N°23

LE RAYON DE SOLEIL

THE SYNCHROTRON MAGAZINE

Crystallography at SOLEIL

SOLEIL SYNCHROTRON

CONTENTS

The magazine of the SOLEIL Synchrotron_N°23 November 2013

To subscribe to
Rayon de SOLEIL
click on
www.synchrotron-soleil.fr

Editorial

Jean Daillant
Director General

2013 has offered rich scientific results as well as national and international events involving SOLEIL teams. We are now a few days away from the launch of the International Year of Crystallography on 20th and 21st January at the UNESCO headquarters in Paris.

Crystallography is a most interdisciplinary science through which major societal challenges do find answers. Synchrotrons are crucial facilities when it comes to studying matter and dedicating this issue to the research carried out at SOLEIL in crystallography was an obvious choice. About half of SOLEIL beamlines, currently operating or under construction, use diffraction or scattering, sometimes coupled with other techniques. Hence, this issue is an opportunity to display the wide experimental field SOLEIL beamlines cover and the complex processes they reveal.

Besides, this issue of Rayon de SOLEIL presents innovative ideas and instrumental developments now available to our users.

IPANEMA's director, Loïc Bertrand, welcoming Genevieve Fioraso, French Minister for Higher Education and Research, and Jean-Paul Huchon, President of the Ile-de-France Region, accompanied by an official delegation of local and regional representatives.

INAUGURATION

IPANEMA

ON SEPTEMBER 12TH, 2013 Geneviève Fioraso, Minister for Higher Education and Research, and Jean-Paul Huchon, President of the Ile-de-France Region, inaugurated IPANEMA (CNRS / Ministry of Culture and communication) on the SOLEIL synchrotron site. IPANEMA is the European research platform for the advanced study of materials relating to archeology, paleontology, ancient environments and cultural heritage. IPANEMA's construction and equipment were funded equally by the State and the Ile-de-France Region, and include a research building adjacent to the SOLEIL synchrotron and the PUMA beamline, optimized for ancient materials.

EUROPE

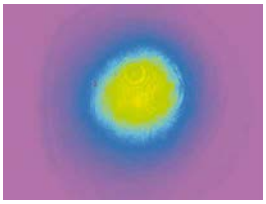
Prize winner

MARIE-EMMANUELLE COUPRIE, HEAD OF THE MAGNETISM AND INSERTION DEVICES GROUP AT SOLEIL, has been awarded an ERC (European Research Council) grant for the COXINEL1 project. COXINEL aims to demonstrate that, by using laser acceleration, it is possible to obtain the free-electron laser (FEL) amplification needed to develop more compact light sources. FEL are the first tunable X-ray lasers and the most intense light sources in the X-ray energy domain. COXINEL benefits from a very favorable environment at SOLEIL and more widely on the Paris-Saclay campus, particularly in terms of engineering, to turn the ideas and theories that physicists have devised into reality.

1. COXINEL : COherent Xray source INferred from Electrons accelerated by Laser.

IN BRIEF

FEMTO-SLICING



August 2013: the first step in the femto-slicing project. The laser beam starting in the laser hutch on the CRISTAL beamline and after a journey of more than 80 meters and guided by several mirrors, is propagated in the part of the storage ring where it will interact with the electron bunches in the wiggler. The goal: to generate pulses of femtosecond synchrotron radiation.

USERS' MEETING

As part of the International Year of Crystallography, the 9th SOLEIL Users' Meeting (23-24 January, 2014) will start with a morning's satellite session: 4 plenary conferences dedicated to crystallography, at Ecole Polytechnique (Palaiseau).

PROTEIN-LIGAND INTERACTIONS

The sensation of astringency in the VUV rays of the DESIRS

Astringency is the feeling of dryness and puckeriness inside the mouth that accompanies the consumption of plant products, such as wine or tea, or unripe fruit. Tannins, secondary plant metabolites, are at the origin of this feeling, which is still poorly characterized. A new approach using mass spectrometry coupled with VUV radiation, developed on the DESIRS and DISCO beamlines has helped to better understand the molecular mechanisms involved in this astringency phenomenon.

The ion trap on its mobile frame (on the right-hand side), installed here on the DISCO beamline, as it was coupled to the DESIRS beamline for the experiments on the IB5 protein.

One of the players involved in this feeling of astringency is a family of salivary proteins, called proline-rich proteins (PRPs), one of the «intrinsically disordered proteins» and therefore flexible. PRPs have a high affinity for tannins, molecules produced by bark, roots, leaves or fruit. These PRPs trap and bind tannin molecules (ref. 1). They are particularly abundant in the saliva of mammals with diets rich in tannins, this function having been selected to protect the body from the anti-nutritional effects of tannins. Indeed, the tannins will also bind to enzymes involved in digestion, rendering them inactive and therefore with repercussions on digestion.

Studying PRPs: a real headache

CAs with other intrinsically disordered proteins, the absence of a well-defined 3D structure and the many repeat PRP sequences makes them and their interactions difficult to study using standard structural biology techniques, such as crystallography or nuclear magnetic resonance.

However, the use of alternative approaches has provided a certain amount of information about these interactions. Thus, using small angle X-ray scattering (SAXS) technique on the SWING beamline has

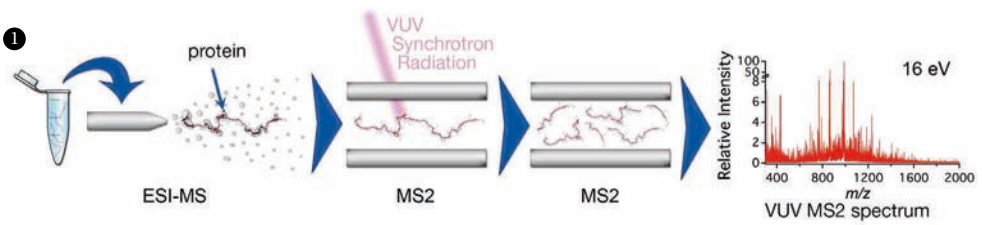


Figure 1 : Diagram of the MS/MS technique based on activation by VUV synchrotron radiation.

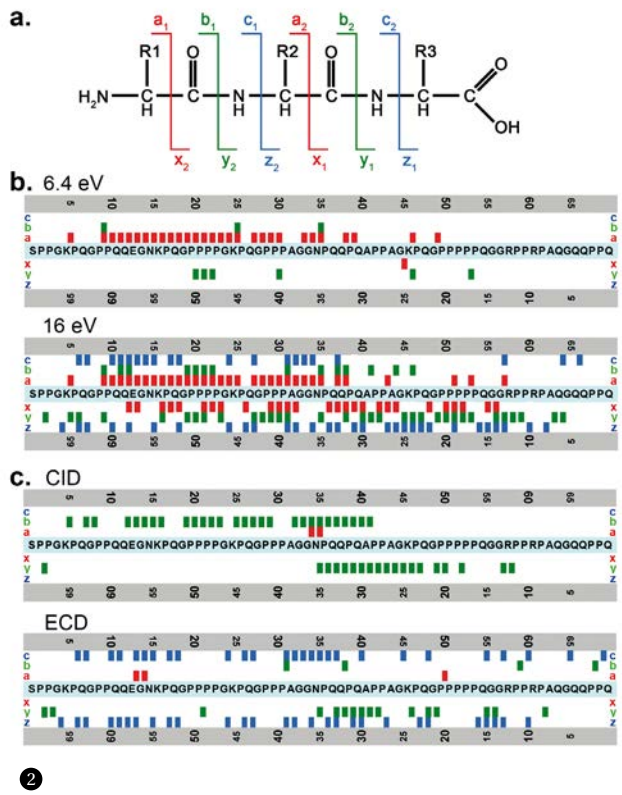


Figure 2 : Nomenclature for MS/MS peptide fragmentation (a). Patterns of $IB5^{7+}$ protein fragmentation after activation at 6.4 and 16 eV (b), by CID and ECD (c).

helped characterize the conformation of these proteins (ref. 2) as well as the supramolecular objects formed during their interactions with tannins (ref. 3).

Using mass spectrometry, the stoichiometries of PRP•tannin (ref. 4) complexes have been determined, and this technique, when coupled with ion mobility, showed that PRP-tannin binding induces a conformational change in PRPs (ref. 5). However, the localization of the tannin-PRP interaction sites had not yet been precisely determined. A new approach using mass spectrometry coupled with VUV radiation, developed on the DESIRS and DISCO beamlines, has answered this question (ref. 6).

Mass spectrometry and reasoned fragmentation

This technique is based on the coupling of a commercial ion-trap mass spectrometer with synchrotron radiation (ref. 7) (Figure 1). The development of sensitive electrospray ionization (ESI) sources, which make it possible to ionize and desolvate molecular and supramolecular biological objects without fragmenting them, now makes mass spectrometry (MS) a powerful tool for the study of biological objects. Indeed, MS is a fast, sensitive and specific technique, but also able to provide information on the structure of molecules. This information can be generated by tandem mass spectrometry experiments (MS/MS) in which an ionized target molecule is selected, then activated and dissociated into fragments, which then are analyzed and identified in a final step. The standard technique for activating ions, called «collision induced dissociation» (CID) and provided on most commercial mass spectrometers, involves slow heating of ions through collisions with a gas. This method is not applicable to locating non-covalent interactions between a protein and another object. To locate interaction sites between a ligand and a protein an activation method is required to fragment the polypeptide chain while maintaining the ligand linked to its interaction site. The technique that has been developed activates the target molecule using active radiation in the ultraviolet range under vacuum (VUV) (Figure 1).

How do VUVs may produce fragments

The relevance of the MS/MS technique is related to the wealth of information it can generate and therefore the number of fragments produced, as well as the quality of

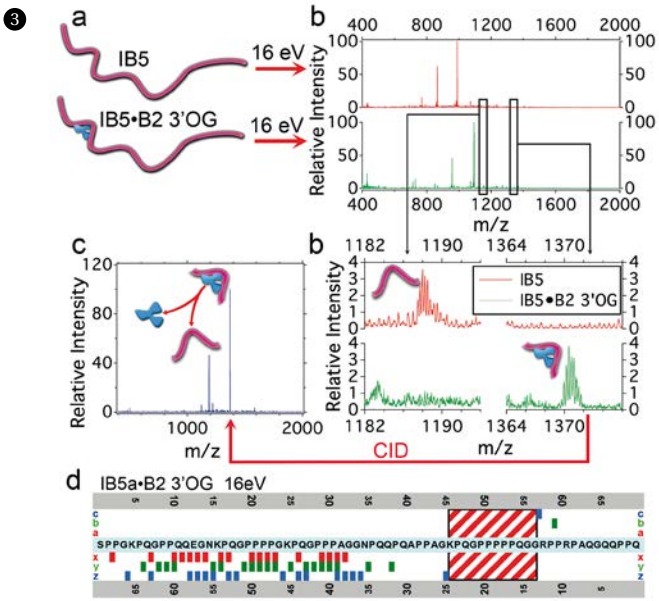


Figure 3 : Localisation of the B2 3'OG binding site on IB5. The objects $IB5^{7+}$ and $IB5•B2\ 3'OG^{7+}$ were selected and irradiated with 16 eV photons (a). Comparison of the MS/MS 16 eV VUV spectra identified specific fragments in the $IB5•B2\ 3'OG^{7+}$ fragmentation spectrum in which the m/z ratio had a mass difference corresponding to that of $B2\ 3'OG^{7+}$ compared with fragments from the fragmentation spectrum of $IB5^{7+}$ (b). CID activation of identified fragments confirmed the presence of the ligand (c). The map of B2 3'OG-carrying fragments identified the 'KPQGPPPPPQGG' sequence as a B2 3'OG binding site on IB5.

the information provided. The first step in validating this method focused on comparing the fragmentation patterns obtained by VUV irradiation with those obtained with standard techniques such as collision-induced dissociation (CID) or electron-capture dissociation (ECD). For this, the human salivary protein IB5 with a +7 charge state ($IB5^{+7}$), was activated by four different radiation wavelengths, and two laboratory techniques (CID and ECD). Figure 2 shows the fragmentation patterns obtained for two photon energies (6.4 and 16 eV), as well as for the CID and ECD experiments. Comparison of fragmentation patterns shows that below the ionization threshold of the protein (6.4 eV) the majority of fragments are those formed by breaking the C-C bond (α-bond type), while above the ionization threshold (16 eV), all types of fragments are present. This observation confirms the existence of two different fragmentation regimes. Below the ionization threshold, the fragments generated result from the photodissociation of the ion precursor, whereas the appearance of radical cations $[M+7H]^{\bullet 8+}$ and $[M+7H]^{\bullet\bullet 9+}$ lead predominantly to a dissociative photoionization mechanism. This mode of fragmentation is the most informative and requires the use of photon energy in the VUV. Thus, thanks to synchrotron radiation, a 91% sequence coverage was obtained while it was only 58% by CID and 68% by ECD.

