped with KB focusing optics, a versatile 3 circle Huber diffractometer, and a set of 12 spherically bent Si(nn0) analyzers rotatable (0-155°) in the vertical scattering plane. Depending on the experiments, users can choose between small- (0.3 eV at 10keV) or large-incident photon bandwidths (1.3 eV at 10keV) with a 5-fold difference in photon flux. Additional measurements, such as x-ray absorption or emission spectroscopy, can be integrated into the XRS setup, allowing one to extract complementary results or facilitate better comparison with existing literature.

# **X-ray Raman Spectroscopy using the LERIX facility at the APS**

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The Lower Energy Resolution Inelastic X-ray Scattering (LERIX) facility, permanently stationed in sector 20 ID-B of the APS, was commissioned and made available to general users in 2006. This instrument was optimized for measurements of momentum dependent X-ray Raman Spectroscopy (XRS) of low-energy excitations from semi-core and core-levels with binding energies from 10 eV to as much as 2000 eV. Taking advantage of the unique traits of this technique, a rich variety of experiments ranging from studies of valence and core excitation in gaseous nitrogen to studies of non-dipole transitions in f-electron systems, from studies of energy storage and fuel cell systems to the genesis of new states of matter under high pressures (generated using a diamond anvil cell, DAC), and from studies of electronic structure of liquid samples to truly bulk sensitive speciation of carbon in soils have been performed, in the past twelve years. In this talk, we will discuss some of the experiments that have been carried out with the LERIX instrument, with emphasis on energy materials, environmental science, high pressure science, and basic chemistry.

# High energy resolution fourteen-crystal spectrometer for high quality fluorescence and absorption measurements on an X-ray Absorption Spectroscopy beamline

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FAME (French Absorption beamline for Material and Environmental sciences) and FAME-UHD (FAME-Ultra High Dilution) are two French CRG beamlines at ESRF dedicated to X-ray Absorption Spectroscopy (XAS) in material science, catalysis and especially in environmental and Earth sciences. The study of the speciation of highly-diluted elements by XAS is experimentally extremely challenging. On the FAME beamline, we developed a CAS in the Johann's geometry, using 1 [1] and 5 crystals [2]. This 5-crystal spectrometer was installed on a dedicated beamline (FAME-UHD), opened to regular users since January 2017. Beginning of 2018 a 14-crystal spectrometer was then installed (Figure 1). Within this approach, measuring the XAS signal in fluorescence mode is performed with a  $\approx 1$  eV energy resolution, for photons energy ranging from 4 to 18 keV. Due to this new tool many restrictions on sample concentrations and multi-fluorescence interferences may be overcome [3]. XAS measurements on a target element down to 1ppm and even below are now possible [4,5], as well as *operando* and *in situ* measurements [6,7].



Figure 1: 14-crystal Crystal Analyzer Spectrometer on FAME-UHD beamline.

## References

- [1] - J.-L.Hazemann et al., Journal of Synchrotron Radiation **16**, 283–292 (2009).
- [2] - I. Llorens et al., Review of Scientific Instruments **83**, 063104 (2012).
- [3] - O. Proux et al., Journal of Environmental Quality **46**, 1146-1157(2017).
- [4] - E. De Santis et al., Condensed Matter **4**, 13 (2019).
- [5] - C. Bissardon et al., Analyst (2019), accepted.
- [6] - G. Dantelle et al., RSC Advances **8**, 26857-26870(2018).
- [7] - A. Aguilar-Tapia et al., Review of Scientific Instruments **89**, 035109 (2018).

# Carbon speciation in ancient and historical systems using X-ray Raman spectroscopy and imaging

L. Bertrand<sup>1,2</sup>, R. Georgiou<sup>1,2</sup>, P. Gueriau<sup>1,3</sup>, C.J. Sahle<sup>4</sup>, A. Mirone<sup>4</sup>, N. Daly<sup>5</sup>,  
R. Garrouste<sup>6</sup>, J. Giaccai<sup>7</sup>, R. Popelka-Filcoff<sup>8</sup>, K. Trentelman<sup>5</sup>, S. Bernard<sup>9</sup>, J.-P. Rueff<sup>2,10</sup>,  
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We investigate and discuss the potentials and limits of X-ray Raman scattering (XRS) to probe carbon speciation in complex heterogeneous solid ancient samples. The hard X-ray inelastic scattering technique was used to collect carbon K-edge XANES data in a non-destructive manner, in air, with bulk sensitivity, to provide information not compromised by surface contamination, thus overcoming important constraints in the characterization of ancient materials. The potential of XRS is demonstrated through the analysis of carbon-based artists' pigments, which are until today poorly understood due to their complex chemistry, based on experiments at SOLEIL and the ESRF in collaboration with SSRL at Stanford [1]. XRS was used to determine the speciation in a consistent set of modern and historical samples used in the arts. Furthermore, we collected XRS-based carbon K-edge XANES on fossil samples. XRS spectra provided information on the degree of aromaticity, the signatures of oxidized COO groups, the presence of carbon bound with heteroatoms and turbostraticity. Additionally, we further tested and developed non-invasive 3D chemical imaging of ancient organic materials by X-ray Raman hyperspectral imaging at the K-edge of carbon [2]. These results show the potential of XRS as a powerful and convenient probe to discriminate carbon-based compounds in complex, heterogeneous samples which can be further applied to a wide range of ancient and historic materials.

## References

- [1] - P. Gueriau, J.-P. Rueff, S. Bernard, J. Kaddissy, S. Goler, C.J. Sahle, D. Sokaras, R.A. Wogelius, P.L. Manning, U. Bergmann and L. Bertrand. *Analytical Chemistry* **89**, 10819 (2017).  
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# Modeling X-ray Raman scattering with XSpectra

G. Radtke<sup>1</sup>, D. Cabaret<sup>1</sup>, E. de Clermont Gallerande<sup>1</sup>, G. Lelong<sup>1</sup>, C. Brouder<sup>1</sup>,  
M.-B. Attaiaa<sup>1</sup>, L. Paulatto<sup>1</sup>, Ch.J. Sahle<sup>2</sup>

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X-ray Raman Scattering (XRS) spectroscopy has become increasingly popular in condensed matter physics and chemistry during the last decades for probing the local atomic and electronic structure of solids, liquids or gases under complex sample environments, opening up a wealth of possibilities for *in situ* experiments. XRS bears a lot of similarities with soft x-ray absorption and electron energy loss spectroscopies, as it probes the same electronic transitions under experimental conditions where the dipole approximation remains valid, but it differs in one essential point from these techniques in that it can allow large momentum transfers and therefore induce high-order electric multipole transitions. Although N<sub>4,5</sub> edges of lanthanides and O<sub>4,5</sub> edges of actinides provide the most striking examples of such high-order transitions, non-dipole transitions can also be probed at K edges of light elements and consist predominantly of monopole or, usually to a much lesser extent, quadrupole transitions.

