N°20

LE RAYON DE SOLEIL

THE SYNCHROTRON MAGAZINE

Light on dynamics

SOLEIL SYNCHROTRON

CONTENTS

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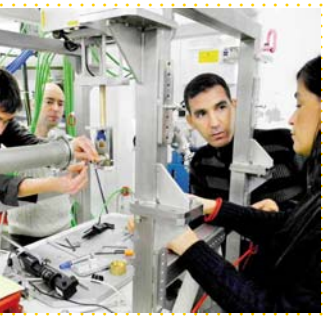

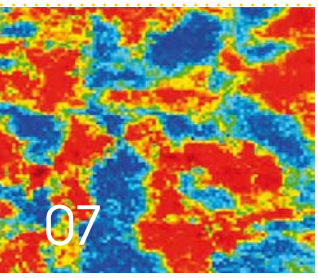

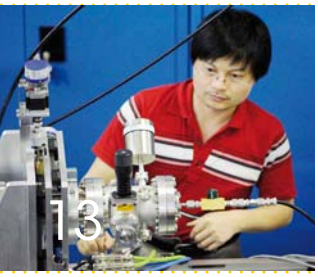

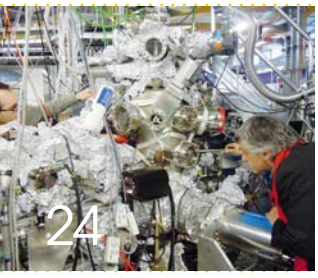

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Editorial

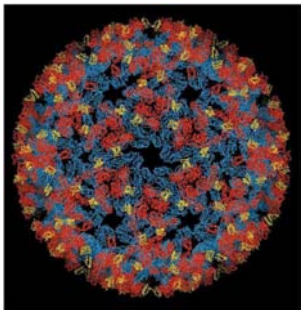
Michel van der Rest
Director General

With about 300 publications in 2010 and nearly 30 at the start of this year, SOLEIL is up there with the best in terms of performance and scientific productivity. Twenty beamlines will be available this year for the scientific community and industrial users aware of the possibilities of synchrotron radiation. This promises to be a busy year, although 2010 ended hectically, this becoming almost a tradition, with great excitement over our budget. The essentials, i.e. our scientific ambitions for today and tomorrow, have nevertheless been preserved. Thus, the phase 2 beamlines will be largely completed by the end of this year, except NANOSCOPIUM, which will take about two further years.

I will return then, as a friend, to discover this very promising imaging beamline and the latest achievements at SOLEIL. Indeed, my term ends in mid-summer after four of the most rewarding years of my career. In the meantime, I will undoubtedly see many first-class results, particularly in one of SOLEIL's flagship areas, the dynamic studies that are the subject of this twentieth issue of the Rayon de SOLEIL. I hope you enjoy reading this issue and see you soon on our beamlines.

BIOCRYSTALLOGRAPHY

Elucidation of the 3D structure of chikungunya virus surface proteins



RESEARCHERS AT THE PASTEUR INSTITUTE AND THE CNRS, in collaboration with the PROXIMA 1 beamline of SOLEIL, have solved the three-dimensional structures of the glycoproteins that envelop the chikungunya virus. This discovery allows us to understand how this protein complex is activated in order to allow the virus to invade target cells. Activation is a key step in the viral life cycle, and its elucidation provides essential information for the development of antiviral strategies, for prevention and treatment. For this work, data were also collected at ESRF and SLS.
Voss, J. E. et al., *Nature,* 2010, 468(7324).

USERS ACCOMODATION

Double capacity for the guest house

FROM MID-JANUARY 2011 THE SOLEIL GUESTHOUSE will double its capacity through the provision of a brand new building, built as an extension to the existing building. The number of bedrooms increases from 40 to 81, one of these rooms being reserved for SOLEIL personnel. This extension will include improvements (e.g. shades to the windows) added following the suggestions of users of the "first section" open since January 2008. An upgrading of both buildings was also carried out with regard to disabled access, the requirements on this subject having changed since 2008.

2 463

In 2010, there have been more than 2,000 users of SOLEIL facilities, with 17 beamlines available.

6

Number of SOLEIL Program Committees after reconfiguration: since September 2010, they evaluate at the same time projects submitted for the SOLEIL beamlines and 4 ESRF beamlines.

$9{,}8.10^{-10}$

Target value, as defined in the detailed pre-project and reached in 2010, for the average pressure (in mbar) in the storage ring, for a current of 500 mA.

IN BRIEF

STRENGTHENING OF PARTNERSHIP BETWEEN THAI SYNCHROTRON SLRI AND SOLEIL

The scientific expertise of the research groups at SOLEIL in the field of infrared microscopy and PhotoElectron Emission Microspectroscopy (PEEM), techniques that are available on the SMIS and HERMES beamlines, will soon benefit scientists from SLRI (Synchrotron Light Research Institute), the Thai synchrotron. A "Memorandum of Understanding" between SLRI and SOLEIL was indeed signed to that end on 25th October 2010 - date of the SLRI official inauguration. The aim of this agreement was also to strengthen transnational cooperation and mutual support between Thailand and France in order to promote scientific activities associated with the use of synchrotron radiation.

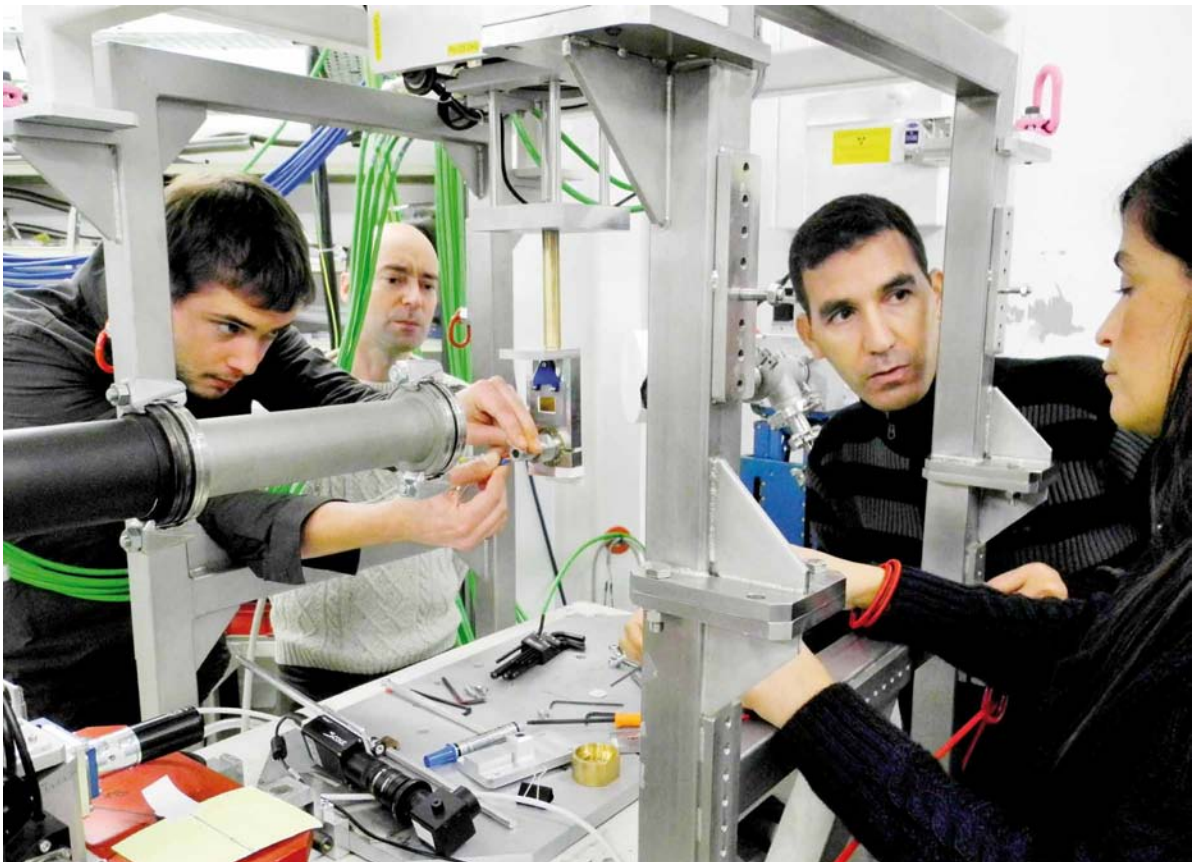
SOLEIL AND "AGENDA 21 DE L'ESSONNE"

Since May 2008 SOLEIL has been a partner in the "Agenda 21 de l'Essonne" initiative. The General Council of the Essonne has just published its report on projects carried out in 2009, including a description of 3 carried out by SOLEIL (offering analytical services for ecologically friendly activities), and a directory of 69 approved projects in 2010, including the 2 contributions by SOLEIL (staff transport respecting the environment and eco-grazing by sheep).

ENERGY

At the core of lithium batteries

How to store electrical energy is the subject of intense economic and scientific research in response to the global energy crisis, diversification of energy sources and changes in the forms of individual transport. A question that brings together four beamlines at SOLEIL, the "Institut des Matériaux" in Nantes and the "Laboratoire de Réactivité et de Chimie des Solides" in Amiens.



Installation of the electrochemical cell on ODE beamline. From left to right: Stéphane Hamelet (Amiens), Patrick Soudan and Miloud Zerrouki (Nantes) and Stéphanie Belin (SAMBA beamline).