Tannin and PRP remain linked

In a second step, the study focused on the interactions between the IB5 protein and a model tannin, B2 3'OG. The non-covalent complex $IB5•B2\ 3'OG^{+7}$ was preserved during the ionization step and was then selected and irradiated by the synchrotron beam. Figure 3b shows the comparison of the MS/MS 16 eV VUV spectra of $IB5^{+7}$ and $IB5•B2\ 3'OG^{+7}$. This comparison made it possible to identify about forty peaks present only on the fragmentation spectrum of $IB5•B2\ 3'OG^{+7}$ and therefore potentially the ligand carrier. This analysis also verified the presence of fragments without the corresponding tannin on the fragmentation spectrum of the protein alone. An additional MS/MS step (MS^3) targeted ligand carrier fragments, but this time they were activated using CID, to separate the fixed tannin and confirm the identity of the fragments. Figure 3c shows the MS^3 spectrum of a tannin-carrying fragment. In this figure, two major peaks are present, corresponding to the selected parent ion and to an ion fragment with a lower mass, corresponding to the lost tannin. The identification of these fragments finally showed that the 'KPQGPPPPPQGG' sequence contains the preferred tannin interaction site on the IB5 protein (Figure 3d). Within this sequence, the 5-proline cluster probably adopts the start of a secondary type I or II polyproline helix structure, forming a rigid element, thus providing an initial anchorage point for tannin (ref. 8).

This study demonstrated the potential of coupling mass spectrometry with the VUV radiations for the structural study of flexible proteins such as IDPs and their supramolecular assemblies. The technique could be applied to other types of protein, but can also be adapted to the study of many other biological structures such as sugars, lipids, DNA and RNA... at the molecular and supramolecular level. Indeed, this technique could also generate specific fragmentation with regard to the structure of the object studied, depending on whether it is folded or completely denatured and thus reveal the tertiary or quaternary structure of proteins in addition to their primary sequence.

→ **Contacts :**
alexandre.giuliani@synchrotron-soleil.fr;
francis.canon@dijon.inra.fr

References :
[1] F. Canon et al. *Anal. Bioanal. Chem.* **2010,** 398, 815-822.
[2] H. Boze et al. *Biophys. J.* **2010,** 99, 656-665.
[3] F. Canon et al. *Langmuir* **2013,** 29, 1926-1937.
[4] F. Canon et al. *Anal. Bioanal. Chem.* **2009,** 395, 2535-2545.
[5] F. Canon et al. *J. Am. Chem. Soc.* **2011,** 133, 7847-7852.
[6] F. Canon et al. *Angewandte Chemie* **2013,** 52, 8377-8381.
[7] A. R. Milosavljevic et al. *J. Sync. Rad.* **2012,** 19, 174-178.
[8] M. Fuxreiter et al. *J. Mol. Biol.* **2004,** 338, 1015-1026.

INSTRUMENT DEVELOPMENT

HAXPES or easy photoemission

Using the HAXPES (hard X-ray photoemission spectroscopy) station on the GALAXIES beamline, it is possible to carry out high kinetic energy photoemission experiments on samples in the solid, liquid or gas phase (ref.1). The ability to analyze kinetic energies ranging from 10 eV to more than 10 keV makes this a unique experimental station at SOLEIL.

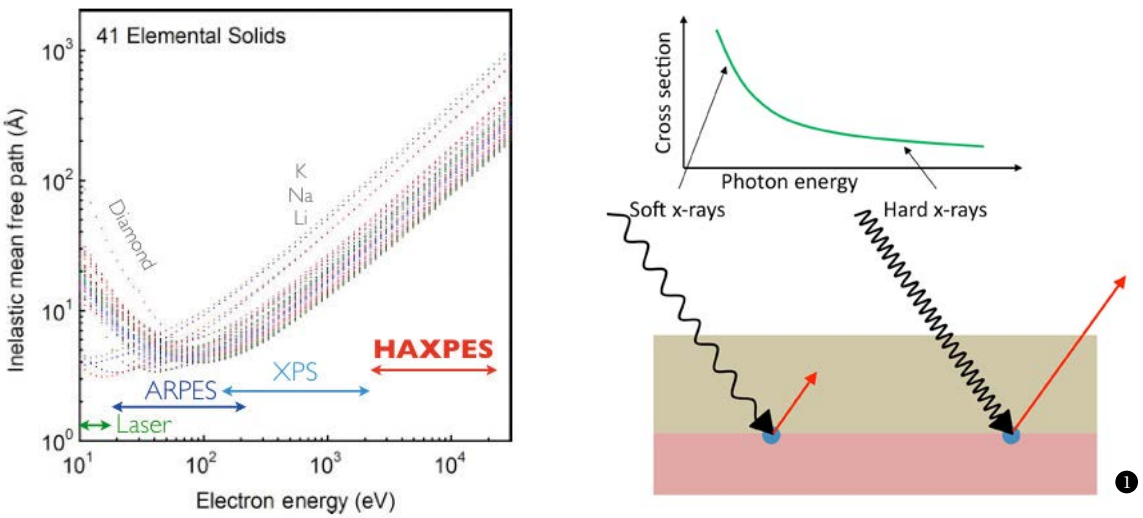


Figure 1:
On the left, the electron inelastic mean free path as a function of its kinetic energy. The high sensitivity of HAXPES in depth is illustrated on the right for a (red) buried interface. With soft X-rays, the electron excited at the interface (red arrow) cannot exit from the material because of insufficient kinetic energy. In contrast, at high photon energy, the electron has a high energy and is able to exit the material and be analyzed. The downside is lower ionization efficiency (green curve).

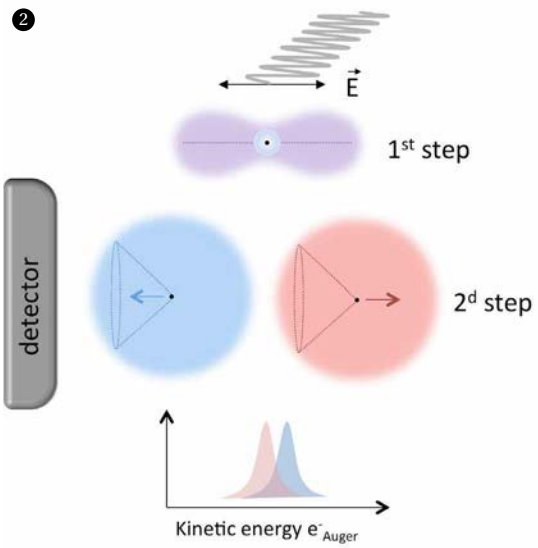
There are several advantages in the use of high energy. First, the energy analysis of the emitted electrons gives specific information about the ionized element and its chemical environment. At high energies, it is possible to reach deeper electronic shells which relaxation is very fast ($t < 10^{-15}$ s). On the other hand, due to the high kinetic energy of the electrons, it is possible to probe about 10 times deeper into the material than with standard photoemission (VUV and soft X-rays), which opens the way to the study of interfaces, buried layers or ion mobility in liquids. HAXPES is generally much less sensitive to the surface condition of materials than standard photoemission techniques and requires no special treatment of the surface. It is particularly well suited for applied materials (multi-layers, buried interfaces and functional materials).

Seeing the movement of atoms

In the case of an isolated atom, ejecting an electron by giving it high kinetic energy leads to nuclear displacement, i.e. a recoil effect. This phenomenon is difficult to identify because of the large mass difference between the electron and the nucleus. To induce a strong effect, the photoelectron must have a high kinetic energy during ejection. At high energies, however, the spectral resolution decreases as well as the effective ionization cross sections, making it difficult to measure. An alternative way is to measure the recoil effect not directly on the photoelectron spectrum, but on the Auger spectrum, which does not depend on the incident energy bandwidth. On the GALAXIES beamline, the high photon flux and large angular acceptance of the electron spectrometer can compensate for the reduction in effective ionization cross-section. These parameters allowed us to make measurements of Auger spectra of ionized neon 1s shells and show that the recoil can be big enough for a separation of Auger lines to be possible. The observed process, equivalent to a Doppler effect, showed that the dependence of the Auger effect on the photon energy was possible because of the nuclear movement (ref.2).

HARPES or bulk band structure

The properties of materials are largely based on their electronic structure. The method often used to visu-



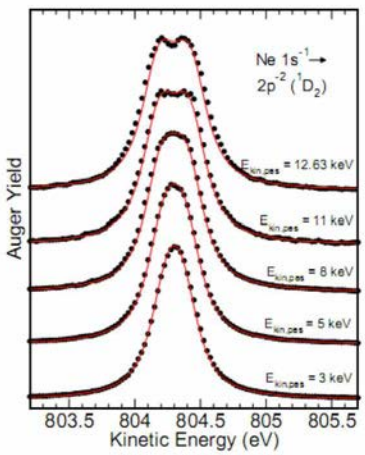


Figure 2: In the first step, an electron from the Neon 1s shell is ejected with a cos² angular distribution with respect to the polarization vector (shown in purple). The Ne⁺ ion recoils in the opposite direction. Auger relaxation occurs in a second step as a result of this ion motion. Auger electrons are emitted (1) isotropically (blue and red clouds) and (2) collected necessarily towards the detector (cone in the figure). Those emitted from the ion whose pulse is directed at the detector (blue arrow) are measured as being faster than the electrons emitted in the opposite direction (red arrow). The experimental results (dots) and numerical simulations (red) are shown on the right for different kinetic energies of Ne1s photoelectron (ref.2).

alize this structure is called ARPES (angle-resolved photoemission spectroscopy). This combines the kinetic energy detection of photo-emitted electrons with emission direction measurements (the electron momentum). When both kinds of information are combined, it is possible to reconstruct the electronic structure.

The development of ARPES is important for the study of fundamental physical phenomena such as electronic correlations, superconductivity or topological insulators. Measurements are traditionally performed with low energy photons to benefit from the high energy and high time resolution and greater cross section. However, this requires having perfectly clean surfaces which limits the method to mostly two-dimensional samples. Moreover, even in ideal cases, ARPES ultimately only provides a picture of the surface electronic properties due to the very short mean free path and not of the bulk state.

Recent studies have shown that it is possible to perform these measurements with high kinetic energy, paving the way for the characterization of the bulk electronic structure of materials, using HARPES (hard x-ray angle-resolved photoemission spectroscopy), based on the traditional technique. The first measurements on the GALAXIES beamline (see Figure 3) show the feasibility of the method and pave the way to new applications, such as the study of the electronic structure of buried layers or interfaces.