Modeling therefore plays a very important role when interpreting the complex *q*-dependence of XRS spectra with the purpose of extracting useful information about the local atomic or electronic structure of a material. In this talk, I will present an efficient technique designed to calculate XRS spectra at the K edge in the framework of a single-particle theory [1]. We have implemented the calculation of the XRS dynamic structure factor in the module XSpectra [2-4] of the Quantum ESPRESSO suite of codes [5] which is based on Density Functional Theory, uses pseudopotentials, a plane-wave basis set and periodic boundary conditions. The calculation is based on an efficient recursive scheme to compute the dynamic structure factor as a continued fraction without requiring the explicit calculation of high-lying unoccupied states. In this framework, multipole transitions are calculated to provide a full account of the *q*-dependence of XRS spectra.

After giving a general presentation of the method, the related approximations and practical issues, I will present the results obtained on a series of K edges recorded in lithium-bearing reference compounds, namely LiBO<sub>2</sub>, Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>O, and LiF.

## References

- [1] - E. de Clermont Gallerande, D. Cabaret, G. Lelong, C. Brouder, M.-B. Attaiaa, L. Paulatto, K. Gilmore, Ch.J. Sahle, and G. Radtke, *Phys. Rev. B* **98** 214104 (2018).
- [2] - M. Taillefumier, D. Cabaret, A.-M. Flank, and F. Mauri, *Phys. Rev. B* **66**, 195107 (2002).
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- [5] - P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, and R.M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).

# X-ray Raman scattering calculations with the OCEAN code

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Many X-ray absorption events can be described accurately within a two-particle framework that accounts for the explicit interactions between the excited electron and the core-hole, as well as an averaged interaction of each particle with the rest of the system. Formally, this amounts to evaluating ladder diagrams and requires solving the Bethe-Salpeter equation. Contrary to common assumption, obtaining X-ray spectra through the Bethe-Salpeter equation is actually quite computationally efficient as it does not require use of supercells, eliminates summations over final states, and allows for a real-space evaluation of the core-hole screening response. I will present the implementation of the Bethe-Salpeter equation within the OCEAN code [1] as it pertains to X-ray Raman scattering and will provide a brief description of the use of the code. Several recent scientific use cases will be presented [2-4]. I will conclude with some thoughts on including additional many-body effects and prospects for applications on strongly correlated materials.

## References

- [1] - K. Gilmore *et al.*, *Computer Physics Communications* **197**, 109 (2015).
- [2] - J. Niskanen *et al.*, *Physical Review E* **96**, 013319 (2017).
- [3] - S. Petitgirard *et al.*, *Geochemical Perspectives Letters* **9**, 32 (2019).
- [4] - G. Spiekermann *et al.*, *Physical Review X* **9**, 011025 (2019).

# Momentum transfer dependence in X-ray Raman Scattering

Y. Joly<sup>1</sup>, C. Cavallari<sup>2</sup>, S.A. Guda<sup>3</sup> and Ch.J. Sahle<sup>2)</sup>

<sup>1</sup>Institut Néel, CNRS, Grenoble, France; <sup>2</sup>European Synchrotron Radiation Facility, Grenoble Cedex, France;

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In X-Ray Raman Scattering (XRS), the momentum transfer,  $\mathbf{q}$ , plays a role equivalent at first order, to the polarization light in X-ray absorption spectroscopy. It has nevertheless been observed for a long time that when this one increases, differences between these techniques become evident, especially at the rising edges.

Our purpose is to present the mathematical expansion of the field-matter interaction versus the momentum transfer. This one explains the differences and shows the appearance of a monopolar term with its  $\Delta\ell = 0$  selection rule. At most of its well established interest for the low energy edge, this phenomena makes XRS also an interesting probe of electronic states not usually accessible by other absorption spectroscopy techniques. To illustrate this, we will give examples showing the good reproduction, by *ab initio* simulations, of the  $\mathbf{q}$ -dependence of spectra recorded at different chemical element edges.

# Statistical view on core-level spectra of liquids

J. Niskanen

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Rather than a single geometry, the atomistic structure of liquid systems is described by a collection of possible configurations, each assigned with a probabilistic weight for occurrence [1]. This fact means that all properties derived from atomistic configurations are averages over the corresponding statistical ensemble. Most notably for spectroscopists, X-ray spectra from liquids are not an exception to this principle.

In this contribution we will discuss the consequences of this idea, using our recently established line of thought [2-4] as an example. We start with the fundamental difference between a gas-phase and a liquid system, and then proceed with the idea of ensemble averages as the only obtainable experimental result.

What follows is a method of analyzing statistical simulations for structural interpretation of the core-level spectra. The protocol [2-3] relies on a a-posteriori analysis of a simulation for the ensemble averaged core-level spectrum to establish a statistical link between structural information and spectral regions of interest. Here, the role of core-level spectroscopy is fundamental: as the 1s orbital is local, each individual transition occurs locally, which allows for connecting the behaviour of averaged spectra to atomistically local structural parameters.

Last, we will quickly refer our current view of what this means for interpretation of the X-ray spectra of liquid water in ambient conditions [4].

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# **X-ray Raman scattering study of hydrothermal fluids: The case of aqueous sodium chloride solutions**

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Aqueous solutions play a key role in many natural and industrial processes. Particularly, hydrothermal fluids (i.e. hot aqueous fluids with dissolved electrolytes, silica, CO<sub>2</sub>, or other solutes) are essential in mass and energy transfer in the Earth's crust and upper mantle, which happens predominantly in subduction zones [1]. These fluids cause the formation of most ore deposits. The system H<sub>2</sub>O + NaCl is of special interest in geosciences as NaCl is long known to be the major solute in aqueous fluids in Earth's crust [2].

Interestingly, the effect of electrolytes on the water structure at sub- and supercritical conditions has only been investigated for a handful of chemical compounds. The role of additional protons and hydroxide ions in aqueous solution is still debated [3,4] and the spatial extend of the ion's influence on the local water structure is controversially discussed [5]. In order to reveal the microscopic structure of this fascinating liquid and to investigate the influence of the alkali halide on the hydrogen bond network up to the supercritical regime, we present an in situ x-ray Raman scattering study of aqueous sodium chloride solutions at high pressure and high temperature. Probing the oxygen K-edge of the salt solution yields unique information about the oxygen's local coordination around the ions, e.g. solvation-shell structure and ion pairing. Using x-ray Raman scattering in combination with yet to perform ab initio modelling of the liquid's molecular structure we aim to constrain the structural effects of sodium chloride on the hydrogen-bond network providing unique understanding of NaCl solvation in hot aqueous fluids.