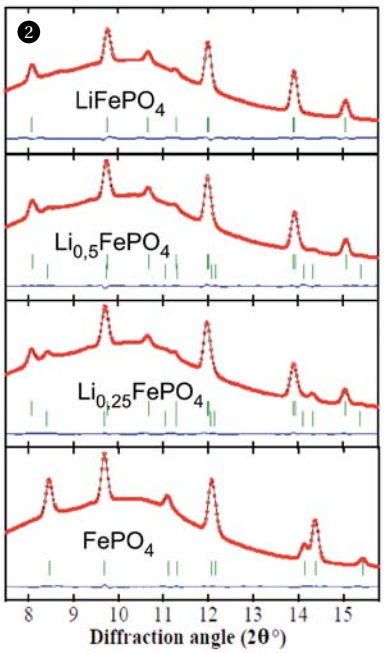
Throughout the world, thousands of researchers are actively looking for batteries that can store the maximum energy possible, at low cost and under the best safety conditions. At present, the greatest number of studies in this field concern lithium batteries (see Rayon de SOLEIL n°16, page 14).

When at rest or in "operando"

A considerable number of studies have been carried out to determine as precisely as possible, the structural and electronic changes in materials during a lithium-ion battery cycle, both when charging and discharging. Among the methods used there are those that are structural, such as X-ray or neutron diffraction and transmission electron microscopy and spectroscopic methods, such as infrared spectroscopy, Raman spectroscopy, electron photoemission, Mössbauer spectroscopy and NMR. X-ray absorption spectroscopy (XAS) is a unique form of spectroscopy, both because it allows, depending on the part of the spectrum studied, characterization of the electronic state (XANES) or the structure of the

Figure 1: X-ray diffraction measurements carried out on CRISTAL at the C/2 charging regime on the $LiFePO_4$/$FePO_4$ system. The written compositions correspond to the average composition of the whole electrode.

Figure 2: Electrochemical cell designed for operando experiments



material (EXAFS) on a localized scale and because it requires the use of synchrotron radiation.

To date, nearly all the experiments mentioned above have been performed on disconnected batteries, thus at equilibrium, or on materials extracted from batteries after use. There are very few results available to directly link the electrochemical performance of the battery and the structural and electronic state of the active component.

To fill this gap a project was set up in 2007 to characterize the electrode materials of the battery during operation, by diffraction and X-ray absorption, using the high X-ray photon flux delivered by SOLEIL. These techniques have already shown their ability to analyze the structural changes and charge transfers occurring within the material, depending on the lithium content.

It therefore became possible to examine the behavior of materials specifically during the operation of the battery (operando experiments) and particularly that of the positive electrode, $LiFePO_4$, currently regarded as one of the most promising materials for the positive electrodes of lithium batteries. This material is known to work mainly on a $LiFePO_4$ / $FePO_4$ two-phase system.

A "transparent" battery

The first phase of the study was to develop an electrochemical cell capable of collecting diffraction and absorption data, in reflection and transmission mode of detection. This cell, like all lithium batteries, had to be completely air and watertight, and reproduce very accurately the electrochemical behavior of the materials under study. This cell was designed with a hollow piston for the transmission experiments. Sealing was ensured by O-rings and beryllium windows (Figure 1). It reproduced exactly the electrochemical curves obtained in the literature for various compounds, regardless of the C / n charging regime*. One of the major advantages of this experimental device is that it can provide the behavior signature of the material when the electrochemical behavior of the battery becomes abnormal.

Complementarity of the SOLEIL beamlines

Addressing how a battery material actually operates in relation to varying numbers of lithium electrons and ions in an electrode requires the introduction of the notion of their diffusion, therefore, possible heterogeneities within the electrode, and the behavior of the materials beyond the steady state and during the process of polarization and relaxation. It is therefore important to be able to study the batteries over several time and space scales, requiring the use of the different beamlines involved in this project.

The system studied has a two-phase electrochemical behavior - the two phases in question being $LiFePO_4$ and $FePO_4$ - shown by galvanostatic cycling experiments.

On CRISTAL, X-ray diffraction measurements with a C/2 charging regime have confirmed this two-phase stage with the presence of two clearly identified XRD patterns. However, it is quite clear (Figure 2) that when the product is charged, the $FePO_4$ diffraction peaks are produced later relative to the amount of lithium extracted electrochemically, since for the overall $Li_{0,5}FePO_4$ composition of the electrode, one would expect equal amounts of both $LiFePO_4$ and $FePO_4$ phases, while on the X-ray diffraction pattern, the initial $LiFePO_4$ phase is clearly in the majority.

The extent of this delay is even more marked when the regime is high. Since the overall electrochemical composition of the electrode is known, this apparent delay may be explained either by the formation of one or more phases that are not detected by diffraction due to their amorphous nature, or because other parts of the electrode are ahead, i.e., more charged and poorer in lithium than the average for the electrode. The first hypothesis is excluded by the fact that $FePO_4$ is formed in correlation with the disappearance of LiFePO4. The only explanation is therefore a highly heterogeneous electrode.

When diffraction is confirmed by absorption

To test this heterogeneity, X-ray absorption experiments were performed on SAMBA. An electrode was

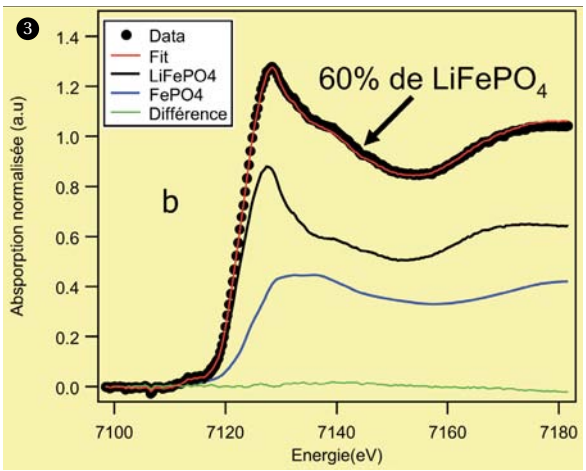


Figure 3: Example of a linear combination calculated for an average $Li_{0.36}FePO_4$ composition, based on $FePO_4$ spectra. The spectra were recorded in the 2C regime on ODE in dispersive XAS mode.

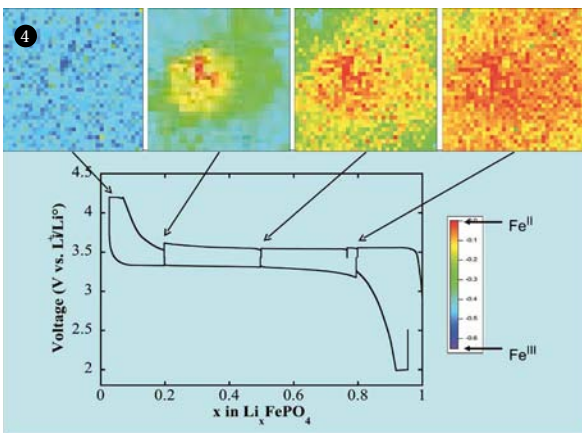


Figure 4: Maps of the distribution of oxidized / reduced iron carried out on a 0.7x 0.7 cm² electrode surface, in 35 x 35 points spaced by 200 µm. Measuring Conditions: charged at 1C, after relaxation of 15 min, for average Li compositions shown by arrows. Measurements were made on LUCIA.

charged up to the $Li_{0.5}FePO_4$ composition, then placed in an airtight sample holder in such a way as to allow access to the entire electrode, in order to record XANES spectra on portions of the electrode located at the edges of the electrochemical cell. The biphase nature of the electrochemical system was indeed confirmed by these measures (presence of isosbestic points), each spectrum being a linear combination of the $FePO_4$ and $LiFePO_4$ spectra. However, as additional information, it was observed that some spectra were behind or ahead of the average $Li_{0.5}FePO_4$ composition, perfectly illustrating the heterogeneity of the system.

A dynamic X-ray absorption experiment was then carried out using the 2C regime on the ODE beamline. A linear combination of the $FePO_4$ and $LiFePO_4$ spectra was calculated from each of the spectra recorded. For example (Figure 3), in the case of $Li_{0.36}FePO_4$, the linear combination gives a true composition of the analyzed area of 60% $LiFePO_4$ and 40% $FePO_4$, instead of the expected 36% $LiFePO_4$. The delay previously observed by diffraction has thus been confirmed, this time with an observed electrode surface about 1,000 times smaller.

However, this delay is not spatially uniform, as shown by mapping the distribution of Fe^{II} and Fe^{III} in the electrode fraction observable in transmission. Performed on the LUCIA beamline, thanks to its 7x7 µm² beam spot, this analysis was very accurate: the signature for the average degree of oxidation could be analyzed at each point of the sample. The measurements, which only took a few seconds each, were carried out at the absorption near-edge for $LiFePO_4$.

Finally, the researchers obtained a map of almost 1,300 points showing the distribution of iron in its oxidized and reduced states when the battery was at rest, and how this distribution changed on a small portion of that surface when the battery was operating through a charge-discharge cycle (Figure 4). These results again illustrate the heterogeneity of the electrode under operation.

Unexpected heterogeneity

Taken together, these results show that the reality of the behavior of a battery electrode, from a structural and electronic standpoint, is far from ideal. Although this conclusion is not entirely surprising given the complexity of the composite structure of the electrodes, it upsets the traditional arguments based on complete homogeneity of the systems.

