



SOLEIL Users' Meeting
January 20th – 21st, 2022

Visioconference
Synchrotron SOLEIL, Saint-Aubin – France

Summary

- Programme
- Plenary Session
- Parallel Sessions:
 - Ancient & New Materials
 - Dynamic, Reactivity & Chemical Analysis Diluted Matter
 - Life & Earth Sciences
- Posters Session
 - List of Posters



Programme

Thursday, January 20th, 2022

VISIOCONFERENCE

- 10:00 – 10:10 **Welcome / Introduction, ORGUES Chair – Rozenn LE HIR**
- 10:10 – 10:20 The word of SOLEIL General Director – **Jean DAILLANT**
- Geosciences:**
10:20 – 11:05 Studying interactions between life and minerals by scanning transmission X-ray microscopy
Karim BENZERARA – IMPMC, Sorbonne Université, Paris
- Diluted matter:**
11:05 – 11:50 High resolution heterodyne and dual comb molecular spectroscopy at AILES beamline
Jean-François LAMPIN – IEMN, Université de Lille
- 11:50 – 12:10 *Peer Review Committee – PRC 3 – David BABONNEAU*
Peer Review Committee – PRC 4 – Lorenzo STIEVANO
Questions 10 min
- 12:10 – 12:20 Presentation of AFURS – **Roland THISSEN**
12:20 – 12:30 Presentation of ESUO – **Cormac MC GUINNESS**
- 12:30 – 14:00 *Break*
- Parallel sessions** (see the detailed programme below)
- 14:00 – 15:45
- Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces) – **Simona Raneri, Chairperson**
 - Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry) – **Heloise Dossmann, Chairperson**
 - Life & Earth Sciences (Biology / Health & Environment / Geoscience) – **Benoit Masquida, Chairperson**
- 15:45 – 16:15 *Break*
- Parallel sessions** (see the detailed programme below)
- 16:15 – 18:00
- Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces) – **Fabien Cheynis, Chairperson**
 - Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry) – **Florent Carn, Chairperson**
 - Life & Earth Sciences (Biology / Health & Environment / Geoscience) – **Rémi Marsac, Chairperson**
- 18:00 – 20:00 Posters session
Asma Tougerti, Chairperson



Programme

Friday, January 21st, 2022

VISIOCONFERENCE

Parallel sessions (see the detailed programme below)

- 9:00 – 10:45
- Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces) – **Emmanouil Frantzeskakis Chairperson**
 - Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry) – **Asma Tougeri, Chairperson**
 - Life & Earth Sciences (Biology / Health & Environment / Geoscience) – **Rozenn Le Hir, Chairperson**
- 10:45 – 11:15 *Break*
- 11:15 – 12:15
- Award of the best student poster
 - Round Table – **Rozenn Le Hir, Chairperson**
 - Update on the upgrade of SOLEIL
- 12:15 – 14:00 *Break*
- 14:00 – 17:00
- Technical workshop on STXM, XPEEM and Ptychography (HERMES beamline) – **Debora Pierucci, Chairperson**



Parallel Session Schedule

Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces)

Chairpersons: E. Frantzeskakis, D. Pierucci, A. Bordage, F. Cheynis and S. Raneri

Thursday, January 20th, 2022

- 14:00 – 14:30
(25'+5')
- The role of SOLEIL in the study of cultural heritage materials: The case of the stained-glass windows of Notre Dame cathedral
Myrtille HUNAULT – Synchrotron SOLEIL, Saint-Aubin, France
- 14:30 – 14:55
(20'+5')
- Migration of metal ions in historical oil-based pictorial paintings
Patrick KEKICHEFF – Institut Charles Sadron, Université de Strasbourg, C.N.R.S., Strasbourg, Synchrotron SOLEIL, Saint-Aubin, France
- 14:55 – 15:20
(20'+5')
- Comparative analysis of prehistoric mammoth ivories and bones at PUMA/SOLEIL and new AGLAE/C2RMF
Laurent TRANCHANT – Synchrotron SOLEIL, Saint-Aubin, France
- 15:20 – 15:45
(20'+5')
- Topological defects in smectic thin films
Jean de Dieu NIYONZIMA – Sorbonne Université, CNRS, Institut des Nanosciences de Paris, Paris, France
- 15:45 – 16:15
- Break
- 16:15 – 16:45
(25'+5')
- Surfaces, interfaces and nano-objets: recent multi-technique studies, beamlines overview and anticipated evolutions in the context of the upgrade @SOLEIL
Alina VLAD & Pavel DUDIN – SIXS/ANTARES beamline, Synchrotron SOLEIL, Saint-Aubin, France
- 16:45 – 17:10
(20'+5')
- XAS and XMCD analysis of the interface between FeRh magnetic nanoclusters and SrTiO₃ crystals
Sara GONZALEZ – Univ Lyon, CNRS, ECL, INSA Lyon, UCBL, CPE, INL, Villeurbanne, France
- 17:10 – 17:35
(20'+5')
- Synthetic antiferromagnet materials studied by soft X-ray magnetic resonant scattering
Cyril LEVEILLE – Synchrotron SOLEIL, Saint-Aubin, France
- 17:35 – 18:00
(20'+5')
- From Synchrotron to lasers infrared photons sources for very high pressure studies: Need and complementary
Paul DUMAS – Synchrotron SOLEIL, Saint-Aubin, France & CEA, DAM, DIF, Arpajon, France



Parallel Session Schedule

Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces)

Chairpersons: E. Frantzeskakis, D. Pierucci, A. Bordage, F. Cheynis and S. Raneri

Friday, January 21st, 2022

- 09:00 – 09:30
(25'+5') Shedding a new “light” onto the puzzles of magnetite
Hebatalla ELNAGGAR – *IMPMC, France / Utrecht Universit , Pays-bas*
- 09:30 – 9:55
(20'+5') Imaging the changes in electronic structure driving the metal-to-insulator transition in V_2O_3
Maximillian THEES – *Universit  Paris-Saclay, CNRS, Institut des Sciences Mol culaires d'Orsay, Orsay, France*
- 09:55 – 10:20
(20'+5') HAXPES study of surface/interface effects by alkali post deposition treatment of (Ag,Cu)(In,Ga)Se₂ thin film solar cell absorbers
Natalia MARTIN – *Solar Cell Technology, Department of Materials Science and Engineering, Uppsala University, Uppsala, Sweden*
- 10:20 – 10:45
(20'+5') Ultrafast light-induced strain and symmetry breaking in ferroic materials
Vincent JUVE – *Le Mans Universit , Le Mans, France*
- 10:45 – 11:15 *Break*



Parallel Session Schedule

Dynamic, reactivity and Chemical analysis (Diluted Matter & Chemistry)

Chairpersons: P. Asselin, A. Tougerti, H. Dossmann, F. Carn

Thursday, January 20th, 2022

- 14:00 – 14:30
(25'+5')
- Providing mechanistic insights into the low-temperature oxidation chemistry by Synchrotron-based VUV PEPICO spectroscopy
Jérémy BOURGALAIS – LRGP, Nancy, France
- 14:30 – 14:55
(20'+5')
- Inner Valence photoionization of small molecules: From spectrally to temporally resolved MFPADs
Jennifer JOSEPH – Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, Orsay, France
- 14:55 – 15:20
(20'+5')
- Multi-electron coincidence spectroscopy of the Ar 2p² double core hole decay
Maximilian REINHARDT – University of Oulu, Oulu, Finlande
- 15:20 – 15:45
(20'+5')
- Post-collision interaction effects in sulfur KLL Auger spectra of thiophene and Thiophene-based polymers
Nicolas VELASQUEZ – Sorbonne Université, CNRS, Laboratoire de Chimie Physique Matière et Rayonnement, Paris, France
- 15:45 – 16:15
- Break
- 16:15 – 16:45
(25'+5')
- Synchrotron insights onto the formation of synthetic and biological magnetite nanoparticles
Damien FAIVRE – Institut de biosciences et biotechnologies, CEA Cadarache, France
- 16:45 – 17:10
(20'+5')
- Pentagonal gold bipyramids self-assemble with long-range triclinic order
Doru CONSTANTIN – Institut Charles Sadron, CNRS and Université de Strasbourg, Strasbourg, France
- 17:10 – 17:35
(20'+5')
- Structural evolution of PT nanoparticles during ammonia oxidation
David SIMONNE – Synchrotron SOLEIL, Saint-Aubin, France
- 17:35 – 18:00
(20'+5')
- Innovative chemical imaging speciation methodology for studying the impact of the impregnation and drying of supported CoMoP/ Al₂O₃ HDS catalysts by quick-XAS and Raman spectroscopies
Beatriz BARATA – IFPEN, Synchrotron SOLEIL, Saint-Aubin, France



Parallel Session Schedule

Dynamic, reactivity and Chemical analysis (Dilluted Matter & Chemistry)

Chairpersons: P. Asselin, A. Tougerti, H. Dossmann, F. Carn

Friday, January 21st, 2022

- 09:00 – 09:30 Microfluidic tools for Synchrotron-based experiments: Applications to chemistry
(25'+5') **Benedikt LASALLE** – *Synchrotron SOLEIL, Saint-Aubin, France*
- 09:30 – 9:55 Photoelectron Circular Dichroism as a probe for conformational isomerism in 1-indanol
(20'+5') **Jennifer DUPONT** – *Institut des Sciences Moléculaires d'Orsay, CNRS, Univ. Paris-Saclay, Orsay, France*
- 09:55 – 10:20 MOSARIX: A Von Hamos spectrometer based on highly annealed pyrolytic graphite crystal
(20'+5') in the tender X-ray domain
Roba MOUSSAOUI – *Sorbonne Université, CNRS, Laboratoire de Chimie Physique Matière et Rayonnement, Paris, France*
- 10:20 – 10:45 Preliminary study on migration of halide ions in metal halide perovskite induced by
(20'+5') electrical field based on nano X-ray fluorescence
Haeyeon JUN – *Synchrotron SOLEIL, Saint-Aubin, France*
- 10:45 – 11:15 *Break*



Parallel Session Schedule

Life & Earth Sciences (Biology / Health & Environment / Geoscience)

Chairpersons: B. Masquida, R. Le Hir and R. Marsac

Thursday, January 20th, 2022

- 14:00 – 14:30
(25'+5')
- Allosteric modulators of force production: Towards precision medicine for different classes of heart diseases
Anne HOUDUSSE – *Institut Curie, Paris, France*
- 15:00 – 15:30
(25'+5')
- HELIOBIO group
Frédéric JAMME – *Synchrotron SOLEIL, St Aubin, France*
- 15:30 – 15:55
(20'+5')
- Structural insights into RNA-mediated transcription regulation in bacteria.
Albert WEIXLBAUMER – *IGBMC, Université de Strasbourg, CRNS, INSERM, Illkirch, France*
- 15:55 – 16:15
- Break*
- 16:15 – 16:45
(25'+5')
- Spatial distribution and speciation of REE in soils and REE accumulating ferns
Emmanuelle MONTARGES-PELLETIER – *LIEC, Nancy, France*
- 16:45 – 17:10
(20'+5')
- Probing the stoichiometry of Fe₃-O₄ nanoparticles by soft XAS and XMCD
Fadi CHOUËIKANI – *Synchrotron SOLEIL, St Aubin, France*
- 17:10 – 17:35
(20'+5')
- Microfluidic production of nanomedecins with in operando SAXS structural investigation of lipid nano-emulsions formulation. Presentation of the galenic on-chip concept
Guillaume BROTONS – *Université Le Mans, France*
- 17:35 – 18:00
(20'+5')
- Dynamics and structural changes of calmodulin upon interactions with its potent antagonist calmidazolium
Corentin LEGER – *Institut Pasteur, Université Paris, France*



Parallel Session Schedule

Life & Earth Sciences (Biology / Health & Environment / Geoscience)

Chairpersons: B. Masquida, R. Le Hir and R. Marsac

Friday, January 21st, 2022

- 09:00 – 09:30
(25'+5') From moss to sequoia, X-rays reveal the metastability of sap transport under tension
Sylvain DELZON – *INRAe Bordeaux, France*
- 09:30 – 09:55
(20'+5') Deep investigation of specificities and behaviours of flax fibers and stems through different SOLEIL beamlines
Alain BOURMAUD – *Université Bretagne Sud, France*
- 09:55 – 10:20
(20'+5') A N7-methyltransferase hidden in the dark proteome of newly discovered nidovirus. Structure, function and evolutionary implications
François FERRON – *AFMB, Université Aix-Marseille, France*
- 10:20 – 10:45
(20'+5') Structural insights onto the ribosome from the human pathogen *C. albicans*
Olga KOLOSOVA – *Department of Integrated Structural Biology, Institute of Genetics and Molecular and Cellular Biology, University of Strasbourg; Illkirch, France*
- 10:45 – 11:15 *Break*

PLENARY SESSION

Rozenn LE HIR, Chairperson

- 10:00 – 10:10 **Welcome / Introduction, ORGUES Chair – Rozenn LE HIR**
- 10:10 – 10:20 The word of SOLEIL General Director – **Jean DAILLANT**
- Geosciences:**
Studying interactions between life and minerals by scanning transmission X-ray microscopy
10:20 – 11:05 **Karim BENZERARA** – *IMPMC, Sorbonne Université, Paris*
- Diluted matter:**
High resolution heterodyne and dual comb molecular spectroscopy at AILES beamline
11:05 – 11:50 **Jean-François LAMPIN** – *IEMN, Université de Lille*
- Peer Review Committee – PRC 3 – David BABONNEAU*
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Questions 10min
- 12:10 – 12:20 Presentation of AFURS – **Roland THISSEN**
- 12:20 – 12:30 Presentation of ESUO – **Cormac MC GUINNESS**

Studying Interactions between Life and Minerals using Synchrotron Radiation

K. Benzerara, R. Bolzoni, D. Chevrier, J. Debie, A. Elmaleh, N. Mehta,
J. Gaëtan, A. Hitchcock, A. Juhin, C. Lefèvre, N. Menguy,
F. Skouri-Panet, A. Somogyi, S. Swaraj, D. Vantelon and the HERMES,
LUCIA, Nanoscopium beamline teams

*Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, Institut de Minéralogie,
de Physique des Matériaux et de Cosmochimie, IMPMC, 75005 Paris, France*

ABSTRACT

A wide diversity of living organisms, especially microbial organisms, can form a large panel of mineral phases (1,2). This process, called biomineralization, has major implications for diverse science topics such as the search of traces of life in ancient and/or extraterrestrial rocks, the design of bio-assisted remediation processes of pollutions, the study of pathological calcification... In this talk, we will go on a naturalistic journey in which we will explore new modes of mineral formation by bacteria, including intracellular amorphous calcium carbonates and amorphous Fe- and Mn-rich silicates, as well as the formation of magnetites by bacteria involved in symbioses with eukaryotes. We will question the geochemical significance of these processes as well as their molecular mechanisms. Moreover, we will illustrate how crucial the use of diverse synchrotron-based technique is for this research, with a special focus on scanning transmission x-ray microscopy (3-5).

REFERENCES

1. J. Cosmidis and K. Benzerara, *Comptes Rendus. Géoscience*, **354**, 1-39 (2022).
2. S. Görgen, K. Benzerara, F. Skouri-Panet. et al. *Discov. Mater.* **1**, 2 (2021).
3. C.L. Monteil, K. Benzerara, N. Menguy, et al. *ISME J* **15**, 1–18 (2021).
4. L. Le Nagard, X. Zhu, H. Yuan, e al., *Chemical Geology*, **530**, 119348 (2019).
5. J. Cosmidis and K. Benzerara, "Soft x-ray scanning transmission spectromicroscopy", in *Biomineralization Sourcebook*, edited by E. DiMasi and L.B. Gower, Boca Raton: CRC Press, 2014, pp. 115-130.

High Resolution Heterodyne and Dual Comb Molecular Spectroscopy at AILES Beamline

M-H. Mammez^{1,*}, T. Hearne³, D. Mammez¹, Z. Buchanan^{2,3}, O. Pirali^{3,4},
M-A. Martin-Drumel³, J. Turut⁵, G. Ducournau⁵, S. Eliet⁵, F. Hindle¹,
S. Barbieri⁵, P. Roy⁴, G. Mouret¹, and J-F. Lampin⁵

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ABSTRACT

Spectroscopy is a powerful non-invasive method that allows to identify atoms and molecules in many different applications. In particular high-resolution spectroscopy allows a high selectivity between molecular species in gas phase and is used in atmospheric molecular physics and astronomy. Spectroscopy in the far-infrared (FIR) and the terahertz ranges (0.1-10 THz corresponding to a wavelength of 30-3000 μm) is particularly rich because a lot of strong lines of many chemical compounds belong to this range. Moreover techniques coming from the radio frequency domain can be applied to this range: here we use the heterodyne detection scheme that allows very high resolutions. Thanks to a new kind of THz laser that is used as a local oscillator, we have demonstrated a broadband THz spectrometer that exploits the synchrotron radiation (SR) at MHz resolution. In another set of experiments we have also demonstrated that it is possible to use the coherent synchrotron radiation (CSR) in a dual-comb spectroscopy setup in the sub-THz range. The results of this work were obtained during the HEROES ANR project.

An introduction to the European Synchrotron and FEL Users Organisation (ESUO) & User survey and questionnaire on impact of absence of Trans-National-Access (TNA) funding

Cormac McGuinness¹, Carla Bittencourt², Federico Boscherini², Tom Hase²,
Rainer Lechner², Derek Logan², Bridget Murphy², Moniek Tromp².

1) President and 2) Executive Board Members of European Synchrotron and FEL Users Organisation (ESUO), www.esuo.eu (1 Trinity College Dublin, Ireland.)

The European Synchrotron and FEL Users Organisation (ESUO) was established for the purposes of advocating on behalf of European SR and FEL users of European facilities. ESUO's vision is to support a thriving (European) synchrotron & FEL user community with equal opportunities of access and participation for all scientists based solely on the scientific merit of their ideas.

European users have benefitted over two decades from the availability of financial support via successive Framework/ Horizon 2020 Integrating Activities programmes providing Trans-National-Access (TNA) funding in accessing SR and FEL facilities, paying travel and accommodation costs for one or more members on a beamtime. Earlier, in 2014, ESUO had been successfully in helping lobby for continuation of TNA in Horizon 2020 via a general access activity giving the CALIPSOplus programme. However, the TNA which was funded by CALIPSOplus ended with the project on 31st October 2021. At present there is no direct replacement by the European Commission in the form of a general access curiosity driven programme that would continue to provide TNA to all researchers from across Europe no matter the topic.

ESUO has initiated a user survey on the possible impacts of the absence of Trans-National-Access (TNA) funding for the user community. This can be completed by going to the following link: <https://www.esuo.eu/possible-impacts-of-the-absence-of-transnational-access-funding-support-for-the-user-community/>

All researchers, young and old, whether Master or PhD students, postdoctoral researchers, academic staff, group leaders or professors are encouraged to complete the survey and to circulate it. Using the survey results, ESUO will continue to advocate to the European Commission, in cooperation with LEAPS facilities, for TNA funding for all science topics and all scientists.

ESUO first established in 2010, in 2021 has become an International non-profit organisation, and is composed of national delegates from all European nations and their National User Organisations (NUOs) and/or Facility User Organisations (FUOs).