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# X-ray Raman scattering for the study of hydrothermal carbon materials

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X-ray Raman Scattering (XRS) is non-resonant inelastic X-ray scattering from core electrons [1]. This technique gives access to soft X-ray absorption edges (e.g. C, N, O) using hard (e.g. 10 KeV) X-rays as the probe. The use of hard X-rays increases the penetration depth from a few tens of nanometers to the order of millimetres, allowing for complex sample environments and bulk material analysis [2]. Here, this emerging synchrotron radiation technique is applied to hydrothermal carbon produced by the decomposition of biomass (Oak wood) under hot-compressed conditions [3]. Despite a wide number of applications (e.g. supercapacitors, renewable fuels), very little is known about the structure and reaction mechanisms responsible for hydrothermal carbon formation. Previously, bulk evidence of carbon speciation for these materials has only been possible using advanced solid-state NMR techniques. However, these techniques have challenges such as low signal to noise ratios and poor resolution of certain carbon environments [4]. Here XRS is applied to better describe the structure of hydrothermal carbon and put it in relationship with more classical pyrolytic carbons (pyrochar). This study offers insight into whether calcined hydrothermal carbon is equivalent to its pyrolytic equivalent and offers an-depth understanding of the reaction mechanism. A molecular understanding of these sustainable carbon materials will allow them to be chemically modified for specific applications such as toxic metal remediation [5].

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# Core-level non-resonant inelastic X-ray scattering (NIXS): Beyond the dipole limit

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We would like to show how wave functions of strongly correlated  $f$  and  $d$ -electron materials can be determined to a great detail with core-level non-resonant inelastic x-ray scattering (NIXS, x-ray Raman). The key issue here is to utilize transitions that go beyond the dipole limit, in the following called *multipole transitions* [1-4]. Multipole transitions can be achieved by carrying out the NIXS experiments at high momentum transfers, e.g. of the order of  $|\vec{q}| \approx 10 \text{ \AA}^{-1}$ .

In the multipole transition limit, the vector  $\vec{q}$  dependence of the scattering function  $S(\vec{q}, \omega)$  can reveal symmetries that are not accessible by experimental methods that are based on dipole selection rules. We will show how NIXS can determine the in-plane orientation of the  $4f$  wave function in tetragonal Ce compounds [5,6] and the crystal-field ground state in cubic CeB<sub>6</sub> [7] and SmB<sub>6</sub> [8], with the latter being considered as *the* candidate material for a strongly correlated topological insulator.

Another important aspect of using multipole transitions is that final states with higher quantum numbers can be reached that are not accessible in a dipole experiment. These high quantum number states tend to have lower energies, making them more excitonic and less mixed with the continuum states. The atomic features will thus show up more clearly. We utilize this effect in our study of U compounds, and we were able to identify the atomic like wave functions that make up the ground state of the often highly itinerant (and certainly highly covalent) U systems [9,10].

Finally, we have explored and developed a new experimental method that directly images the active local wave function in solids. This is achieved by measuring the angular distribution of the integrated intensity of the  $s$ -core-to-valence NIXS. We can directly map the orbitals when using the dipole forbidden  $3s \rightarrow 3d$  ( $M_1$ -edge) transitions in  $3d$  transition metal compounds [11]. There is no need to do spectroscopic analysis or calculations. This provides a purely experimental and thus unbiased determination of the orbitals that actively drive the ground-state properties in many modern day solid state materials.

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# Electronic excitations and momentum densities in oxides studied by inelastic X-ray scattering

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The background signals of X-ray Raman scattering experiments, i.e. valence electron excitations and the Compton peak, are wealthy sources of information on the electronic structure and dynamics in condensed matter systems. A very particular strength of non-resonant inelastic X-ray scattering (IXS) is that the scattering cross section can be accurately calculated from state-of-the-art first principles theory, and the probed response function is in fact a fundamental quantity in modern theories of electronic structure of condensed matter. [1,2] This combined with the low interaction cross section, that guarantees bulk sensitivity and minor multiple scattering effects, makes IXS an uniquely clean experiment. Furthermore, IXS experiments can also give insight into complementary methods such as photoemission spectroscopy and resonant inelastic X-ray scattering.

Transition metal oxide compounds are widely studied compounds, in which interesting physical properties arise from electron correlation effects, electron-phonon coupling, magnetic interactions, and combinations thereof. This talk will focus on applications of IXS to two canonical materials: SrVO<sub>3</sub> and VO<sub>2</sub>. The former is considered a prototypical correlated metal, and is often used as a test case for theoretical development. Recent experimental and theoretical studies have raised an interest in the role of collective electronic excitations in SrVO<sub>3</sub>, and some first steps in their characterization will be discussed. [2,3,4] The latter compound VO<sub>2</sub> exhibits a metal-insulator transition that is accompanied by a structural phase transition. The Compton profile difference between the metallic and insulating phases will be discussed alongside comparisons to theoretical calculations. [5,6]

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# Polyamorphism in oxide glasses

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*Polyamorphism*, which is the ability for a system to form several distinct amorphous phases of identical composition, is an intriguing and yet poorly understood phenomenon. Prototypical systems exhibiting polyamorphism (PA) during compression include H<sub>2</sub>O, SiO<sub>2</sub>, GeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> which all exist in low- and high-density amorphous states.[1] These states generally differ in their properties (e.g., density and rigidity) and PA may have practical implications for the design and control of new materials with specific properties.[2] From a fundamental point of view, this phenomenon is of tremendous importance since, in addition to an obvious connection with crystalline polymorphism, PA likely may reflect the existence of liquid-liquid transitions at higher temperatures.

In this presentation, we will present the important contribution of XRS spectroscopy in the understanding of the pressure-induced modifications of some glassy oxides (borates, germanates, ...) view through the modifications of the local environment of low-Z elements.[3]

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# Magma properties at deep earth's conditions from electronic structure of silica measured using X-ray Raman Spectroscopy

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Melt properties at high pressure are crucial to model the evolution of the deep part of the Earth formation and evolution. SiO<sub>2</sub> is the main component of silicate melts in the Earth's deep mantle and controls their network structure and physical properties with pressure, e.g. density, viscosity. Knowledge of the short-range atomic and electronic structure in melts brings important constraints about their compressibility and viscosity at depth. We measured the O K-edge and the Si L<sub>2,3</sub>-edge in silica up to 110 GPa using X-ray Raman scattering spectroscopy, with a striking match to calculated spectra of the quenched high-pressure melt based on structures from molecular dynamics simulations [1]. Our data show two major discontinuities at high pressure that are related to coordination changes. Between 20 and 27 GPa, at the transition zone (660 km), <sup>4</sup>Si species are converted into a mixture of <sup>5</sup>Si and <sup>6</sup>Si species. Between 60 and 70 GPa, in the lower mantle, a further transition marks the decrease of <sup>5</sup>Si species with <sup>6</sup>Si becoming dominant above 70 GPa without crossing-over the 6-fold references stishovite and CaCl<sub>2</sub> phases up to at least 110 GPa. These two discontinuities are found at the same pressure of change in compressibility and density measured on the same SiO<sub>2</sub> glass using the X-ray absorption method [2]. The changes of coordination and density measured on SiO<sub>2</sub> may have direct influence on the properties of silicate melts at depth with changes in viscosity and partitioning of elements at such pressures. Higher coordination than 6 only takes place beyond 140 GPa corroborating brillouin scattering measurements in agreement with our results with a further increase in density at such pressure. Silicate melts containing network modifiers elements may potentially densify at a lower pressure making magmas neutrally buoyant at the depth of the core-mantle boundary.