Many parameters were taken into account, some of them permitting electrochemical behavior and heterogeneity to be correlated: cycle speed, active material particle size, pressure on the electrodes and the preparation of electrodes. This last point seemed to be quite decisive and corroborated the electrochemical measurements showing that the best performance resulted from a compromise on the nature and proportion of phases included in the formulation of a composite electrode. This is a key element in industrial development aimed at optimizing the formulation for a given active component and preselected construction method.

The original objective of this work was to show the potential of synchrotron radiation for characterizing battery materials in operando mode. The results exceeded expectations, thanks to the spatial resolution analysis. X-ray diffraction and absorption experiments, as these are easy to carry out, appear to be excellent methods for characterizing electrodes, at least on a scale of a few microns, which is appropriate for the composites.

Developments are possible on several fronts. The first is to examine the behavior of other electrode materials. Then it would be quite conceivable to systematically test, using the synchrotron, numerous possible combinations of parameters involved in the development of electrodes and to correlate perfectly their heterogeneity and electrochemical performance.

Finally, can we imagine the time when test samples and elements of industrial production will be examined using synchrotron radiation, before finding their way into our laptops and electric cars?

*C/n charging regime: conditions (current strength) applied to achieve the complete charge of the battery in n hours. In the case of 1C, for LiFePO4, 100% of the Li^+ ions had migrated to the positive electrode in 1 hour – in 2 hours for C/2, in 30 minutes for 2C.

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References :
Rossignol C. et al., J. Electrochem. Soc., 148 A869-877 (2001)
Leriche J. B. et al., J. Electrochem. Soc., 157 (5) A606-A610 (2010)

METAL-INSULATOR TRANSITION

The Mott transition in the light of synchrotron radiation

The Mott transition reflects the transition between the insulating state of a system of correlated electrons and a metallic phase (see box). Understanding this metal-insulator transition is essential, not only from a fundamental point of view but also to control the electronic properties of materials, with major technological implications in the search for faster and more efficient electronic devices.

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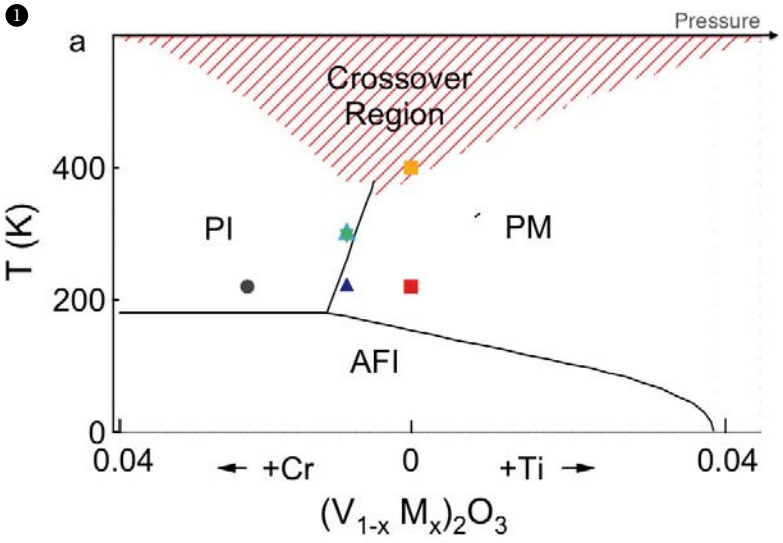

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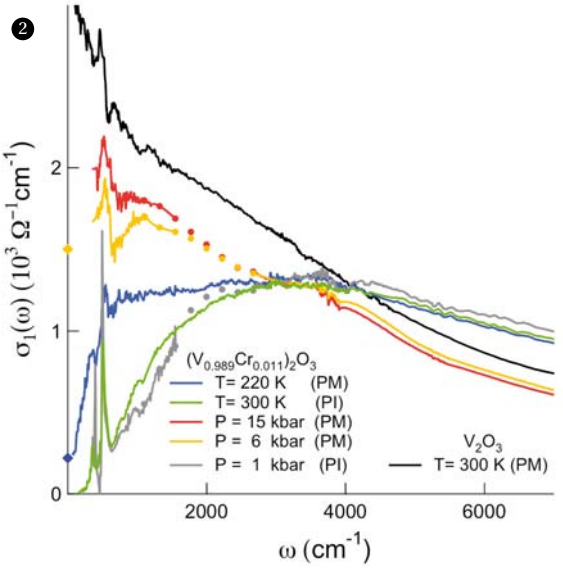

The Mott transition remains poorly understood and highly complex: the material has an intermediate behavior between metal and insulator that is poorly described by theory and difficult to characterize experimentally. The most advanced spectroscopic techniques using synchrotron radiation can provide answers to these open questions. As part of an international collaboration involving the University of Rome "La Sapienza" and the Laboratoire de Physique des Solides (LPS) at Orsay, researchers on the GALAXIES, PSICHE and CRISTAL beamlines, at SOLEIL undertook a study of the metal-insulator transition in Cr-doped V_2O_3, a model material of strongly correlated electron systems, using different techniques from infrared to X-rays. This work, which started as part of a SOLEIL/LPS PhD. thesis [1,2] has recently led to spectacular results obtained through an original approach combining electronic and structural probes.

Not as simple as it seems

The phase diagram of V_2O_3 was established in the 1970's as a function of temperature, doping and pressure (Figure 1). Based on this diagram, V_2O_3 is metallic at room temperature (Paramagnetic Metallic phase, PM) and becomes insulating at low temperatures (Antiferromagnetic Insulating phase, AFI) or by doping with Cr (Paramagnetic Insulating phase, PI); in the latter case, it is possible to restore the metallic phase by applying external pressure (upper scale) from a doped sample or through temperature and appropriate doping (triangles). We focused more specifically on the PM-PI transition in V_2O_3-1.1% Cr doped compound. Unlike the PM-AFI transition, the PM-PI transition occurs without structural change and as such is considered as a pure manifestation of electron correlations and thus of the Mott transition. It soon became clear, however, that the apparent simplicity of the phase diagram masked great physical complexity: the behavior in the PM phase is that of a poor metal, the structure of V_2O_3-1.1% Cr has a mixture of phases; doping induces local distortions in the structure; finally, the transition mechanism remains poorly understood.

A first confirmation of this complexity came from measurements of optical conductivity in the infrared (Figure 2) obtained at ELETTRA. Although the PI phase clearly shows an energy gap - this is the signature of an insulator - (green curve), the spectra obtained in the metallic phase is highly sensitive to

Figure 1: Phase diagram of V_2O_3 as a function of temperature (left scale), doping (below) and pressure (above). PI, PM are insulating and metallic paramagnetic phases, respectively, and AFI, the insulating antiferromagnetic phase.

Figure 2: Optical conductivity measured in the infrared region under different temperatures and pressures.

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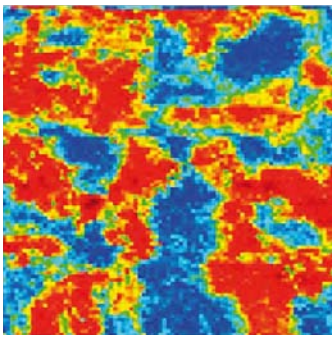

Figure 3: Coexistence of metallic (red) and insulating (blue) phases observed by X-ray spectromicroscopy. The image covers an area of 50 x 50 µm².

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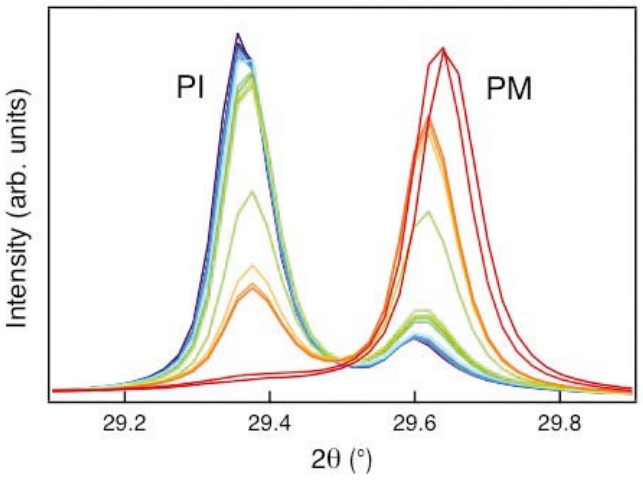


Figure 4: The metal-insulator transition observed by X-ray diffraction. Starting from the insulating phase (PI, blue), only the metallic phase (PM, red) remains at high-pressure.

the point considered in the "PM" region of the phase diagram: We can find a poor metal (blue curve, T = 220 K, x = 1.1%), a good metal (black curve, T = 300 K, x = 0) and intermediate cases (yellow and red curves). We confirmed these observations using the effective medium approximation (EMA) of the optical conductivity. These calculations showed that all spectra can be described by a mixture of various concentrations of metal and insulator. Thus, the «PM» spectrum measured at 220 K is composed of 45% metallic phase and 55% insulating phase, far from the image of a pure phase!

Imaging the mixing of phases

It is even possible to directly visualize this mixing of electronic phases with X-ray spectromicroscopy, a technique which consists of measuring a photoemission spectrum at each point of the sample. The images obtained at ELETTRA and processed here in false colors, clearly show a coexistence of insulating and metallic phases on the microscopic level at the metal-insulator transition induced by temperature (blue and red zones in Figure 1). Even more surprising, the measurements show that the system keeps track of the pattern formed by the different phases, even after a complete cycle through the transition, probably due to the presence of Cr impurities that serve as nucleation centers.