PARALLEL SESSION

Ancient & New Materials

(Cultural heritage / Structure / Electronic Properties /
Surfaces & Interfaces)

VISIOCONFERENCE

Thursday, January 20th

Chairpersons:

E. Frantzeskakis, D. Pierucci, A. Bordage, F. Cheynis and S. Raneri

- IT-01 The role of SOLEIL in the study of cultural heritage materials: The case of the stained-glass windows of Notre Dame cathedral
M. Hunault
- OC-01 Migration of metal ions in historical oil-based pictorial paintings
P. Kekicheff
- OC-02 Comparative analysis of prehistoric mammoth ivories and bones at PUMA SOLEIL and new AGLAE C2RMF
L. Tranchant
- OC-03 Topological defects in smectic thin films
J. de D. Niyonzima
- IT-02 Surfaces, interfaces and nano-objets: Recent multi-technique studies, beamlines overview and anticipated evolutions in the context of the upgrade @SOLEIL
A. Vlad & P. Dudin
- OC-04 XAS and XMCD analysis of the interface between FeRh magnetic nanoclusters and SrTiO₃ crystals
S. Gonzalez
- OC-05 Synthetic antiferromagnet materials studied by soft X-ray magnetic resonant scattering
C. Léveillé
- OC-06 From Synchrotron to lasers infrared photons sources for very high-pressure studies: Need and complementary
P. Dumas

PARALLEL SESSION

Ancient & New Materials

(Cultural heritage / Structure / Electronic Properties /
Surfaces & Interfaces)

VISIOCONFERENCE

Friday, January 21st

Chairpersons:

E. Frantzeskakis, D. Pierucci, A. Bordage, F. Cheynis and S. Raneri

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|-------|---|
| IT-03 | Shedding a new “light” onto the puzzles of magnetite H. Elnaggar |
| OC-07 | Imaging the changes in electronic structure driving the metal-to-insulator transition in V_2O_3 M. Thees |
| OC-08 | HAXPES study of surface/interface effects by alkali post deposition treatment of (Ag,Cu)(In,Ga)Se ₂ thin film solar cell absorbers N. Martin |
| OC-09 | Ultrafast light-induced strain and symmetry breaking in ferroic materials V. Juvé |

The Role of SOLEIL in the Study of Cultural Heritage Materials: The Case of the Stained-glass Windows of Notre Dame Cathedral

Myrtille HUNAUT

Synchrotron SOLEIL, Saint-Aubin, France

Migration of metal ions in historical oil-based pictorial paintings

P. Kékicheff^{1,2}; R. Adamski¹; T. Roland¹; A. Egele¹; D. Favier¹;
S. Schoeder²; L. Tranchant²; Ł Bratasz³;
F. C. Izzo⁴; L. Fuster-López⁵; M. F. Mecklenburg⁶

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²*Synchrotron SOLEIL, Saint Aubin, 91192 Gif-sur-Yvette, France*

³*Jerzy Haber Institute, Polish Academy of Sciences, 30-239 Kraków, Poland*

⁴*Università Ca' Foscari Venezia, Dipartimento Scienze Ambientali, Mestre Venezia, Italy*

⁵*Universitat Politècnica de València, Dept. Conservación y Restauración de Bienes Culturales, Spain*

⁶*Museum Conservation Institute, Smithsonian Institution, Suitland, Maryland 20746, USA*

ABSTRACT

Oil-based easel paintings are subject to slow deterioration processes that affect their appearance and structural integrity. Ongoing reaction between metal ions (from metal-containing pigments) and free fatty acids (from hydrolyzed triglycerides of the oil binding medium and additives) leads to the formation of metal carboxylates (soaps). These complexes of metal ions (usually lead and zinc) and long-chain saturated fatty acids can form large crystalline aggregates that may protrude through the paint surface and lead to crack formation, brittleness, delamination, and to the disruption of the painted surface. Despite progress in the understanding of metal soap formation, many issues are still unresolved. One concerns the migration of metal cations likely to diffuse in their hydrated form through the paint matrix assisted by the diffusion of water via interconnected channels and pores of various sizes.^{1,2} However, the exact mechanism of metal ion diffusion remains difficult to quantify, especially since no direct measurement of their coefficient of diffusion, D , has so far been reported for paint layers that have naturally aged.

To address this question, we set a procedure on PUMA to measure D for Fe ions in well controlled 2-layers paints. These oil films belong to the Mecklenburg's Paint Reference Collection at the Smithsonian Museum Conservation Institute, USA. A white lead pigment in cold pressed linseed oil was applied on polyester film in 1990. In 1999 a second coloured paint film (ochre-orange; iron-based pigment) was applied on top. The Fe concentration profile across the interface separating the ochre layer with the pure Pb-white layer is measured by μ -XRF mapping. XANES and XRD investigations confirm the presence of Fe ions that have migrated into the pure Pb-white layer over this ~20 years period. From the concentration profile a coefficient of diffusion is inferred: $D \sim 10^{-17} \text{ m}^2/\text{s}$ (i.e. $\sim 300 \text{ }\mu\text{m}/\text{year}$). The analysis uses numerical simulations comparing a diffusion mechanism that follows Fick's law with a non-Fickian behavior.³ To our knowledge, this is the first time that a coefficient of diffusion of metal ions migrating in-between the different paint layers in a painting is reported.

REFERENCES

1. M. F. Mecklenburg *et al.*, Structural response of painted wood surfaces to changes in ambient relative humidity. In: V. Dorge & F. C. Howlett (Eds.), *Painted Wood: History and Conservation*, Los Angeles: The Getty Conservation Institute, 464-483 (1998).
2. G. J. A. M. Eumeelen, *et al.* A computational model for chemo-mechanical degradation of historical oil paintings due to metal soap formation. *J. Mech. Phys. Solid.* **132**, 1-21 (2019).
3. P. Kékicheff; R. Adamski; T. Roland; A. Egele; D. Favier; L. Tranchant; S. Schoeder; Ł Bratasz; F. C. Izzo; L. Fuster-López; M. F. Mecklenburg, *to be submitted*.

Comparative Analysis of Prehistoric Mammoth Ivories and Bones at PUMA/SOLEIL and New AGLAE/C2RMF

L. Tranchant¹, K. Müller², Q. Lemasson^{3,4}, L. Pichon^{3,4}, C. Pacheco^{3,4}, S. Schöder¹ and I. Reiche³⁻⁵

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⁴Fédération de recherche NewAGLAE, FR3506 CNRS/Ministère de la Culture/ENSCP, C2RMF - Palais du Louvre, 75001 Paris, France

⁵PSL Université, ENSCP, Institut de recherche de Chimie Paris, UMR 8247 CNRS, Équipe PCMTH, 75005 Paris, France

ABSTRACT

The PUMA beamline at the SOLEIL synchrotron and New AGLAE accelerator at the C2RMF are two facilities dedicated to heritage science. They provide complementary analysis tools to characterize diagenetic and biogenic elements present in Paleolithic mammoth ivories and bones. In this work we study samples coming from the *Hohle Fels* site in the South-west of Germany and dating from the Aurignacian period (45 000 – 35 000 BP). This site is of high interest for prehistorians because one of the earliest examples of human figurative art (Venus figurine) and some of the earliest musical instruments have been discovered in this cave [1,2].

Study of prehistoric ivories enables to address different questions such as their provisioning during the Aurignacian period, the relative dating and the degradation process during the burial time (diagenesis) [3, 4]. The objective of this communication is to highlight the different analysis possible at PUMA and at New AGLAE and how they can provide a more comprehensive understanding of ancient materials.

Mappings of chemical elements obtained by X-ray fluorescence (XRF) at PUMA and particle induced X-ray emission (PIXE) at New AGLAE are compared and show that the sensitivity for heavy elements ($Z > 17$) is better with the XRF technique at PUMA. The New AGLAE facility is very adapted to the detection and quantification of light elements ($Z < 30$). Moreover, complementary to PIXE, the particle induced gamma ray emission (PIGE) analysis and Rutherford backscattering spectroscopy (RBS) at New AGLAE respectively allow to quantify very light elements ($Z < 15$) for the former and to detect organic phase for the latter technique. The use of all these methods offered by PUMA and New AGLAE enables to detect every element from carbon to uranium and to determine whether they are major, minor or trace elements in a non-destructive way.

REFERENCES

1. N. J. Conard (2003). *Nature*, **426**(6968), 830-832.
2. N. J. Conard, M. Malina & S. C. Münzel (2009). *Nature*, **460**(7256), 737-740.
3. C. Heckel, K. Müller, R. White, S. Wolf, N. J. Conard, C. Normand, H. Floss, & I. Reiche, I. (2016). *Quaternary International*, **403**, 40-50.
4. I. Reiche, C. Heckel, K. Müller, O. Jöris, T. Matthies, N. J. Conard, H. Floss & R. White (2018) *Angewandte Chemie International Edition*, **57**(25), 7428-7432.

Topological Defects In Smectic Thin Films

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ABSTRACT

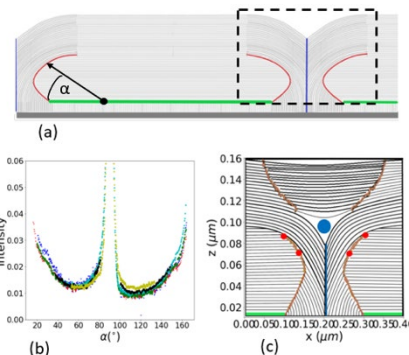
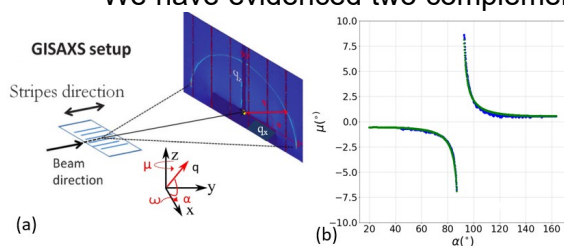
Topological defects are ubiquitous in nature but their intimate structure is still poorly known. Using GISAXS at the SIXS beamline of Soleil Synchrotron facility, we studied the internal structure of arrays of linear topological defects in thin smectic-A liquid crystal films (thickness = 180nm) of 4-n-octyl-4'-cyanobiphenyl (8CB). The smectic film is composed of flattened hemicylinders made of superimposed smectic layers (Figure 2a). Bragg x-ray intensity is proportional to the number, $n(\alpha)$, of smectic layers, whose normal, parallel to the wave-vector transfer makes an angle α with the substrate (Figure 2a) [1]. We have therefore determined how to obtain Bragg's condition for a given α in the hemicylinders. Using the Bragg's intensity, we are now able to reconstruct the structure of the smectic film with high resolution for a nanoscale determination of the topological defect structure.

We have evidenced two complementary methods to determine the smectic layers Bragg's condition inside the hemicylinders, based on the rotation of the smectic films around two orthogonal axes through the respective angles ω and μ (figure 1a). We calculated the theoretical Bragg's angles. The comparison of the theoretical μ_{Bragg} (in green) and experimental position of maximum intensities (in blue) confirms that the maximum intensities are the Bragg's values (Figure 1b).

The reconstruction of the smectic layers reveals 3 types of topological defects shown in figure 2c: dislocations (in red), disclinations (in blue) and 2D ribbon-like grain boundary (in green). The localization of the two first defects is now known and their core estimated to be around 10nm. We are ready to study how these structures locally vary in presence of ordered nanoparticle assemblies that become confined in the defect cores when smectic oily streaks are formed in presence of nanoparticles [2].

References:

- [1] D. Coursault *et al.*, "Self-organized arrays of dislocations in thin smectic liquid crystal films," *Soft Matter*, vol. 12, no. 3, pp. 678–688, 2016.
[2] S.-P. Do *et al.*, "From Chains to Monolayers: Nanoparticle Assembly Driven by Smectic Topological Defects," *Nano Lett.*, vol. 20, no. 3, pp. 1598–1606, 2020.



Surfaces, Interfaces and Nano-objets: Recent Multi-technique Studies, Beamlines Overview and Anticipated Evolutions in the Context of the Upgrade @SOLEIL

Alina VLAD & Pavel DUDIN

SIXS/ANTARES Beamline, Synchrotron SOLEIL, Saint-Aubin, France

XAS And XMCD Analysis Of The Interface Between FeRh Magnetic Nanoclusters And SrTiO₃ Crystals

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ABSTRACT

Nanomultiferroic composites are promising systems where the interfacial coupling between ferroics can drive the appearance of new features absent in the individual constituents. Magnetic, voltage and strain mediation approaches have driven research activities to explore nanomultiferroics for technological applications [1].

We propose to study ultimately small nanomultiferroic systems, based on magnetic nanoclusters (NCs) and ferroic oxides. Material choices are made based on structural compatibility, thus epitaxy, of nanomagnets depicting remarkable strain-mediated magnetic properties, *i.e.* FeRh, and prototypical perovskite oxides, ferroelastic SrTiO₃ and ferroelectric,-elastic BaTiO₃. Indeed, when chemically ordered in the CsCl-type phase, or B2 phase, the FeRh alloy is expected to transit from antiferromagnetic to ferromagnetic around 370 K. Remarkably, in NCs as small as 5 nm, B2 phase is attainable through UHV annealing, and depicts high magnetization down to 3 K [2], confirming the stabilization of ferromagnetism in NCs and differing from bulk behavior.

Here, we focus on studying FeRh NCs (3 to 7 nm size, of different densities) on TiO₂-terminated atomically flat SrTiO₃ (001) crystals. Determination of NCs distribution, their shape and crystalline state were performed by atomic force microscopy, grazing incidence small-angle X-ray scattering and X-ray diffraction (BM32-ESRF, SixS-SOLEIL), respectively. At DEIMOS-SOLEIL beamline, using different end-stations to cover a wide range of temperatures (4 K up to 950 K), we have investigated interface chemistry mechanisms through different thermal and environmental cycling using X-ray absorption spectroscopy, and determined NCs magnetic properties, including NCs Curie temperature, by X-Ray magnetic circular dichroism spectroscopy. These latter results and the *in situ* investigations of the chemically disordered to chemically order NC phase transition, with diffraction and magnetic fingerprints determined from GIXRD and XMCD respectively, will be discussed in the framework of NCs epitaxial growth on oxide and interface/surface chemistry of these nanomultiferroic composites.

REFERENCES

1. W. Eerenstein, N.D. Mathur, J.F. Scott, *Nature*, **442**, pp. 759-765 (2006); N. A. Spaldin and R. Ramesh, *Nature Mater.* **18**, 203 (2019)
2. A. Hillion et al., *Phys. Rev. Lett.* **110**, 087207 (2013); V. Dupuis et al. *Beilstein J. Nanotechnol.* **7**, 1850 (2016)

Synthetic Antiferromagnet Materials Studied by Soft X-ray Magnetic Resonant Scattering

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ABSTRACT

Soft ferromagnetic (FM) materials are widely used in data storage technology due to small size of magnetic bit allowing high reliable storage capacity and our capabilities to control/read at microscopic scale in the GHz regime. Synthetic AntiFerromagnetic (SAF) systems are made of FM films with an antiferromagnetic coupling. SAF materials have been proposed for future magnetic devices since they emit less stray field, are thermally more stable and have a higher storage density. Moreover, the AF coupling between two ferromagnetic films composing a SAF could lead to an enhanced domain wall velocity that is linked with chiral stability or to the stabilization of small AF skyrmions with no transverse deflection while moving. It has been recently demonstrated that the amplitude and sign of the circular dichroism in X-ray resonant magnetic scattering (XRMS) give direct information on the type (*i.e.* Néel or Bloch) and on the chirality (clockwise or anticlockwise) of the domain walls in ferromagnetic films. In this contribution, we demonstrate that the same approach is also valid for SAF system. It allows us to extract chirality information about the spin spiral optimized magnetic texture. We also report XRMS dichroic signal's temperature dependence that indicates the temperature evolution of the different magnetic interactions at play (*i.e.* magnetic anisotropy, interfacial chiral interaction and exchange interaction) through significant modifications on the spin textures stabilized in such SAFs. Last, we show the agreement of simulations performed with a distorted wave Born approximation (DWBA) with the specular and off-specular experimental data which can become a powerful tool to retrieve samples 3D magnetization profile.



Figure 1 : (Left) Cross section of a calculated magnetic configuration of spin spirals antiferromagnetically coupled in a bilayer (from W. Legrand et al. Nat. Mater. **19**, 34 (2020))

(Right) Corresponding experimental diffraction pattern at an angle that corresponds to half of the Bragg angle.

From Synchrotron to Lasers Infrared Photons Sources for Very High Pressure Studies: Need and Complementary

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ABSTRACT

Reaching pressure over 400 GPa using a Diamond Anvil Cell (DAC) has been, for long, a hard limit to overcome. Recently, the use of toroidal-shape diamond (t-DAC) [1] has allowed to reach pressures up to 600 GPa which opens the exploration of the properties of matter under extreme pressure. In particular, the use of t-DAC has been essential to reach the metallic state of both hydrogen and deuterium, respectively at 425 GPa [2], and 460 GPa[3], which could be characterized in front of the SMIS beamline at SOLEIL.

Being a non-invasive approach, IR absorption spectroscopy is well appropriate to measure the structural, chemical and electronic properties of matter under extreme pressure. The synchrotron source has been of paramount importance in providing the necessary brightness to record spectra at small sample dimensions (about 6 microns in diameter), accessible in the 400 GPa range. However, in the 500 GPa pressure range, the sample is more of 4 μm in diameter and then the IR signal becomes almost undetectable.

The way to continue the exploration of matter under extreme pressure using IR spectroscopy is to use recently developed IR laser sources. Despite a limited spectral range at present compared to the synchrotron source, infrared lasers are much brighter sources, and transmission/reflection IR studies on a less than 3 μm in diameter sample is feasible.

We will illustrate the performances of a supercontinuum infrared lasers in the range of 2-4 microns wavelength, associated with a supercontinuum visible lasers (0.45- 2.3 microns) both in transmission and reflections for very small sample diameter and discuss the necessary complementarity between the two sources that would provide outstanding infrared probing capabilities for very high pressures studies .

REFERENCES

[1]- *Toroidal diamond anvil cell for detailed measurements under extreme static pressures* Dewaele, A., Loubeyre, P., Occelli, F., Marie, O. and Mezouar, M.. **Nature Comm.** 9, 2913 1-9 (2018)

[2]- *Synchrotron Infrared spectroscopic evidence of the probable transition to metal hydrogen* Paul Loubeyre , Florent Occelli and Paul Dumas **Nature**, volume 577 (30 janvier 2020)

[3]- *Isotopic shift in the transition to metal hydrogen.* Paul Loubeyre, Florent Occelli, Paul Dumas Submitted

Shedding a New “Light” onto the Puzzles of Magnetite

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ABSTRACT

Magnetite (Fe_3O_4) is one of the most abundant Fe bearing minerals on Earth and it finds many applications in areas such as paleomagnetism, medicine, data recording, and engineering [1]. It is believed to have governed the early Martian climate and favoured biologically relevant chemical reactions [2]. Fe_3O_4 is known to man as the first compass [3] and an intriguing half metallic oxide of interest to spintronics applications [4]. It also undergoes a metal to insulator transition at $T_V \sim 125\text{K}$ which is referred to as the Verwey transition [5, 6, 7]. Ever since the work of Verwey, Fe_3O_4 was considered as an archetype of strongly correlated oxide systems. This gave rise to considerable efforts devoted to understanding the origin of the Verwey transition. It has however remained a daunting task to determine the driving force of the transition due to its complexity: Fe_3O_4 is a mixed valence, strongly correlated system where many interactions such as Jahn-Teller (dynamical and static), spin-orbit and phonons are very close in energetics. Several decades of research have deduced that in the insulator phase of magnetite, an intricate, long-range network of linear magnetic molecules called “trimerons” form, with the linear structure $\text{Fe}^{3+}\text{-Fe}^{2+}\text{-Fe}^{3+}$ [8]. The trimerons are associated with compressive tetragonal Jahn-Teller distortion at the Fe^{2+} central ion of the trimeron. But recently, trimerons have also been suggested to exist in the high-temperature metallic-like phase, just above the Verwey transition as short range. It is not straightforward to establish the existence of high temperature trimeron correlations because of their dynamical nature and associated small local Jahn-Teller distortion, which renders standard techniques such as x-ray diffraction, UV-Vis and NMR spectroscopy ineffective. As it stands to date, both possibilities were suggested [9,10,11,12].