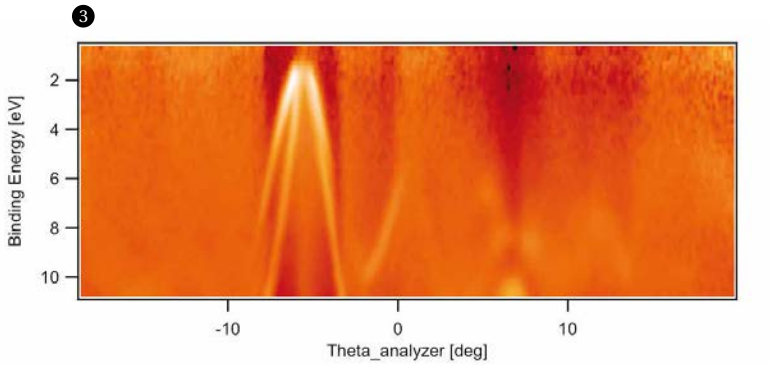


Figure 3: High kinetic energy band structure or HARPES in doped diamond obtained on the GALAXIES beamline. The measurements were performed at 15 K with incident photons of 2.5 keV (ref.3).

Conclusion

The HAXPES station on the GALAXIES beamline has extended the photoemission field to high kinetic energy. This method allows materials to be probed in depth, providing so far unexplored photoemission opportunities to study materials and diluted (gaseous, liquid) phases. The reduced surface sensitivity makes HAXPES measurements easy to perform.

→ **Contacts :**
denis.ceolin@synchrotron-soleil.fr ;
jean-pascal.rueff@synchrotron-soleil.fr ;
marc.simon@upmc.fr

References:
[1] D. Céolin et al. J. Electr. Spectr. and Relat. Phenom. (accepted)
[2] M. Simon et al. Phys. Rev. Lett. (submitted)
[3] C. Fadley et al., in preparation

FOCUS ON

AILES/Ultra-high vacuum group: a long-path cryogenic cell for IR absorption

The AILES beamline, which exploits the brillance of SOLEIL for spectroscopic analysis in the infrared (IR) field, has linked up with the Ultra-High Vacuum Group and LISA[1], to develop the first long-path cryogenic cell for the quantitative analysis of gas in the IR - THz[2].

IR spectroscopy plays a key role in the remote sensing of molecules in inaccessible environments (plasmas, combustion, astrophysics, etc.) or for the quantification of molecules in the atmosphere. The interest of the scientific community has motivated the development of a long-path cryogenic gas cell. Low temperature measurements are used to study these molecules in situ or even to depopulate the excited vibrational or rotational levels, an essential prerequisite for analysis and modeling.

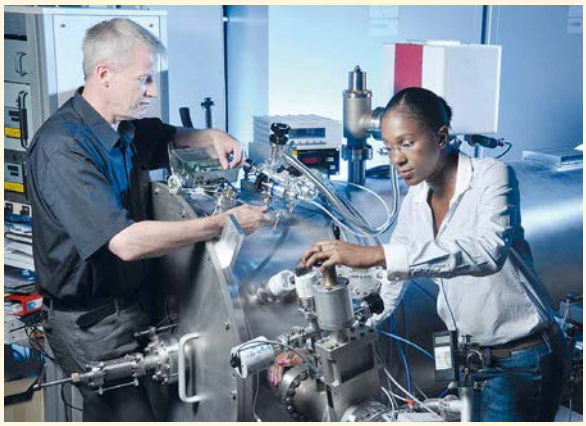
The aim was to have a cryogenic gas cell, homogeneously cooled, compact enough to be used on the AILES beamline but capable of generating optical paths over one hundred meters long. A specific device was developed, optimized for both the mid and far IR ranges, allowing easy switching between these two ranges on the same samples or a rapid change of optical path, while being compatible with oxidizing or halogen gases. Such an instrument is unique, as far as we know.

Cryogenics and IR optics, a long-pathway and stability: conflicting demands...

Many challenges had to be met: in addition to obtaining a long optical path, the distance light traveled had to be controlled between 3 and more than 140 meters, but also at temperatures between -190 and +100°C, with a perfect seal and the use of materials resistant under vacuum and to the gases to be studied, IR optics compatible with low temperatures, together with ultra-high vacuum and cryogenic systems that do not generate any acoustic vibration. With solutions relying heavily on vacuum technology, a close collaboration developed between the AILES group and the Ultra Vacuum Group. Other skills present at SOLEIL were also mobilized: the Design/Engineering Group for the mechanics and modeling of thermal constraints, together with the Pulsed Elements Group for electronic wiring.
In addition to the commitment and skills of SOLEIL, a key element of success has been the ability to rely on the technical expertise of local industrial partners: the mechanical precision design of the quadruple cryogenic cell (STIM, Cachan), and optics and thin films (MAT Technology, OPTIMASK, Morangis).

A need for precision metrology...

One specific requirement was for the development of a pressure sensor in the sub-millibar range, for accurately measuring the pressure of the gases for which the profiles and IR absorption cross-sections are being determined. Such a device was developed at SOLEIL in collaboration with the Ultra-High Vacuum Group.



Laurent Manceron and Laetitia Lago setting up the cryogenic cell...

Up and running at the end of 2012!

After more than two years of development and testing, the first measurements were carried out in late 2012[3] and since then there have been increasing numbers of requests for studies on anthropogenic atmospheric gases (SF_6, CF_4, CF_3I, C_3H_8 or volatile organic compounds) in collaborations or as user requests (U. Bourgogne, LISA, U. Aachen, IMK Karlsruhe, etc.)

1. LISA: Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS - U. Paris Diderot et Paris Est (contact: Fridolin.Kwabia@lisa.u-pec.fr)
2. Range covered: wavelengths from 2 to 1000 µm
3. See http://www.synchrotron-soleil.fr/Soleil/ToutesActualites/2013/AILES-Modelisation

→ **Contacts :**
laurent.manceron@synchrotron-soleil.fr;
laetitia.lago@synchrotron-soleil.fr

EXPERT PORTRAIT

RYUTARO NAGAOKA, HEAD OF THE "ACCELERATOR PHYSICS" GR

With a PhD in theoretical nuclear physics from the University of Tokyo, Ryutaro Nagaoka very quickly decided to specialize in accelerator physics. A change of direction that reflected his desire to work in a scientific field that applied more directly to society. In his view, the work of his nuclear physicist colleagues was too «solo». Synchrotrons have allowed him to work as part of a group, and SOLEIL even asked him to head one. The career path of an accelerator globetrotter.

What led you to work at SOLEIL?

When I decided to leave the nuclear physics field for that of accelerators, that is to say after my PhD, I started at the RIKEN laboratory in Tokyo. I joined SPring-8, but I quickly left Japan for Europe, where my career took off: in Italy at Elettra for six years, then to France at the ESRF for another six years and finally SOLEIL since 2002. Each time I moved following a proposal to join a group. These successive posts have allowed me to intervene each time at a different stage of the synchrotron: the SPring-8 storage ring complex had not yet been built when I worked on its lattice design and optimization, I participated then in the commissioning of the machine at Elettra, then was asked to improve the performance of the ESRF ring. It was while I was at the ESRF that I met Jean-Marc Filhol. Shortly after leaving to form part of the SOLEIL project, which had not yet been built, Jean-Marc proposed me to join the "Accelerator Physics" group here.

So what was your task at SOLEIL?

My role, as I was already doing in part at the ESRF, was to study the instability of the electron beam: determine its level of interaction with the environment, simulate the beam dynamics... all this in order to ensure that the intensity of the beam could ultimately reach 500 mA. It was in this context that I was put in charge of the development of the transverse feedback system (see Rayon de SOLEIL N° 19, p. 11). This maintains, by means of continuous corrections, a stable high-intensity beam, by keeping the transverse beam sizes very close to the theoretical values. This system, necessary in continuum for the beam's performance to remain

OUP AT SOLEIL

optimal, is now routinely used. To develop it, several SOLEIL groups were brought together: Diagnostics, Radio Frequency and Design Engineering.
Then, in 2011, I replaced Amor Nadji, who had been appointed Director of the Sources and Accelerators Division on Jean-Marc Filhol's departure. I became head of the Accelerator Physics group.
This management role was a big change and a novelty for me as, until then I had just concentrated on my own projects. I am now committed to also monitoring and supervising those in my group!

And now, what are the challenges?

When I started working with synchrotrons 26 years ago, no 3rd generation machines were yet in operation. At that time the main concern was how to store the electron beam.
When this was met, the next was to characterize the machines and improve their performance. SOLEIL, which was built a few years later than the first 3rd generation synchrotrons such as the ESRF, represents a state-of-the art 3rd generation light source, of which we can be proud. But we must think of the future.
Now, physicists have a new challenge: to push the performance of synchrotron storage rings to their limits – referred to as «Ultimate Storage Rings» or USRs. The goal is to reduce the horizontal emittance, which is the key parameter in greatly increasing the flux density of photons emitted and achieving transverse coherence of the beam. This emittance is aimed to be reduced by an order of magnitude from 4 nm, currently at SOLEIL, down to a value of 400 pm! Studies are already under way; several models are now feasible thanks to advances in technology, especially in magnetism. Very high fields are required, provided by electromagnets that are not superconductors but very thin and placed close to the electron beam. This in turn requires designing smaller vacuum chambers, to tolerate fewer errors on the beam path ... In other words, there will be an impact on the entire machine. Such USRS are already under construction in Sweden (MAX IV) and Brazil (Sirius). These synchrotrons have been designed from the outset to be USRs. In the case of SOLEIL - but also the ESRF, Diamond or SPring-8, who are working on it as well – what is involved is an upgrade of an existing machine. Such an adaptation is more complex to implement than designing from the start and also risks closing access to users. Modifications must be carried out in such a way as to minimize as much as possible the duration of shutdown. For the ESRF, the upgrade is planned to take effect by 2020 with a year of shutdown, and Diamond and SPring-8 are considering similar timetables. To maintain SOLEIL "in the race", a lot of work therefore lies ahead of us.
And that's not all: a theoretical study is underway, initiated by Amor Nadji with an interest of laboratories such as the ESRF, SLAC, and MAXLAB. This concerns the production of a completely round beam in a straight section of the ring. The study uses the 12-meter long straight section of SOLEIL as a test bench, in which are arranged "skew quadrupoles", a solenoid and an insertion device to produce the radiation. Preliminary calculations show that an emittance of 200 pm could be locally achieved. We would like to go further by showing the experimental feasibility of such a scheme when undertaken in a collaborative venture among the four laboratories.

And looking back at 11 years at SOLEIL?

They have flown fast... And I would like to express my gratitude to SOLEIL because I felt integrated into the project as soon as I arrived. I much appreciated the open-mindedness of all of my colleagues. And with these new challenges, the coming years will no doubt pass very quickly too!

→ **Contact :**
ryutaro.nagaoka@synchrotron-soleil.fr

SPOTLIGHT ON

Storage ring filling patterns for time-resolved based experiments: measuring the purity of electron bunches

When the storage ring operates in top-up injection mode, electrons can accumulate in parasitic bunches, deteriorating the purity of the electron beam filling patterns and hence the quality of time structure of the photon beams provided to the beamlines. But did you know that it is possible to clean out a bunch of electrons?

Different ways of filling up the storage ring

In a storage ring, the accelerating voltage of the radiofrequency (RF) cavities compensates for the energy loss of electrons due to synchrotron radiation and allows them to be regrouped into bunches. In the SOLEIL storage ring (354-meter circumference), the electrons revolve with a 1.18 µs revolution period or a revolution frequency of 846 kHz. As the RF frequency in the accelerating cavities is 352 MHz, the electrons can regroup into 416 separate bunches evenly spaced by 2.84 ns intervals. Each bunch is spread out longitudinally with an approximately Gaussian distribution with a standard deviation (sigma) typically of the order of 12 ps RMS (i.e. 28 ps Full Width Half Maximum) under normal operating conditions (nominal alpha, RF voltage of 3 MV and about 1 mA per bunch).

The photons emitted by these electron bunches are also produced in form of bunches.