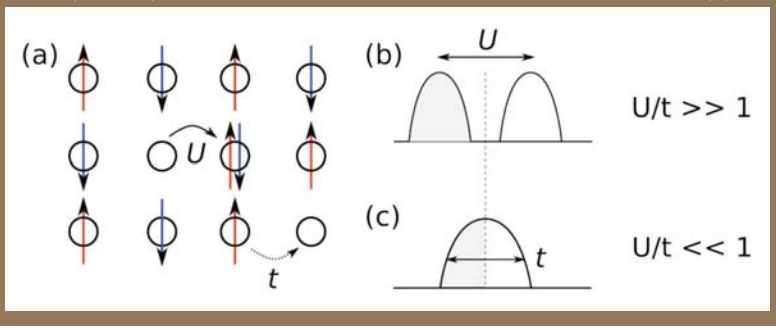
Phase mixing is particularly marked in the transition induced by temperature. In contrast, during the transition under pressure, the coexistence of phases observed indirectly by X-ray diffraction (Figure 4) on the CRISTAL beamline at SOLEIL, almost completely disappears at high pressure, leaving a more homogeneous and pure metallic phase. This result corroborates the optical conductivity measurements performed under pressure (Figure 2) which show growing metallic character as pressure increases.

A combination of techniques is required

In conclusion, the measurements clearly evidence a mixing of metallic and insulating phases on the microscopic scale in V_2O_3, through the Mott transition induced by temperature, doping or pressure. The degree of purity of the metallic phase depends markedly on external parameters, but also on the impurities present in the sample. In general, this study highlights the complexity underlying the phase diagram of correlated materials and the need for a multimodal approach.

The Mott transition

Like Kondo, Anderson, or de Gennes, Mott is one of the few eminent scientists who have lent their names to a physical effect that is still very relevant today. The Mott insulator model explains why some materials are insulators rather than conductors (metals) as expected from the filling of electronic shells, while the Mott transition focuses on the transition from one state to the other under the influence of external parameters (doping, pressure, temperature, etc.) The two phenomena are closely related to the Hubbard model that describes the behavior of an electron moving in an antiferromagnetic network (a). In this model, electrons can move from site to site through the hopping interaction t, identified to the electronic bandwidth. When a site is doubly occupied, it costs an extra energy U, the Coulomb interaction. It is the *U/t* ratio which determines the nature of the system: if *U/t <<1* - (c), the electron band is half-filled (gray area) and the electrons are free to move by thermal excitations into the empty states (in white): the systems behaves as a metal. However, if *U/t >>1* - (b) the interaction U opens up an energy gap that the electrons cannot cross. They are trapped: the behavior is that of an insulator, induced here by correlations.



➔ **For more information :** Lupi, S. et al., Nature Communications 1, 105 (2010)

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References :
• F. Rodolakis, Thesis Université Paris XI (2009) - Direction: J.-P. Rueff & M. Marsi.
• F. Rodolakis et al., Phys. Rev. Lett. 102, 066805 (2009), J. Phys: Conf. Series 190, 012092 (2009) & Phys. Rev. Lett. 104, 047401 (2010).

FOCUS ON

An in-vacuum wiggler for the PSICHE beamline

The PSICHE beamline, expected to be available to users in 2012, will be partly dedicated to high energy X-ray diffraction under extreme conditions and partly to microtomography. Its light source will be an in-vacuum wiggler, designed and built at SOLEIL.

How to obtain a photon energy of 70 keV , the upper limit of the spectral range available at SOLEIL? For insertion device specialists, the answer seems obvious: a wiggler is required, as undulators do not allow such high energies to be reached . However, even with a wiggler, producing such hard X-rays is far from being conventional.

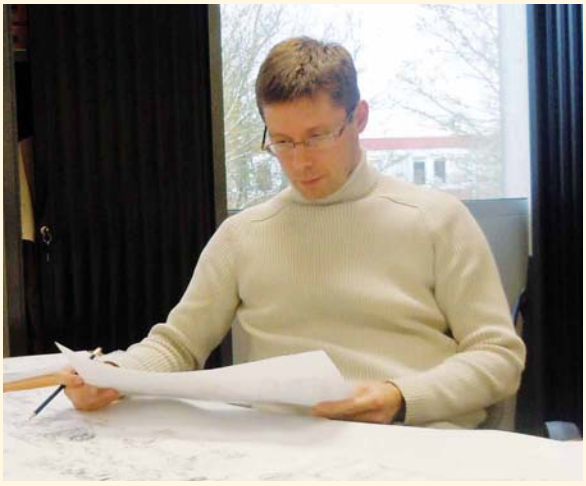
Superconductor or in- vacuum technology?

When it came to choosing the PSICHE light source, two technical solutions were explored: the technology of superconductors, used especially in the DIAMOND synchrotron in Britain and the CLS in Canada on wigglers in comparable energy ranges, and in-vacuum insertion technology, for which there were no reference points. Both approaches were explored right up to the setting up of the tender, the time required to evaluate the impact of both solutions on the infrastructure, the investment and the running costs and, on the other hand, the expected performance levels. This comparative study showed that the manufacture of an in-vacuum wiggler at SOLEIL was less restrictive and less costly than a superconducting wiggler, despite a slightly lower flux. The final choice was validated in July 2006.
But everything remained to be done!

A solid in-house experience

Olivier Marcouillé then tackles the task. His advantage: three years experience, with his colleagues in the "Magnetism and Insertions" group at SOLEIL, on in-vacuum undulators. Most of them are already installed on six beamlines and two additional ones are planned to be installed in the next two years. Innovation does not really appear in the technology, similar to that used for undulators, but rather in the engineering required to design the carriage that underpins this particular insertion device. Indeed, the magnetic forces are 4 times larger than those produced in the undulators, due to the increase of the magnetic field. The forces reach 10 tons, which unusually constraints the carriage and mainly the girders. To overcome this difficulty, Keihan Tavakoli and SOLEIL's engineering group proposed an original compensation solution consisting of springs installed between the wiggler girders, in order to cancel the forces.

The permanent magnets of the PSICHE wiggler, before being put under vacuum.



Olivier Marcouillé is already busy designing new magnetic devices for SOLEIL

Ready for 2012

The permanent magnets equipped with their holders, girders and carriage were made separately by outside companies. SOLEIL was responsible for integrating the various components and for carrying out the magnetic measurements and corrections. Particular attention was paid to the tools used to assemble the parts due to the large magnetic forces that required heightened safety considerations. The wiggler was installed on the machine last June. Initial tests showed that its operation matched with specifications, except for one unexpected effect – now understood - of the wiggler on the beam lifetime. Olivier Marcouillé is currently working with the "Machine Physicists", to correct this default.
The first experiments on PSICHE beamline will be carried out in 2012!

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EXPERT PORTRAIT

JEAN-PAUL RICAUD, ELECTRICAL ENGINEER

Coming from industry, a specialist in electronic development, Jean-Paul Ricaud joined the Control and Acquisition Electronics group in SOLEIL's Computing Division in 2004.

In what context did you start working at SOLEIL?

When I was recruited, Alexandre Loulergue, Head of the "synchronization machine" project, had just finished writing all the specifications for this system. My mission was to develop the technical side and to establish the specifications necessary to order from outside sources, the different elements involved. Once this "machine" component was in operation - this was in 2006 - I was put in charge of its monitoring and maintenance, as is still the case.
And, in parallel, I was assigned to the beamline synchronization system, available now on six beamlines that carry out time-resolved experiments: DESIRS, DISCO, LUCIA, METROLOGIE, PLEIADES and TEMPO. This system is up and running.

What is the "synchronization machine" system?

Electrons are generated by the electron gun, accelerated in the LINAC and then injected into the Booster where their acceleration continues until their extraction and injection into the storage ring. This trajectory requires the perfectly synchronized triggering of a variety of instruments: the electron gun, magnets and diagnostic devices of the beam. Hence the need to set up "clocks" and trigger signals to temporally link the various devices to each other.
In addition, we must manage the various ways of filling the Ring (ring "full" with 416 bunches, or 8 bunches, a single bunch, or even a hybrid mode), and the top-up operation (filling of about 2 mA every 2-6 minutes).

What does it consist of?

Once the role and characteristics of the system were specified, developing the appropriate electronics was entrusted to the French company Greenfield Technologie, which had already supplied similar equipment to the CEA.
A real mini network of optical fibers was installed to dispatch the synchronization messages from the «central brain» - a computer located in the control room - towards local boards situated throughout the machine.
Each board can then generate trigger signals through eight outputs. The mainframe itself is synchronized with the clock of the very accurate radio-frequency system (352.196 MHz) that sends their power to accelerator cavities.
To compensate for the time it takes for the signal to travel the length of cable between devices, and also compensate for the latency of the equipment, the system includes time delays that the user can specify. Thus, in the control room, operators can program into the mainframe computer - using a LabVIEW application - preset delays in order to trigger the series of events that will get the desired filling mode of the storage ring.
The triggering accuracy is 5.7 ns for all equipment, and even up to 80 ps in the case of the electron gun.

And what about the beamlines?