In this talk, I will discuss a series of x-ray spectroscopic measurements that shed new light on the open questions regarding trimeron correlations in magnetite. I will present $2p3d$ RIXS magnetic angular dependence measurements that provide new insights regarding the short-range dynamical correlations and their evolution with temperature across the Verwey transition. Fe $2p3d$ RIXS magnetic angular dependence has the required sensitivity to track the evolution of local Jahn-Teller distortion at the formal Fe^{2+} sites in Fe_3O_4 . This is because one efficiently uses the x-ray polarization and magnetic angular dependence to differentiate between the close-lying distortion-induced states through the strong symmetry constraints imposed. This type of advanced RIXS-dichroism measurements is uniquely possible at the MAGELEC sample environment now available at the (RIXS) end-station of the SEXTANTS beamline. The combination of state-of-the-art $2p3d$ RIXS dichroism measurements and theoretical simulations based on Ligand Field Multiplet Theory provides an insightful picture of the Verwey transition and the interplay of the degrees of freedom in this complex oxide.

REFERENCES

- [1] D. W. Dunlop and  .  zdemir. *Rock Magnetism*. Cambridge University Press, 1997.
- [2] N. J. Tosca, et. al., *Nat. Geoscience*, 11(9):635–639, 2018.
- [3] W. Lowrie. *Fundamentals of Geophysics*. Cambridge University Press, 2 edition, 2007.
- [4] J. P. Hong, et. a., *Appl. Phys. Lett.*, 83(8):1590–1592, 2003.
- [5] E. J. W. Verwey, *Nature*, 144(3642):327–328, 1939.
- [6] E. J. W. Verwey and P. W. Haayman, *Physica*, 8(9):979 – 987, 1941.
- [7] E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.*, 15(4):174–180, 1947.
- [8] Senn, et. al., *Nature* 2012, 481, 173–176.
- [9] Huang et. al., *Nat. Commun.* 2016, 7, 12017.
- [10] Perversi et. al., *Nat. Commun.* 2019, 10, 2857.
- [11] Elnaggar et. al., *Phys. Rev. Lett.* 2019, 123, 207201.
- [12] Elnaggar et. al., *Phys. Rev. B* 2020,101, 085107.

Imaging the Changes in Electronic Structure Driving the Metal-to-insulator Transition in V_2O_3

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ABSTRACT

In solids, strong repulsion between electrons can inhibit their movement and result in a “Mott” metal-to-insulator transition (MIT), a fundamental phenomenon whose understanding has remained a challenge for over 50 years. A key issue is how the wave-like itinerant electrons change into a localized-like state due to increased interactions.

In bulk V_2O_3 , a first-order Metal-to-Insulator Transition occurs at a transition temperature of $T_{MIT} \approx 160$ K, as evidenced by a sharp rise in resistivity of more than 6 orders of magnitude [1-7] and the opening of a gap of about 750 meV [8,9].

We will present a comprehensive study of the electronic structure using angle-resolved photoemission spectroscopy (ARPES), including measurements from the CASSIOPEE beamline at SOLEIL, across the temperature-induced MIT in V_2O_3 films [10], whose crystal integrity, contrary to single crystals, is not affected by the transition.

We found dispersive quasi-particle and Mott-Hubbard bands in the metallic state, and observe unique spectral signatures, different to those of a conventional Fermi-surface instability, accompanying the MIT: opening of a gap at the Fermi level associated to a decrease in spectral weight of the quasiparticle band, without any change in its effective mass, while the Mott-Hubbard-band remains unaffected by the MIT. The spectral weight is transferred from the conduction band to a non-dispersive band of different orbital character, as the latter moves down in binding energy. We furthermore observe a clear thermal hysteresis in the gap and the quasi-particle's spectral weight, which we interpret in terms of the evolution of ratios of metallic/insulating microscopic domains, and that precisely capture the hysteresis in resistivity measured in the same samples [10].

REFERENCES

1. P. Fulde, *Correlated Electrons in Quantum Matter* (World Scientific, 2012); www.worldscientific.com/doi/pdf/10.1142/8419.
2. N. F. Mott, Metal-insulator transition. *Rev. Mod. Phys.* 40, 677–683 (1968).
3. D. B. McWhan, T. M. Rice, J. P. Remeika, Mott transition in Cr-doped V_2O_3 . *Phys. Rev. Lett.* 23, 1384–1387 (1969).
4. D. B. McWhan, J. P. Remeika, T. M. Rice, W. F. Brinkman, J. P. Maita, A. Menth, Electronic specific heat of metallic Ti-doped V_2O_3 . *Phys. Rev. Lett.* 27, 941–943 (1971).
5. N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, 2004).
6. M. Imada, A. Fujimori, Y. Tokura, Metal-insulator transitions. *Rev. Mod. Phys.* 70, 1039–1263 (1998).
7. V. Dobrosavljevic, N. Trivedi, J. M. Valles Jr., *Conductor-Insulator Quantum Phase Transitions* (Oxford Univ., 2012).
8. M. J. Rozenberg, G. Kotliar, H. Kajueter, G. A. Thomas, D. H. Rapkine, J. M. Honig, P. Metcalf, Optical conductivity in mott-hubbard systems. *Phys. Rev. Lett.* 75, 105–108 (1995).
9. M. J. Rozenberg, G. Kotliar, H. Kajueter, Transfer of spectral weight in spectroscopies of correlated electron systems. *Phys. Rev. B* 54, 8452–8468 (1996).
10. M. Thees, M.-H. Lee, R. L. Bouwmeester, P. H. Rezende-Gonçalves, E. David, A. Zimmers, F. Fortuna, E. Frantzeskakis, N. M. Vargas, Y. Kalcheim Yoav, P. Le Fèvre Patrick, K. Horiba, H. Kumigashira Hiroshi, S. Biermann, J. Trastoy, M. J. Rozenberg, I. K. Schuller, A. F. Santander-Syro, Imaging the itinerant-to-localized transmutation of electrons across the metal-to-insulator transition in V_2O_3 . *Sci. Adv.* 7, eabj1164 (2021)

HAXPES Study of Surface/Interface Effects by Alkali Post Deposition Treatment of (Ag,Cu)(In,Ga)Se₂ Thin Film Solar Cell Absorbers

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ABSTRACT

Cu(In,Ga)Se₂ (CIGS) thin film solar cells have shown high and stable efficiencies for both laboratory cells and industrial modules with record cell efficiencies of 23.4% [1]. To reach closer to the theoretical maximum efficiency of around 30%, further reductions of optical and electrical losses are needed. Recent works show that silver (Ag) alloying in CIGS to form (Ag,Cu)(In,Ga)Se₂ (ACIGS) leads to higher device efficiencies as compared to similar CIGS devices without Ag [2]. More, Ag incorporation increases the band gap, which can be exploited to pave the way for high band gap applications such as tandem solar cells. Further, a postdeposition treatment (PDT) based on alkali metal fluorides [3] after absorber formation has been studied recently and is known to improve the efficiency in CIGS solar cells. The exact role of the silver and/or alkali elements is intensively discussed, but it is clear that interface and grain boundary effects are important in (A)CIGS solar cells. It is likely that a redistribution of the absorber elements near the surface region may occur during the alkali PDT and some works show interface formation in CIGS solar cells subjected to a metal fluoride post deposition treatment [4].

In this work we employed HAXPES at the Galaxies beamline at SOLEIL to study the interface between CdS buffers and PDT-ACIGS absorbers, which have been exposed to different metal fluoride PDT. Two different alkali PDT are compared, RbF and CsF, to investigate how the choice of the metal fluoride treatment affects the buffer/absorber interface. In particular, the chemical and electronic properties of CdS/ACIGS interfaces in terms of intermixing, energy band alignment and composition for a set of device relevant samples have been studied. The results show that the electronic structure at the CdS/ACIGS interface does not change for the different PDTs. However, the ACIGS composition at the near surface region seems to change depending on the applied PDT process. Possible reasons for this will be discussed. The results give insights into how selective alkali PDT could change the ACIGS surface composition, which may influence the solar cell behavior.

REFERENCES

1. M. Nakamura, et al., *IEEE Journal of Photovoltaics* **9**, 1863 (2019).
2. M. Edoff, et al., *IEEE J. Photovoltaics* **7**, 1789 (2017).
3. S. Siebentritt et al., *Adv. Energy Mater.* **10**, 1903752 (2020).
4. E. Handick et al., *ACS Appl. Mater. Interfaces* **9**, 3581 (2017); J. Bombsch et al., *ACS Appl. Mater. Interfaces* **12**, 34941 (2020).

Ultrafast Light-induced Strain and Symmetry Breaking in Ferroic Materials

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ABSTRACT

The understanding of the lattice dynamics in ferroic compounds driven by an ultrashort light pulse is an exciting research direction due to the exceptional non-linear properties (optical, elastic, electric and magnetic) of ferroic and multiferroic materials [1-5]. Photoinduced strain in ferroic materials is driven by a complex interplay between charge, phonon and spin dynamics with microscopic mechanisms that still need to be determined[5-10]. We present recent experiments where ultrafast photoinduced strain is evaluated in BiFeO₃-based multiferroic materials, with a focus on the description of the ultrafast symmetry change of the unit-cell that appears after an ultrashort laser pulse. A combination of optical and X-ray time-resolved techniques enables to clearly demonstrate how the light excitation can lead to a modulation of the symmetry in ferroic materials[11]. By studying two asymmetric Bragg reflections (i.e. $h0l$ and $-h0l$ for instance) of a (001)_c single BiFeO₃ crystal, we show how it is possible to disentangle at the picosecond time scale the light-induced longitudinal and shear strain in the unit cell[11]. Due to a difference between the value of the longitudinal and shear velocities, the strain develops at the picosecond timescale within a two-step mechanism. This temporal evolution of the strain within the unit cell highlights the transient symmetry breaking of the pseudocubic unit cell of BiFeO₃. Moreover, recent experiments carried out at SOLEIL (Cristal beamline) with thin films of multiferroic nanostructures having different ferroelectric domain organizations and different elastic and electrostatic boundary conditions will be presented. In these systems, we discuss the different physical mechanisms at play in the light-induced strain and in the ferroelectric polarization modulation. All these new results provide rich insights for the understanding of the physics of photo-induced strain, in relation with the light-induced ferroelectricity modulation in nanostructured ferroic compounds.

REFERENCES

- [1] H. J. Lee et al, Phys. Rev. X, 11, 031031 (2021)
- [2] E. Collet et al, Science 300 (5619), 612-615 (2003)
- [3] X. Li et al Science 364, 1079-1082 (2019)
- [4] H. Akamatsu et al Phys. Rev. Lett. 120, 096101 (2018)
- [5] M. Lejman et al, Nat. Comm. 7, 1-10 (2016)
- [6] B. Kundys, Appl. Phys. Rev. 2, 011301 (2015).
- [7] P. Ruello, V. Gusev, Ultrasonics, 56, 21-35 (2015).
- [8] C. Paillard et al, Phys. Rev. Lett. 116 (24), 247401 (2016).
- [9] B. Kundys et al, Nat. Mater. 9, 803-805 (2010).
- [10] M. Lejman et al., Nat. Comm. 5, 4301, (2014).
- [11] V. Juvé et al, Phys. Rev. B 102, 220303(R) (2020).

PARALLEL SESSION

Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry)

VISIOCONFERENCE

Thursday, January 20th

Chairpersons:

P. Asselin, A. Tougerti, H. Dossmann, F. Carn

- IT-04 Providing mechanistic insights into the low-temperature oxidation chemistry by Synchrotron-based VUV PEPICO spectroscopy
J. Bourgalais
- OC-10 Inner Valence photoionization of small molecules: From spectrally to temporally resolved MFPADs
J. Joseph
- OC-11 Multi-electron coincidence spectroscopy of the Ar 2p-2 double core hole decay
M. Reinhardt
- OC-12 Post-collision interaction effects in sulfur KLL Auger spectra of thiophene and thiophene-based polymers
N. Velasquez
- IT-05 Synchrotron insights onto the formation of synthetic and biological magnetite nanoparticles
D. Faivre
- OC-13 Pentagonal gold bipyramids self-assemble with long-range triclinic order
C. Doru
- OC-14 Structural evolution of PT nanoparticles during ammonia oxidation
D. Simonne
- OC-15 Innovative chemical imaging speciation methodology for studying the impact of the impregnation and drying of supported CoMoP/ Al₂O₃ HDS catalysts by quick-XAS and Raman spectroscopies
B. Barata

PARALLEL SESSION

Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry)

VISIOCONFERENCE

Friday, January 21st

Chairpersons:

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- IT-06 Microfluidic tools for Synchrotron-based experiments: Applications to chemistry
B. Lasalle
- OC-16 Photoelectron Circular Dichroism as a probe for conformational isomerism in 1-indanol
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- OC-17 MOSARIX: A Von Hamos spectrometer based on highly annealed pyrolytic graphite crystal in the tender X-ray domain
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Mechanistic Insights on the Gas-phase Low-temperature Oxidation Chemistry for Combustion using SVUV PEPICO Spectroscopy

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ABSTRACT

Understanding the auto-ignition chemistry of a fuel-air mixture, especially at low temperature (<1,000K) is mandatory for the design and optimization of low-emission and high-efficiency internal combustion engines. The low temperature oxidation of hydrocarbon fuels is relatively well understood and already implemented in detailed chemical kinetic models. However, quantitative agreement between measurements and simulations is not always achieved because oxidation intermediates, especially structural isomers and conformers are not always unequivocally identified.

In this talk, I will present how synchrotron-based mass-selected photoion photoelectron coincidence spectroscopy (PEPICO) is a suitable analytic tool to decipher isomers. I will take as an example, our recently published work on the low-temperature oxidation of n-pentane, a prototype molecule for gasoline and diesel fuels. I will show how the use of the PEPICO technique at the SOLEIL synchrotron allowed to solve the discrepancies in the literature on the quantification of ketohydroperoxides. Those intermediates play a central role in oxidation chemistry by triggering autoignition in internal combustion engines.

Inner Valence Photoionization of Small Molecules: From Spectrally To Temporally Resolved MFPADs

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ABSTRACT

Studies on angular distribution of photoelectrons in molecular frame (MFPADs) significantly advanced the investigation of photoionization (PI) dynamics of diatomic molecules. These observables provide magnitudes and phases of the partial wave dipole matrix elements (DMEs), leading to a complete description of photoionization [1]. In the complex inner valence region they provide in particular new insight into the PI dynamics of highly excited ionic states involving shape resonances, Rydberg progressions and autoionizing states. In our work, using PLEIADES and DESIRS beamlines of Synchrotron SOLEIL, we take advantage of electron-ion 3D momentum spectroscopy to investigate dissociative photoionization (DPI) of molecules such as N₂, CO, NO, N₂O covering a photon energy range of 25 eV to 60 eV.

The complete PI experiments performed using circularly polarized light at SOLEIL, operated in a few bunch mode, address three main aspects. Firstly, the spectrally resolved experiments add to the existing spectroscopic knowledge of the inner valence region and provide crucial references for future temporally resolved experiments involving XUV attosecond pulses, as scheduled on the FAB-10 beamline at ATTOLAB [2]. In the reported experiment on N₂, various DPI processes are identified by the binding energy of the ionic states and their dissociation limits, and characterized by their MFPADs [3,4]. Secondly, the energy dependence of the measured MFPADs and subsequent DMEs provide information on PI dynamics of ionic states involving shape resonances. For DPI of N₂, these observables are reported for the two dominant DPI processes, corresponding to PI into the $F^2\Sigma_g^+$ state and H band. Their comparison to those calculated by Pr. R. R. Lucchese using MCSCF calculations deepens the understanding of the $2\sigma_g \rightarrow \sigma_u$ shape resonance in N₂. Thirdly, we discuss the conditions to determine MF angle resolved emission times delays in molecular photoionization from such spectrally resolved experiments. For the $4\sigma \rightarrow \sigma^*$ shape resonance in NO, experimental ionization delays after XUV ionization are obtained from the MFPADs and the corresponding DMEs measured at a series of well-resolved photon energies, selecting one common reference phase [5]. The angular dependence of emission delays (in a few hundreds of as) is interpreted in the frame of a multichannel Fano model.

REFERENCES

1. Dill, D. 1976 J Chem Phys 65, 1130–1133; Lucchese, R. R. & Dowek, D. 2014 Attosecond and XUV Physics, 293–320
2. J Joseph et al 2020 J. Phys. B: At. Mol. Opt. Phys. 53 184007
3. Baltzer et al 1992 Phys Rev A 46, 5545; Aoto et al 2006 J Chem Phys 124, 234306
4. Hikosaka, Y. & Eland, J. 2000 J. Phys. B: At. Mol. Opt. Phys. 33, 3137; Motoki S et al 2002 J. Phys. B: At. Mol. Opt. Phys 35, 3801
5. Holzmeier et al 2021 [arXiv:2107.09915v2](https://arxiv.org/abs/2107.09915v2) (in press)

Multi-electron Coincidence Spectroscopy of the Ar $2p^{-2}$ Double Core Hole Decay

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ABSTRACT

The full set of decay pathways of Argon $2p^{-2}$ double core hole states has been investigated using a magnetic bottle type spectrometer, of the kind developed by John Eland *et al* [1], coupled with an ion time-of-flight spectrometer. This experiment allows efficient multi-electron / ion coincidence measurements. It has been performed at the GALAXIES [2] beamline at SOLEIL.

Recently, double core holes have been largely studied by populating them by single photon double ionization at synchrotron centers. These are difficult experiments due to the very low cross sections of this process. A more efficient alternative method exists when it is possible to populate double core hole states by the decay of a deeper inner shell hole. This is the case for L-shell double core holes, which are the dominant products after 1s ionization and decay. The Ar $2p^{-2}$ double core hole states are for instance dominantly populated by decay of the Ar 1s core hole (with a probability of 46.3%, see Guillemin *et al* [3]).

Both electron- and ion-filtering have been used here. This made it possible to follow the Auger cascade step-by-step in detail. The Ar³⁺ intermediate and Ar⁴⁺ final stages of the dominant decay pathway leading to Ar⁴⁺ final states have been observed. The resulting experimental binding energies are compared to theoretical *ab initio* calculations, revealing the precise states involved in the transitions. The agreement with theory is very good.