If the aim is to have the flux (or brightness) as high as possible, regardless of its temporal distribution, the preferred filling pattern would be 416 bunches as uniform as possible. In the case of SOLEIL, the production of electrons by the linear accelerator (Linac) is then done in the so-called long pulse mode (LPM), which produces 295 ns macropulses, corresponding to a quarter of the storage ring circumference. This injection mode is called "4 quarter injection mode" which is close to uniform filling pattern and achieves a maximum stored beam intensity of 500 mA.

On the other hand, some users of synchrotron radiation take advantage of the time structure of radiation, in particular to study the dynamic properties of materials by means of time-resolved pump-probe experiments. At SOLEIL, this is particularly the case of the TEMPO and CRISTAL beamlines.

However, the time scales of observed phenomena (and detector response) are rarely of the order of magnitude of the 2.84 ns separating two subsequent bunches, but rather in the order of magnitude of a few tens of nanoseconds: the 8 bunch (8 bunches evenly spaced by 148 ns) and 1 bunch (1.18 µs between two bunches) filling patterns answer this strong need.

Although intensities per bunch are higher than in the uniform filling mode, the total intensity that can be stored in these modes is limited: 120 mA (8 x 15 mA) in 8 bunches and 20 mA in 1 bunch. These values originate partly from the collective effects exacerbated by the high density of electrons per bunch and partly from the interactions with the vacuum chamber pipe of the storage ring.

In order to simultaneously meet the needs of high-flux high brilliance experiments and temporal structures, the most commonly used filling pattern in radiation centers are the so-called hybrid modes, where most of the intensity is given by a large number of small contiguous bunches, followed by a window in the middle of which a single (usually higher intensity) bunch is located.

At SOLEIL for the production of these isolated bunches, the Linac works in short pulse mode (SPM): electrons from the cathode are extracted by high-voltage pulses of about 2 ns long RMS in such a way as to minimize the acceleration of electrons out of the targeted bunch; however despite various measures implemented to prevent this phenomenon, some electrons are ex-

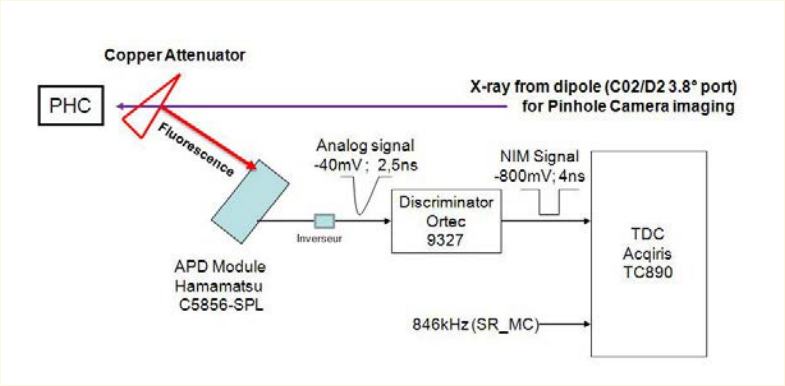
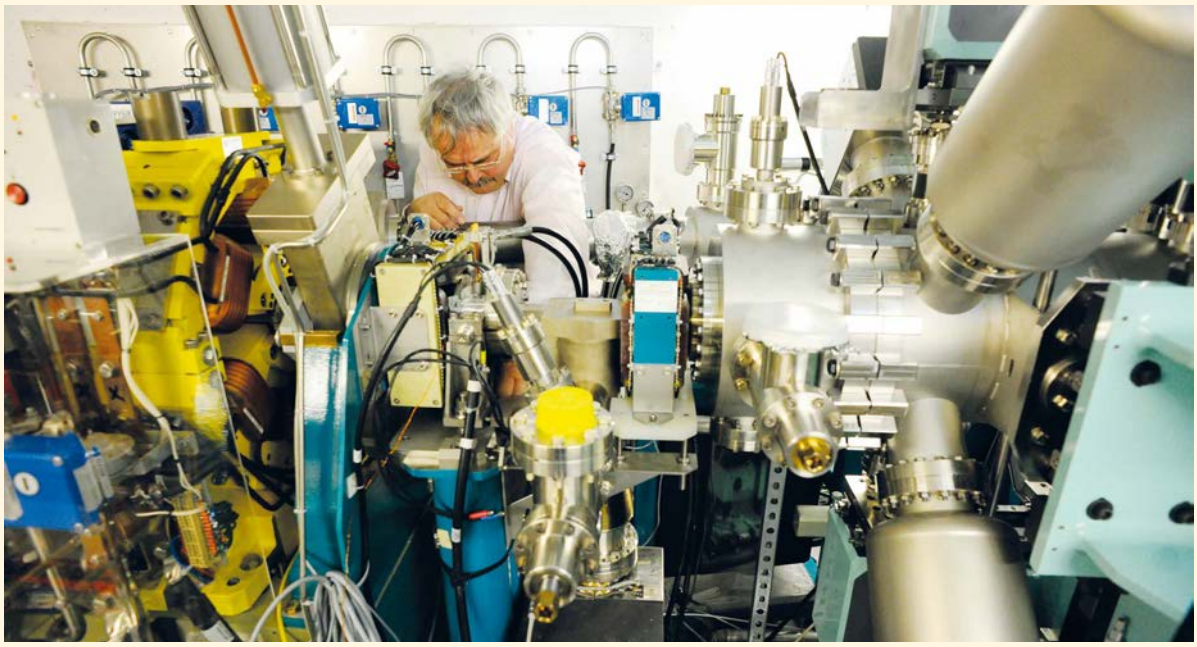


figure 1 : Purity measurement: acquisition scheme.



Lodovico Cassinari, in charge of the Diagnostics Group, working in the tunnel of the storage ring.

tracted from the cathode outside of this time period and accelerated by the Linac.

The purity of stored bunches

Purity is defined as the ratio between the number of photons emitted by undesirable electrons in a supposedly empty bunch and the number of photons emitted by the electrons of the desired bunch (assumed to be isolated), which comes down to be the ratio between the numbers of electrons in the respective bunches.

The injection is done in quarters (corresponding to 295 ns macropulses); the pulsed kicker magnets that allow the incident beam to be injected into the ring are sized accordingly: they are active for time spans slightly longer than these 295 ns. During injection of the isolated bunch, these very pulsed magnets can unfortunately allow the injection of undesirable electrons collected at different stages of the acceleration process ("dark" current emitted by the LINAC gun, for example).

Parasitic bunches thus created with very low intensity: an electron circulating in the ring corresponds to a 13.5 pA current, compared to the current stored in the desired bunches (of the order of a few milliamperes).

However, in the top-up injection mode, as the lifetime of these parasitic bunches is significantly larger than that of the main bunch, the reinjection process may lead to an accumulation of electrons in the parasitic bunches while keeping the intensity of the main bunch constant.

This could result in a deterioration of the purity, lead to a degradation of the time resolution, and worsen the signal to noise ratio of the beamline time-resolved experiments.

Measuring the purity

The system setup at SOLEIL (figure 1) is based on one of the ESRF facility (Ref. 1), using a well-known method (Ref. 2) called time-correlated single photon counting (TC-SPC).

Advantage is taken of the X-ray radiation used for measuring the transverse dimensions of the beam: a thin (1 mm thick) aluminum window allows the highest energy photons produced by a dipole magnet to come out to be imaged by

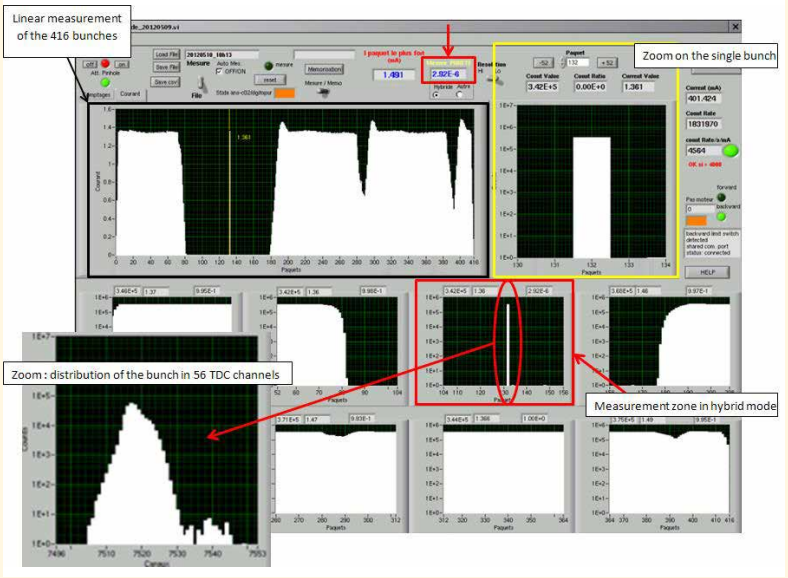
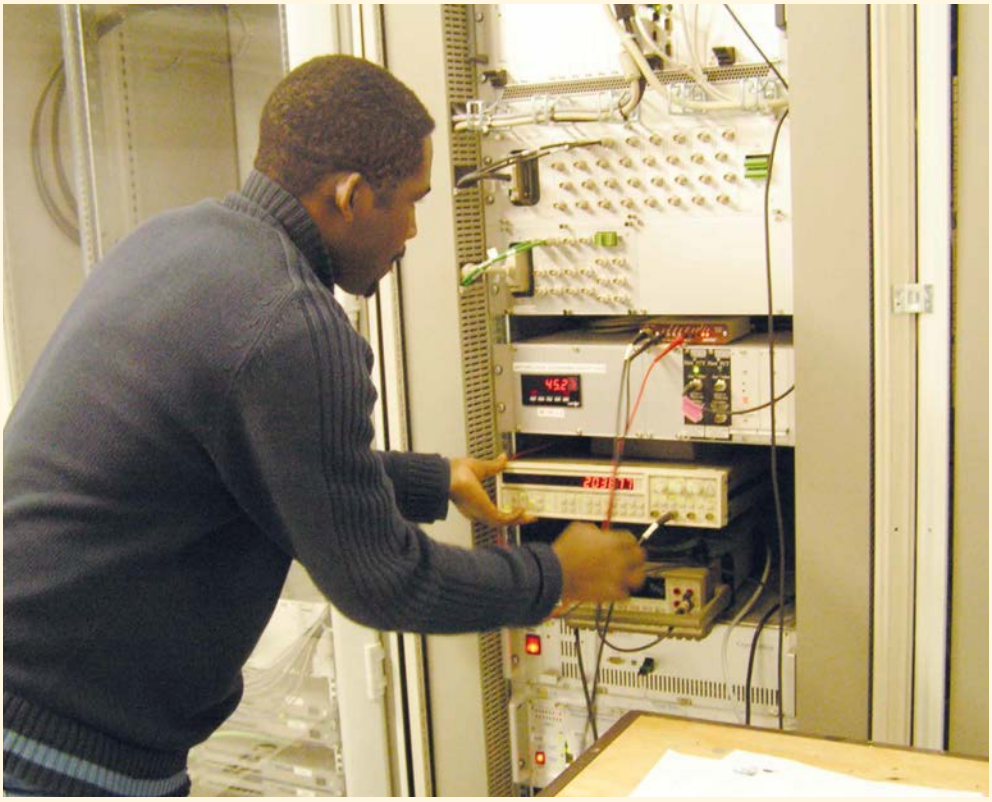


figure 2 : Purity measurement application in the control room.