The machine synchronization system already provided beamlines with the storage ring master clock (846 kHz, the frequency of revolution of an electron bunch), as well as the warning signals at the beginning and end of each injection during the top-up operation.
For most beamlines this information is sufficient, but not for those who perform time-resolved experiments, the principle of which is to synchronize the acquisition of their detector to the photons emitted by the passage of one or more electron bunches.
When a bunch passes in front of the beamline, it causes a extremely short flash of synchrotron radiation: 20 to 50 ps (time related to the length of the bunch).
The flash occurs at a very stable and high frequency (846 kHz in single bunch mode, 6.77 MHz in 8-bunch mode) and its very short duration can freeze the exact condition of the sample studied. Successive flashes during the following passages will then "photograph" the sample during its evolution over time.
The challenge is to trigger the analysis just as flashes occur. As electrons turn at more or less the speed of light, accuracy is required!
This is why we set up a complementary synchronization system adapted to the specific needs of these beamlines: their measuring instruments are triggered during the passage of the electron bunch.
This system is very flexible and versatile. It can accommodate a maximum of different instruments, a vital quality in a research center such as SOLEIL, where each beamline has its specific equipment.

This diversity can also be found in the people that I have the opportunity to encounter in the course of my work, since it has led me to interact with most beamline teams and SOLEIL sources, but also with some external users.
It is a very enriching human environment, which contributes to making my work at SOLEIL interesting.

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SPOTLIGHT ON

Towards the generation of femtosecond pulses at SOLEIL*

In a 3rd generation light source, the photon pulse length, in usual operation, allows dynamic phenomena to be studied on the scale of a few tens of picoseconds. However, thanks to a new technique called "slicing", it is becoming possible to produce sub-picosecond pulses short enough to probe ultra-fast dynamic structures.

SOLEIL is a 3rd generation synchrotron light source producing photon beams of very high brilliance, from infrared (IR) to hard X-rays. This radiation is emitted in very short pulses which duration is determined by that of the electron bunches circulating in the storage ring. For reasons intrinsic to the dynamics of electrons in storage rings, it is very difficult, under normal operating conditions, to obtain electron bunches with temporal widths below 30 picoseconds (ps = 10^{-12} sec) FWHM (1). Although the corresponding photon pulse durations, can be used to study a large number of dynamic phenomena, they are still too long to probe ultra-fast dynamic structures such as chemical reactions, phase transitions, rapid structural changes in crystals and other intra-atomic phenomena that occur on the 100 femtosecond scale (fs = 10^{-15} sec). Unlike the 3rd generation sources, the 4th generation ones, such as free-electron lasers based on linear accelerators, are capable of producing fs pulses. However, a recent technique called "slicing" enables to generate sub-picosecond pulses on storage rings.

The principle of the Slicing

A powerful and ultra short laser pulse (~50 fs - FWHM) co-propagates with an electron bunch (30 ps of duration) oscillating in the periodic magnetic field of a wiggler (called "modulator") (Figure 1). The electrons that are affected by the electromagnetic field of the laser change energy, since inside the wiggler their velocity acquires a transverse component parallel to the laser's electric field: some electrons gain and others lose energy. This concern only the electrons which are entering the wiggler at the same time as the laser pulse (in the 50 fs «slice»).

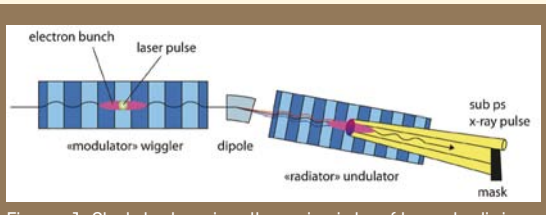

Figure 1: Sketch showing the principle of bunch slicing to generate femtosecond pulses of synchrotron radiation. From S. Khan, EPAC 2002.

The laser-electron interaction is maximum when the central wavelength of the spontaneous emission from an electron passing the wiggler λ_{rs} satisfies the following resonance condition:

$$\lambda_{rs} = \lambda_L = \frac{\lambda_w}{2\gamma^2}\left(1 + \frac{K^2}{2}\right)$$

where λ_L is the laser wavelength, γ is the Lorentz factor, λ_w is the wiggler period and K its deflection parameter.

When this electron bunch then passes through a dispersive magnetic field (bending magnet) or a zone where the dispersion function is non-zero, the energy modulation generated inside the wiggler translates itself into a spatial or angular separation: the sliced electrons and those of the core bunch not having undergone the laser action have different trajectories. Thus one can spatially separate the radiation produced by these different electrons in a «radiator» that can be a bending magnet or an undulator (Figure 1).
This technique, which has been validated experimentally for the first time at ALS (Berkeley, USA), is currently operated on sources such as BESSYII (Germany), SLS (Switzerland), the new ALS project and on UVSOR (Japan). However, as the laser-electron interaction involves only a small part of the electron beam, the photon flux coming from the slice is consequently much lower than the one produced by the whole electron beam. The values reported from the experiments cited above are around 10^5 photons/s/0.1% b.w(2) for pulse durations between 150 and 200 fs FWHM.
The SOLEIL Femto-Slicing project differs from the projects cited above by at least three major points of view:

- several beamlines (instead of a single one) will be able to use these ultrashort pulses simultaneously. CRISTAL (4 to 30 keV) and TEMPO (50 eV to 1.5 keV) will be the first two beamlines. They are respectively interested in sub-picosecond diffraction and time-resolved photoelectron spectroscopy. Later, the DEIMOS and GALAXIES beamlines would also benefit from these ultra short pulses. Thus fs pulses will be produced at SOLEIL covering the soft and hard X-rays energy range.
- the geometric separation between the slice and the core is generated without using any extra magnetic element. The scheme takes advantage from the linear optics of the ring that has a natural non-zero horizontal dispersion in all straight sections.
- the radiation emitted by the modulator will be routinely and independently used as a source for a dedicated beamline, the PUMA beamline (for the study of ancient materials).

The modulator

The magnetic and geometric parameters for the choice of the wiggler (modulator) must take into account some

Breaking news

*** This ambitious project is not being funded by SOLEIL at present, the Council gathered on March 2, 2011, having asked that outside funding be found to carry it out.**

constraints. The wiggler must emit radiation at the same wavelength as the laser (800 nm), the total radiated power must be below the limit set by the front-end of the beamline and the performance of the ring, in terms of emittance and beam lifetime, must be preserved. In addition, the wiggler must yield a high photon flux up to 50 keV to satisfy the PUMA beamline specifications. The magnetic studies, in one hand, and beam dynamics, on the other, have converged on to a wiggler with 20 magnetic periods of 164 mm, a length of 3.28 m and a maximum magnetic field of 1.63 T. The power emitted is 20 kW.

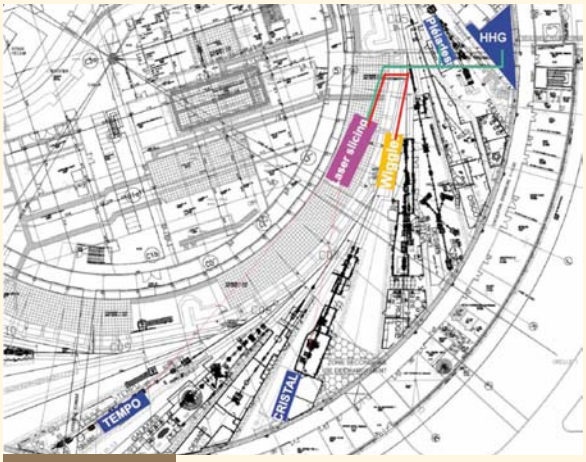

Figure 2: Diagram showing the location of the Femto-Slicing laser hutch, of the wiggler modulator, of the TEMPO and CRISTAL beamlines and of the HHG and PLEIADES experimental hutches.

The laser

The laser must be able to deliver ultra short pulses and an energy output large enough to ensure an effective separation between the slice and the core. Moreover, since the frequency of the electron bunches is very high (352 MHz) and the expected flux of fs pulses is rather low, it is important that the repetition frequency of the laser is as high as possible. Table 1 summarizes the main specifications of the selected laser system.

The Femto-slicing laser system hutch will be located in the inner service area of the synchrotron. The stability criteria of the laser required the replacement of the existing 20 cm thin slab which rested directly on a raft, unlike the storage ring tunnel that is resting on piles. Part of the existing slab was cut, removed and replaced by a thicker and more stable slab. The operation took place during the machine shut down of January 2011.

Transport of the laser beam

The laser beam will be propagated under vacuum from the exit of the hutch to its injection point into the wiggler. It must therefore cross the inner radiation shielding wall of the storage ring and a dedicated shield of the penetration is of course foreseen. To enable the laser beam entering the ring vacuum, a new bending magnet vacuum chamber is under construction. Studies concerning the transport of the laser beam, its alignment and focusing towards the wiggler are also underway. In addition, the laser beam must be matched temporally, spectrally and spatially to the electron beam in the wiggler. For this, an IR diagnostics beamline will be installed at the 0° output of the wiggler, inside the tunnel.

The laser beam and the synchrotron radiation from the wiggler at 800 nm will be extracted at very low current, using a retractable mirror, and then transported to a diagnostic station to make temporal, spectral and spatial measurements. To measure and optimize in real time the efficiency of the slicing at high current, an indirect method will be used, the analysis of Coherent Synchrotron Radiation (CSR) in the THz range generated from the bending magnets of the ring. The intensity of the CSR is directly related to the efficiency of the energy modulation in the wiggler. The extraction of THz radiation will be carried out at the bending magnet exit of the Machine Diagnostics beamline MSRV (Mirror Synchrotron Radiation in the Visible) which will be optimized for this purpose.

Use of femtosecond radiation

Slicing experiment will be performed with a 10 mA electron bunch, with the storage ring topped up in either single bunch mode, in 8-bunch mode to 90 mA, or in hybrid mode at 390 mA + 10 mA.