The weak L²₂₃-M³ auger transition (simultaneous filling of the two L-shell holes, with emission of one M-shell electron) leading to Ar³⁺ final states has been observed at 458.5 eV kinetic energy. We measured a branching ratio of $1.9 \cdot 10^{-3}$ in comparison to the total decay of the $2p^{-2}$ double core vacancy, which agrees very well to previous work by Žitnik *et al* [4].

Furthermore, the remaining decay paths of the Ar 1s⁻¹ core hole and their respective contributions to the total yield have been analyzed and compared to theory to very good agreement.

REFERENCES

1. J. H. D. Eland, O. Vieuxmaire, T. Kinugawa, P. Lablanquie, R. I. Hall, and F. Penent, *Phys. Rev. Lett.* **90**, 053003 (2003).
2. 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**, 175-179 (2015).
3. R. Guillemin, K. Jänkälä, B. Cunha de Miranda, T. Marin, L. Journel, T. Marchenko, O. Travnikova, G. Goldsztejn, I. Ismail, R. Püttner, D. Céolin, B. Lassalle-Kaiser, M. N. Piancastelli, and M. Simon, *Phys. Rev. A* **97**, 013418 (2018).
4. M. Žitnik, R. Püttner, G. Goldsztejn, K. Bučar, M. Kavčič, A. Mihelič, T. Marchenko, R. Guillemin, L. Journel, O. Travnikova, D. Céolin, M. N. Piancastelli, and M. Simon, *Phys. Rev. A* **93**, 021401 (2016).

Post-collision Interaction Effects in Sulfur KLL Auger Spectra of Thiophene and Thiophene-based Polymers

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ABSTRACT

Electronic correlations in inner-shell ionized molecules can be probed via Auger spectroscopy. After high-energy photons ionize the atomic core shell close to the ionization threshold, a slow photoelectron leaves the atom, not without interacting with the ionic field. Decay may take place via emission of an Auger electron, with which the photoelectron may interact. This Coulombic interaction between the three parties is known as post-collision interaction (PCI). From a classical perspective PCI occurs due to an energy exchange between the ejected Auger electron, photoelectron and the remaining ion. PCI visibly affects photoelectron and Auger spectra in two ways: the energy distribution represented by the lineshape, becomes distorted, and the position of the lines in the energy spectrum may shift considerably¹. PCI has been extensively studied in gaseous systems, such as argon² and carbonyl sulfide³. However, little is known on the manifestation of PCI in solid systems. Using the HAXPES experimental end-station at the GALAXIES beamline of the SOLEIL French synchrotron facility⁴, we measured high-resolution KLL Auger spectra at photon energies between 0 and 200 eV above the sulfur 1s ionization threshold of: 1) thiophene, an aromatic molecule in the gas phase, 2) polythiophene, a thiophene-based π -conjugated polymer, powder mixed with graphite, and 3) P3HT, another thiophenic polymer, prepared as a film. A stronger PCI shift was observed in polythiophene and P3HT compared to thiophene, which can be potentially interpreted in terms of screening of the photoelectron field in the solids, by taking into account the electric permittivity of the respective polymer, and the hindering of the photoelectron propagation within the polymer media, leading to loss of kinetic energy.

REFERENCES

1. M. Yu. Kuchiev, S. Sheinerman, *Sov. Phys. Usp.* **32**, 569 (1989).
2. R. Guillemin, S. Sheinerman, R. Püttner, T. Marchenko, G. Goldsztejn, L. Journal, R. K. Kushawaha, D. Céolin, M. N. Piancastelli, and M. Simon, *Phys. Rev. A* **92**, 012503 (2015).
3. C. Bomme, R. Guillemin, S. Sheinerman, T. Marin, L. Journal, T. Marchenko, R. K. Kushawaha, N. Trcera, M. N. Piancastelli, and M. Simon, *J. Phys. B: At. Mol. Opt. Phys.* **46**, 215101 (2013).
4. D. Céolin, J. M. Ablett, D. Prieur, T. Moreno, J.-P. Rueff, T. Marchenko, L. Journal, R. Guillemin, B. Pilette, T. Marin, and M. Simon, *J. Electron Spectrosc. Relat. Phenom.* **190**, 188 (2013).

Synchrotron Insights onto the Formation of Synthetic and Biological Magnetite Nanoparticles

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ABSTRACT

Magnetite is a ubiquitous minerals formed in varying environmental settings that can also be simply synthesized in the lab. Magnetite nanoparticles have a variety of applications. The particles formed by magnetotactic bacteria are particularly interesting because they exhibit controlled dimensions and morphologies. The microorganisms produce chains of stable single domain magnetite nanoparticles via a transient protein-stabilized ferric (oxyhydr)oxide directing crystal growth as shown by X-ray absorption spectroscopy (XAS).[1] We used recent advancements in synchrotron light to study the process at the single cell level. We demonstrate that scanning X-ray fluorescence microscopy (SXFEM) and nanoscale X-ray absorption near-edge structure (nano-XANES) mapping can spatially and chemically identify intracellular iron species.[2]

Inspired by the biomineralization process, we developed a synthetic route to produce magnetite nanoparticles in the presence of a polypeptide. *In situ* small-angle x-ray scattering in combination with *ex situ* cryogenic XAS enables us to present a comprehensive mechanism of the formation of magnetite in the presence of the additive where wettability of magnetite is key to guide growth via amorphous ferrihydrite precursor.[3] This mechanism can be compared to the one we determined for the case without additive. Using *in situ* X-ray scattering, we indeed showed that nucleation propagates at the nanometer scale within amorphous precursors [4]. We find that the self-confinement by an amorphous precursor slows down crystal growth by two orders of magnitude once the crystal size reaches the amorphous particle size (c.a. 3 nm).

Accordingly, magnetite formation at low temperature involves poorly crystalline intermediates that play a central role in the process.

REFERENCES

- [1] J. Baumgartner et al., *PNAS* **2013**, 110, 14883-14888
- [2] D. Chevrier et al., *Small Science*, in press.
- [3] L. Kuhrts et al., *Journal of American Chemical Society* **2021**, 143 (29), 10963-10969
- [4] J. Baumgartner. et al., *Nano Lett.* **2020**, 20 (7), 5001–5007.

Pentagonal gold bipyramids self-assemble with long-range triclinic order

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ABSTRACT

The packing of solid bodies is one of the oldest problems in the natural sciences. Among the various shapes, spindles (elongated objects with two sharp tips) yield a surprising variety of arrangements, depending on their cross-section. We elucidate for the first time the three-dimensional stacking of spindle-shaped objects, experimentally and via simulations, by focusing on bipyramids of regular polygonal base with n sides. For $n=5$ the crystal symmetry is triclinic, with lower symmetry than the building blocks of the structure and with two particles per unit cell. Further simulations confirm that these features are present for other odd n values: they can be attributed to the non-centrosymmetric shape of the particles. Surprisingly, this symmetry reduction is accompanied by a lower packing fraction than in the even n case [1].

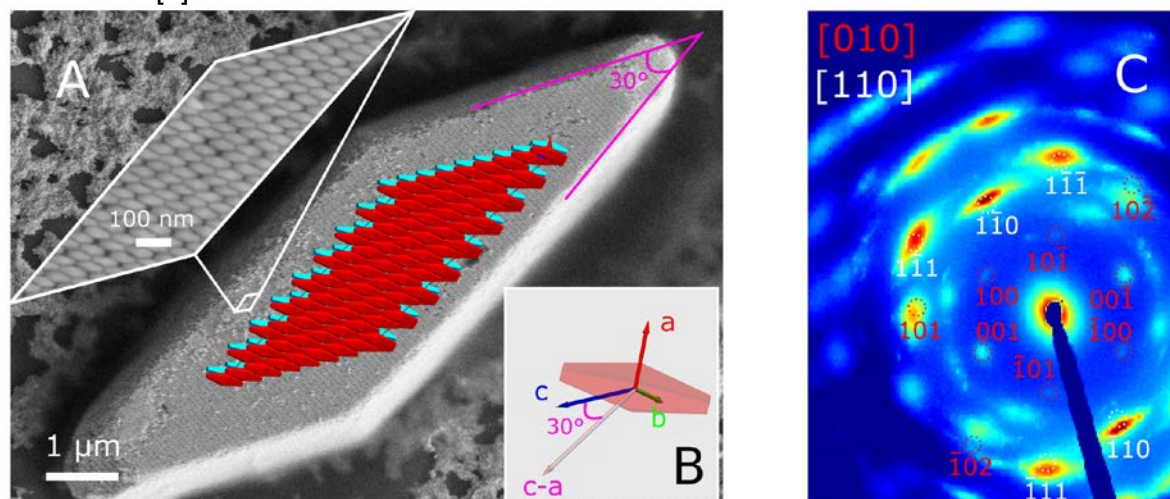


Figure: A) SEM image of one supercrystal, with superimposed model (the unit cell contains one red and one blue particle, rotated by $2\pi/5$ with respect to each other). Inset: magnified image of the supercrystal surface. B) Unit cell of the model oriented along the c and $c-a$ vectors of the triclinic lattice. C) 2D SAXS image (in log intensity scale). The Miller indices corresponding to the triclinic lattice are indicated on some Bragg spots. Two colors (red and white) are used for the indexing of two supercrystals with different orientation defined by the corresponding zone axis [UVW].

REFERENCES

1. J. Lyu, W. Chaabani, E. Modin, A. Chuvilin, T. Bizien, F. Smallenburg, M. Impéror-Clerc, D. Constantin and C. Hamon, in preparation.

Structural Evolution of Pt Nanoparticles During Ammonia Oxidation

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ABSTRACT

We aim at investigating in situ and operando the catalytic structure-activity relationships to optimise nanoparticle catalysts. We focus on the ammonia (NH₃) oxidation of Pt nanoparticles.

The gas flow reactor (XCAT) at the SIXS beamline allows us to perform near ambient pressure measurements under variant gas flows. A graphite layer below the sample's surface is used as a heater by tuning the input current. The multi-environment diffractometer (MED), has recently been updated for Coherent Diffraction Imaging (CDI) via a new set of coherence optics.

On one hand, we explore the surface evolution of the ensemble of Pt nanoparticles using surface X-ray diffraction (SXRD), allowing us to extract information about the surface structure. The analysis of Crystal Truncation Rods (CTRs) and low incident angle reflectivity for different gas conditions and temperature allows one to have a precise idea of the evolution of the surface (roughness, thickness, density, formation of new layers). Reciprocal space maps are collected simultaneously and then projected onto a plane perpendicular to the nanoparticle facets for details about each facet's evolution.

On the other hand we perform in-situ and operando Bragg Coherent Diffraction Imaging (BCDI) measurements of isolated Pt nanoparticles during the oxidation of Ammonia, for the same gas and temperature conditions. By following the evolution of multiple parameters in 3D (size, strain, shape, re-faceting) of the reconstructed nanoparticle, we gain important insight into the structure dependence of the catalytic properties of the nanoparticle which provides information on the catalytically active facets and on the deactivation process of the particles.

During both experiments, the evolution of the reaction is followed by mass spectroscopy with a direct link from the chamber to a residual gas analyser (RGA), allowing us to connect the dynamical structural changes of Pt nanoparticles to the catalyst activity.

REFERENCES

- [1] Resta, A. *et al.* 2020) Ammonia Oxidation over a Pt₂₅Rh₇₅(001) Model Catalyst Surface: An Operando Study. *Journal of Physical Chemistry C*
- [2] Li, N. *et al.* (2020) Continuous scanning for Bragg coherent X-ray imaging. *Scientific Reports*
- [3] Wang, H. *et al.* 2016) Direct and continuous strain control of catalysts with tunable battery electrode materials. *Science*
- [4] Kim, Y. *et al.* 2021) Single Alloy Nanoparticle X-Ray Imaging during a Catalytic Reaction.

Innovative Chemical Imaging Speciation Methodology for Studying the Impact of the Impregnation and Drying of Supported CoMoP/Al₂O₃ HDS Catalysts by Quick-XAS and Raman Spectroscopies

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The controlled dispersion of phosphorus-based molybdenum heteropolyanions (P-HPAs) on alumina support at the expense of polymolybdates is highly demanded since they result upon sulfidation to a higher HDS catalytic activity¹. Despite the recent progress in Raman and NMR imaging techniques², which both reveal the heterogeneous distribution of oxidic species on alumina extrudates, the identification and quantification of those species remain a major challenge.

In this presentation, we will present results gained at the ROCK beamline during the *in situ* monitoring by Full Field (FF) XAS imaging of the impregnation of a 1.5 to 1.7 mm thick alumina extrudate with a solution of metallic precursors and phosphorus, followed by *in situ* drying using two specially designed cells. The FF XAS imaging methodology developed consists in the recording of space-energy resolved 3D data cubes using a pixelated ORCA Flash 4.0 V3 CMOS camera³. Each data cube consists typically of 580 absorption images recorded between 19800 and 21200 eV, leading roughly to one image every 2-2.5 eV. The first steps after data extraction comprise binning of pixels in order to improve the signal-to-noise (S/N) ratio and extraction of the edge jump, which are performed stepwise in a single cube of data. The typical pixel size enabled using the camera equipped with a X4 magnification objective is 1.625 μm. The methodology developed includes adjusting the spectra normalization parameters, resulting in the absorption map (**Fig. 1a**), followed by binning, 30x30 pixels in this case (**Fig. 1b**), which ensures that the signal is well resolved and with acceptable S/N ratio for the post treatment. The recording time for the space-energy resolved 3D data cube is \approx 5.5 s leading to hundreds of cubes of spectra to be handled during the 3-hours impregnation and subsequent 2h-drying monitoring. Using Jupyter notebooks, the binning and normalization parameters chosen for a cube can be massively applied to all the cubes measured in an experiment. The next post-processing regards the EXAFS extraction for each pixel of the binned image and their subsequent linear combination fitting (LCF), using a library of EXAFS spectra of bulk references⁴ providing for the first time a quantification of Mo-based species dispersed on the support (**Fig. 1c**), given in relative fraction of spectrum. The replication of this methodology of analysis over the time of acquisition of *in situ* experiments provides valuable spatial and time-resolved information on the complex physico-chemical phenomena and enables to establish a relationship between speciation and preparation parameters, as precursor solution and support compositions. This is complemented with Raman hyperspectral imaging of the dried extrudates, which results in qualitative mapping of the location of the P-HPAs (**Fig. 1d**).

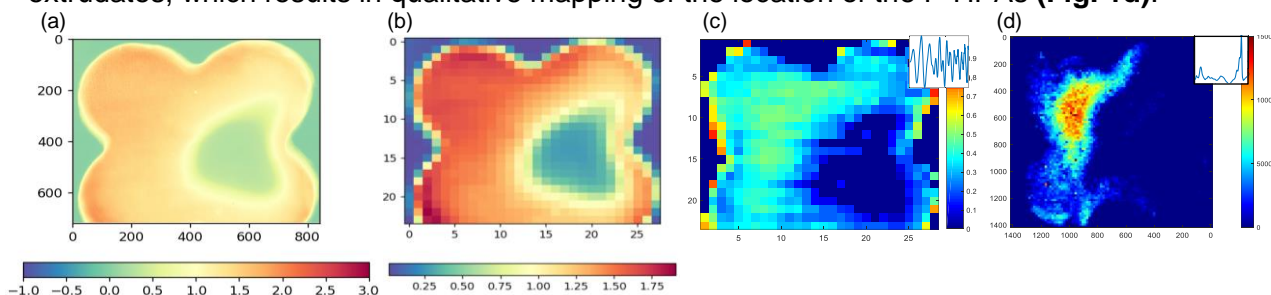


Figure 1: (a) Absorption map after normalization and (b) absorption map after normalization and binning of a dried extrudate of CoMoP/Al₂O₃ at 8 wt.% MoO₃, Co/Mo 0.4, P/Mo 0.56, (c) result of LCF analysis as a mapping of the relative fraction of lacunar Keggin's HPA with a 49x49 μm resolution, (d) Raman hyperspectral imaging of the same HPA with a 16x16 μm resolution.

(1) Frizi, N. et al. Catal. Today 130 (2008), (2) Catita, L. et al. A. Catal. A 547 (2017) 164-175, (3) La Fontaine, C. et al. Synch. Rad. News 33(1) 20-25 (2020), (4) Lesage, C. PhD Thesis (2019)

Microfluidic Tools for Synchrotron-based Experiments: Applications to Chemistry

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ABSTRACT

Microfluidics is a rapidly evolving field, mostly driven by biomedical and life science applications. The existence of physical phenomena specific to the micron scale (laminar flow, interface/bulk ratio) allows manipulating small amounts of liquids with high precision. The combination of synchrotron techniques with microfluidic devices can provide useful tools to understand the behavior of microfluidic systems, but also to deliver samples before an X-ray beam, under very specific conditions. Although life sciences are the first to benefit from the coupling of microfluidics with synchrotron techniques, chemical sciences can also take advantage from it. I will show in this presentation a few examples where microfluidic systems can be helpful to understand a chemical problem.

Photoelectron Circular Dichroism as a Probe for Conformational Isomerism In 1-indanol

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ABSTRACT

Photoelectron circular dichroism (PECD) consists in a forward/backward asymmetry with respect to the light propagation axis in the photoelectron angular distribution after ionization of a chiral molecule by a circularly polarized light. PECD has shown a strong sensitivity to molecular conformations.¹ This is the reason why we applied this technique to a chiral flexible molecule: 1-indanol. Indeed, this molecule exists in one or two conformers in a supersonic beam, depending on the nature of the carrier gas (Figure 1).²

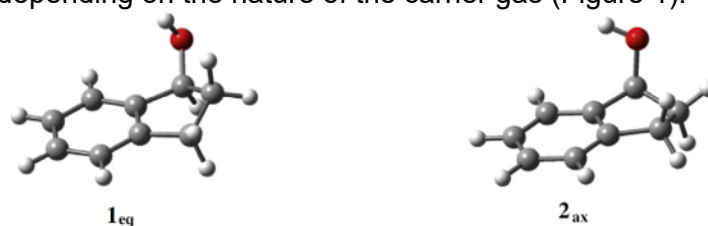


Figure 1 : Conformations of the jet-cooled 1-indanol in argon (1_{eq}) and in helium (1_{eq} and 2_{ax})

Photoelectron spectra (PES) and PECD spectra of jet-cooled (S)-1-indanol and (R)-1-indanol were recorded in helium and argon at several photon energies on the DESIRS beamline at the SOLEIL Synchrotron. The PECD spectra exhibit a very good mirroring between the two enantiomers of 1-indanol in both carrier gases and show differences when changing the carrier gas (Figure 2) that we attribute to a clear conformational change.