Purity measurement: Francis Dohou, from the Diagnostics Group, is checking the acquisition electronics.

an optical device called a pinhole camera.
A strip of copper serving as an attenuator is inserted between the X-ray beam and the pinhole camera.
Fluorescent radiation from copper is collected by an avalanche photodiode (APD) radiation hardened by a lead shield. This assembly is motorized to allow the block containing the photodiode to move from its measuring position to its rest position (protection against radiation induced damages in the tunnel).
Given the dynamics required by the system (5-6 orders of magnitude between the intensity of the main bunches and the parasitic bunches), the diode is not used in a linear, but rather in a stochastic mode (hence the use of an avalanche photodiode).
Going through the intermediary of the copper fluorescence, the amplitude of the pulses generated by the avalanche diode is no longer a function of the bunch intensity. On the other hand, at any time, the probability of photons emitted by electrons and deflected by the dipole exciting a copper atom recorded by the photodiode is proportional to the number of these electrons.
Thus, the temporal distribution of the pulses emitted by the diode reflects the temporal distribution of electrons circulating in the ring.
After data processing (discriminator to eliminate diode noise), the pulses are stored in 23624 channels, 50 ps wide, of a TDC (Time-to-Digital Converter), thus covering the 1.18 µs storage ring revolution period (figure 2).
The 50 ps resolution of the TDC would not give a good representation of the distribution within a bunch (of the order of 20 ps RMS); however, this resolution is sufficient to distinguish two consecutive bunches (separated by 2.84 ns).
To achieve the resolution required for measuring the purity (10^{-6}, i.e. a factor of one million between the intensity of the main bunch and the residual bunch), the pulses are accumulated until they reach a million hits in the main bunch. With 4000 counts/mA/s and 5 mA for the main bunch in hybrid mode, the measurement takes 50 seconds.
Typically, the purity achieved during the filling up of the storage ring in hybrid mode (from 0 to 430 mA) is of the order of a few 10^{-6} for supposed empty bunches, except for the bunch that immediately follows the isolated bunch, which is usually of the order of 10^{-5}. However, poor adjustment of the injection parameters (especially in the dephasing of the Linac pulse or of the pulsed magnets) can lead to higher values. Moreover, the situation can only deteriorate progressively over successive injections in top-up mode (see above). It is not uncommon to achieve a purity of 10^{-4} after a few days of uninterrupted beam. This value is within the tolerance of the current demand of the beamlines.

Cleaning out the bunch

Being not immune from an incident that could lead, for example, to the unexpected injection in the empty quarter, it is therefore useful to be able to clean the stored beam by removing unwanted bunches. This means being able to excite a bunch strongly enough to make it unstable without affecting the other bunches. This is accomplished by using the bunch per bunch transverse feedback (FBT) that suppresses the transverse oscillations of individual bunches, which are induced by the interaction of each bunch with its environment (other bunches, vacuum chamber, and ions, etc.).
The transverse feedback used by SOLEIL has sufficient resolution to be able to reverse the polarity of the deflection applied to a particular bunch (anti-feedback). It is thus possible to resonantly excite the targeted bunch, while keeping the feedback function on other bunches.
Developments are underway to implement this "bunch cleaning" function during the machine operation.

→ **Contact :**
Lodovico.cassinari@synchrotron-soleil.fr

References:
[1] B. Joly, G.A. Naylor "A High Dynamic Range Bunch Purity Tool", DIPAC 2001 – ESRF, Grenoble, France.
[2] S. Takano "Beam Diagnostics with Synchrotron Radiation in Light Sources", IPAC,2010, Kyoto, Japon.

Crystallography at SOLEIL

On their beamline SIXS, Alina Vlad and Alessandro Coati are setting up the diffractometer coupled to a ultra-high vacuum chamber.

The International Year of Crystallography in 2014 will celebrate the centenary of Max von Laue being awarded the Nobel Prize in Physics,"for his discovery of the diffraction of X-rays by crystals". This is a small review of the history of crystallography, from ancient times to the latest synchrotrons.

Crystallography at SOLEIL

Erik Elkaïm, scientist at CRISTAL beamline, and one of the three diffractometers of the beamline, dedicated to powder diffraction.

Although crystallography or the "study of crystalline materials at the atomic level" has experienced unprecedented growth due to X-ray diffraction techniques, Man's interest in crystals did not, of course, start just a century ago.

Crystallography before X-rays

Since ancient times, crystals and gemstones have fascinated and made people reflect. The word "krystallos" or ice in Greek was used for the first time in the first century BC to denote quartz. Their geometric shapes, their different faces and translucent aspect evoking purity intrigued many, and these minerals quickly became subjects for study. And Plato gave his name to the definition of the five types of "Platonic solids", classified according to the shape of the regular polygons that constitute their convex faces.

Moving on to the end of the 18th century, Jean-Baptiste Romé de l'Isle and his assistant Arnoult Carangeot noticed that, the angles between the crystal faces of a given species are constant, whatever the lateral extension of these faces and the origin of the crystal. He thus established the law of the constancy of interfacial angles, paving the way for the scientific study of crystals.

At the same period, Abbé Haüy first had the idea (legend has it that he let a calcite crystal drop and continued to break the already broken pieces) that a crystal is a periodic stacking of small entities, creating facets and then faces on a large-scale. From this fundamental discovery was born the "integrant molecules" concept, later called the unit cell, corresponding to the basic unit or building block from which crystals are periodically assembled.

In about 1840, Auguste Bravais, going back to the integrant molecule, translated into mathematical functions the notion of periodicity. Using the concept of

DIFFABS

Ultra-fast acquisition of pole figures: a remarkable change in texture during silicidation

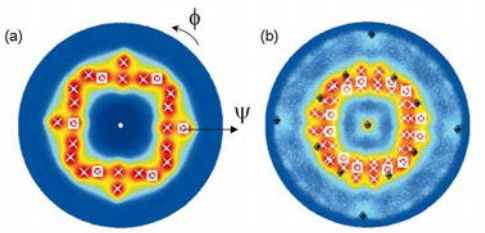


Figure 1 : (a)-(b) Pole figures measured for a Pd_2Si film on Si(001) around $111Pd_2Si$ and $212Pd_2Si$ reflections. $0° \leq \phi \leq 360°$ and $2° \leq \psi \leq 88°$. The white crosses (black diamonds) show the simulated position of the Pd_2Si film peaks (substrate).

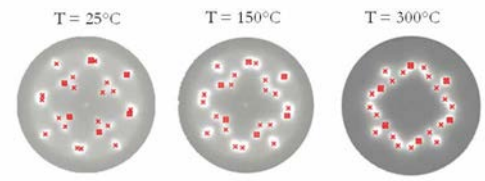


Figure 2 : Pole figures measured *in situ* for a Pd_2Si film on Si(001) around the $111Pd_2Si$ reflection at different temperatures.

Many physical properties of materials are closely related to their microstructure. The crystal structure of a material and its degree of crystalline order are significant parameters. Its texture can be described as the preferred orientation of crystallites in the material. In thin films, the texture influences, in particular, their mechanical, thermo-electric and magnetic properties.
The use of X-ray diffraction to obtain pole figures is a well-established method of characterizing texture. Recently, the use of a two-dimensional detector (XPAD) combined with continuous scanning of the motors on the DiffAbs beamline made it possible to collect complete pole figures in less than a minute.
To validate this original new experimental approach, the texture of the Pd_2Si phase was characterized *in situ* during its formation during the annealing of a thin film (<100 nm) of palladium (Pd) deposited on a silicon substrate (Si). Figure 1 shows two pole figures around the $111Pd_2Si$ and $212Pd_2Si$ peaks obtained after annealing at 200°C. They were used to determine the orientation of the (111) and (212) planes and the texture of Pd_2Si. The figures show the remarkable texture of the Pd_2Si phase characterized by four crystallographic orientation variants. Figure 2 shows changes to the pole figure around the $111Pd_2Si$ peak, as a function of temperature. The figures reveal a continuous rotation of Pd2Si grains around a crystallographic axis during annealing. This remarkable change in the texture can be explained by a diffusion mechanism during the formation of the Pd_2Si phase.
The ultra-fast acquisition of pole figures opens the way to *in situ* monitoring and analysis of the crystallography and texture formation in (ultra) thin films.

→ **Contacts :**
marie-ingrid.richard@im2np.fr;
cristian.mocuta@synchrotron-soleil.fr

"ALTHOUGH THE SEDUCTIVE POWER OF SOLID MATTER HAS LONG DEPENDED ON ITS PERFECT ATOMIC ORDERING, NOWADAYS ONE IS INCLINED TO VALUE THE LACK OF SUCH PERFECT PERIODICITY..."
HUBERT CURIEN, BORDEAUX IUCR CONFERENCE, 1990.

symmetry, he concluded that there are only 14 ways to periodically assemble sets of virtual points, the so-called lattices, where these virtual points are then not identified specifically. But it already appeared that 5-fold symmetry posed a problem.
This first "mathematization" of crystals was completed at the end of the 19th century by several scientists. They showed that, if each point in such lattices is identified by a motif, the constraints dictated by symmetry limited the number of different assemblies, and therefore the possible types of crystals to 230. This gave birth to the theory of space groups, still in use today.
It was not until the 20th century that this pattern was defined as a set of atoms, since the existence of atoms was not yet fully accepted at the time by all physicists.

From theory to practice

The discovery of X-ray diffraction by crystals in the early 20th century was made possible by the convergence of several streams of scientific research and a supportive environment at Munich University. On the one hand, researchers were working on X-rays, electromagnetic waves with such a short wavelength that no slit was thin enough to diffract them. On the other hand, scientists were trying to show that a crystal was indeed an assembly of atoms. This time, the notion of atoms was

To be continued on page 18...

PSICHE

Studying materials in extreme conditions

Figure 1 (up): Paris-Edinburgh cell
Figure 2: multi-anvil cell.

In the universe, materials are found much more rarely at "ambient" pressure and temperature than under extreme thermodynamic conditions; these include very high temperatures in stars and planets (including the depths of the Earth) and very low or zero temperatures in space. Being able to reproduce such conditions is therefore of major importance to geophysicists and geochemists, in order to understand these extreme environments better.
It is also now clear that there is a link between the form and function of materials, and changes to one will also lead to changes to the other. This is true in biology; a protein acquires its function through folding, but also in physics, since a change in the inner structure of the material affects its properties (mechanical, electrical, electronic and magnetic, etc.). In the first case, applying moderate pressure can force the molecule to take on this or that form, which it naturally adopts under given biological conditions, and studying the stability of these forms is often associated with different functions. In physics, due to much higher pressures, the interatomic distances of the sample are modified. Numerous possibilities to "play" with material properties present themselves to the scientists. Finally, in chemistry, in addition to the standard "initial composition" and "temperature", the 3rd parameter "pressure" also opens up numerous possibilities to synthesize new materials. Exploring all the conditions of this three-dimensional matrix is no longer possible by trial and error. The answer lies in in situ analysis: for a given composition, the pressure and temperature can be made to vary, and diffraction can track the creation of new phases until the material of interest is obtained. The aim is then to optimize the thermodynamic path that was followed.
Several facilities are available on the PSICHE beamline to tackle these issues:
• Diamond anvil cells, to achieve the highest pressures (300 GPa), at very low (10 K, cryostat) or very high temperatures (3000 K, laser heating). The volumes are, however, limited to a few µl, thus preventing re-use of the sample.
• Paris-Edinburgh cells, for larger volumes (a few ml) and high temperatures (2000 K) ; the pressure is limited to 15 GPa (IMPMC, P. and M. Curie University collaboration).
• Multi-anvil cells, which, thanks to a press weighing more than 2 tons, can be used to increase samples of a few ml to 40 GPa (in collaboration with the "Laboratoire des Magmas et Volcans", Clermont-Ferrand and the Néel Institute, Grenoble).
Finally, to cite some results already obtained on this beamline, opened to users in 2013: synthesis of Mg carbide (Paris-Edinburgh cell, an IMPMC and P. and M. Curie University collaboration) and using diffraction to determine its crystallographic form; study under pressure of the charge transfer in Prussian blue analogues in order to optimize their response to a light stimulus (ICMO, Paris-South University collaboration); monitoring the compressibility of nanoparticles, of Prussian Blue analogues, depending on their size (Coordination Chemistry Laboratory, Toulouse).