Performance in terms of photon flux must be calculated accurately including all the contributing factors. However, initial calculations give sample fluxes between 10^6 and 10^7 photons/s/0.1% b.w. The duration of the photon pulse emitted in each of the radiators will be longer than the duration of the laser pulse, due to the effect of slippage (electrons drift with respect to the wavelength of light in the wiggler) and due to the effects of the emittance and energy dispersion of the electron beam during its transport from the modulator to the radiators.

The total duration of the pulse expected at CRISTAL and TEMPO beamlines is given in Table 2, taking into account the different uncorrelated contributions.

Synchronization

As the experiments on TEMPO and CRISTAL beamlines will be of «pump-probe» type (stimulation of a sample by a laser beam, prior to analysis by the photon fs beam), this will require synchronization between the stimulating lasers pulses and the slicing laser pulse with an accuracy of a few tens of fs. Given the large distances between the different systems (~ 50 m) this remains one of the major difficulties to overcome. Several options are under consideration.

Other uses for laser slicing

The laser for the slicing has outstanding characteristics in terms of power and repetition rate, making it a very interesting tool for complementary applications when not being used for slicing:

- experiments on the PLEIADES beamline, coupling synchrotron radiation with the laser for spectroscopy experiments in strong fields
- experiments without synchrotron radiation, through generating high order harmonics in gases (HHG) for experiments in dilute phase and for imaging.

The Femto-Slicing project requires development and equipment that are under the responsibility of the Sources & Accelerators and Experiments Divisions. Amor Nadji is the project leader on the Machine side and Jan Luning is the project leader on the Experiments side, responsible for the scientific coordination of the project. They are assisted by Marie-Emmanuelle Couprie and Pascale Prigent, respectively.

1 FWHM: full width at half maximum
2 b.w.: bandwidth

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Table 1: Main characteristics of the laser system at SOLEIL

Central wavelength (nm)	800 Titanium :Sapphire
Minimum pulse duration (FWHM) (fs)	30
Output energy 800nm (mJ)	5
Repetition frequency (kHz)	10

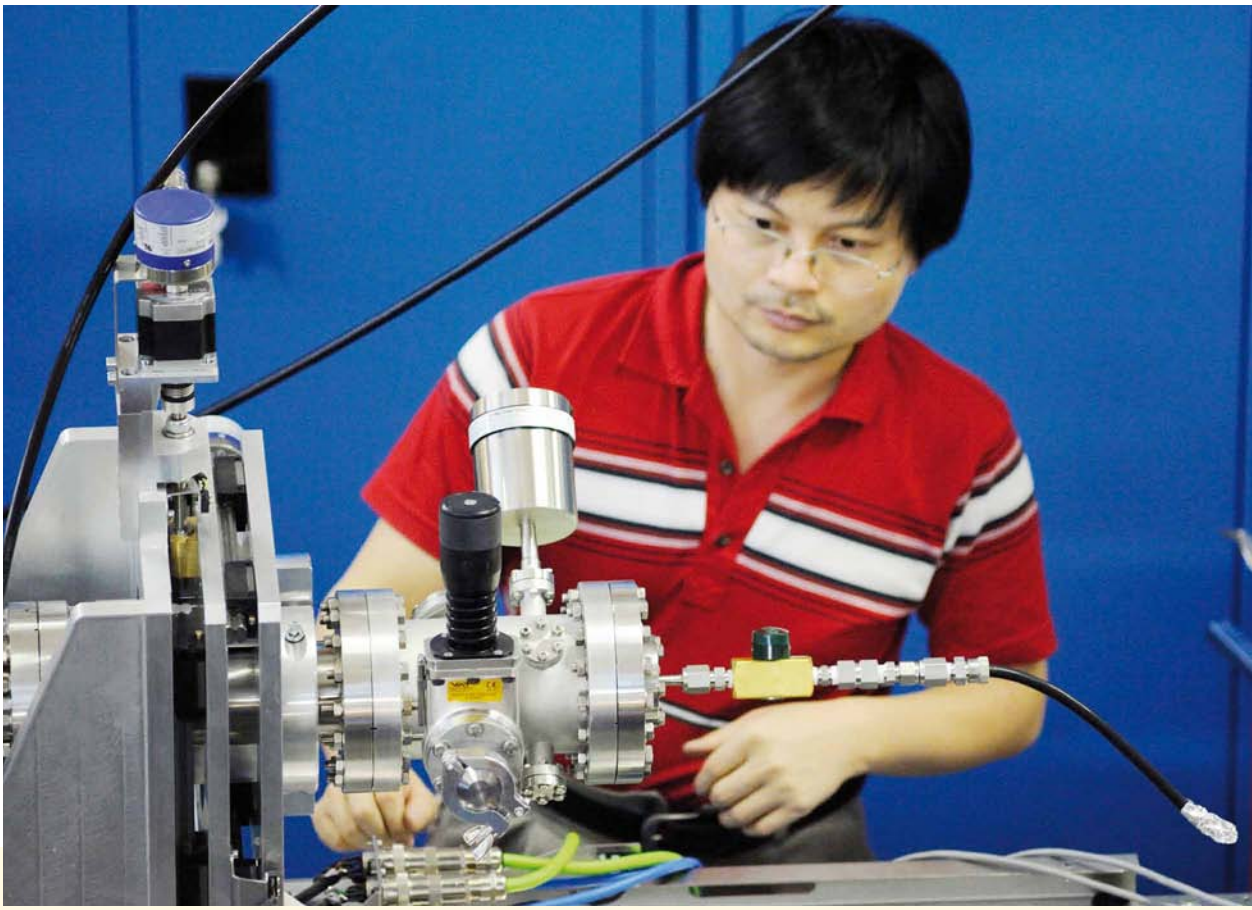
Table 2: Total pulse durations (FWHM in fs)

Radiator	Laser	Slippage	Emittance	Energy Dispersion	Total
CRISTAL	50	53	54	52	104
TEMPO	50	53	47	117	145

Light on dynamics

Dynamics at SOLEIL involves a very wide timescale, ranging from milliseconds to a few hundred femtoseconds! Similarly, it covers a wide range of applications, since it starts with the study of atomic motion and the local properties of atoms and moves on to phase transition at the macroscopic scale by using cooperative or reactional effects that develop at different times.

Light on dynamics



Xiaojing Liu, scientist on PLEIADES beamline, setting up the isolated nano-objects source based on an aerosol generation technique, which is developed for the Nano-PLEAIDES ANR project.

Synchrotron radiation is an ideal tool for developing time-resolved studies both because it has a naturally pulsed structure (the pulses are a few tens of ps, or even a few ps in low-alpha mode or about 100 femtoseconds in slicing mode), but also because its brightness allows acquisitions with very short integration times (a few seconds or a few milliseconds or tens of microseconds with ad hoc detectors), allowing, for example, reaction monitoring. Another complementary approach, from the point of view of quantum mechanics, is to develop spectroscopic studies at very high spectral resolution. It is then possible, following the uncertainty principle, to access temporal information at even shorter time scales, as far as the total achieved resolution is good enough. The examples brought together here are certainly not exhaustive (almost all beamlines are presently or will be involved in dynamic studies) but help to illustrate some of these general considerations, over a wide scientific field.

Studies of nano-objects

The strong interest in nano-objects, which have unique properties related to confinement effects linked to their size, has prompted numerous dynamic studies aimed at understanding both nucleation and growth phases. Experiments carried out on SAMBA and SWING, combining time-resolved absorption and scattering, or on ODE (XANES dispersive mode), further our understanding of these complex phenomena which often involve transient states. The aim of such studies, through greater control of the nucleation conditions, is to control the synthesis of nanoparticles and to optimize their final properties. Studies on aerosols and free nanoparticles (DESIRS, PLEAIDES) will complement these approaches.

TEMPO

Magnetization dynamics in nanowires revealed by time-resolved XMCD-PEEM

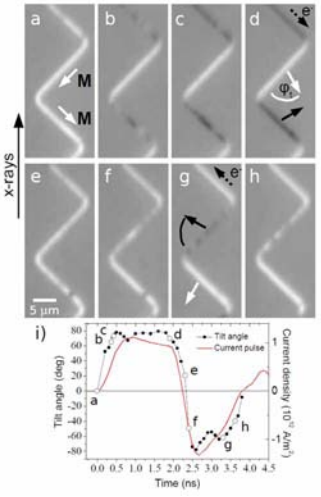


Figure 1: Time-resolved XMCD-PEEM images of the magnetic domains in the NiFe layer of a 400 nm wide nanostripe. The upper part of the figure presents 8 of the tens of images recorded, every 100 ps, during the bipolar current pulse (4.5 ns). Part (i) of the figure shows with what time delays these images were recorded, together with the magnetization tilt angle Φt.

Domain walls in magnetic nanowires have been proposed to constitute a new type of fast and cheap magnetic storage medium, the so-called race-track memory [1]. The displacement of the domain walls in these nanowires is induced by short current pulses, through the so-called spin-transfer-torque (STT) effect. Many experimental studies have used magnetic microscopy to investigate current-induced domain wall motion, but all of them used quasi-static measurements, imaging the position and shape of the magnetic domain wall before and after a current pulse. For a better theoretical and experimental understanding of the interaction between spin polarized currents and domain walls it is crucial to directly observe the magnetic configuration of the nanowires during the current pulses.