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# Pressure-driven changes in XRS spectra of compressed amorphous MgSiO<sub>3</sub> glass

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The atomic structure of silicate melts at high pressures is intimately linked to macroscopic properties such as density and viscosity [1]. MgSiO<sub>3</sub> end-member composition is a key to understand the properties of mafic melts in Earth's deep mantle, and MgSiO<sub>3</sub> glass is considered as a good analog of the melt due to the structural similarity.

Experimental structural changes in MgSiO<sub>3</sub> glass at high pressures have been investigated using X-ray diffraction (e.g. [2]) and X-ray Raman scattering spectroscopy (XRS) [3,4]. While XRS is the only technique to access the electronic structure of the light elements O, Si and Mg in a confined environment like a diamond anvil cell (DAC), the hitherto recorded spectral quality demands improvement in signal-to-noise ratio and energy resolution because of the high absorption of the diamonds. Further development for XRS high pressure are thus needed to investigate amorphous material.

We present XRS spectra of the oxygen K-edge, the silicon L<sub>2,3</sub>-edge and the magnesium L<sub>2,3</sub>-edge of compressed amorphous MgSiO<sub>3</sub> up to 60 GPa. Owing to the strongly reduced absorption by using miniature diamonds [5] an improved signal-to-noise ratio by about a factor of 10 compared to commonly sized diamonds was obtained and the experiment was conducted at lower photon energies resulting in a higher energy resolution below 1 eV. Additionally, the imaging properties at beamline ID20 at the ESRF allow for selective evaluation of the sample signal and thereby further increase the spectral quality.

Bethe-Salpeter spectral calculations [7] of silicate minerals with different coordinations for magnesium allow us to interpret the observed changes in the Mg L<sub>2,3</sub>-edge.

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# Fingerprinting reaction pathways of lightweight compounds by X-ray Raman scattering Spectroscopy: Application to hydrogen storage materials

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In situ and in operando studies of chemical reactions by X-ray absorption spectroscopy allows for precise characterization of reaction products and reaction intermediates via fingerprinting by reference compounds [1]. As the spectral shape of the absorption edge is highly sensitive to the chemical environment of the absorbing atom, e.g. its oxidation state, local coordination, spin state and type of bonding, multicomponent fits of known references can be utilized to determine changes in the phase composition during reaction. However, this method is limited to the study of high Z elements whenever the sample environment (chemical reactor, high pressure cell, electrochemical cell) or the reaction conditions (pressurized gas atmosphere, solid-liquid interfaces) cause strong absorption of X-rays. In those cases X-ray Raman scattering offers a powerful approach to study absorption edges of low and intermediate Z elements bulk sensitively [2] and is particularly valuable for the analysis of amorphous reaction products and liquid phases. Thanks to the recent development of large solid-angle spectrometers, in situ / in operando X-ray Raman scattering experiments became feasible nowadays [3,4] which opens an exciting field for new applications in e.g. catalysis, reaction kinetics, battery research, and fuel cell technology. The capabilities and limitations of the method will be discussed and exemplified by the study of decomposition pathways in the potential lightweight hydrogen storage materials  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Ca}(\text{BH}_4)_2$ , during thermally induced hydrogen release [5-7].

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# The effect of Ni doping on the performance and electronic structure of LSCF cathodes used for IT-SOFCs

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We investigated the effect of nickel doping on the electronic structure and performance of nanostructured  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8-0.03}\text{Ni}_{0.03}\text{O}_{3-\delta}$  prepared by the one pot sol-gel method. The undoped  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF0.8) provided by PRAXAIR was used as reference. Moreover, for comparison, Ni (3 mol%) was deposited by wetness impregnation over the  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ . We show by in-situ X-ray absorption spectroscopy (XAS) at 900°C under air flow that nickel enters the B perovskite site of the material and favors the stabilization of the cobalt oxidation state, as evidenced by the delay in the decrease of the average Co valence with respect to undoped samples. Our results are further supported by in-situ X-ray Raman spectroscopy (XRS) that allowed us to monitor the temperature evolution of the O K-edge. XRS evidences that nickel-doped LSCF shows unmodified  $\text{O}2p\text{-TM}3d$  density of states, which proves that the Co oxidation state is preserved. Electrochemical impedance spectroscopy (EIS) measurements were carried out over half-cell systems consisting of LSCF-based materials deposited onto a  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  electrolyte. The improvement of the electrochemical performances of the Ni-doped  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8-0.03}\text{Ni}_{0.03}\text{O}_{3-\delta}$  sample with respect to a reference Ni-impregnated LSCF is attributed to the stabilization of the TM-O<sub>6</sub> structural units, which were recently proposed as the functional units for oxygen reduction.

## Bulk sensitive soft X-ray edges probing in electrodes for battery application

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To this day, elucidating the charge transfer process in electrode material upon electrochemical cycling remains a challenge, primarily due to the complexity of chemical reactions at the electrode surfaces. Here we present an elegant and reliable method to probe bulk sensitive soft edges for elucidating anodic and cathodic charge compensation contribution via x-ray Raman scattering spectroscopy. By using hard x-ray incident beam this technique circumvents surface limitation and avoids self-absorption problematic. In addition it does not require complex sample preparation or experimental setups, making it an ideal tool for potential *in situ* analysis of electronic structure of electrode materials. For the first time we monitored bulk soft edges of both oxygen and transition metal of the cathode material Li<sub>2</sub>FeSiO<sub>4</sub> during one complete electrochemical cycle. We reveal that redox mechanism relies primarily on iron (cathodic) contribution, but that the oxygen (anodic) plays an active role in the charge compensation process throughout the electrochemical reaction. Moreover, we were able to support the experimentally observed changes of the electronic structure with *ab initio* based simulation.