→ **Contact : jean-paul.itie@synchrotron-soleil.fr**

... Continued from page 17

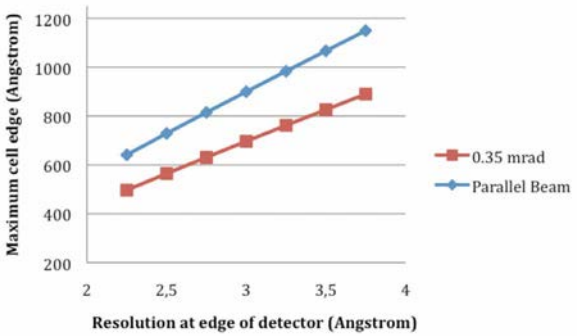
acquired, fractions of nanometers apart. And Max von Laue, a specialist on interference phenomena, urged that this form of radiation must diffract on such objects. In view of the results obtained in 1912 on a crystal of copper sulfate, it is clear that these scientists needed all their motivation to persevere and ultimately record the spots showing that diffraction had occurred. Von Laue received the Nobel Prize in Physics for this discovery two years later.
Then the Bragg, father and son, took up the mantle and improved the experimental setups, developed the first X-ray spectrometers and determined the first structures (KCl, NaCl, then ZnS, FeS_2, etc.). They received the 1915 Nobel Prize in Physics for "services in the analysis of crystal structure by means of X-rays" and founded a school that would train for decades prestigious crystallographers, such as Watson and Crick, co-discoverers of the double helical structure of DNA (Nobel Prize in Medicine in 1962), with Maurice Wilkins and Rosalind Franklin, unjustly forgotten at the time.

X-Rays, electrons and neutrons; crystals and quasicrystals...

Crystallography will then benefit from the development of knowledge and theories in quantum mechanics, which were able to show in 1930 that diffraction was not limited to X-rays, other particles than x-rays could be used as complementary probes: electrons and neutrons.
More recently, in 1982, the discovery of quasicrystals represented the last major paradigm shift in crystallog-

PROXIMA1

Bio-crystallography of macromolecules



Resolution of the unit cell on PROXIMA1, for parallel and divergent beams.

The PROXIMA 1 beamline is used to collect X-ray diffraction data from crystals of biological macromolecules (proteins, nucleic acids and their complexes). In particular the advanced properties of the SOLEIL source allow the beamline to provide a small, intense X-ray beam whilst preserving the beam parallelism (beam divergence around 0.3 milliradian at the sample position). Thus the beam produced by PROXIMA 1 is very well matched to the size, unit cell dimensions, resolution limit and sample mosaicity of large macromolecular complexes such as the ribosome. This point is illustrated in Fig 1 below, which illustrates the maximum unit cell dimension resolvable on PROXIMA 1 as a function of the resolution of the diffraction pattern, and for two different beam divergences (firstly with the beam divergence at the sample position of 0.3 mrad, which is the normal focused condition, and secondly with the beam rendered close to parallel after the mirrors, with a net divergence of 0.05 mrad). PROXIMA 1 uses a variable focus "bimorph" mirror system, coupled with spatial filtering, to adapt the size and divergence of the X-ray beam to the size and divergence acceptance of the crystal samples under study. In addition the possibility, given by the 3 circle "kappa" geometry goniostat, allows the crystal to be orientated in order to position a specific crystal axis in the X-ray beam (for example, to orient a long axis in a direction in which it is easy to control the beam divergence). Using this technology has enabled a number of large macromolecular complexes to be studied on the beamline. An example, where data collection needed careful optimization of the X-ray beam, is given below.

→ **Contact :**
andrew.thompson@synchrotron-soleil.fr

Diffraction of X-rays leads to a diffraction image in "reciprocal space", where large distances in the real world lead to short distances in the diffraction pattern. Hence diffraction spots from large molecules tend to be much more closely spaced in the diffraction pattern than those from small molecules. In order to solve a structure with X-rays, the intensity of a maximum of Bragg reflections must be accurately measured. When the diffraction spots are too close together, this measurement is subject to error (or even impossible). Hence the X-ray beam size, crystal to detector distance and X-ray beam divergence have to be matched to the diffraction properties of the crystal.

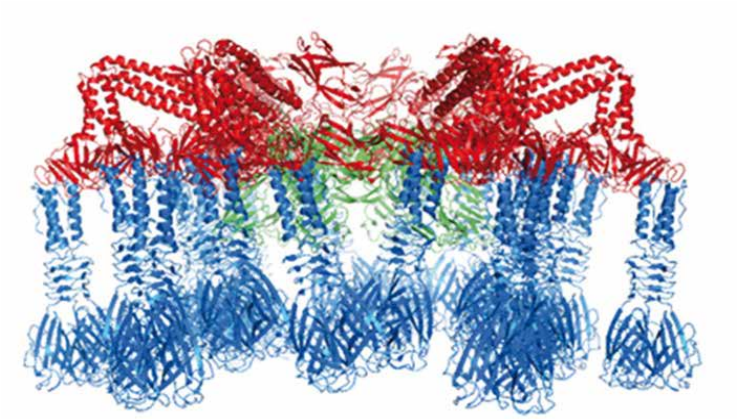
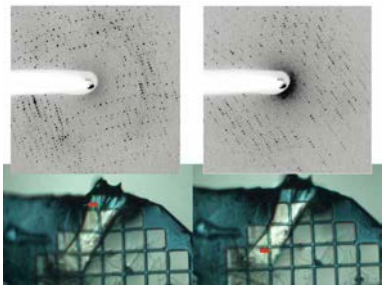


Figure 2 : The structure of the 1.8 MegaDalton baseplate of the phage TP901-1, composed of 78 proteins that self-assemble spontaneously, revealed an unexpected result: an alternative host adhesion mechanism. Unlike the infection strategy known for other phages of lactic bacteria, the Calcium ions, very present in the milk, do not play any role in the case of TP901-1. Furthermore, the way the 78 proteins forming this enormous complex articulate with each other once self-assembled is also original. These results are published in PNAS. Ref: Veesler, D. et al. PNAS, 2012, 109(23): 8954.

PROXIMA 2

Micro-focused X-rays for the Good, the Bad and the Ugly in Bio-crystallography



Two X-ray diffraction images taken from an "ugly" crystal on PROXIMA 2: On the left, a zone at the top of the crystal was exposed, and the diffraction pattern is messy with spots at irregular spacings. On the right, a zone at the bottom of the crystal was exposed, and the diffraction pattern is clean with spots at regular spacings. The red rectangle marks the position and size of the X-ray beam. The sample is mounted on a plastic support with a 25 micron mesh.

The 3-dimensional structure of a biological macromolecule (proteins, DNA, RNA, complex assemblies, viruses, etc) can often explain its function and even help the pharmaceutical industry to make new, more potent and tailor-made drugs.
X-ray crystallography is the most common method used to determine the structure of a biological molecule, but one of the biggest challenges faced by the scientist is to grow single crystals of sufficient size and quality. Typically, hundreds of crystallization conditions are tested before finding one that will produce crystals, which at first are often "ugly" – in other words, clumped, cracked and/or very small – just a few microns in size. Very rarely are these first crystals "good" – nicely shaped, big, single crystals which diffract X-rays well, and sometimes they are "bad" - nicely shaped, big crystals which DO NOT diffract X-rays at all. The bio-crystallographer needs to know whether his crystals are "good, bad or ugly", so that he can optimize the crystallization conditions to produce "good" crystals, which will lead to an atomic 3-dimensional model of the biological macromolecule under study.
On PROXIMA 2, which opened in March 2013, the powerful flux of X-rays are focused down to less than 10 x 5 microns (HxV, FWHM*) to allow users to collect from either very small crystals, or to single out the best zone of an "ugly" crystal. This fine focus improves the signal to noise ratio of the X-ray diffraction pattern from small crystals, but more importantly it can also avoid spurious X-ray diffraction patterns from unwanted material (precipitates, cracks or neighboring crystals). In larger X-ray beams, this extra unwanted material adds extra noise and/or complicates the diffraction pattern, which becomes impossible to process. The micro-focusing of X-rays is crucial for success in the most important and difficult structural projects. For the scientist wishing to obtain good diffraction, it can save months of work preparing better crystals. The screening for the best zone of a crystal is being automated on PROXIMA 2 with 2-dimensional "grid" scans. The diffraction images from these scans will be processed on-the-fly to score the zones and permit the scientist to choose the optimal part of the crystal to collect from. As such, PROXIMA 2 is complementary to PROXIMA 1, where the former permits scientists to screen "ugly" crystals, while the latter employs more specialized structure determination methods.

*FWHM: Full width at half maximum

→ **Contact :**
William.shepard@synchrotron-soleil.fr

... Continued from page 18

raphy, with the questioning of one of the fundamentals of this science: the possibility of 5-fold symmetry in materials with long-range ordered atomic structure (proved by X-ray diffraction). Quasicrystals still remain a relevant research topic.
In synchrotrons, crystallography naturally occupies a prominent place. But structure determination is not limited only to studies using X-ray diffraction, absorption spectroscopies (XANES and EXAFS) can also bring essential structural information...

Thirteen SOLEIL beamlines

Indeed, although crystallography and X-ray diffraction have been historically linked for over a century, the International Union of Crystallography has enlarged the circle by adding X-ray absorption in the study techniques. At SOLEIL, thirteen beamlines are diffraction or scattering beamlines, and two of them allow X-ray diffraction and absorption to be combined. Five research areas emerge from studies conducted on these beamlines.

■ Structural biology

PROXIMA1, the first biocrystallography beamline at SOLEIL, has published more than 300 scientific articles since its opening to users in 2008, reflecting the quality and efficiency of the beamline and its running group, notably in solving such structures as macromolecular complexes, as explained in more detail on page 19. Since March 2013, PROXIMA2 complements PROXIMA1, opening up prospects in terms of crystal screening (see above) and in situ data

CRISTAL

Distribution of cations in materials for photovoltaic cells - resonant X-ray scattering on a Cu_2ZnSnS_4 single crystal

The development of thin film photovoltaic cells without Si, but with high conversion efficiency, is a very active area of research in the current economic climate. Although thin film solar cells based on Cu(In,Ga)Se_2 (CIGS) have already proven themselves, finding new non-toxic materials containing elements abundant on Earth is crucial for the large-scale production of photovoltaic cells. Compounds derived from Cu_2ZnSnS_4 (CZTS) appear to be very good candidates as absorbents in such solar cells [1]. A detailed knowledge of the crystal structure is crucial for improving performance. As Cu and Zn can occupy the same crystallographic site [2,3], the nature of the distribution of these atoms (ordered or disordered, in this case leading to a more symmetrical structure - see figure 2) is crucial in order to link it with their electronic properties. However, as the atomic scattering factors of these atoms are too similar, conventional X-ray diffraction experiments are not suitable in this case. The technique called "resonant diffraction" (or anomalous diffraction) is then essential to differentiate these atoms of adjacent atomic numbers that can occupy the same crystallographic site.

The energy of the X-ray beam has to be adjusted very precisely, so that it is near the absorption edge of one of the elements. As a result, for this element, the number of electrons contributing to the X-ray diffraction is artificially reduced (figure 1), thus increasing the contrast with the adjacent element. The use of synchrotron radiation is therefore essential since only this X-ray source allows for a precise adjustment of the beam energy. The precision required for the beam energy is very high ($\Delta E/E \sim 0.01\%$) and must be maintained over the entire duration of the experiment (from a few hours to several days). A resonant x-ray diffraction experiment at the K-edge of Cu on a CZTS single crystal was performed for the first time, on the CRISTAL beamline. The results obtained made it possible to clearly distinguish the Cu and Zn atoms and thus specify the nature of the distribution of this disordered kesterite-type structure within the cationic planes (figure 2b). The study will now continue to try to understand why a deviation from a 2: 1: 1: 4 stoichiometric ratio seems to improve the conversion efficiency.