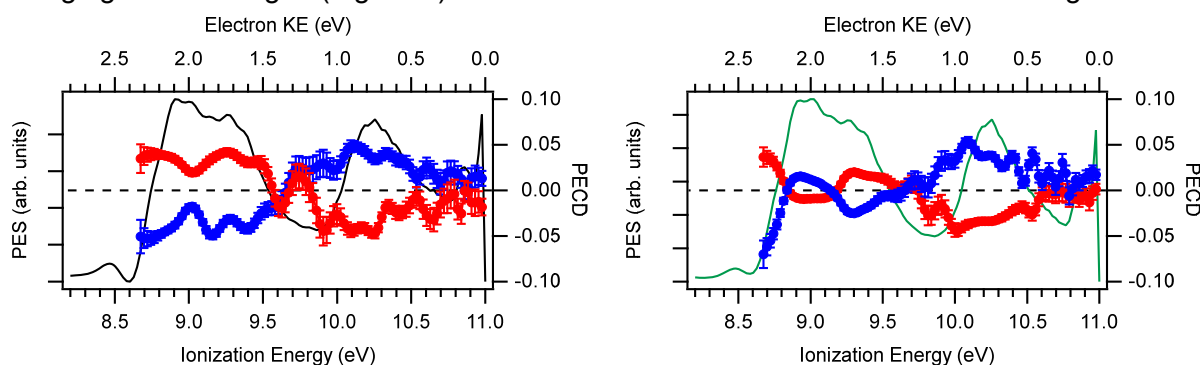


Figure 2: Photoelectron (left scale) and PECD (right scale) for (S)-1-indanol (red) and (R)-1-indanol (blue) in Ar (left) and in He (right), at $h\nu = 11.0$ eV

REFERENCES

1. R. Hadidi, D. K. Božanić, H. Ganjitarbar, G. A. Garcia, I. Powis, and L. Nahon, *Communications Chemistry* **4**, 72 (2021).
2. A. Bouchet, J. Altnöder, M. Broquier, A. Zehnacker, *Journal of Molecular Structure* **2014**, 1076, 344–351

MOSARIX: A Von Hamos spectrometer based on Highly Annealed Pyrolytic Graphite crystal in the tender x-ray domain

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ABSTRACT

MOSARIX is a collaborative project between three research group in Sorbonne University to build an x-ray spectrometer (2-5 keV) portable to large scale facilities with high efficiency and good resolution. X-ray spectroscopy and coincidences experiment are planned. A prototype with a single Highly Annealed Pyrolytic Graphite (HAPG) crystal with von Hamos geometry has been tested (resolution and efficiency). A spectral resolution $E/\Delta E=4000$ was achieved by recording the elastic peak of photons issued from the GALAXIES-SOLEIL synchrotron beamline.

We plan to build the spectrometer with 9 HADP crystals under Helium atmosphere using a TimePix3 or a CCD camera.

REFERENCES

1. Iyas ISMAIL, et al. A von Hamos spectrometer based on HAPG crystal in tender x-rays domain, submitted RSI
2. Iyas ISMAIL, Marc SIMON, Francis PENENT, MOSARIX: Progress Report, hal- 02504347
3. Iyas ISMAIL, et al. Review of Scientific Instruments 89, 113101 (2018)

Preliminary Study on Migration of Halide Ions in Metal Halide Perovskite induced by Electrical Field based on Nano X-ray Fluorescence

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ABSTRACT

Organic inorganic halide perovskite solar cells (PSCs) have attracted a lot of attention because of their excellent optoelectronic properties. Their power conversion efficiency has reached 25.5 % within around ten years [1]–[4]. However, they show degradation of their performance under operational conditions (light, bias, environmental stress, etc.) [5], [6]. Among several degradation mechanisms caused by various operating conditions, the degradation mechanism induced by the electrical field in operation conditions is required to be elucidated to increase their long-term stability. Characterizations that provide nano- and microscale details concerning the chemical and electronic factors are required to understand the detailed mechanism.

Synchrotron-based characterizations have recently been used to strengthen our understanding of the structural properties of halide perovskites and the dynamics of halide perovskite solar cells. Because of highly collimated monochromatic x-rays produced by synchrotron radiation, chemical and physical information at high resolution can be achieved [7]. In this study, we observed degradation with halide ion migration caused by applied electrical field (ex-situ) using nano-X-ray fluorescence (n-XRF). n-XRF has a high sensitivity of chemical components, including lead and iodine, and it provides spatially resolved spectra at the nanoscale.

Here, we prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3), one of the representative organic inorganic halide perovskites, film on custom fabricated biasing electrode chips. We applied 2.5 V to the halide perovskite film for 30 minutes and 60 minutes (ex-situ) and obtained n-XRF. With increase in time of applied electrical biasing, the fluorescence intensity of iodine on the left electrode gradually decreases. It indicates that iodine ions move from cathode (left electrode) to anode (right electrode) under electrical field. In addition to these studies, we have also investigated the effect of X-ray radiation damage, which will also be presented.

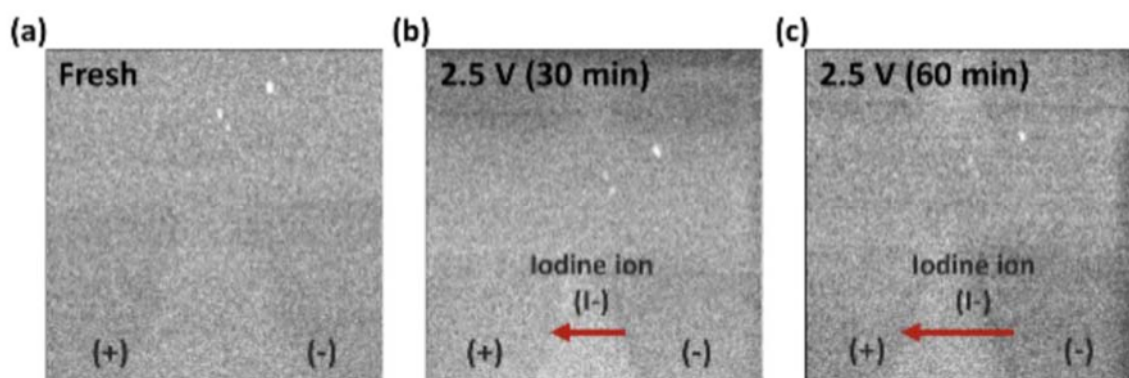


Figure 1 Iodine n-XRF map of (a) fresh MAPbI_3 , images acquired after biasing for (b) 30 minutes and (c) 60 min. [Images have the same intensity scale]

REFERENCES

- [1] N. G. Park *et al.*, *MRS Bull.*, 43, 7, 527–533 (2018).
- [2] M. A. Green *et al.*, *Nat. Photonics*, 8, 7, 506–514 (2014).
- [3] J. Chen *et al.*, *J. Mater. Chem. C*, 4, 1, 11–27 (2015).
- [4] "NREL efficiency chart." [Online]. Available: <https://www.nrel.gov/pv/cell-efficiency.html>.
- [5] F. El-Mellouhi *et al.*, 9, 18, 2648–2655 (2016).
- [6] Y. Wang *et al.*, *Science*, 365, 6454, 687–691 (2019).
- [7] S. Rahimabadi *et al.*, *X-Ray Spectrometry*, 49, 348–373 (2020).

PARALLEL SESSION

Life & Earth Sciences
(Biology / Health & Environment / Geoscience)

VISIOCONFERENCE

Thursday, January 20th

Chairpersons:

B. Masquida, Y. Gohon and R. Marsac

- IT-07 Allosteric modulators of force production: Towards precision medicine for different classes of heart diseases
A. Houdusse
- IT-08 HELIOBIO group
F. Jamme
- OC-19 Structural insights into RNA-mediated transcription regulation in bacteria
A. Weixlbaumer
- IT-09 Spatial distribution and speciation of REE in soils and REE accumulating ferns
E. Montarges-Pelletier
- OC-20 Probing the stoichiometry of Fe₃₋₅O₄ nanoparticles by soft XAS and XMCD
F. Choueikani
- OC-21 Microfluidic production of nanomedecins with in operando SAXS structural investigation of lipid nano-emulsions formulation. Presentation of the galenic on-chip concept
G. Brotons
- OC-22 Dynamics and structural changes of calmodulin upon interactions with its potent antagonist calmidazolium
C. Leger

PARALLEL SESSION

Life & Earth Sciences
(Biology / Health & Environment / Geoscience)

CENTRALE-SUPELEC-GIF-SUR-YVETTE - MICHELIN AUDITORIUM #1

Friday, January 21st

Chairpersons:

B. Masquida, Y. Gohon and R. Marsac

- | | |
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| IT-10 | From moss to sequoia, X-rays reveal the metastability of sap transport under tension S. Delzon |
| OC-22 | Deep investigation of specificities and behaviours of flax fibers and stems through different SOLEIL beamlines A. Bourmaud |
| OC-23 | A N7-methyltransferase hidden in the dark proteome of newly discovered nidovirus. Structure, function and evolutionary implications F. Ferron |
| OC-24 | Structural insights onto the ribosome from the human pathogen <i>C. albicans</i> O. Kolosova |

Allosteric Modulators of Force Production: Towards Precision Medicine for Different Classes of Heart Diseases

A. Houdusse

UMR-144 CNRS, Curie Institute, Paris, France.

ABSTRACT

Hypertrophic and dilated cardiomyopathies are highly prevalent cardiac diseases. They result from distinct single-point mutations in sarcomeric proteins that lead to muscle dysfunction. Most of the current treatments for end-stage cardiomyopathies such as heart transplantation or implantable-cardioverter are highly invasive. Recently, a new approach using small-molecules able to modulate myosin force production has been proposed to treat cardiac disease. Some of these small molecules such as the activator Omecamtiv mecarbil (OM) and the inhibitor Mavacamten (Mava) are currently in late phase 3 clinical trials. Aficamtem is another specific cardiac myosin inhibitor currently in phase 2 clinical trials, while MPH-220 is specific for skeletal muscle myosin. In this study, we used a combination of X-ray crystallography and molecular dynamics in order to decipher the specificity and the mechanism of action of these drug candidates. Our results describe the binding pocket of these drugs and highlight the basis of their specificity. The comparative study of the mode of action of an activator and an inhibitor of Pi release in cardiac myosin provides the blueprint for allosteric modulation of force production by a myosin, but also opens the road to the design of new treatments.

HELIOBIO Group

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ABSTRACT

Synchrotron radiation enables measurements across a wide variety of length and time scales whilst exploiting different probing energies to provide chemical specificity. An upgrade of SOLEIL synchrotron will encourage the emergence of methods to study biological molecules at high spatial and temporal resolution and at physiological temperatures.

The combined expertise of the life sciences beamline teams at SOLEIL forms the HELIOBIO Group. The HELIOBIO Group has been very active in adopting a multidisciplinary and integrated approach. However, the success of a multidisciplinary approach depends critically on the strength of partnerships with other laboratories and the level to which common objectives can be defined.

The HELIOBIO Group will be presented and his approach towards an integrated integrative biology at SOLEIL synchrotron.

This work is presented on behalf of the members of the HelioBio scientific section at SOLEIL (<https://www.synchrotron-soleil.fr/en/research/house-research/biology-health-heliobio>).

Structural Insights into RNA-mediated Transcription Regulation in Bacteria

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ABSTRACT

Cis-regulatory RNA elements exert control over their own transcription from DNA. For example, intrinsic terminators encode structured RNA elements, which trigger transcription termination in bacteria. In contrast, the *cis*-regulatory RNA *putL* suppresses RNA polymerase (RNAP) responses to pause and termination signals without auxiliary proteins. Here we present cryo-EM reconstructions of co-transcriptionally assembled complexes of *E. coli* RNAP and *putL* variants halted at pause and intrinsic termination sites. The reconstructions suggest how *putL* suppresses transcriptional pausing and highlight inactive RNAP states before and after RNA release during termination. When RNAP transcribes a U-rich sequence, its interactions with DNA and the RNA-DNA hybrid are destabilized before transcript release. We describe how an RNA transcript regulates its own synthesis and provide the framework to understand RNA-mediated transcription termination.

Spatial Distribution and Speciation of REE in Soils and REE Accumulating Ferns

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ABSTRACT

The rare earth elements (REEs) are strategic metals strongly involved in low-carbon energy conversion but are also emerging contaminant due to their spreading in soils and surface waters. In industrial materials, REEs come at 90% from South China ion-adsorption deposits, from which they are recovered by heap leaching. Such large-scale process produces not-reclaimed tailings. In that context, evidencing REE-bearing phases is critical for predicting REE dynamics in these materials and designing a successful sustainable reclamation strategy, phyto-stabilization being currently tested. Furthermore, as pivotal elements toward REE transfer to the trophic chain and potential remediation tools, studying REE accumulating plants are of high concern in this context of large-scale remediation.

To investigate REEs in soils (tailings with and without phyto-stabilization). X-ray fluorescence and X-ray absorption analyses were performed at SOLEIL (LUCIA), targeting the most concentrated REEs, i.e., La, Ce and Nd. XAS data at REE L-edge allowed us to detect very low quantities of REEs that were not detectable in global fluorescence spectra. The combination of micro-spectroscopy and fluorescence mapping was crucial and powerful to detect low levels of REEs in this heterogeneous material, evidencing the co-localization of REEs with iron (hydr)oxide; and in reclaimed samples the presence of REEs in roots.

In order to evidence REE storage in accumulating ferns, different specimen were exposed to a mixture six different REEs (La, Ce, Gd, Sm, Y and Yb). microXRF experiments were performed on two imaging beamlines, P06 (PETRA, Hambourg), LUCIA beamline (SOLEIL). Experiments at PETRA provided high resolution element mapping from fresh and hydrated samples, completed with micro-analyses on frozen-hydrated thin sections on LUCIA. We could decipher the REE storage sites of the light REE-accumulating fern *Dryopteris erythrosora*. Comparing the REE distribution in the green and necrotic parts of the frond sheds light over the differential mobility between LREEs and HREEs and shows that necrotized areas are not REE-accumulating sites. Also, the absence of cell-to-cell mobility of REEs in the gametophyte suggests the absence of REE compatible transporters in photosynthetic tissues.

The two studies finally illustrate the benefits of synchrotron-based techniques for the study of REE distribution and speciation in biological or non-biological matrices.

Probing the Stoichiometry of $\text{Fe}_{3-d}\text{O}_4$ Nanoparticles by Soft XAS and XMCD

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ABSTRACT

For several years now, magnetite (Fe_3O_4) nanoparticles are well known by their spinel structure with a specific coordination of iron cation Fe^{2+} and Fe^{3+} . They have aroused great interest due to their many synthesis method, large reactive surface area, good inherent magnetism, and redox properties¹. Thus, they have been used in various domains going from medicine² to magnetic storage as well as environment³. However, the control of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (in other words the stoichiometry) is very important factors in order to control the reactivity on the nanoparticles surface and then the adsorption capacity of organic compounds, the sorption and redox speciation of inorganic contaminants.

Thanks to their chemical selectivity and valence state sensitivity, X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) are unique tools to separately probe the electronic properties of the 3d transition element Fe. They allow to determine the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio but also to distinguish the tetrahedral (Td) and octahedral (Oh) iron and their oxidation state in magnetic compounds⁴.

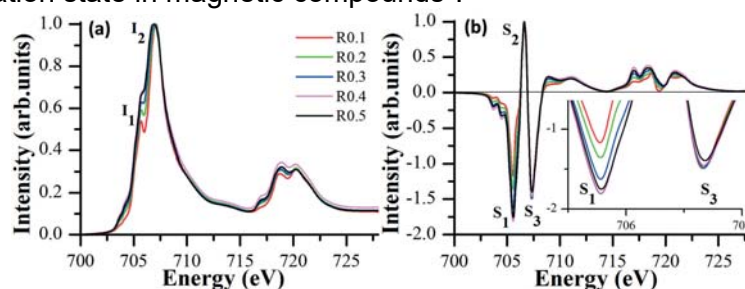


Figure: The evolution of the XAS (a) and XMCD (b) signature versus the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio S.

In this framework, we propose a complete investigation of the valence state and the structure (Oh vs Td) for 10 nm sized nanoparticles that prepared via coprecipitation method. The effect of the stoichiometry (intermediate state between magnetite and maghemite), the redox conditions and the dissolved Fe^{2+} are studied. The magnitude of the XMCD signature is correlated to the stoichiometry that give a full calibration curve⁵.

REFERENCES

1. M. Usman, et al. Chem. Rev., 2018, 118, 3251–3304
2. C. Li, Nat. Mater., 2014, 13, 110–115
3. P. V. Nidheesh, RSC Adv., 2015, 5, 40552–40577; P. Xu et al., Sci. Total Environ., 2012, 424, 1–10.
4. P. Ohresser, Rev. Sci. Instrum., 2014, 85, 013106; N. Daffé et al., J. Magn. Magn. Mater., 2018, 460, 243–252
5. Ph. Jungcharoen et al. Environ. Sci.: Nano, 2021, 8, 2098

Microfluidic Production of Nanomedecines with *in-operando* SAXS Structural Investigation of Lipid Nano-Emulsions formulation. Presentation of the Galenic-on-chip Concept

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ABSTRACT

Continuous production of drug delivery systems (DDS) assisted by microfluidics has drawn a growing interest because of the high reproducibility, low batch-to-batch variation of formulations, narrow and controlled particle size distribution and scale-up facilities induced by this process. Besides, microfluidics offers opportunities for high throughput screening of process parameters and the implementation of Process Analytical Technologies (PAT) as close to the product.

In this context, we propose to spotlight the GALECHIP concept [1] through the development of an instrumented microfluidic pilot considered as a **Galenic Lab-on-Chip** to formulate nanomedicines, such as Lipid Nano-Emulsions (LNE), under controlled process conditions which are essential to obtain DDS with controlled sizes and properties.

With this microfluidic pilot, we conducted:

(i) an *in operando* Small Angle X-ray Scattering (SAXS) investigation along the microfluidic channels in order to understand the physicochemical and hydrodynamical mechanisms involved in the formation of well controlled LNEs (25, 50 and 100nm in size). Starting at the mixing point of pure water and non-ionic surfactants in a pharmaceutical oil, we studied the phase inversion process that occurs during the Lipid Nano Emulsion formation and the DDS maturation pathway. The mapping of the SAXS signal from the chip in continuous production, was obtained with sufficient time and spatial resolution, by combining a tailored silicon/glass chip, high speed SAXS “fly-scans” and the use of X-ray Compound Refractive Lenses.

(ii) a technological development of affordable 3D printed plastic microfluidic chips (PEEK & ABS) in order to encourage the use of such formulation platforms at low costs; and

(iii) the application to the formulation in sterile production of loaded-LNE for medical treatments involving hydrophobic drugs.

REFERENCES

1. Nicolas Rolley, Marie Bonnin, Guillaume Lefevbre, Sylvain Verron, Sylvester Bargiel, Laurent Robert, Jérémie Riou, Carl Simonsson, Thomas Bizien, Jean-Christophe Gimel, Jean-Pierre Benoit, Guillaume Brotons* and Brice Calvignac *, *Nanoscale*, 13, 11899-11912 (2021), DOI <https://doi.org/10.1039/D1NR00879J>

Dynamics and Structural Changes of Calmodulin upon Interaction with Its Potent Antagonist Calmidazolium

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ABSTRACT

Calmodulin is a eukaryotic multifunctional, calcium-modulated protein that regulates the activity of numerous effector proteins involved in a variety of physiological processes. Calmidazolium is one of the most potent antagonist inhibitors of calmodulin and one the most widely used inhibitor of calmodulin in cell biology. However, the structure of the calmidazolium-bound calmodulin as well as the dynamics and conformational changes of the protein induced by the drug are unknown.

Here, we report an integrative structural biology approach, which combines SRCD (DISCO), SEC-SAXS (SWING), X-ray crystallography (PROXIMA 1 & 2A), HDX-MS and NMR. Our results provide molecular insights into the CDZ-induced dynamics and structural changes of calmodulin leading to its unavailability to its various intracellular partners. CDZ-binding induces an open-to-close conformational change of CaM associated with a strong stabilization of the structural elements and reduction of protein dynamics. We further show that the effects of CDZ are similar to those induced by CaM-binding protein-derived peptides despite their distant chemical nature. The residues involved in the stabilization of the CaM:CDZ complex and the residues in close contact with CDZ have been identified.