## XRS study of medium range order in crystalline alkali borates

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The alkali borate binary system is peculiar as the short-range order around the network former element can be modified with alkali content. When adding alkali ion into vitreous B<sub>2</sub>O<sub>3</sub>, a <sup>[3]</sup>B to <sup>[4]</sup>B coordination change occurs, ensuring the charge neutrality of the system with the formation of negatively charged BO<sub>4</sub><sup>-</sup> tetrahedra. Above 40-50wt.% of alkali ion, the borate network experiences a progressive depolymerization of the borate network pairing with appearance of non-bridging oxygens (NBO). NBOs are defined as atoms bound to only one network former and bearing a negative charge, whereas bridging oxygens (BO) are bound to two network former cations. The structure of alkali borates is peculiar since it presents a short-range order (<sup>[3]</sup>B, <sup>[4]</sup>B) but also an unusual medium range order with formation of superstructural units [1]. Those units impact both the mechanical and thermodynamical properties.

X-ray Raman Scattering coupled to theoretical calculations [2] has already proved its efficiency to study the local structure around low-Z elements such as lithium, boron and oxygen atoms. By revealing the boron coordination number and the presence of non-bridging oxygens in alkali borates, XRS is thus relevant to find spectral signatures related to superstructural units on the B and O *K*-edge spectra. Thanks to the recent implementation of XRS in Quantum Espresso [3] and the comparison with calculation of density of states, we are now able to understand the spectral features of the oxygen and boron atoms in alkali borates in terms of short- and medium-range order in crystalline structures.

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# X-ray Raman scattering study of Li-based compounds at high temperature

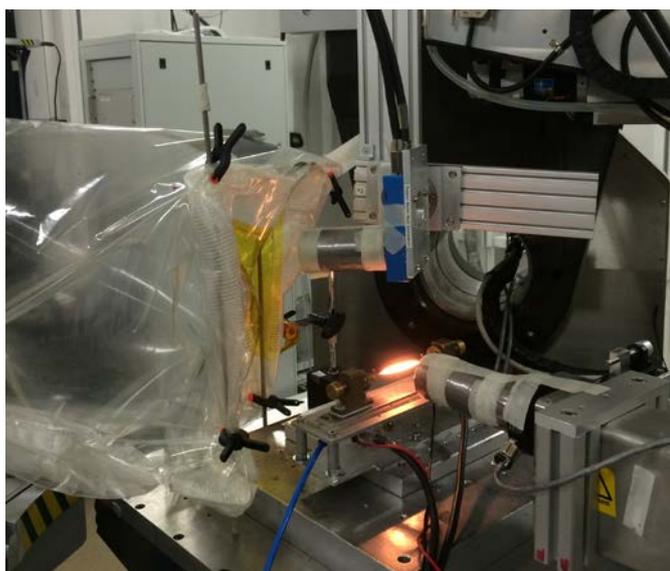
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Lithium (Li) is an important industrial metal. It is principally used in Lithium batteries but is also a very important element for various other applications such as glass and glass-ceramics (*e.g.* Zerodur® Schott AG).

X-ray Raman scattering data have been collected, at high temperature, for several Li-bearing compounds (lithium minerals, salts and glasses) at the GALAXIE beamline (SOLEIL, F) by using a heating wire system [1] (Figure 1).

We will present the results obtained at high temperatures, and we will compare Li K-edge data obtained at room temperature [2]. In particular, we will focus on the specific spectral features observed in crystalline and amorphous compounds, which are related to the Li ions local bonding environment.



**Figure 1:** heating wire system on GALAXIE beamline (SOLEIL synchrotron, F)

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# XRS study of metal hydride nanocomposites for energy storage applications

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Efficient energy storage is crucial for the use of renewable energy from intermittent sources such as solar and wind. Metal hydride based nanocomposites (e.g.  $\text{LiBH}_4/\text{C}$  and  $\text{LiBH}_4/\text{SiO}_2$ ) have attracted attention as a multifunctional materials for a variety of energy storage applications, including reversible hydrogen storage, rechargeable batteries, ammonia storage/decomposition.<sup>1-6</sup> Characterization of metal hydride nanocomposites is often hampered by their lack of long range crystallinity, the presence of mostly light (low Z) elements, and low concentration of the active phase(s). In this presentation, I will use examples from reversible hydrogen storage and all-solid-state batteries to demonstrate the efficacy of X-ray Raman Scattering (XRS) for the ex-situ and in-situ study of metal hydride nanocomposite materials in energy storage applications.<sup>7-8</sup> I will show that XRS is particularly ideal for probing the electronic (K and/or L edges) and structural changes in light elements such as Li, B, Ca, Na, Mg, N, K, Al, O and Si) which are often the main contents of metal hydride nanocomposites. I will discuss some of the experimental and challenges, and the effort to solve them.

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# X-ray Raman scattering of photocharged BiVO<sub>4</sub> reveals beneficial effect on the space charge region

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Photoelectrochemical (PEC) water splitting is a promising method to directly convert sunlight and water into hydrogen, a promising material that could become very important in the oncoming energy transition. Bismuth vanadate (BiVO<sub>4</sub>) is an extensively investigated ternary metal oxide semiconductor that has shown interesting properties for PEC water splitting. It is the best performing metal oxide photoanode to date and the band gap of 2.4 eV is suitable to make BiVO<sub>4</sub> a good top absorber in tandem with a low band gap bottom absorber to perform highly efficient solar water splitting.

One of the main drawbacks of BiVO<sub>4</sub> is charge recombination at the surface. Recently, it was found that a technique called photocharging creates a thin layer on the surface of BiVO<sub>4</sub>, improving its performance as a photoanode drastically. [1,2] To understand the electronic implications of this surface layer on the bulk of the BiVO<sub>4</sub>, X-ray Raman scattering (XRS) spectroscopy was performed to study the V L<sub>3</sub> and L<sub>2</sub>, and the O K-edge of the material. Through grazing incidence XRS spectroscopy measurements, it was found that the oxidation state of vanadium is altered in the first 60 nm of the material. The O K-edge spectrum was simulated using FDMNES, which revealed a change in electron confinement and occupancy in the oxygen pre-edge. These insights, combined with ultraviolet-visible spectroscopy (UV-vis) and X-ray photoelectron spectroscopy (XPS) data, revealed that the surface layer forms a heterojunction with BiVO<sub>4</sub>, leading to favourable band bending and strongly reduced surface recombination.

During the talk I will also discuss possibilities for performing operando (photo)-electrochemical XRS experiments that could become feasible after the current ESRF upgrade. Both cell design and limitations of these operando experiments will be discussed.