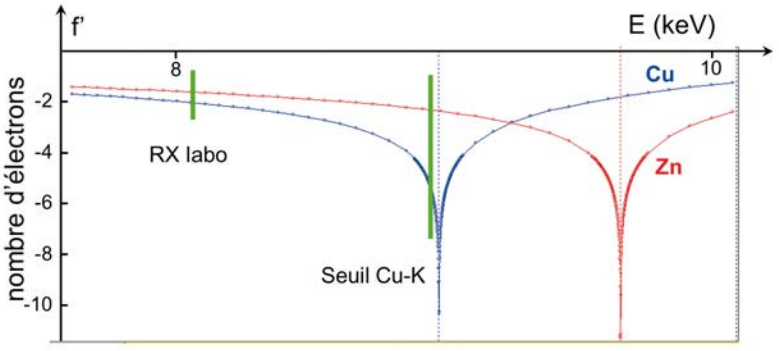


Figure 1 : Evolution of the f' component of the X-ray diffusion factor as a function of energy. The Cu/Zn contrast increases markedly close to the absorption edge of copper.

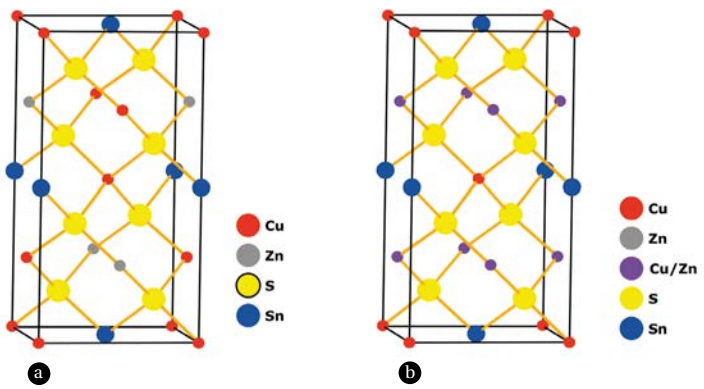


Figure 2 : Kesterite-type structure of Cu_2ZnSnS_4 a) ordered (space group $I\bar{4}$) or b) disordered (space group $I\bar{4}2m$)

→ **Contacts :**
pierre.fertey@synchrotron-soleil.fr ;
Alain.Lafond@cnrs-imn.fr

References:

[1] Todorov, T. K. et al. Adv. Energy Mater. **3,** 34 (2013)
[2] Fontané, X. et al. Alloys Compd. **539,** 190 (2012)
[3] Choubrac, L. et al. Phys. Chem. Chem. Phys., **15.** 10722 (2013)

SIXS

Nanoalloys: crystallographic structure and stability

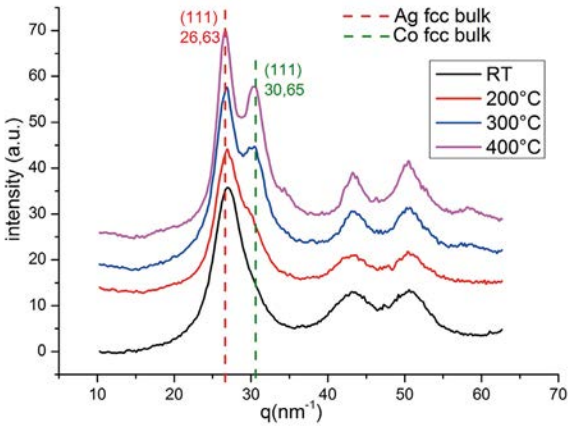


Figure 1 : X-ray diffraction spectra of a Ag@Co nanoalloy during annealing.
Figure 2 : schematic representations of a nanoparticle, at room temperature (a) and after annealing (b).

The physicochemical properties of materials change deeply depending on the amount of material involved. Thus, by adjusting the size of objects, in particular on the nanometric range, it is possible to highlight or reveal new properties.
A very significant example is that of metal nanoparticles, potentially very interesting for use in the catalysis or magnetic memories fields. Their properties can be tailored by the size reduction and also by alloying with other metals on the nanoscale. These «nanoalloys», the composition of which can be controlled, can be obtained by various methods, either from chemical solutions, or physically via deposits on substrates, etc.
The SixS beamline can be used to study nanoalloys prepared either by the simultaneous deposition (co-deposition) or by sequential deposition of different elements. The properties of nanoalloys depend on their size, their crystallographic structure and the organization of the chemical species. The beamline's experimental setup allows to prepare the nanoalloys in situ in order to study the evolution of their structure, organization and morphology during growth and/or heat treatment, or even a chemical reaction. In addition, using anomalous X-ray scattering (energy measurement close to the absorption edge of elements), the measurements can be selective to one element of the alloy.
The example shown in Figure 1 is that of an Ag@Co nanoalloy obtained by co-deposition under UHV. This is wide-angle x-ray diffraction spectrum, which permits to follow the evolution of the alloy atomic structure during thermal annealing. At room temperature, the Co signal is not present, so it can be inferred that the nanoparticle is composed of a core of Ag atoms surrounded by an ultra-thin Co shell stabilized on the surface by partial oxidation, a metastable configuration, as sketched in Figure 2a. During annealing under UHV of the sample, the emergence of a contribution corresponding to metallic Co is increasingly observed, suggesting

... Continued from page 20

collection, for example in microfluidic chips.
Small-angle X-ray scattering (SAXS) is also one of the techniques used in structural biology. The SWING beamline has provided users, since 2009, with a versatile sample environment (see Rayon de SOLEIL 18, p.9) for automatically injecting and/or purifying biological samples before SAXS analysis. The device has been optimized since February 2013 to gain even more time in sample studies.

■ *In situ* and *operando* experiments

The experiments carried out at SOLEIL are tending to become more often a study of a process over time, not only to characterize a "frozen" sample. Fine examples have been obtained on CRISTAL, when monitoring the composition of lithium batteries in operation (see Rayon de SOLEIL 20, p.4) or the growth of carbon nanotubes. The box on p. 17 describes how DIFFABS provided in situ analysis of crystallography and texture formation in thin films. For its part, the SIXS beamline allows the *in situ* study of thin layer formation or the evolution of a surface, interface or nano-objects during deposition, thermal treatment or reaction (see example above). In this case, the coupling of diffraction and scattering (GISAXS) is used to monitor changes in samples on different scales, from atomic structure to the morphology of nano - objects. The SIRIUS beamline, complementary to SIXS with lower energy X-rays, will soon extend these possibilities.

a segregation of the Co and Ag; in this case, the nanoparticles can present a configuration so-called Janus nanoparticles, as sketched in Figure 2b.
Although wide-angle X-ray diffraction give insights on the atomic structure, SixS allows to perfom grazing incidence small angle X-ray scattering measurements, which provide information on the shape, size and dispersion of nanoparticles on the substrate. In the case of Ag@Co nanoalloys, we observed that the nanoparticles average size increases from 2.6 nm (about 800 atoms) up to 4.1 nm under annealing and their average distance from 3.4 nm to 5.7 nm. This information is essential for interpreting the link between their structural, chemical and morphological reorganization.

→ **Contacts :**
pascal.andreazza@univ-orleans.fr ;
alessandro.coati@synchrotron-soleil.fr;
yves.garreau@synchrotron-soleil.fr

Extreme conditions

On the PSICHE, CRISTAL and DIFFABS beamlines, high pressure analytical techniques are available by using different press systems (see PSICHE insert p.18). Various experiments can be performed: powdered samples or single crystal, angular or energy dispersive diffraction eventually coupled with absorption spectroscopy measurements. The coupling is even more important in this field than in others, in order to obtain a full structural characterization.
These studies are often carried out as a function of temperature, which in some cases can also be extremely high or low.
However, at SOLEIL, "extreme conditions" also include the "radioactivity" issue. The MARS beamline is now authorized by the Nuclear Safety Authority (ASN) to receive samples whose radioactivity is equivalent to 15 kg of uranium isotope 238; the first experiments took place on 20 September 2013. MARS has a unique setup capable of combining diffraction and X-ray absorption measurements on the same radioactive sample, with the additional possibility of using a microbeam, particularly suited to the study of heterogeneous materials.

"Playing" with the X-ray beam characteristics

Being able to distinguish between two elements with neighboring atomic numbers and likely to occupy the same crystallographic site has been made easier by the use of the neutron diffraction technique. When using X-rays, the technique known as resonant or anomalous diffraction, requiring the fine energy tuning of the available synchrotrons beam, is often the only solution (see CRISTAL insert p.21). CRISTAL, SIXS, DIFFABS, SIRIUS, PROXIMA1 and PROXIMA2 beamlines use resonant diffraction.

Another feature of the X-ray beam is coherence, the use of which has flourished with the development of third generation synchrotrons. This gives access to both slow dynamics through the study of the speckle intensity fluctuations (as with lasers), and imaging, by solving the phase determination problem encountered in conventional diffraction techniques.

In the hard X-ray field, there have been impressive results on CRISTAL (see Rayon de SOLEIL 22, p.24) and, in weaker energy ranges, magnetic-domain imaging, based on holographic techniques, gives images with almost nanometric resolution. (cf www.synchrotron-soleil.fr/Soleil/ToutesActualites/2012/SEXTANTS-IMAGERIE).
From 2014, it will be possible to carry out tomography experiments on the nanoscale, using the coherence properties of hard x-ray beams, on the Nanoscopium beamline (see Rayon de SOLEIL 21, p.9).

Time-resolved experiments and femtoslicing

Time-resolved experiments are central to the research strategy at SOLEIL in order to "see" processes on different time scales. One of the most recent developments has been operating the storage ring in the so-called "low alpha" mode (see Rayon de SOLEIL 22, p.14), making it possible to go down to temporal resolutions of a few picoseconds; On CRISTAL this type of mode is used to study ultrafast phenomena.
By the end of 2013 the first tests will have been carried out with the so-called "slicing" technique (see Rayon de SOLEIL 20, p.11). Resolutions of the order of hundreds of femtoseconds will then be reached. SOLEIL will ensure the development of all possible complementary techniques for experiments using X-ray lasers (European XFEL, LCLS).

Specialized platforms
for new user communities

16 April, 2013; signature of the contract for the Cosmétomique platform, at salon In-Cosmetics, Paris. From left to right: François Germinet, president of the University of Cergy-Pontoise ; Elian Lati, director of BIO-EC; Marc-Antoine Jamet, president of Cosmetic Valley; Jean Daillant, general director of SOLEIL; Marie-Madeleine Mialot, vice-president of région Centre.

Beside the "one-shot" use of beamlines for generally short-term academic or industrial research projects, SOLEIL is in the process of creating research platforms and specialized services in specific fields to host external, public and/or private communities, carrying out medium and long-term synchrotron projects.

These specialized hosting platforms have at least two of the following three characteristics:
• installed in dedicated premises on the SOLEIL site, in the synchrotron building or close by,
• run by an external R & D interface and support group able to translate the specific problems of the applicative domain into synchrotron solution needs,
• access to beamlines and complementary non-synchrotron equipment necessary to the specific needs of this applicative domain.

The first construction at SOLEIL has been agro-food platform proposed on the basis of the collaborative research beteween INRA (Institut National de Recherche Agronomique) and SOLEIL. Initially, three INRA engineers have been integrated since 2007 to the SOLEIL SMIS, DISCO and SWING beamlines to meet the needs of the agriculture and food industry sectors, notably, expressed by INRA groups and their academic and industrial partners.
Furthermore, a services and research platform for ancient materials (IPANEMA), was created in 2010 in partnership with the French Ministry of Culture and the CNRS around the establishment of a specialized group, a specific building with laboratories and offices and the PUMA beamline optimized for ancient materials.
• Two new projects involving specialized platforms were launched in Spring 2013 by SOLEIL and its partners:
• The **MICASOL** platform, supported by the "materials" laboratories of the CNRS and two universities in the Alsace region, in conjunction with the MICA (Materials Institute Carnot Alsace) Carnot Institute, is open to Alsace companies from all sectors interested in nanotechnology and the multi-scale characterization of materials. SOLEIL and its academic partners signed a collaboration agreement on March 18th, 2013.