These results open the way to rationally design new drugs more selective to CaM.

From Moss to Sequoia, X-rays Reveal the Metastability of Sap Transport under Tension

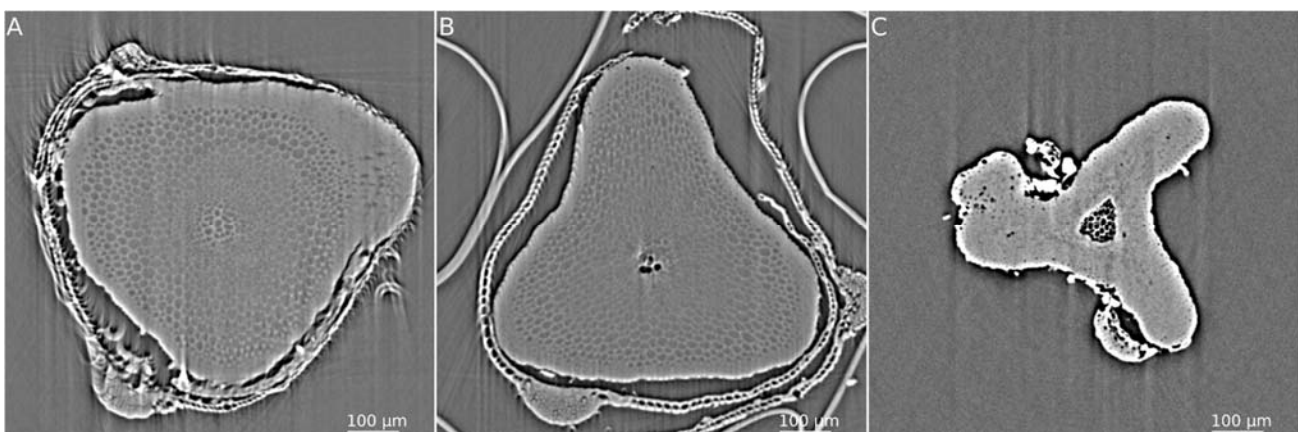
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ABSTRACT

The mechanism of sap ascent in plants and the content of xylem vessels have been the subject of intense debates over the age. Plants, and most remarkably trees, are capable of rapidly transporting water to the leaves at considerable heights by a transport system that relies on water sustaining a tensile force. However, this transport mechanism comes with its own set of problems, most notably that water under tension is in a metastable state and prone to cavitation. This has strong implications for (i) the survival of plants under drought conditions and (ii) the determination of this drought tolerance by measuring xylem hydraulic conductivity in the laboratory, which is subject to bias when measuring cut samples where the vessels are open to air. For this reason, X-ray imaging has become a very important technology over the last decade in the field of plant physiology, allowing scanning of intact plants. The aim of my talk is to illustrate some of the scientific advances that have been made using this technique to determine the contents of vessels in a non-invasive manner. For instance, our results document a remarkable convergence between the functionality of moss and vascular plants. Using x-ray micro-computed tomography at the PSICHE beamline, we show that a common tall moss species not only transports water under tension, but also protects its vascular system from cavitation by regulating transpiration in a similar fashion to vascular plants. We also used this non-invasive technique to study the impact of vascular diseases on plant physiology and survival, showing that grapevine leaves with esca symptoms had a significantly high level of nonfunctional vessels resulting from the presence of nongaseous embolisms.



Deep investigation of Specificities and Behaviours of Flax Fibres and Stems through Different SOLEIL Beamlines

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ABSTRACT

This presentation proposes a review of three works carried out between 2017 and 2021 at the SOLEIL Synchrotron on different beamlines. They all concern the study of flax fibres and stems. Flax is one of the first plants domesticated by man and its fibres have been used for textile purposes for thousands of years. In recent decades, new uses have been developed. Indeed, the mechanical and environmental properties of these fibres make them an ideal reinforcement for the composites industry.

Firstly, on the DISCO line, we studied the impact of a gravitropism phenomenon on the biochemical structure of the plants and fibres; we evidenced that the impact of gravitropism was different depending on the areas of the plant considered but also according to their stage of maturity. The second part concerns the microfibrillar angle (MFA of flax fibres), which is one of their major structural characteristics; firstly, multi-photon microscopy (SHG) of the DISCO beamline was used to estimate this MFA on elementary fibres; secondly, work carried out on SWING revealed a reorientation of cellulose microfibrils during tensile tests in a range of relative humidities. Finally, the third section of this presentation is dedicated to the study of kink-bands, major structural defects of the fibres whose origin remains uncertain. Here again, the SHG (DISCO) has made it possible to highlight disorganization of cellulose in these zones; then microtomographic explorations, conducted on ANATOMIX, were carried out on flax stems and fibres; They provide initial answers by clearly highlighting altered zones at the level of the kink bands on the fibres, whatever their level of transformation; on the other hand, the stems analysed did not reveal the presence of kink-bands, which seems to confirm that their origin is caused by the mechanical extraction of the fibres and not by the growth of the plants

REFERENCES

1. Melelli A, Jamme F, Legland D, Beaugrand J, and Bourmaud A, Industrial Crops and products, 2020, 156, 112847.
2. Melelli A, Durand S, Arnould O, Richely E, Guessasma S, Jamme F, Beaugrand J, Bourmaud A, Industrial Crops and products, 2021, 164, 113368.
3. Beaugrand J, Goudenhooff C, Alvarado C, Devaux M-F, Rivard C, Durand S, Chauvet H, Réfrégiers M, Jamme F, Guillon F, Baley C, Bourmaud A, Industrial Crops and products, 2022, 175, 11425

A N7-Methyltransferase hidden in the dark proteome of newly discovered Nidovirus. Structure, function and evolutionary implications.

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ABSTRACT

The order *Nidovirales* is a diverse group of (+)RNA viruses, classified together based on their common genome organisation and conserved replicative enzymes, despite drastic differences in size and complexity¹. One such difference is reflected into the mechanisms and enzymes responsible for viral 5' RNA cap synthesis. Within the *Coronaviridae* family, two separate methyltransferases (MTase), nsp14^{2,3} and nsp16⁴⁻⁶, perform the RNA-cap N7-guanine and 2'-OH methylation respectively for generation of the proposed m7GpppNm type I cap structure⁷. For the majority of other families within the *Nidovirales*, the presence, structure and key enzymes involved in 5'capping still remain uncertain⁸. These viruses either lack completely an RNA MTase signature sequence, or lack an N7-guanine methyltransferase signature sequence, obscuring our understanding about how RNA-caps are N7-methylated for these families. Here, we report in newly discovered members of *Tobaniviridae*⁸ the discovery of a hidden Rossmann fold RNA N7-guanine methyltransferase in Orf1a, an unusual genome locus for this gene.

REFERENCES

1. A.E. Gorbalenya et al. *Virus Res* 2006, 17,17–37.
2. Y. Ma, et al. *Proc. Natl. Acad.Sci. U.S.A.*, 2015 112, 9436–9441.
3. F. Ferron,et al. *Proc. Natl. Acad. Sci.U.S.A.* 2018, 115, E162–E171.
4. E. Decroly,et al. *J. Virol.*,2008, 82, 8071–8084.
5. E. Decroly,et al. *PLoS Pathog.*, 7, e1002059. 2011
6. Y. Chen, et al. *PLoS Pathog.*, 7, e1002294. 2011
7. E. Decroly,F. Ferron, J. Lescar,J. and B. Canard, *Nat. Rev.Microbiol* 2011, 10, 51–65.
8. F. Ferron et al., *NAR Genomics and Bioinformatics*, 2020, Vol. 2, No. 1 1-10

Structural Insights onto the Ribosome from the Human Pathogen *C. Albicans*

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ABSTRACT

The human pathogen *Candida albicans* causes potentially deadly infections, known as candidiasis. Few drugs are available against *C. albicans* and all of them have several side effects. Moreover, an increasing number of cases of drug resistance has been reported. These deficiencies in the available treatment for candidiasis are due mainly to the fact that they are not directed against one of the most useful targets of antibiotics – the protein synthesis apparatus. Eukaryotic ribosome is known target for the inhibitors [1], but the main challenge nowadays is to find specific inhibitors, which only act against the chosen target, such as the *C. albicans* ribosome.

It is known that some mutations in functional sites of the ribosome affect the binding of inhibitors. For instance, resistance of *C. albicans* to the inhibitor cycloheximide is most likely caused by a mutation, P56Q, in the ribosome protein uL42 which forms the E-tRNA binding site on the 60S subunit [2,3]. The structural basis of this inhibition has not been known yet.

To find the structural determinates of the *C. albicans* ribosome we need to know its three-dimensional structure. Among all available methods X-ray crystallography is often applied for investigation of the binding mode for distinct compounds known to inhibit or modulate the protein-translation function of the ribosome.

Here, we report the X-ray crystal structure of the 80S ribosome of *C. albicans* in complex with the novel A-site inhibitor ailanthone. Also, we compared the main functional centres with those of *S. cerevisiae* and *H. sapiens* and identified several structural differences in functional sites that may help in the search for a specific inhibitor.

Improving these results and performing further screens of potential compounds we aim to find highly specific inhibitors of protein translation in *C. albicans*.

REFERENCES

1. N. Garreau de Loubresse et al., Structural basis for the inhibition of the eukaryotic ribosome. Nature 513, 517-522 (2014).
2. J. H. Bae, B. H. Sung, J. H. Sohn, Site saturation mutagenesis of ribosomal protein L42 at 56th residue and application as a consecutive selection marker for cycloheximide resistance in yeast. FEMS Microbiol Lett 365, (2018)
3. L. Shen et al., Structure of the translating Neurospora ribosome arrested by cycloheximide. PNAS, (2021).

List of Posters

In blue student posters

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| PO-01-AM 18:00 | Electronic-structure origin of the high thermoelectric coefficient in hole doped CuRhO ₂ A.J. Thakur |
| PO-02-AM 18:07 | In situ electrical and mechanical study of Indium Tin Oxide films deposited on flexible substrate: A Synchrotron investigation T. Chommaux |
| PO-03-DR 18:14 | Bimetallic M-N-C catalysts for oxygen reduction reaction in proton exchange membrane fuel cells: An operando X-ray absorption study A. Khan |
| PO-04-DR 18:21 | Operando study of macrocycle molecular catalysts for CO ₂ reduction reaction S.T. Dong |
| PO-05-DR 18:28 | Investigation of ligand electronic effects on iron cyclopentadienyl complexes using photoelectron spectroscopy L. Bourehil |
| PO-06-DR 18:35 | Auger spectroscopy of fulminic acid, HCNO M. Gerlach |
| PO-07-LS 18:42 | Morphological variations of calcite microfossils based on synchrotron microtomography data to reveal the last 200 years of environmental changes in the Danish strait C. Choquel |
| PO-08-LS 18:49 | Monitoring food structure in plant protein gels during digestion F. Boué |
| PO-09-LS 18:56 | X-ray compatible microfluidic platforms for in situ serial Synchrotron crystallography R. Vasireddi |
| PO-10-DR 19:03 | Hall-petch relationship in thermosensitive micellar copolymer polycrystals with embedded colloidal nanoparticles A. Mourchid |
| PO-11-AM 19:10 | Spectral ptychography at the SWING beamline A. Kulow |
| PO-12-AM 19:17 | Temperature and doping dependence of the crystal field excitations in La _{1-x} Sr _x VO ₃ family of compounds near the Mott insulator limit A. Nicolaou |
| PO-13-AM 19:24 | Correlation between strain, ferroelectricity and oxidation state in epitaxial multiferroic Fe ₂ O ₃ /BaTiO ₃ heterostructures H. Lin |
| PO-14-AM 19:31 | In-situ study of the photomagnetic effect in RbCoFe Prussian blue analogues nanoparticles embedded in an ordered SiO ₂ matrix L. Altenschmidt |
| PO-15-AM 19:38 | Evolution of electronic structures and charge density wave properties in layered LaSb ₂ L. Chen |

PO-16-AM
19:45

Unveiling the electronic state interplay at organic DBP/4P-NPD exciton blocking interfaces in organic solar cells

M. Ahmad

PO-17-AM
19:52

Decompression failure in hydrogen-exposed rubbers: Insights from in-situ tomography at Anatomix beamline

S. Castagnet

PO-18-AM
19:59

Structural, magnetic and magnetocaloric transitions in $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Fe}_2\text{D}_{3.5}$ deuteride

V. Paul-Boncour

Electronic-structure origin of the high thermoelectric coefficient in hole doped CuRhO_2

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ABSTRACT

CuRhO_2 is a delafossite with CdI_2 type layered structure. Its crystal structure consists of layers of RhO_2 stacked between triangular Cu layers which exhibit dumbbell like O-Cu-O coordination. CuRhO_2 is an insulator with a semiconducting band gap of about 1.9 eV and displays good thermoelectric properties with a Seebeck coefficient of the order of 200 $\mu\text{V}/\text{K}$. Doping the system with Mg^{2+} introduces hole carriers, which leads to a transition to a metallic state also showing an unusually large Seebeck coefficient. Such a large thermoelectric coefficient has been hypothesized to originate on “pudding mold” type bands for other materials, such as cobalt oxides [1]. Here we report the observation of the theorized “pudding mold” type band structure in 10% Mg doped CuRhO_2 through angle resolved photoemission spectroscopy (ARPES) and accompany our measurements with density functional theory (DFT) calculations along with transport calculations based on the DFT band structure. The DFT calculations of the undoped material are found to fit very well with the measurements after applying a rigid band shift of the calculated bands to simulate the hole doping. The calculated Seebeck coefficient of $\sim 200\mu\text{V}/\text{K}$ also matches the transport measurements done on this material [2].

REFERENCES

1. Kuroki, K., & Arita, R. (2007). “Pudding mold” band drives large thermopower in Na_xCoO_2 . *Journal of the Physical Society of Japan*, **76**(8), 083707. <https://doi.org/10.1143/jpsj.76.083707>
2. Maignan, A., Eyert, V., Martin, C., Kremer, S., Frésard, R., & Pelloquin, D. (2009). Electronic structure and thermoelectric properties of $\text{CuRh}_{1-x}\text{Mg}_x\text{O}_2$. *Physical Review B*, **80**(11). <https://doi.org/10.1103/physrevb.80.115103>

In situ electrical and mechanical study of Indium Tin Oxide films deposited on flexible substrate: a synchrotron investigation

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Keywords: In situ deformation; synchrotron x-ray diffraction; electro-mechanical properties; ITO; thin films

Transparent conducting oxides (TCOs) combine two interesting behaviours: low electrical resistivity and good optical transmission in the visible spectral range. Indium Tin Oxide (ITO) exhibits this precious compromise, which allows it to be a key material found in many optoelectronic devices such as photovoltaic cells, screens and smart devices or electromagnetic shielding [1]. However, the electrical properties of ITO thin films under mechanical stress are not well understood, although they are part of a promising field open to many applications such as stretchable microelectronics [2].

ITO is a degenerate semiconductor, its electrical properties are modified when it is subjected to deformation. The electro-mechanical behaviour of thin films is studied as a function of different deposition parameters (sputtering ion, O₂ flow, deposition temperature). From these parameters, microstructure and electrical properties can be related.

Initial microstructural, electrical and optical characterizations of ITO thin films deposited onto polyimide substrates are performed at the Institut P'. The core of the experimental work is then carried out at the synchrotron SOLEIL. The synchrotron environment allows, through X-ray diffraction experiments, a detailed characterization of the mechanical behavior of ITO subjected to a continuous biaxial tensile test. These in situ experiments allow measuring the applied strains in the polyimide thanks to digital image correlation, the applied strains or stresses in the ITO films thanks to X-ray diffraction and, electrical resistivity thanks to four point probe method.

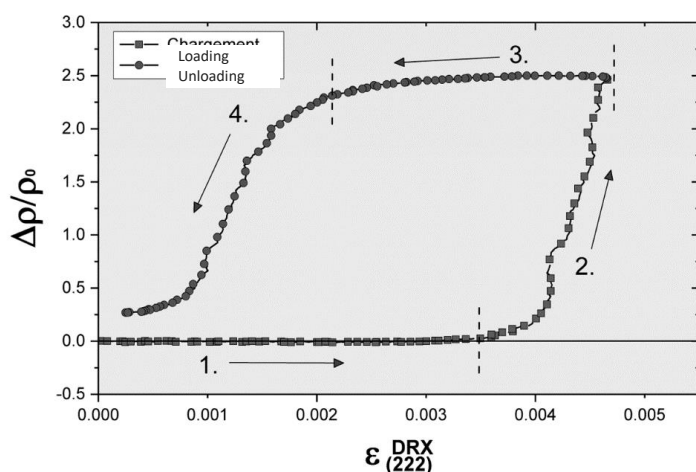


Figure 1: Relative variation of resistivity as a function of out-of-plane deformation of the ITO (400 nm thick fabricated by ion sputtering with Xe ion in a flow of O₂ at Room Temperature) during a tensile test (loading + unloading). Four main domains can be observed: (1) Elastic domain, (2) ITO crack's growth in ITO and propagation in polyimide substrate, (3) Crack's closure in substrate and finally (4) crack's closure in ITO thin films

The unique experimental set-up at the DiffAbs synchrotron beamline allows detailed characterization and determination of the electro-mechanical behavior of the ITO thin films (see figure 1). Depending on the microstructure of the thin film, the electrical response as a function of applied strain is clearly observed. In particular, crack onset can be determined very precisely using in situ resistivity measurements. This latter device, coupled with finite element simulations, will permit to analyse and understand the electrical behaviour of anisotropic thin films.

[1] A. Facchetti, T.J. Marks, Transparent electronics: from synthesis to applications. John Wiley & Sons (2010).

[2] J. A. Rogers, T. Someya, Y. Huang, Materials and mechanics for stretchable electronics, Science, 327 (2010), 1603-1607.

Bimetallic M-N-C Catalysts for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cells: an *operando* X-ray absorption study

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ABSTRACT

Nowadays the low activity and high cost of catalysts remain the main limiting factor for the widespread use of fuel cells and other new energy supply technologies. Pyrolyzed iron-based non-noble metal catalysts showed themselves as a promising alternative to replace platinum-based catalysts for catalyzing the oxygen reduction reaction (ORR) in acid medium.

Bimetallic FeSn-NC and FeCo-NC catalyst exhibit higher ORR activity and promising higher stability than the parent FeNC materials¹. In this study, we employed *operando* X-ray absorption measurements to identify potential-induced structural and electronic changes. Specifically, the X-ray absorption near edge structure (XANES) spectra show a change in the oxidation state of Fe in FeSn-NC and FeCo-NC, while the Sn and Co K-edge XANES spectra are independent of the electrochemical potential in the ORR range.

An accurate structural characterization of the catalytic active sites was carried out by studying the extended X-ray absorption fine structure (EXAFS) region too. The EXAFS analysis revealed the existence of atomically dispersed FeN₄ and SnN₄ moieties in FeSn-NC, and FeN_x and CoN_x moieties in FeCo-NC, that is also characterised by the presence of metal nanoparticles.