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# Posters



EBS workshop on X-ray Raman Scattering spectroscopy  
3, 4 & 5 April 2019  
ESRF Grenoble

## List of Posters

- **S. Delhommaye:** Modeling nuclei quantum thermal fluctuations and core-hole effects in X-ray Raman Scattering spectroscopy
- **E. De Clermont Gallerande:** DFT modelling of X-ray Raman Scattering: Applications to lithium model compounds
- **M. Elbers:** Pressure induced changes of the hydrogen-bond network in water and aqueous TMAO solutions
- **B. Evans:** Structural characterization of organic salts by combined X-ray Raman Scattering and excited-state DFT calculations
- **A.-P. Honkanen:** Li K edge EXAFS via X-ray Raman spectroscopy
- **A.-P. Honkanen:** HelXAS: a low-cost home laboratory instrument for X-ray absorption spectroscopy
- **F.G.B. Ooms:** XRS study on 5V  $\text{LiCr}_{0.08}\text{Ni}_{0.42}\text{Mn}_{1.50}\text{O}_4$  battery electrodes
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- **J.E. Rodrigues:** Spin-phonon coupling in uniaxial anisotropic spin-glass based on  $\text{Fe}_2\text{TiO}_5$  pseudobrookite
- **Ch.J. Sahle:** Microscopic structure of water at high pressure and high temperature
- **R. Sakrowski:** Structural changes in a natural basalt glass at high-pressure by means of X-ray Raman Scattering
- **G. Spiekermann:** Amorphous  $\text{SiO}_2$  and  $\text{GeO}_2$  at extreme pressures: Insights from X-ray Raman and valence-to-core emission spectroscopy
- **R. Verbeni:** CAL: The Crystal Analyser Laboratory
- **R. Verbeni:** CAL production for multi-analyser crystal spectrometers at the ESRF
- **C. Weis:** Combining X-ray emission and X-ray Raman Scattering spectroscopy for the study of Earth materials at high pressure and high temperature
- **D. Zapata Dominguez:** Post mortem investigation of the chemical environment in silicon-based lithium-ion batteries by XRS

# Modeling nuclei quantum thermal fluctuations and core-hole effects in X-ray Raman scattering spectroscopy

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X-ray absorption spectroscopy (XAS) has recently been shown to be sensitive to nuclei quantum thermal vibration effects at the K edge of light elements like low-Z cations in oxides [1,2], with a main effect in the pre-edge of the spectra. The pre-edge peak is dominated by *s* empty states that are probed indirectly through electric dipole transitions thanks to vibration-induced hybridization between *s* and *p* empty states. X-ray Raman scattering spectroscopy (XRS), relying on non-resonant inelastic X-ray scattering, can provide both information equivalent to what is accessible by soft XAS, and information inaccessible to soft XAS. For low momentum transfer value *q*, the dipole electronic transitions dominate in the XRS spectra leading to a spectrum similar to a XAS spectrum. At high *q* value however, monopole electronic transitions that are forbidden in XAS become a significant part of the XRS spectrum. In this study, we focus on the Al *K* edge of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> measured in XRS and study the quantum nuclei quantum thermal vibrations effects on the electric dipole and monopole transitions.

The XRS spectra is calculated using the Xspectra module of Quantum-Espresso, using pseudopotentials, plane-wave basis sets and periodic boundary conditions, within a density functional theory framework [3,4,5,6]. The core-hole electron interaction is modelled using the final state rule in the FCH (Full Core-Hole) approach (1*s* core-hole taken into account during the pseudopotential generation, compensated by a background charge on all the cell). The nuclei quantum thermal vibrations effects are modelled in the Quasi-Harmonic Approximation (QHA), allowing the generation of temperature-dependent atomic configurations that are then used to compute an XRS spectrum with Xspectra. The theoretical spectrum is obtained by calculating the average of all the configuration spectra, and compared to experimental XRS spectra measured at the ID20 beam line of ESRF.

A good agreement between experience and calculation is achieved. Calculation allows the separation between contributions of electric dipole and monopole transitions. The Al *K* edge XRS spectrum of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> features an intense pre-edge peak due to direct and indirect 1*s*-3*s* transitions, indirect ones being caused by nuclei vibration-induced hybridization of 3*p* and 3*s* states, allowing to probe the 3*s* states of Al through the dipole transitions. This theoretical study shows thermal effects on XRS spectra at the Al *K* edge that could be of crucial importance in systems relevant for catalysis.

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# Structural characterization of organic salts by combined X-ray Raman Scattering and excited-state DFT calculations

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Formulating active pharmaceutical ingredients (APIs) as salts can provide favourable biopharmaceutical and physicochemical properties, such as physical and chemical stability, and increased solubility [1]. Predictive modelling of organic salt crystallisation from solution requires knowledge of speciation in solutions, as structural and electronic properties impact on the crystal structure and morphology of the final product. Core level X-ray Absorption Spectroscopy (XAS) has recently been used to probe the properties of organic ions in solution through the Near-Edge X-ray Absorption Fine-Structure (NEXAFS) region, which is highly sensitive to hydrogen bonding and protonation and hence changes in solvation structure [2]. However, currently available vacuum instruments for soft XAS studies of solutions rely on the use of microjets and similar liquid sample dosing technologies, which are prone to nozzle blockage by spontaneous crystallisation of concentrated solutions. Moreover, expansion into vacuum precludes the high degree of temperature control required for nucleation and crystallisation studies.

Detection of the near-edge fine-structure spectra by X-ray Raman Scattering (XRS), which utilizes hard X-rays (photon energy  $\sim 10$  keV), has allowed us to work around these limitations. We obtained C and N K-edge fine-structure spectra of imidazolium salt solutions (pH 3) at ambient pressure. Comparison with results for neutral imidazole species (pH 10) confirms that the near-edge fine-structure in low momentum transfer XRS agrees well with previously obtained NEXAFS data. The imidazolium cation exhibits N K-edge fine-structure that is fundamentally different from that of imidazole due to equivalence of the nitrogen moieties in the ion. The two  $\pi^*$  resonances of the non-equivalent nitrogen moieties in imidazole result in a single  $\pi^*$  resonance, in agreement with previous observations for the N 1s binding energies by X-ray Photoelectron Spectroscopy (XPS). Time-dependent density functional theory (TD-DFT) calculations were performed for a number of solvation structures, including implicit and explicit solvation models. They reproduce the peak positions and intensities of the K-edge fine-structure features for both neutral imidazole and the cationic imidazolium species. In summary, we have demonstrated that soft K-edge measurement via XRS permits characterization of organic solutes in solution at ambient pressure. TD-DFT calculations model the observed changes successfully and provide an understanding of the effect of solute-solvent interactions.