• The shared innovation platform (PFMI) **"Cosmétomique",** supported by the Cosmetic Valley center of excellence for French companies in the cosmetics industry and dedicated to the characterization and measurement of the effectiveness and safety of products.
It is based on a partnership with the Bio-EC company and the University of Cergy Pontoise signed on April 16th, 2013 at the Paris international In-Cosmetics exhibition.
The PFMI has already started its first concrete actions: collaborative R&D projects, a poster presentation at the CosmInnov fair in early October 2013, exchanges with Ile de France companies able to provide complementary skills and an international collaborative project with Quebec.

→ **Contact :**
philippe.deblay@synchrotron-soleil.fr

EN BREF

↘ TRAINING
For the coming weeks, the training course diary for SOLEIL is full: on November 25th, a joint training program with LLB for firms in the metallurgy sector interested by the use of large instruments; on November 26th, a presentation during the "basic characterization of materials in contact with food" workshop organized by the Federation of glass industries ; on December 3rd, a lecture during the "Non Destructive Testing" training day organized by the European Ceramics center of excellence at the Ester Limoges Technopole ; finally, an in-company seminar for a R&D center from an international world-leading cosmetics company, in early 2014.

↘ SIXTH PARTICIPATION TO "RENDEZ-VOUS CARNOT"
SOLEIL had an exhibition stand and participated to business meetings during the 6th "Rendez-Vous Carnot" in Lyon the 9th and 10th October 2013, with 800 other major R&D players in partnership with industry.

WHAT DOES SOLEIL DO WHEN THE TOWN IS ASLEEP?

Like most synchrotrons in the world, research groups also work here at night: users carry out one experiment after another, while operators ensure the availability and quality of the beam. Coordinators meet the needs of scientific teams on site by finding the material they lack and colleagues, on-call, monitor their emails and mobile phones... a hive of activity that about 500 people discovered this year on September 27th, 2013, when they were hosted from 18:00 to midnight.

Web TV

As with the 2013 edition of the Users' Meeting, you will be able to follow the SOLEIL users web TV on the 23rd-24th January 2014 on **www.dailymotion.com/SynchrotronSOLEIL**

IYCr2014

International Year of Crystallography: D-40

Wherever you are in 2014, there will no doubt be an activity to discover: wonderful collections of crystals, experimental workshops to discover diffraction and amazing Penrose patterns, conferences, bars of science, laboratory visits, research meetings... The SOLEIL program and many others will be available on the aicr2014.fr website. So follow this exceptional year's twitter feed: @IYCr2014

12

Feel free to send greetings from SOLEIL by sending one of the 12 postcards now available in the reception area.

Our job is to position, to the tenth of a millimeter, equipment carrying electron and photon beams, using techniques and tools that were invented and optimized three centuries ago.

Manuel Ros, assistant Engineer, Alignment/Metrology Group

15th iWoRiD Workshop

THIS YEAR, SOLEIL WAS CHOSEN TO ORGANIZE THE 15TH INTERNATIONAL WORKSHOP on Radiation Imaging Detectors (iWoRiD). This series of annual conferences, the first of which was held in Sweden in 1999, aims to bring together experts in imaging detectors for different communities, such as particle physics, nuclear physics, astrophysics, synchrotrons, medical imaging, neutrons, etc. Indeed, the technologies used for these different applications are often similar and the bringing together of these different points of view often leads to fruitful exchanges. Over the years iWoRiD has become a rendezvous for detector developers, where gas detectors, scintillators, semiconductors, etc., are discussed. The latest advances in electronics, detection materials, data acquisition and interconnecting technologies are presented here by international experts.
The conference was held from 23rd to 27th June 2013, on the Cordeliers campus in the heart of Paris. SOLEIL was very pleased to have broken the attendance record for iWoRiD, with 269 participants from 32 countries, 10 invited speakers, 40 lectures and 130 posters. In addition, eleven companies in the detectors and electronics business provided financial support for the event.

The conference kept its scientific promises, and it was possible to catch a glimpse of exciting prospects for the world of synchrotrons. There were presented, for example, detectors with high dynamics integrating electronics, but still with single-photon sensitivity and without count rate limits, which will perhaps become successors to the current hybrid pixel detectors such as XPAD. Great strides have also been made in developing materials that will improve high energy efficiency, such as gallium arsenide AsGa or cadmium telluride CdTe.

The next iWoRiD conference will be held in June 2014 in Trieste, Italy.

→ **Contact:**
stephanie.hustache@synchrotron-soleil.fr

Science at femto-slicing facilities

FEMTO-SLICING FACILITIES AT SYNCHROTRON RADIATION STORAGE RINGS ARE ONE OF THE FEW SOURCES which provide sub-picosecond pulsed X-rays covering the entire photon energy range of X-ray science.
With commissioning of SOLEIL's femtoslicing facility scheduled to start in December 2013, the goal of this workshop was to gather scientists interested in ultrafast phenomena to give them an overview of the state-of-the-art of science realized at the existing slicing sources and to present to them the novel experimental capabilities becoming available at SOLEIL in 2014.

The workshop, co-organized by the researchers from the CRISTAL and TEMPO beamlines, received strong attention as demonstrated by the participation of close to 100 scientists, primarily from France, but also from other European countries. The speakers of the first session gave an overview of the evolution and operation's details of the femto-slicing facilities at BESSY and SLS and the scientific exploitation of these sources since their commissioning.
A point emphasized by all the speakers concerned the very high oversubscription of the existing sources and that this demand is still increasing. This reflects the increasing interest of researchers in ultrafast phenomena occurring in a variety of scientific domains and the complementarity of experiments realized at femto-slicing sources and x-ray free electron lasers. A second point made by these speakers concerned the need for optimization of the

RF **Superconductivity**

SRF2013, THE 16TH INTERNATIONAL CONFERENCE ON RADIOFREQUENCY SUPERCONDUCTIVITY, was held at the Cité Universitaire Internationale, Paris, on September 22-29, 2013. The aim of this biennial conference is to provide a forum for scientists, engineers, students and industrial partners working in the field of superconducting RF (SRF), applied to accelerators for particle physics, nuclear physics or light sources.
These specialists had the opportunity to present and discuss the latest advances in SRF science, technology and applications. As a preliminary, special tutorials for scientists or engineers new to the SRF field were held on September 19-21 at GANIL, Caen. On this occasion, the participants could visit the GANIL accelerator facilities and, in particular, the Spiral2 linac (linear accelerator), which is currently under assembly.
SRF2013 welcomed nearly 400 participants for about 70 lectures, 300 poster presentations, debates on "hot topics" and 25 industrial exhibition stands. The participants could also enjoy tours of the laboratories at LAL, IPN Orsay, CEA Saclay and SOLEIL.
The main topics can be classified into three broad categories:
• **Design and manufacture of SRF cavities (accelerating or deflecting and electron guns):** optimizing geometries, selecting materials, various treatments and manufacturing techniques to improve performance in terms of accelerating gradient and Q-factor; theory, calculations and simulations, experimental results, mass production, etc.

• **Design and manufacture of equipment associated with SRF cavities:** power couplers, frequency tuning systems, higher order mode damping, diagnostics and controls, cryostats and cryogenic sources ...
• **Accelerators using SRF technology:** progress on projects under consideration or under construction (EXFEL, ILC, ESS, heavy ion accelerators, energy recovery linacs, etc.) and operational results (LHC, CEBAF, SNS, synchrotron light sources and FEL, etc.).

In addition to its participation in the local organizing committee with the CEA and the CNRS, SOLEIL also contributed by presenting three posters, two on the operational experience with the storage ring RF and cryogenic systems and one on the progress of the LUNEX5 project.

→ **Contact:**
patrick.marchand@synchrotron-soleil.fr

---

femto-slicing facilities to produce and to harvest the highest number of femto-second sliced X-ray photons possible. This first session was concluded by a presentation of the femto-slicing facility currently under construction at SOLEIL.

The need for more beamtime at femto-slicing sources and their complementarity to X-ray free electron lasers was reiterated during the presentations of the second session, which were given by users of the existing sources and illustrated the variety of scientific phenomena explored today at femtoslicing facilities.
The speakers of the final session presented experiments in preparation for the SOLEIL femto-slicing facility. Emphasis was placed on how those experiments will complement their current time-resolved studies relying on alternative pulsed X-ray and other sources.
The workshop was concluded by a round table discussion on the experimental capabilities to be made available at the TEMPO and CRISTAL beamlines, the first foreseen experiments and how interested scientists can get involved in the ongoing exciting development.
The strong interest in the workshop and the active participation of all workshop participants in these discussions are a clear sign that the community is waiting for the start of the operation of the SOLEIL femto-slicing facility.

→ **Contact : jan.luning@synchrotron-soleil.fr**

See also:
→ **www.synchrotron-soleil.fr/Soleil/ToutesActualites/Workshops/2013/Slicing/Welcome**

FOOD

SOLEIL **on a plate**

Milk, wine, foie gras, meat, chips and tomatoes, these foods all have one thing in common: they have all ended up in the SOLEIL's light. Using X-rays, UV or infrared rays, studies are based on analyses at several different scales, from atoms to tissues, in these samples that we consume every day.

There is no shortage of examples: studies on the structure of wheat proteins implicated in allergies to this cereal; following the oxidation of a fat emulsion, the major cause of loss of food quality; tensile tests on the walls of wheat grains, removed in white flour but with high nutritional potential; identifying on the molecular level mechanisms responsible for the astringency sensation caused by tasting a glass of wine or under-ripe fruit ; characterization of the protein component of foie gras to prevent them melting during cooking; analysis of the heat denaturation of muscle fibers to preserve the tenderness of meat, etc. The aim of all this research is to both improve the taste, nutritional qualities or food preservation, as well as the methods for preparing processed products, but also how to optimize these processes to reflect the consumption patterns of the future.

On the DISCO beamline, scientists from INRA (Montpellier and Nantes) are collecting images of maize stem walls.

On the menu at SOLEIL

1 **Since 2006,** a special partnership binds INRA (Institut National de Recherche Agronomique) and SOLEIL, on agriculture, food and environment topics.

2 **The DISCO, SMIS, SWING, DESIRS and PROXIMA1** beamlines are the most involved in these studies, covering almost the whole range of wavelengths and techniques available at SOLEIL.

3 **Soon,** with the long Nanoscopium and ANATOMIX beamlines, this range of techniques will be complemented by nanoscale X-ray imaging.

LE RAYON DE SOLEIL is a publication of the Synchrotron SOLEIL civil company **General director** Jean Daillant. **Chief editor** Marie-Pauline Gacoin. **Writing and Coordination** Isabelle Quinkal. **Contribution to this issue** Pascal Andreazza, Alain Buléon, Francis Canon, Lodovico Cassinari, Denis Céolin, Alessandro Coati, Jean Daillant, Philippe Deblay, Francis Duhou, Pierre Fertey, Alexandre Giuliani, Stéphanie Hustache, Jean-Paul Itié, Alain Lafond, Laetitia Lago, Jan Luning, Laurent Manceron, Patrick Marchand, Cristian Mocuta, Amor Nadji, Laurent Nadolski, Ryutaro Nagaoka, Laurent Nahon, Dominique Pedeau, Sylvain Ravy, Manuel Ros, Jean-Pascal Rueff, William Shepard, Andrew Thompson. **Conception** CITIZENPRESS **Art director** David Corvaisier. **Page layout** Fabienne Laurent. **Printing by** Chartrez. **Cover** Florian Kergourlay on the DIFFABS beamline, copyright: SOLEIL. **Copyrights** Francis Canon, Grégory Chabasse, Claude Mennéglier, Vincent Moncorgé, Thinkstock. **Impression** 3500 copies **N° ISSN** 1767-4824 **Legal copyright** november 2013.