REFERENCES

1. Zitolo, A., Goellner, V., Armel, V. et al. Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials. *Nature Mater* 14, 937–942 (2015)

Operando Study of Macrocycle Molecular Catalysts for CO₂ Reduction Reaction

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ABSTRACT

The generation and storage of clean energy is a crucial challenge due to the high accumulation of atmospheric CO₂ by the extensive use of fossil fuels, which is threatening human life on Earth. One route towards the generation of green fuels is the electrochemical reduction of CO₂ towards carbon-containing chemical building blocks, such as CO, HCHO or C₂H₄. Due to the kinetic stability and thermodynamic inertness of CO₂, catalysts are required for the reactions to be carried out efficiently. In the field of molecular catalyst, metal macrocycles such as iron porphyrin¹, cobalt phthalocyanine² or nickel cyclam³ emerge as economical, robust, and effective catalysts for the electro-reduction of CO₂ to CO and other products in smaller quantity. In order to improve the performance of the catalysts, the reduction mechanism needs to be well-understood. Although a variety of studies propose pathways for the reduction of CO₂, there is limited operando data demonstrating the proposed mechanism^{1,4}. Operando X-ray absorption spectroscopy is one of the state-of-the-art techniques to study molecular catalysts as the oxidation states, geometry and surrounding environment of the catalysts can be derived from the spectroscopic data⁵.

Here, we show the state of various metal porphyrins and phthalocyanines electro-catalyst under CO₂ reduction catalysis conditions. Using a 3D-printed spectro-electrochemical flow cell, we demonstrate the integrity of the catalyst during operation as well as shine light on the mechanism of the heterogeneous catalytic reaction. The cell can be easily adapted to different catalysts, electrodes and membranes, providing a versatile platform to study a variety of heterogeneous electrocatalysts at different conditions for CO₂ reduction.

REFERENCES

- (1) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. A Local Proton Source Enhances CO₂ Electroreduction to CO by a Molecular Fe Catalyst. *Science* **2012**, *338* (6103), 90–94. <https://doi.org/10.1126/science.1224581>.
- (2) Wang, M.; Torbensen, K.; Salvatore, D.; Ren, S.; Joulié, D.; Dumoulin, F.; Mendoza, D.; Lassalle-Kaiser, B.; Işci, U.; Berlinguette, C. P.; Robert, M. CO₂ Electrochemical Catalytic Reduction with a Highly Active Cobalt Phthalocyanine. *Nature Communications* **2019**, *10* (1), 1–8. <https://doi.org/10.1038/s41467-019-11542-w>.
- (3) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. Nickel(II)-Cyclam: An Extremely Selective Electrocatalyst for Reduction of CO₂ in Water. *2*.
- (4) Corbin, N.; Zeng, J.; Williams, K.; Manthiram, K. Heterogeneous Molecular Catalysts for Electrocatalytic CO₂ Reduction. *Nano Res.* **2019**, *12* (9), 2093–2125. <https://doi.org/10.1007/s12274-019-2403-y>.
- (5) Liu, Y.; Deb, A.; Yee Leung, K.; Nie, W.; S. Dean, W.; E. Penner-Hahn, J.; L. McCrory, C. C. Determining the Coordination Environment and Electronic Structure of Polymer-Encapsulated Cobalt Phthalocyanine under Electrocatalytic CO₂ Reduction Conditions Using in Situ X-Ray Absorption Spectroscopy. *Dalton Transactions* **2020**, *49* (45), 16329–16339. <https://doi.org/10.1039/D0DT01288B>.

Investigation of Ligand Electronic Effects on Iron Cyclopentadienyl Complexes using Photoelectron Spectroscopy

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ABSTRACT

Organometallic complexes are key compounds in homogenous catalysis and their reactivity is closely related to the steric and electronic effects of the ligands within the complex. [1, 2] Photoelectron spectroscopy (PES) may be used as a fine probe of the electronic interaction between the ligand and the metal centre[3]. This method has been applied here to study tricarbonyl iron complexes of the type $(\text{Fe}(\text{CO})_3\text{L})$ with L being substituted cyclopentadiene ligands. Such complexes take part in hydrogen alkylation reactions[4] and reduction reactions[5]. The experiments were carried out on the DESIRS beamline at the synchrotron SOLEIL facility, using e^-/i^+ coincidence techniques to obtain mass-selected PES of jet-cooled complexes. These spectra provide access to the ionisation energies and state-selected Fe-CO dissociation energies. Rationalization of the experimental results is further made using density functional theory and bond description methods to get information on the electronic structure of the complex and thus on the metal-ligand interaction.

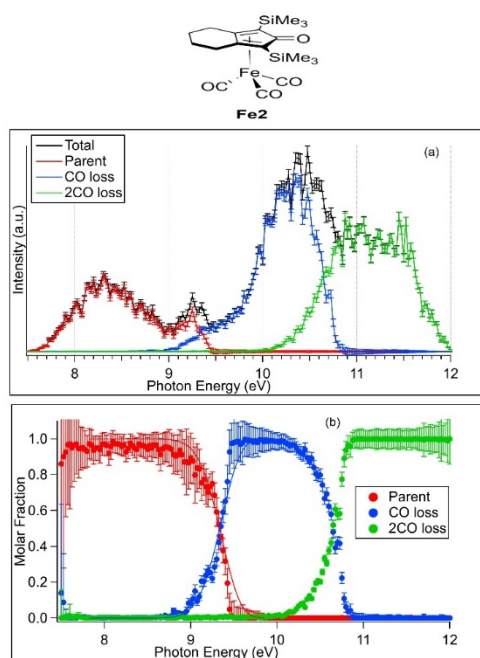


Figure 1. (a). Slow Photoelectron Spectra (SPES) of state-selected Fe2 recorded in the 7.5 - 12.0 eV energy range. (b). Breakdown diagram of Fe2 recorded in the 7.5 - 12.0 eV energy range and obtained with a 150 meV energy resolution. The SPES provide access to the electronic structure of the complex and allow us to draw fragmentation diagrams, from which we can determine the appearance energies of the different fragments.

REFERENCES

1. Constable, E.C., *In Metals and Ligand Reactivity*. 2005. 22-45.
2. Zecchina, A.C., S., Eds., *The Development of Catalysis: A History of Key Processes and Personas in Catalytic Science and Technology*. John Wiley and Sons, 2017.
3. Dossmann, H. Gatineau, D. Clavier, H. Memboeuf, A. Lesage, D. Gimbert, Y., *Exploring Phosphine Electronic Effects on Molybdenum Complexes: A Combined Photoelectron Spectroscopy and Energy Decomposition Analysis Study*. *J Phys Chem A*, 2020. 124(42): p. 8753-8765.
4. Bettoni, L.G., S. Renaud, J. L., , *A phosphine-free iron complex-catalyzed synthesis of cycloalkanes via the borrowing hydrogen strategy*. *Chem. Commun.*, 2020., 56(85): p. 12909-12912.
5. Moulin, S.D., H. Pagnoux-Ozherelyeva, A. Gaillard, S. Poater, A. Cavallo, L. Lohier, J.-F. Renaud, J.-L., , *Bifunctional (Cyclopentadienone) Iron-Tricarbonyl Complexes: Synthesis, Computational Studies and Application in Reductive Amination*. *Chem. Eur. J.*, 2013. 19: p. 17881-17890.

Auger Spectroscopy of Fulminic Acid, HCNO

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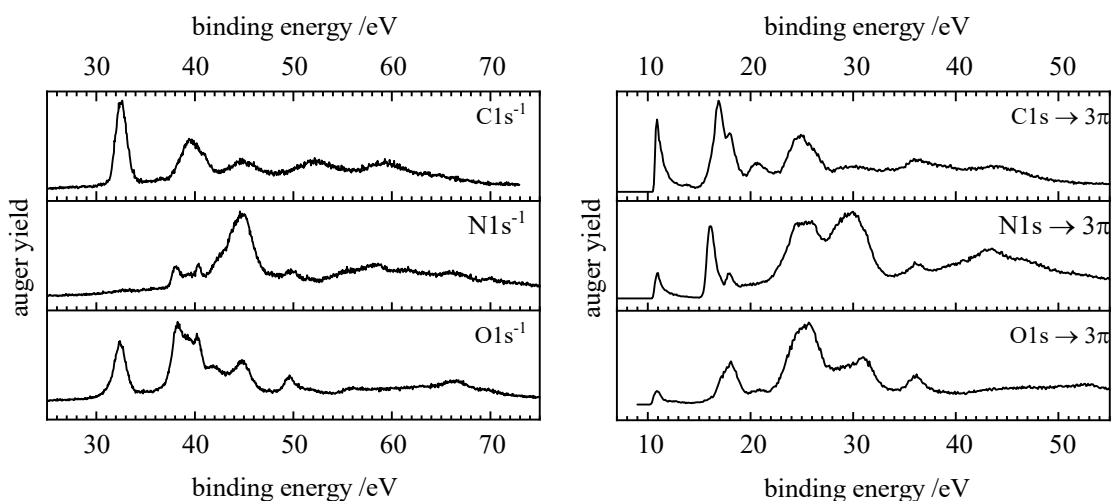
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ABSTRACT

Fulminic acid, HCNO, was first detected in space in 2009 in the three starless cores B1, L1544 and L183.[1] The isomer isocyanic acid, HNCO, is also ubiquitous in interstellar systems.[2] Due to their composition of the atoms Hydrogen, Carbon, Nitrogen and Oxygen a prebiotic role has been suggested for these molecules. Investigating the interaction of these molecules with X-ray radiation is critical in understanding their fate in space.

As such, we present the gas phase auger electron spectra of fulminic acid which were recorded at the PLEIADES beamline at the Synchrotron SOLEIL in France. Fulminic acid was prepared by preparative pyrolysis of the precursor 3-phenyl-4-oximino-isoxazol-5(4H)-one as described by Wentrup et al..[3] Normal and resonant auger electron spectra, XPS as well as NEXAFS spectra were recorded at all three edges. To give further insights into the observed transitions we compare the spectra to the spectra of isocyanic acid, as well as theoretical simulations.



REFERENCES

1. N. Marcelino, J. Cernicharo, B. Tercero, E. Roueff, *Astrophys. J.*, **690**, L27-L30 (2009)
2. Nguyen-Q-Rieu, C. Henkel, J. M. Jackson, R. Mauersberger, *Astron. Astrophys.*, **241**, L33 (1991)
3. C. Wentrup, B. Gerecht, H. Briehl, *Angew. Chem. Int. Ed.*, **18**, 467-468 (1979)

Morphological variations of calcite microfossils based on synchrotron microtomography data to reveal the last 200 years of environmental changes in the Danish strait

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ABSTRACT

Human activities in coastal areas are accelerating in the last 200 years, increasing pressures as warming, oxygen depletion, and ocean acidification on organisms and ecosystems⁽¹⁾. These environmental changes can lead to multiple social-ecological problems. To better understand these potential future threats, we need to develop tools to compare our present situation and events that happened in the past. Foraminifera are tiny marine microorganisms. Their shells are made of calcium carbonate and abundantly fossilized in marine sediments. Foraminifera are currently used as recorders of the past as the chemical composition of their shells reflects environmental conditions⁽²⁾. Their changes in morphology are recently used thanks to the high-resolution 3D development imagery acquired with microtomography (μ CT)^(3,4,5). However, the current method used is time-consuming and allows a few specimens analyzed (one specimen every 24h). In this project we are developing protocols and post-data analysis by using synchrotron facilities (SPRING-8 and SOLEIL), allowing us to generate long time series of hundreds of specimens (one specimen every 30min) required to obtain statistically valid conclusions. In this project, we analyzed a set of 126 specimens (performed at SPING-8) recording the period from pre-industrial conditions into present-day conditions of the Danish strait. We hypothesize that the foraminiferal calcite will respond to the environmental variations by having changed shell morphology. Biometric measurements were analyzed with free software; Image J (thickness) and Meshlab (surface, volume, pore density). Our preliminary results indicate that the shell thickness decreased significantly in the last 200 years, and the shell volume seemed to show an opposite trend. The surface/ volume ratio and pore density did not show a significant trend due to large intra-specific variability between years. These large intra-specific fluctuations could reflect periods of major environmental changes. Finally, our ongoing project demonstrates that the synchrotron-based μ CT approach is a high-resolution, non-destructive, and time-efficient method to reveal past environmental evolution. Therefore, we plan to continue data acquisition with specimens from the last deglaciation (18 to 11 ka BP into Holocene) on beamline ANATOMIX at SOLEIL in Spring 2022.

REFERENCES

1. Bindoff et al. 2019, *Chp 5 In IPCC Special Report on the Ocean and Cryosphere in a Changing Climate* [Pörtner et al (eds.)] In press
2. Filipsson et al. 2010, *Biogeosciences* 7, pp 1335–1347
3. Filipsson et al. 2019, 3D imaging of calcite microfossils – messengers of recent environmental changes. *INQUA, Dublin, Ireland*, 2019
4. Iwasaki et al. 2015, *Paleoceanography* 30, pp 317-331
5. Ni et al. 2020, *Chemical Geology* 558, pp 119871

Monitoring Food Structure in Plant Protein Gels during Digestion

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ABSTRACT

Proteins are essential macronutrients in the human diet, being fundamental in body structure and functions. Their digestibility depends not only on their composition but also on their structure, which in turn can be influenced by different types of processing.

We monitored degradation kinetics of food structures during simulated gastro-intestinal digestion and analyzed an impact of the food structure on the digestibility. As a model solid-like food (most often ingested form of protein) we used plant protein gels - from rapeseed (napin and cruciferin) and potato (patatin). The gels were synthesized by heat-treatment of the solutions at different concentrations and pHs. By the use of UV fluorescence imaging (DISCO) and X-ray scattering (SWING) at SOLEIL synchrotron, we expected to obtain structural information at different length scales: 20-200 μm and 1-500 nm, respectively. It is a continuation of the work on dairy proteins (Floury et al 2018).

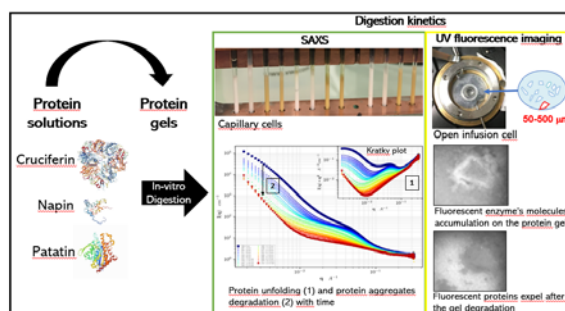
Due to differences in samples dimensions for the two methods used, i.e. gels in thin capillaries for SAXS and gel pieces of $\sim 100\text{-}300\ \mu\text{m}$ in open infusion cell for microscopy, the access of the enzyme and its diffusion through the sample were different.

For SAXS, sampling resolution (beam size) was several hundred μm with table spectrometers (Xeuss, CEA Saclay) but much thinner for SWING (100 μm): we observed enzyme's reaction on the gel surface, progressing over several hours downward the capillaries, limiting the gastric digestion of the protein gels by the enzyme's diffusion. This digestion was much slower than for protein solutions: gelation of proteins could alter the process of their digestion by hindering the access of the enzymes to peptide bonds. Gastric digestion at low pH provoked unfolding of proteins and initial destruction of protein aggregates. The intestinal step at basic pH was more profound in aggregate's destruction, while simultaneous protein re-folding has also been observed. During the fluorescence imaging of the gel pieces under digestion, sampling resolution was several tenths of μm ; we observed (i) enzyme's accumulation on the surface of the gel, with rather fast progression inside (several min) and (ii) a simultaneous expel of proteins from the degraded aggregates.

In both experiments, the effect of digestion depended on the type of protein and the pH of protein solution during gelation – provoking different protein compactness/unfolding and thus different aggregation state of the gels. Intestinal digestion was always more profound and faster compared to gastric digestion. We undoubtedly remarked that protein digestion is determined by the effect of food microstructure, influencing the diffusion and hydrolysis rates.

REFERENCES

1. J. Floury, T. Bianchi, J. Thévenot, D. Dupont, F. Jamme, E. Lutton, M. Panouillé, F. Boué, S. Le Feunteun, "Exploring the breakdown of dairy protein gels during in vitro gastric digestion using time-lapse synchrotron deep-UV fluorescence microscopy" in *Food Chemistry* **239**, 898-910 (2018).



X-ray Compatible Microfluidic Platforms for In Situ Serial Synchrotron Crystallography

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ABSTRACT

Recent developments in ultra-brilliant synchrotron and hard X-ray free electron lasers (FEL) open very exciting possibilities in structural biology, such as in situ serial crystallography¹ and time resolved structural studies of bio-macromolecules. These techniques already contribute to high impact science, yet both require high consumption of crystals and generate large data volumes for structural analysis, potentially requiring long periods of beamtime acquisition on oversubscribed central facilities. These issues can be somewhat mitigated with efficient sample delivery under the X-ray beam. Microfluidic and microscale technologies have played a critical role in facilitating both protein crystallization and structure determination.² The transfer of microfluidic technology experiments is, however, technically challenging due to the requirement of X-ray compatibility of the different device materials. In the current presentation we will review the impact of X-ray compatible microfluidic device technologies on protein crystal growth and X-ray diffraction analysis. We focus on applications of X-ray compatible microfluidics for use in situ serial crystallography experiments at synchrotron sources. At Synchrotron SOLEIL, the microfluidic team, together with the life sciences scientists provides expertise in the design, manufacturing, and experimental implementation of X-ray compatible microfluidic devices optimized for synchrotron experiments. We also provide facilitated means of sample handling and specialized sample environments that address specific experimental conditions at synchrotrons and XFEL facilities. Finally, we are attempting to prepare standardized X-ray compatible microfluidic trapping devices for biomacromolecular structural studies at Synchrotron SOLEIL and other synchrotron facilities.³

REFERENCES

1. H. N. Chapman, P. Fromme, A. Barty, T. A. White, R. A. Kirian, A. Aquila and U. Weierstall, *Nature*, **470(7332)**, 73-77 (2011).
2. R. Vasireddi, A. Gardais and L. M. G. Chavas "Diffusion-based crystal formation in microdevice for high-throughput in situ X-ray screening and data collection at room temperature" (Under Review)-2021.
3. I. Chaussavoine, A. Beauvois, T. Mateo, R. Vasireddi, N. Douri, J. Priam, Y. Liatimi, S. Lefrançois, H. Tabuteau, M. Davranche, D. Vantelon, T. Bizien, L. M. G. Chavas and B. Lassalle-Kaiser; *Journal of Synchrotron Radiation* **27**,230-237, 2020.

Hall-Petch Relationship in Thermosensitive Micellar Copolymer Polycrystals with Embedded Colloidal Nanoparticles

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ABSTRACT

We study the rheological properties of copolymer-nanoparticle aqueous solutions and their relationship to the structure at both nano and microscales [1]. The samples are formed of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer micellar solutions with embedded spherical silica nanoparticles. The concentrated micellar solutions exhibit a phase transition from fluid to crystal induced by temperature. Addition of nanoparticles is found to trigger the formation of polycrystallized micellar micrograins, above the transition temperature, instead of a cubic monocrystal. This transition is associated with the segregation of the nanoparticles, which play the role of impurities, in the interstices between the grains.