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# Li K edge EXAFS via X-ray Raman spectroscopy

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Lithium is the backbone of today's high-capacity battery technology. As a highly mobile, light, and rather abundant element, it is well suited for an ionic charge carrier for energy storage purposes. Its lightness can also be a complication as its small scattering cross-section and spectral overlap of Li K edge with valence-electron excitations, such as the plasmon, make it an elusive element to study. For example, X-ray absorption fine-structure (XAFS) measurements commonly used to derive the oxidation state and the local environment of an element have limited bulk-sensitivity and are restricted to simple sample environments due to the low energy of the photons. However, in order to gain comprehensive understanding of kinetics of Li in realistic electrochemical situations, *in situ* investigation methods are essential.

X-ray Raman spectroscopy (XRS) is a unique method giving the access to low energy excitations using hard x-rays allowing the study of light elements in complex environments [1-3]. Therefore it is a suitable candidate for *in situ* Li studies [4]. We investigated the utilization of XRS as a practical method to obtain high quality extended X-ray absorption fine structure (EXAFS) of Li K edge at ID20 at multiple momentum transfers from various Li compounds.

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## XRS study on 5V $\text{LiCr}_{0.08}\text{Ni}_{0.42}\text{Mn}_{1.50}\text{O}_4$ battery electrodes

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Here we report the study of the  $\text{LiCr}_{0.08}\text{Ni}_{0.42}\text{Mn}_{1.50}\text{O}_4$  cathode material by means of x-ray Raman spectroscopy at ESRF ID20 [1]. Li K-edge, Ni and Mn M-edges, as well as Ni L-edges were measured at various states of charge. We identify the nickel as the main actor in the charge compensation mechanism, showing how the initial  $\text{Ni}^{2+}$  state oxidise during the charge to  $\text{Ni}^{4+}$  through an intermediate state of  $\text{Ni}^{3+}$ . The theoretical calculation of the Ni L edge spectra confirm the interpretation of the experimental results. The complementary truly bulk-sensitive results reported here draw the attention on the ability of x-ray Raman spectroscopy as an useful tool for Li-ion battery studies.

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# An X-ray Raman scattering study of the Li core excitation spectrum in LiH

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X-ray Raman scattering (XRS) spectroscopy was used to study the Li 1s core excitation spectra in LiH in a wide range of momentum transfers  $q$ . The analysis of the near-edge region of the measured spectra in combination with  $q$ -dependent *ab initio* calculations of XRS spectra based on the Bethe–Salpeter equation (BSE) reveals that the prominent peak at the excitation onset arises from two main contributions, namely a pre-edge peak associated to a  $p$ -type core exciton and strong transitions to empty states near the bottom of the conduction band, which is in contrast to previous experimental studies that attributed that feature to a single excitonic peak. The  $p$ -like angular symmetry of the core exciton is supported by BSE calculations of the relative contributions to the XRS spectra from monopole and dipole transitions and by the observed decrease of its normalised intensity for increasing momentum transfers. BSE, as well as real-space multiple-scattering calculations, also reproduced spectral features observed at higher energies and their momentum transfer dependence.

# Spin-phonon coupling in uniaxial anisotropic spin-glass based on $\text{Fe}_2\text{TiO}_5$ pseudobrookite

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The ferric pseudobrookite is a rare example of uniaxial anisotropic spin-glass insulator, depicting a multiglass behaviour and magnetoelectric coupling. Here, we present Raman spectroscopy results in order to elucidate the spin-phonon coupling in  $\text{Fe}_2\text{TiO}_5$  for the first time. The experimental data are supported by computational simulations performed in view of density functional theory, which allowed us to assign the main Raman-active modes. Temperature-dependent phonon behaviour exhibited anomalous evolution around 55 and 80–200 K, which was explained as successive coupling between lattice and spin configuration arising from spin freezing and short-range magnetic correlation, respectively. Arguments that the magnetoelectric effect in  $\text{Fe}_2\text{TiO}_5$  is mediated by spin-phonon coupling are presented.

# Structural changes in a natural basalt glass at high-pressure by means of X-ray Raman Scattering

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Basalt is one of the most common products of mantle melting on the Earth's surface. At mid-ocean ridges, the decompression of the mantle causes the partial melting of peridotite into basaltic magmas forming the oceanic crust. At subduction zones basalt can be recycled down to the mantle and replenish the deep Earth. Basaltic melts are much more mobile than their counterpart solids and any changes in density and viscosity could have strong influence on the chemical and thermal differentiation of the Earth's interior. Basaltic melts could form at partial melts from peridotitic mantle at various locations within the Earth's mantle, such as at the core-mantle boundary [1], at the transition zone [2], at subduction zones [3] or at the lithosphere-asthenosphere-boundary [4]. Knowledge of the short-range atomic and electronic structure in melts brings important constraints about their compressibility and viscosity at depth beyond the transition zone between 20 to 27 GPa (660km). In order to reveal the coordination changes in a natural depolymerized basaltic sample and to study the role of cation network modifiers and their influence on the local environment of Si, Ca and O in high-pressure melts, we measured and analysed the near edge X-ray Raman scattering signal at the Si L-edge, Ca L-edge and O K-edge in a natural basalt glass up to 36 GPa using a new design of conical diamond anvils [5]. These data give a first insight into the influence of cation network modifier, like Ca and are compared to fully polymerized SiO<sub>2</sub> glass at the pressure of the lower mantle [6]. The results will be discussed in view of recent density data [7], X-ray total scattering data [8] and calculated structures and coordination from ab-initio calculation [9].

## References

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# Post mortem investigation of the chemical environment in silicon-based lithium-ion batteries by XRS

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Lithium ion batteries are one of the best solutions for energy storage firstly due to the lighter weight of the lithium conferring high energy density. This also enables the flexibility in design and the portability that facilitates the use in several applications ranging from mobile devices to automobile market. In the research for materials that can reversibly host or release large quantities of lithium ions, it has been realized that silicon offers interesting possibilities because of its high theoretical capacity (3579 mAh/g) and natural abundance, compared to the usual commercial electrode, graphite (372 mAh/g). However, silicon suffers large volume expansion upon the insertion-disinsertion of the lithium ions, which results in the continuous formation of solid electrolyte interphase (SEI), leading to Li trapping and capacity loss. This continuously happen, leading to irreversible capacity and electrical contact loss [1].

One way of limiting volume expansion is using silicon nanoparticles, where the small size enables Li transportation and strain relaxation. These nanoparticles can also be embedded into a matrix to form a composite electrode. Using composites can mitigated volume changes, therefore reducing the capacity loss. However, the changes on the chemical environment of the composite and nanoparticles silicon based-electrodes are not well known.