The time structure of the SOLEIL synchrotron radiation source and the equipment of the Louis Néel Laboratory in Grenoble have been used to perform time-resolved x-ray photoemission electron microscopy (PEEM) experiment in real time, with 100 ps time resolution. In pump/probe experiments, the effect of nanosecond current pulses applied to spin-valve-like FeNi/Cu/Co magnetic nanostructures was directly observed. The microscope images have been taken during the current pulses and clearly reveal a tilt of FeNi magnetization in the direction perpendicular to the stripe. It is associated to the Oersted field accompanying the current pulse. For 400 nm wide stripes, average current densities of 10^{12} A/m^2 lead to tilt angles as large as 80 degrees. These measurements give the first direct evidence for the importance of Oersted fields for current-induced domain wall motion in these trilayered structures. This effect should also play a role for samples where the magnetic layer is surrounded by metallic buffer or protection layers.

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References :
Parkin S.S.P. et al., Science 320, 190 (2008).
Uhlíř, V. et al. arXiv:1002.1302v2 [cond-mat.mtrl-sci].
Grollier, J. et al., Appl. Phys. Lett. 83, 509 (2003).
Uhlíř, V. et al., Phys. Rev. B 83, 020406 (2011).

Dynamics modelisation

The example described on the DISCO beamline involves a completely different field because it is the in situ measurement of the diffusion dynamics of trace elements within complex systems such as food, for example. A major challenge for public health is the problem of food contamination by certain additives found in their packaging. The objective behind modeling their dynamics at the molecular level, based on these measurements, is to understand the role that the size of these solutes plays in their diffusion rate.

"THE OVERARCHING QUESTION IN STRUCTURAL DYNAMICS IS TO UNDERSTAND HOW ATOMIC AND ELECTRONIC INTERACTIONS DRIVE MOLECULAR MACHINES."

FRANCESCO SETTE, DIRECTOR GENERAL OF ESRF, GRENOBLE.

Pump-probe

Much shorter time-scale studies involve more fundamental aspects. While in the previous examples, the element triggering the temporal process to be followed did not require extensive synchronization, this is no longer the case for very short time scales, where this synchronization is usually obtained by pump-probe type experiments. In short, very fast excitation is created by interaction of the system with a pulsed laser, and further evolution of the system is probed means of synchrotron radiation, by adjusting the delay between two pulses. This type of experiment, based on sufficient

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PLEIADES

Circularly polarized light - a probe of nuclear dynamics in achiral species

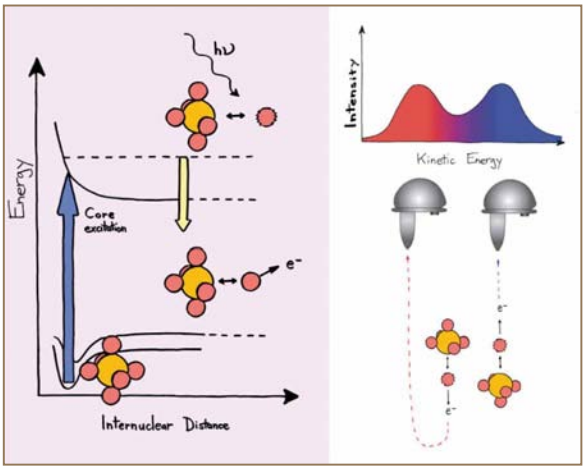

Figure: Left panel: Schematic diagram of the ultrafast dissociation and formation of atomic-like Auger lines observed in Resonant Auger Spectroscopy (RAS).
Right panel: Schematic diagram of the Auger-Doppler effect observed in RAS due to the emission of electrons from the forward/backward travelling core-excited atomic fragments.

Circularly polarized light (CPL) finds numerous applications ranging from modern displays and RealD 3D cinema technology, to circular dichroism of magnetic materials or chiral macromolecules in structural biology, and allows addressing the fascinating origin of the homochirality of life.
For the first time, on the PLEIADES beamline, circularly polarized light has been used to probe nuclear dynamics of highly excited neutral molecules, which dissociate within a few femtoseconds (10^{-15} s) only after absorption of the X-ray photon.
The highly excited SF_6 species $F1s^{-1}a^{*}_{1g}$ experience electronic relaxation by emitting a valence electron, a so-called "Auger electron". However, since the fragmentation process is very fast, the ejection of the Auger electron may occur from already dissociated fragments.
As it has been observed before using linearly polarized light, one is able to distinguish Auger electrons ejected from the fragment atoms moving either towards or away from the electron detector owing to the small differences in their kinetic energies. This effect, called Auger-Doppler by analogy with acoustical Doppler effect, is observed for the first time using CPL despite the uniform distribution of the dissociating chemical bonds induced by the CPL.
Based on the present results, it will be possible to use the circular dichroism in Auger-Doppler profiles as an efficient probe of the photoionization dynamics as well as of the molecular structure and chemical environment, even in achiral species.

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Reference: O. Travnikova et al., Phys. Rev. Lett 105, 233001 (2010)

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statistical analysis, requires the recording of a large number of measurements and thus applies only to reversible phenomena in the analysis time window. In materials science, we can thus probe phase transition dynamics using a photo-triggered system recording time-resolved diffraction patterns. The CRISTAL beamline will soon be equipped with such a system for dynamic studies of a few ps and a eventually a few fs (see prospects offered by the slicing project). The PLEIADES and TEMPO beamlines are, or soon will be, equipped with lasers synchronized with the synchrotron pulses for experiments in dilute phase (fragmentation dynamics) and surface dynamics (reactivity, magnetism) again on a scale of a few tens of ps (then fs with slicing). The insert, showing results from studies on the TEMPO beamline, concerns the magnetization dynamics induced by injecting current into magnetic nanowires. These studies form part of the optimization of materials for information storage of ever increasing density and with switching times as short as possible. It should be noted that, for these studies, the temporal resolution (here about 100 ps) is combined with the spatial resolution (sub-micron) using the XPEEM technique, the magnetic properties being revealed by circular dichroism analysis.

An electronic hole used as an internal clock

The example described on the PLEIADES beamline belongs to another category as it concerns dynamic effects

To be continued on page 18...

DISCO

In-situ measurements of trace diffusion coefficients in polymers

Determining the relationship between the chemical structure of solutes with intermediate molecular weights (e.g. monomers, plastic additives, residues) and trace diffusion coefficients *(D)* in polymers is of significant concern in various domains including the contamination of food products by packaging constituents, polymer ageing, reactivity in solids… For a reason that is still not completely understood, the molecular mass dependence is found much greater in semi-crystalline than in melts. The general goal of this study is to contribute to the development of single-molecule spectroscopy technique than can be applied to monitor trace diffusion in polymer or nanocomposite materials on DISCO beamline.

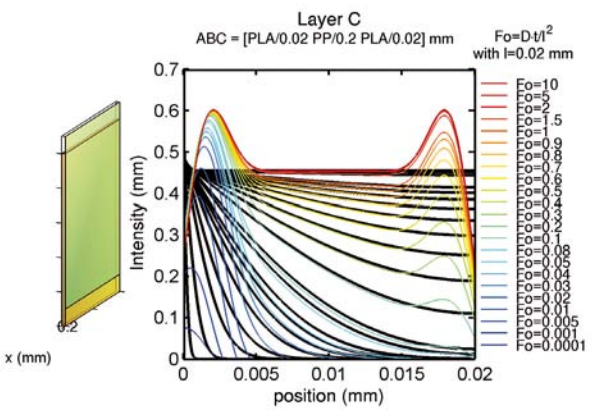

Figure 1: Conditions of diffusion (B=source, A=C=destination) and simulated profiles (black lines= concentration profile without diffraction, colored lines=intensity profiles as measured including light diffraction).

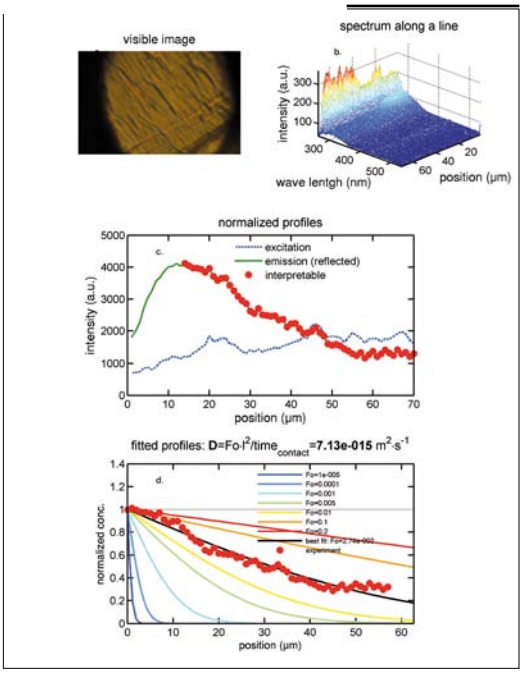

Figure 2: Typical profiles: a) overview of the cross-section of B (PP) in the visible range, b) spectra along a line, c) integrated intensities, d) numerical fitting.