The experimental data show that the variation of nanoparticle concentration has the effect to modify both the yield stress and simultaneously the size of the polycrystalline micrograins observed by optical microscopy: indeed, the yield stress rigorously obeys Hall-Petch law. We also show that the grain size evolves non-monotonically with the nanoparticle concentration without affecting the Hall-Petch relation. We believe that our experimental approach offers new possibilities to study poorly understood mechanical aspects of polycrystalline and nanocrystalline structures, such as their plasticity, with non-destructive techniques.

REFERENCES

[1] A. Mouchid, I. Boucenna, F. Carn, Mechanical strength enhancement by grain size reduction in a soft colloidal polycrystal, *Soft Matter* 2021, Doi:10.1039/D1SM01486B

Spectral Ptychography at the SWING Beamline

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ABSTRACT

The nanoprobe endstation at the SWING beamline allows for 2D-nano-ptychography and 3D-nano-tomo-ptychography [1]. Ptychography is a scanning coherent diffractive imaging technique [2]. A probe with size in the micrometer range is used to scan a sample, with an overlap between adjacent scan positions. The complex-valued object function is iteratively retrieved, using the diffraction patterns measured at each scan position. The resolution is not limited by X-ray optics, the probe size, or the scanning step width, but only by the maximum angle at which speckles can be recorded with a reasonable signal-to-noise-ratio. A further advantage of ptychography is that both phase and absorption contrast can be exploited, thus allowing the investigation of only weakly absorbing samples. In 3D-nano-tomo-ptychography, ptychographic projections are recorded at different angles in a range of 180°. From these projections, a 3D tomogram of the δ and β values can be reconstructed, with δ and β being the components of the complex refractive index, which is related to the complex scattering factor :

$$n - 1 - \delta + i\beta - 1 = \frac{r_e}{2\pi} \lambda^2 \cdot \sum_{at} n_{at}^2 [(f_{0,at} + f'_{,at} + if''_{,at})] \quad (1)$$

with r_e the classical electron radius, λ the wavelength of the incoming X-rays, n_{at} the atomic density, $f = f_0 + f' = f''$ the atomic scattering factor, and the sum goes over all components of the sample. This offers the possibility to get quantitative information of the sample, as δ is directly proportional to the electron density [3].

Performing ptychographic measurements at different incident energies including the energy of the absorption edge of an element of interest (resonant or spectral ptychography) adds spectral information. As the scattering factor varies only slowly with energy far from absorption edges, the differences between the tomograms recorded at resonant energy and off resonant energy can be attributed to the element of interest [4].

Here, we will show measurements on a Ni wire performed at SWING to show the principle of 2D spectral ptychography and 3D resonant ptychographic X-ray computed tomography (R-PXCT) and the performance of the nanoprobe endstation. We can extract an absorption and a δ spectrum from the measured ptychographic projections, and determine the electron and atomic density from the reconstructed tomogram.

REFERENCES

1. C. Engblom et al., 17th Int. Conf. on Acc. and Large Exp. Physics Control Systems ICALEPCS2019, New York, NY, USA
2. J.M. Rodenburg and H.M.L Faulkner, *Appl. Phys. Letters* **85**, 4795-4797 (2004).
3. A. Diaz et al., *Physical Review B* **85**, 020104 (R) (2012).
4. C. Donnelly et al., *Physical Review Letters*, PRL **114**, 115501 (2015).

Temperature and Doping Dependence of the Crystal Field Excitations In $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ Family of Compounds near the Mott Insulator Limit

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ABSTRACT

I will present a temperature and doping-dependent resonant inelastic x-ray scattering (RIXS) study on $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ thin films with $x = 0$ and $x = 0.1$. Bulk $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ canonical example of a compound that exhibits a filling-control metal-insulator transition and undergoes orbital ordering and antiferromagnetic transitions at low temperature [1,2]. In order to understand the rich phase diagram of this family of rare-earth vanadates electronic, lattice, spin and orbital degrees of freedoms have to be taken into account. RIXS is a bulk-sensitive element-specific technique that can be used to probe the neutral excitations of a system. In particular, RIXS is able to directly probe spin and lattice dynamics simultaneously with the orbital excitations, and therefore offers an unprecedented view on the low energy properties of $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$. We have used this emergent technique to investigate doping and temperature dependence of the low energy crystal field excitations in high quality $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ thin films near the Mott insulator limit ($x=0$, $x=0.1$) both at O K and V L_{23} edges. Temperature-dependent measurements at the V L_3 edge reveal an intra- t_{2g} excitation that blueshifts by 40 meV from room temperature to 30 K at a rate that differs between the para- and antiferromagnetic phases. The line shape can be partially explained by a purely local model using crystal field theory calculations. For the low Sr concentration $x=0.1$, the doping is shown to affect the local electronic structure primarily on the O sites, beyond a simple Mott-Hubbard picture [3].

REFERENCES

1. S. Miyasaka, T. Okuda, and Y. Tokura, Phys. Rev. Lett. 85 5388 (2000)
2. F. Inaba, T. Arima, T. Ishikawa, T. Katsufuji, and Y. Tokura, Phys. Rev. B 52 R2221 (1995)
3. Kari Ruotsalainen, Matteo Gatti, James M. Ablett, Flora Yakhou-Harris, Jean-Pascal Rueff, Adrian David, Wilfrid Prellier, and Alessandro Nicolaou, Phys. Rev. B 103 235158 (2021)

Correlation between Strain, Ferroelectricity and Oxidation State in Epitaxial Multiferroic Fe₂O₃/BaTiO₃ Heterostructures

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ABSTRACT

Artificial multiferroic heterostructures, realized by associating ferroelectric and ferromagnetic layers, are of high interest for fundamental research seeking to understand of the correlation between ferroelasticity, ferroelectricity and ferromagnetism, as well as for their strong industrial impact in major fields like spintronics, multiple state memory cells and sensors.[1-4]

In previous experiments, we have been focusing on multiferroic MFe₂O₄ (M=Co, Ni, Mn and Fe) ferrites / epitaxial BaTiO₃ (001) (BTO) heterostructures[5] and observed complex local situations due to correlative chemical reduction mechanisms occurring during the local electric polarization of the layers, likely driven by magneto-electrical couplings as observed by previous combined Piezo Force Microscopy (PFM) [6] and X-Ray Photo-Emission Electron Microscopy(XPEEM) spectromicroscopy experiments [7].

In the present study we considered Fe₂O₃/BaTiO₃(001) heterostructures capable of strong chemical reduction mechanisms in order to better understand the correlation between PFM writing and chemical evolution of the oxide overlayer. We therefore vary the oxidation conditions inside Fe₂O₃/BaTiO₃(001) heterostructures and adjust the PFM writing voltage using as well combined μ -XPEEM and XRD measurement. The XPEEM measurements were realized at the MAX IV synchrotron (Lund, Sweden) while the XRD measurements were done at SOLEIL, DiffAbs beamline. The over-layers were air annealed at increasing temperature to obtain compounds ranging from as-grown γ phase Fe₂O₃ to a mixture of α & γ phases Fe₂O₃, as observed by normal and grazing incidence X-ray diffraction at DiffAbs beamline. Subsequently, the pristine samples of variable compositions were cut into four parts and vacuum annealed at increasing temperatures to artificially create a controlled state of oxygen vacancies. Crystalline structure variations and chemical reduction state were investigated in detail. With these samples of different oxidation states, we proceeded with PFM writing at increasing voltage. The XAS spectrum shows the increase and saturation of chemical reduction with increasing PFM write voltage. Interestingly, the reduction percentage appeared different for each initial oxidation level but the resulting saturation state was found to have similar values. The correlation and origin of these effects will be discussed.

REFERENCES

1. C. A. F. Vaz, J. Phys.: Condens. Matter 24 (2012) 333201;
2. C. A. F. Vaz et al., Adv Mater. 22 (2010) 2900-1;
3. M. Bibes, J. E. Villegas, and A. Barthelemy, Advances in Physics 60 (2011) 5
4. A. Barbier, "Chap.23 - Single and Heterostructure Multiferroic Thin Films" in Magnetic, Ferroelectric, and Multiferroic Metal Oxides, Elsevier, January 2018, ISBN: 9780128111802
5. N. Jedrecy et al., ACS Applied Materials & Interfaces 10 (2018), 28003
6. D. Stanescu et al., ACS Appl. Nano Mater. 2 (2019) 3556-3569;
7. T. Aghavonian, PhD Thesis Paris-Saclay (2016);

In-situ study of the photomagnetic effect in RbCoFe Prussian blue analogues nanoparticles embedded in an ordered SiO₂ matrix

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ABSTRACT

We are interested in the photoswitching properties of CoFe Prussian blue analogues (PBA) nanoparticles embedded in the ordered mesoporosity of a silica monolith. Thanks to the use of an ordered mesoporosity, we are able to control the morphology, the size and the spatial organization of the PBA nanoparticles.^{1,2} This approach also allows the synthesis of nanoparticles with a well-controlled chemical composition, including the amount and nature of alkali cations inserted in the well-known fcc structure of PBAs, which play a key role in the switching properties. Furthermore, a core-shell structure of these PBA nanoparticles with a peculiar surface structure was recently evidenced by a combined X-ray absorption spectroscopy, X-ray diffraction and IR spectroscopy study.³

Here, we present our recent work on the AILES beamline in which we compared the photoswitching properties of the nanoparticles (5 nm) with a chemical composition of Rb₂Co₄[Fe(CN)₆]_{3.3} (called RbCoFe in the following) to the one of the free powder (100 nm grain size) with the same chemical composition. The photoexcitation occurs at low temperatures when the RbCoFe PBA is irradiated with red light ($\lambda = 785$ nm). During this process, the Co^{III}Fe^{II} \rightarrow Co^{II}Fe^{III} charge transfer between the Co and Fe ions occurs which is accompanied by changes in the metal-ligand bonds and thus in their vibrational properties. The comparison of the spectra of the nanocomposites to the ones of the free powder, diluted in silica powder or not, allows for a better understanding of size reduction and surface effects on the photoswitching properties, as well as the influence of the presence of the silica powder or matrix on the efficiency of the photoexcitation.

REFERENCES

1. E. Delahaye, R. Moulin, M. Aouadi, V. Trannoy, P. Beaunier, G. Fornasieri, A. Bleuzen, *Chemistry* **21**, 16906-16916 (2005).
2. P. Durand, G. Fornasieri, C. Baumier, P. Beaunier, D. Durand, E. Rivière, A. Bleuzen, *Journal of Materials. Chemistry* **20**, 9348-9354 (2010).
3. A. Bordage, R. Moulin, E. Fonda, G. Fornasieri, E. Riviere, A. Bleuzen, *Journal of the American Chemical Society* **140**, 10332-10343 (2018).

Evolution of Electronic Structures and Charge Density Wave Properties in Layered LaSb₂

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ABSTRACT

The charge density wave (CDW) state with a periodic distortion of the atomic position and a corresponding modulation of the electron density has brought great interest in condensed matter physics due to its competition or even coexistence with superconductivity [1-2]. In this work, we have studied the temperature-dependent electronic structures and charge density wave properties of light rare-earth antimonide LaSb₂ by combining the angle-resolved photoemission (ARPES) measurements and density functional theory (DFT) calculations. Interestingly, based on ARPES data, it is observed clearly that replicas of electronic bands and fermi surfaces appear at low temperature, which is a typical feature of CDW formation to lower down the electronic energy by fermi surface nesting effect [3-4]. Besides, the band structure and fermi surface DFT calculations are performed based on the corresponding new modulated periodic structure, which indeed show replicas of electronic bands and fermi surface. It further confirms that the replicas origin from the charge density wave formation and evidences the existence of interesting charge density wave state in layered LaSb₂ material at low temperature.

REFERENCES

- [1] Carpinelli, J.M. *et al.* Direct observation of a surface charge density wave, *Nature*. 381 (1996) 398–400.
- [2] Hill, H.M. *et al.* Phonon origin and lattice evolution in charge density wave states, *Phys. Rev. B*. 99 (2019) 174110.
- [3] Lee, E. *et al.* Angle-resolved and resonant photoemission spectroscopy study of the Fermi surface reconstruction in the charge density wave systems CeTe₂ and PrTe₂, *Phys. Rev. B*. 91 (2015) 125137.
- [4] Wu, D. *et al.* Layered semiconductor EuTe₄ with charge density wave order in square tellurium sheets, *Phys. Rev. Mater.* 3 (2019) 024002.

Unveiling the Electronic State Interplay at Organic DBP/4P-NPD Exciton Blocking Interfaces in Organic Solar Cells

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ABSTRACT

We have recently demonstrated that ultra-thin films of 4P-NPD can function as efficient exciton blocking layers in organic solar cells, resulting in up to 24% enhancement of the power conversion efficiency (PCE) by minimizing exciton losses. The increase in PCE was only observed when ultra-thin 4P-NPD films were used (>1nm) giving the interface a major role in this process. In this study, we have conducted an all in-situ photoelectron study to uncover the full energy level alignment at the interface between DBP (electron donor in organic solar cells) and 4P-NPD (exciton blocker) to understand the mechanisms behind the improved performance in devices with ultrathin 4P-NPD layers. We have gained information of the core levels, HOMO levels, LUMO levels and work functions and observed a mixed interface region with energetic shifts due to charge transfer and band bending, and a corresponding energy alignment that shows minimum HOMO offsets at the interface, and a HOMO energy offset that increases with the 4P-NPD thickness. The HOMO offset represents a barrier for hole extraction, and thus the optimum thickness of 0.7nm for 4P-NPD exciton blocking layers in organic solar cell devices can be confirmed and understood from the detailed energy alignment across the interface.

Decompression Failure In Hydrogen-Exposed Rubbers: Insights From In-Situ Tomography At Anatomix Beamline

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This work was partially funded by the French Government program "Investissements d'Avenir" LABEX INTERACTIFS (reference ANR-11-LABX-0017-01)

ABSTRACT

Exposure of rubber materials to high-pressure diffusive gases and subsequent decompression can lead to cavitation and cracking depending on the exposure conditions. This phenomenon has been evidenced for several gas-polymer systems in the past [1-3] but the failure mechanisms and the multiple couplings between mechanics and diffusion have never been elucidated. The recent interest in hydrogen as an alternative energy carrier and the use of rubbers for sealing components makes the issue of first importance. The relatively high pressures in use, combined with the safety risk associated with hydrogen leakage makes specific demands on the rubber materials used as seals in terms of durability. Decompression failure can be addressed at two different scales. At the macroscopic scale, the main challenge is to capture the statistics of cavity fields and its dependence on the mechanical loading, decompression conditions and material properties, in order to model the residual mechanical and permeation properties.

At the cavity scale, the issue is that of the elementary mechanisms, especially of the relative contribution of macromolecular network swelling and cracking to the cavity inflation and deflation. The role of intrinsic properties of the rubber (stiffness, strain-hardening and toughness) at different steps of cavity growth is not clear either. A major difficulty to handle the problem is the complex loading of the cavity, due to full diffuso-mechanical couplings. Indeed, the expansion and deflation of the cavity depends on the balance between the external hydrostatic pressure and the internal pressure, which depends itself on the volume of the cavity and the gas content inside it, possibly varied by the gas flux at the cavity wall. A precise tridimensional and time-resolved tracking of cavities is thus needed. It was the aim of the reported work, based on an in-situ X-ray tomography experiment initially developed on a laboratory source (spatial resolution 16 μm , temporal 100s) [4-5] and extended under a synchrotron environment on the Anatomix line of SOLEIL synchrotron. The gain in spatial (3 μm) and temporal (4s) resolution made it possible to access the very first stages of growth, to properly quantify anisotropy and to detect residual damage. These different elements showed the existence of a first rapid spherical growth regime which then evolved into an anisotropic regime which reflected an underlying mechanism of cracking. The correlation with the intrinsic fracture properties of the rubber is discussed.

REFERENCES

1. Gent, A. N. & Tompkins, D. A. *J. Appl. Phys.* 40, 2520–2525 (1969).
2. Briscoe, B. J., Savvas, T. & Kelly, C. T. *Rubber Chem. Technol.* 67, 384–416 (1994)
3. Yamabe, J. & Nishimura, S. *Journal of Materials Science*, 46, 2300–2307 (2011).
4. S. Castagnet, D. Mellier, A. Nait-Ali, *Polymer Testing*, 70, pp. 255-262, (2018).
5. M. Fazal, S. Castagnet, A. Nait-Ali, S. Nishimura., *Polymer Testing*, 91, 106723, (2020).

Structural, Magnetic and Magnetocaloric Transitions in $Y_{0.9}Pr_{0.1}Fe_2D_{3.5}$ Deuteride

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ABSTRACT

Hydrogen absorption in rare earth (R) and transition metal intermetallic compounds has raised broad interest not only for hydrogen storage applications, but also for the modification of their physical properties [1]. Several studies have been performed on RFe_2 hydrides as they can absorb up to 5 H/f.u. and form several intermediate phases with various crystalline structures and magnetic properties depending on the H content (1,2). Unusual giant isotope effect has been observed on the magnetic properties of $Y_{1-x}R_xFe_2(H,D)_{4.2}$ compounds which present an itinerant electron metamagnetic behavior for a ferromagnetic-antiferromagnetic transition (3). This first order transition is associated to a large magnetocaloric effect accompanied by a cell volume contraction (4). But, whatever R substitution rate, the transition temperature remains below 200 K which is too low for practical application. We have therefore investigated $Y_{1-x}R_xFe_2(H,D)_{3.5}$ compounds presenting magnetic transitions near room temperature. The structural and magnetic properties of $Y_{0.9}Pr_{0.1}Fe_2D_{3.5}$ deuteride have been studied by combining synchrotron and neutron diffraction versus temperature, magnetic measurements, and differential scanning calorimetry (5). The synchrotron diffraction experiments were performed on the CRISTAL beam line at SOLEIL. Deuterium insertion induces a lowering of crystal symmetry compared to the cubic C15 parent compound ($Fd-3m$ SG). The deuteride is monoclinic ($P2_1/c$ SG) below 330 K and undergoes a first order transition between 330 and 350 K towards a pseudo-cubic structure ($R-3m$ SG) at $T_{O-D} = 342(2)$ K (6). The compound is ferromagnetic with $T_C = 274$ K. Upon cooling below T_C , a large magnetostrictive effect with an expansion in the basal (a , c) plane has been observed by the analysis of the cell parameter variation and of the magnetic critical exponents. Magnetic entropy variations characteristic of direct and reverse magnetocaloric effects have been observed at T_C and T_{O-D} respectively. As these effects are near room temperature, they are promising for applications.

REFERENCES

1. G. Wiesinger and G. Hilscher, *Handbook of Magnetic Materials*; Vol. 17, edited by K. H. J. Buschow, Elsevier North-Holland, Amsterdam, 2008, p. 293-456.
2. V. Paul-Boncour, S. M. Filipek, I. Marchuk, G. André, F. Bourée, G. Wiesinger, and A. Percheron-Guégan, *J. Phys.: Condens. Matter* **15**, 4349-4359 (2003).
3. V. Paul-Boncour, M. Guillot, G. Wiesinger, and G. André, *Phys. Rev. B* **72**, 174430 (2005).
4. V. Paul-Boncour and T. Mazet, *J. Appl. Phys.* **105**, 013914 (2009).
5. V. Paul-Boncour, A. Herrero, V. Shtender, K. Provost, E. Elkaim, *J. Appl. Phys.*, **130**, 113904 (2021).