We investigated the variations of the chemical environment in fresh and aged Silicon-anodes by XRS, in particular to study the formation and composition of the SEI in function of the materials morphology (e.g. NPs versus composite, see Fig 1. a. & b.) and state of charge (lithiated and delithiated states after typically few cycles and/or long-term cycling). XRS experiments were performed on ID20 at the ESRF on reference samples (pure compounds) and electrodes in specially designed airtight cell. We scanned the energy at the edges of C, O, F, Li and Si. The analysis of the spectra allowed us to observe qualitatively the formation of organic and inorganic species during cycling, and a quantitative attempt to deconvolute the spectra based on available references was performed to extract the amount of species on the SEI (see Fig 1. a. & b.).

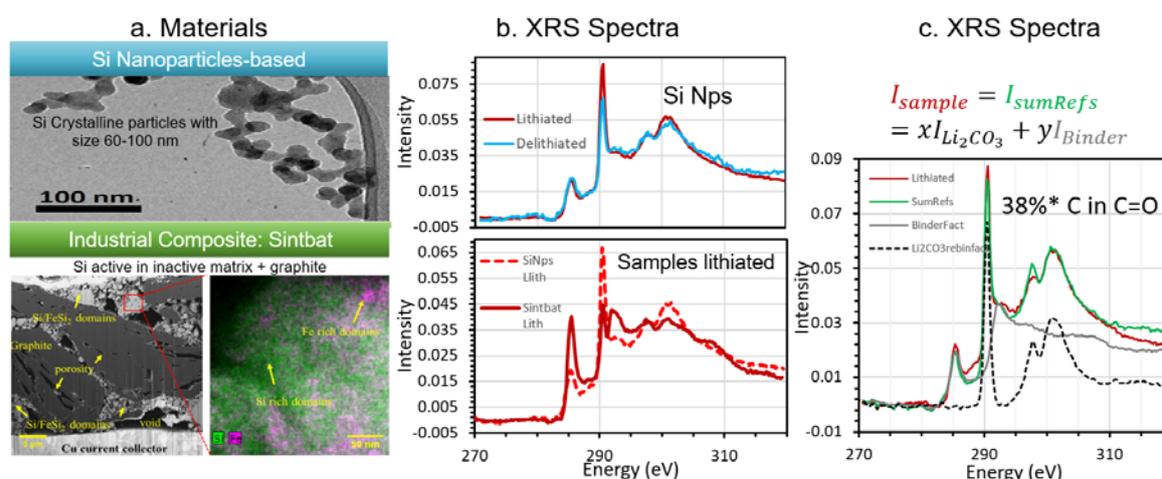


Figure 1: a. Materials investigated. b. Data obtained in the electrodes at different states. c. Analysis using references

## References

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Wednesday 3<sup>rd</sup> April 2019

Thursday 4<sup>th</sup> April 2019

Friday 5<sup>th</sup> April 2019

11:00	Registration with welcome coffee in the ESRF Central Building entrance hall	
12:00	Lunch at the EPN campus restaurant	
13:30	Welcome/Introduction by H. Reichert	
13:45	Session Instrumentation Chair: C. Sternemann	Considerations on the capabilities of ID20 X-ray Raman spectrometer S. Huotari
14:15		XRS at the GALAXIES beamline, SOLEIL Synchrotron J.-P. Rueff
14:45		Inelastic X-ray scattering at P01, DESY M. Sundermann
15:00	Coffee	
15:30	Session Instrumentation Chair: C. Sternemann	X-ray Raman spectroscopy using the LERIX facility at the APS M. Balasubramanian
16:00		High energy resolution fourteen-crystal spectrometer for high quality fluorescence and absorption measurements on an X-ray Absorption Spectroscopy beamline O. Proux
16:20	Discussions on Instruments	
16:40	Session Imaging Chair: S. Huotari	Carbon speciation in ancient and historical systems using X-ray Raman spectroscopy and imaging L. Bertrand
17:20	Beamline Visit ID20	
19:00	Dinner onsite	

9:00	Session Theory Chair: G. van der Laan	Modeling X-ray Raman Scattering with Xspectra G. Radtke
9:20		X-ray Raman Scattering calculations with the OCEAN code K. Gilmore
9:50		Momentum transfer dependence in X-ray Raman Scattering Y. Joly
10:10	Discussions on Calculs	
10:30	Coffee	
11:00	Session Liquids Chair: G. Lelong	Statistical view on core-level spectra of liquids J. Niskanen
11:30		X-ray Raman Scattering study of hydrothermal fluids: The case of aqueous sodium chloride solutions M. Elbers
11:50		X-ray Raman Scattering for the study of hydrothermal carbon materials L. Higgins
12:10	Discussions on Liquids	
12:30	Lunch at the EPN campus restaurant	
14:00	Session Correlated Electron Systems Chair: K. Gilmore	Core-level non-resonant inelastic X-ray scattering (NIXS): Beyond the dipole limit H. Tjeng, A. Severing, A. Amorese, M. Sundermann
15:00		Electronic excitations and momentum densities in oxides studied by inelastic X-ray scattering K. Ruotsalainen
15:30	Discussions on Correlated Electron Systems	
15:45	Coffee	
16:15	Session High Pressure Chair: M. Wilke	Polyamorphism in oxide glasses G. Lelong
16:45		Magma properties at deep earth's conditions from electronic structure of silica measured using X-ray Raman spectroscopy S. Petitgirard
17:15		Pressure-driven changes in XRS spectra of compressed amorphous MgSiO <sub>3</sub> glass G. Spiekermann
17:35	Discussions on High Pressure	
20:00	Workshop dinner at the restaurant L'Epicurien (1 place aux herbes - Tram B stop Ste Claire Les Halles)	

9:00	Session Energy Materials Chair: J.-P. Rueff	Fingerprinting reaction pathways of lightweight compounds by X-ray Raman Scattering spectroscopy: Application to hydrogen storage C. Sternemann
9:30		The effect of Ni doping on the performance and electronic structure of LSCF cathodes used for IT-SOFCs A. Longo
9:50		Bulk sensitive soft X-ray edges probing in electrodes for battery application M. Fehse
10:10	Coffee	
10:40	Session Energy Materials Chair: M. Balasubramanian	XRS study of medium range order in crystalline alkali borates E. de Clermont
11:00		X-ray Raman Scattering study of Li-based compounds at high temperature M.R. Cicconi
11:20		XRS study of metal hydride nanocomposites for energy storage applications P. Ngene
11:40		X-ray Raman Scattering of photocharged BiVO <sub>4</sub> reveals beneficial effect on the space charge region N. Fret
12:00	Discussions on Energy Materials	
12:15	Future of XRS / XRS workshop 2	
12:35	Lunch at the EPN campus restaurant	
14:00	End of workshop	

**EBS Workshop on X-ray Raman Scattering spectroscopy**  
**3, 4 & 5 April 2019 - ESRF Grenoble**