As an intermediate step, a reference was devised and a microscopic technique tailored to assess D values for arbitrary homologous series of tracers and diffusion coefficients as low as 10^{-17} $m^2.s^{-1}$.
The developed methodology relies on 2D spectra profile (wavelength×position) measurements in epi-configuration along cross-sections of materials. The only requirements are that the studied substances present some absorption bands (e.g. aromatic rings or conjugated double-bonds) in the energy range accessible on DISCO beamline, and a corresponding fluorescence that can be separated from the natural fluorescence of the polymer or of its constituents.
Three layers of materials, denoted ABC, are put in contact in controlled thermodynamic conditions (Fig. 1 shows one of the tested configurations) and subsequently microtomed for observations. Layer B is formulated with the desired substance by a prior sorption experiment, and acts as a source. A and C are reception layers that do not contain the substance to test. Determined fluorescence intensities along each sample thickness are compared to numerical solutions of a transport model by diffusion (including partitioning effects if required). In practice, light diffraction due to defocus (imperfect cutting, non-planar samples) and optical aberration must be included.
A typical fit is described in Fig. 2 for an excitation wavelength of 275 nm. A semi-supervised method has been developed to extract baselines, to integrate specific emission peaks (Figs. 2b and 2c) and finally to fit *D* values or equivalently layer dimensionless Fourier numbers, *Fo*.
Plotting activation energies and *D* scaling relationships identified on DISCO beamline for a series of biphenyl molecules in polypropylene (PP) and in poly(lactic acid) (PLA), it appeared that adding one carbon between two phenyls lower *D* values by a factor 3. This scaling was unexpected.
Such results that do not depend on polymer details (similar slopes) are currently analyzed by molecular dynamics simulation to reach a theory.

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ODE

Gold nanoparticles: subsecond kinetics and mechanisms of formation

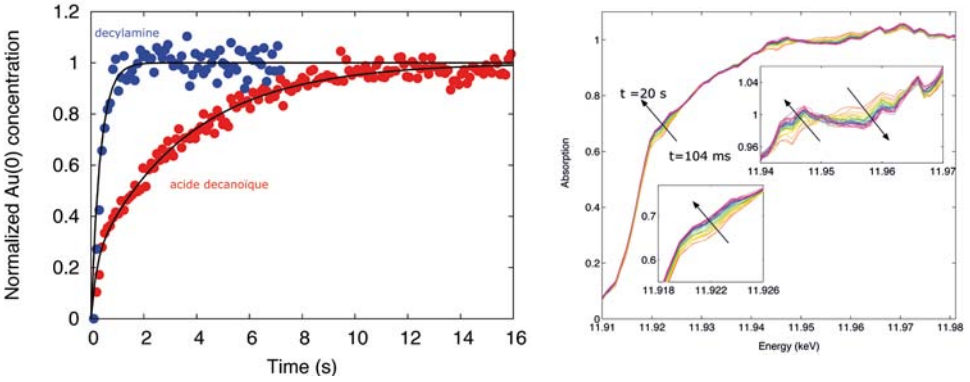

Figure 1 : (left): Formation rate of Au(0) in solution for the 2 ligands (decanoic acid or decylamine) resulting from in situ XANES experiments (right): absorption spectra (XANES) at the L(III)-gold edge for different time periods of gold nanoparticle synthesis in the presence of decanoic acid.

The potential applications of gold nanoparticles aim to exploit their unique intrinsic properties (color, reactivity, etc.) due to their large surface to volume ratio, their shape and polydispersity.
Many synthetic routes can be used to obtain these nanoparticles, though it is difficult to control their size distribution and the underlying mechanisms are still poorly understood. The first stages of synthesis are difficult to observe experimentally and, as a result, there is very little control over the nucleation phase.
Studies on ODE fall within this context and aim to develop in situ follow-up experiments on the formation of gold nanoparticles in terms of the structure of the material being formed and the chemical speciation of the medium. The goal is to understand the mechanisms of metallic nanoparticle formation in order to control their synthesis.
One of the approaches was to couple X-ray absorption near-edge structure (XANES) with a rapid mixing stopped-flow Bio-Logic © system by developing a cell adapted to gold concentration ranges (3 mM). Nanoparticles were formed by borohydride reduction of a solubilized gold salt. These reactions can be very fast (one to a few seconds for spherical particles). The measurement of the absorption spectrum in dispersive mode achieved at the near-edge of gold (XANES) was used to quantitatively access the different oxidation states of gold (Au (III), Au (I), Au (0)) during the synthesis of nanoparticles in the presence of ligands (decanoic acid or decylamine) (Fig 1).
The very high temporal resolution (~ 100 ms) of these experiments helped establish the rules of Au (0) formation rate in the solution, and demonstrate its fundamental role in controlling the final size of nanoparticles.
In particular a very strong transient supersaturation of Au (0) monomers was shown to occur at the peak of nanoparticle nucleation (1s), and a lack of secondary aggregation for this synthesis process.
These key experiments to understand the reaction mechanisms involved in the formation of nanoparticles are also used to understand the development of anisotropy.

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Reference : Abécassis B. et al, Langmuir 2010,(26)17, 13847–13854

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using so-called sub life-time spectroscopy applied to an isolated molecule. In short, the very short life time of a hole created in the inner shell of an atom is used as the internal clock of the changes in the core excited system. The condition required to extract the relevant information, is to combine an overall resolution, both in terms of excitation and analysis that is less than the widening induced by the finite lifetime of the inner hole (in this example 100 meV corresponds to dynamics of tens of femtoseconds).
To conclude this brief overview of opportunities offered at SOLEIL in the field of time-resolved studies, we would like to point out two future actions over the longer term:
• Plans for a beamline optimized for short time kinetics for nanomaterials in heterogeneous catalysis and energy (batteries). This project, accepted by the EQUIPEX call for proposals, will give communities the opportunity to use rapid X absorption (QuickEXAFS) techniques under *in situ* conditions.
• Generation of femtosecond pulses by interaction of a high- intensity fs laser with the electron bunch stored in the ring. The X-ray pulses thus generated in the TEMPO and CRISTAL insertions will then be extracted on these beamlines for dedicated pump-probe experiments (see article p.11).

These actions will directly benefit from specific developments undertaken at the detection level (Xpad detector, local beam deviation, etc.)

SAMBA- SWING

In situ UV-Vis/SAXS and UV-Vis/XAFS Time-Resolved Studies of ZnO Quantum Dots Formation and Growth

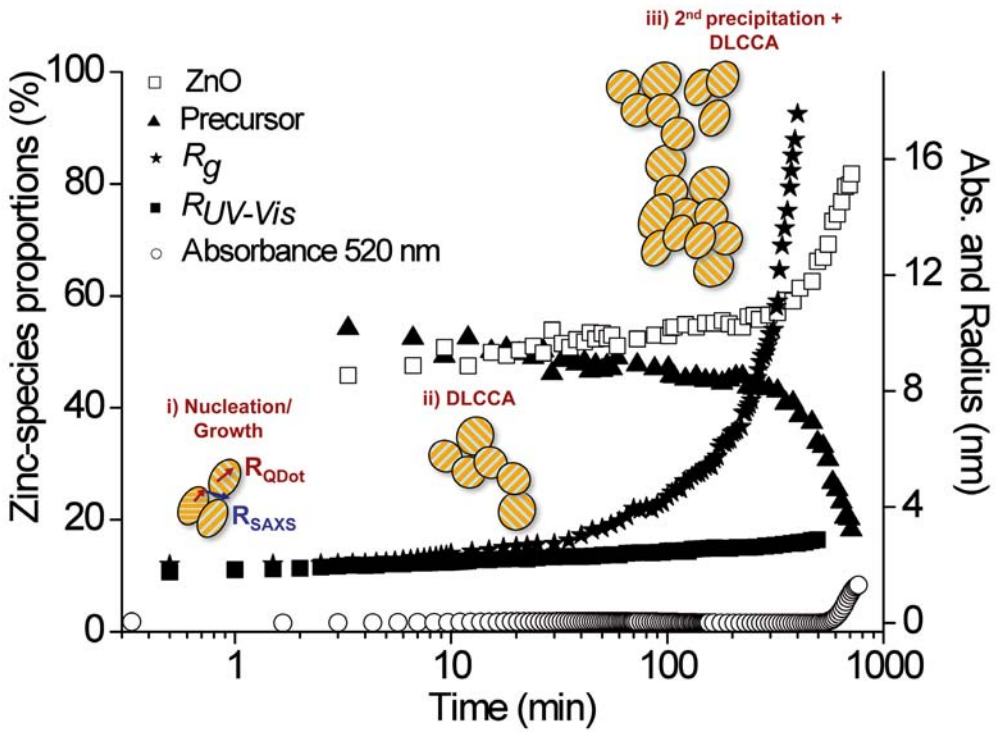

Figure 1 :
Time evolution of the proportion of different zinc species determined by EXAFS (ZnO Q-dots and precursors), of the absorbance value at 520 nm and of the radius of Q-dots determined by UV-Vis, RUV-Vis, and of the gyration radius of scatters determined by SAXS, Rg.

In recent years, the synthesis of nanoparticles has strongly attracted the attention of researchers due to their electronic, luminescent, optoelectronic and catalytic properties varying significantly with particle size. The study of increasing band gap with decreasing particle size is one of the most studied in the field of semiconductor nanoparticles. The understanding of the nucleation and growth processes of such nanoparticles is of prime importance for tailoring their size and then their properties.
In this context, the results gathered at SOLEIL using both the SWING and SAMBA beamlines during the in situ monitoring of the formation of ZnO quantum dots (Qdot), induced by the addition of KOH solution ([OH]/[Zn] = 0.5) to zinc oxy-acetate ethanolic solution at 40°C, were successfully combined in order to unravel the complexity of the involved mechanisms.
In situ time-resolved UV-Vis absorption was combined with Small Angle X-ray Scattering (SAXS) and X-ray Absorption Fine Structure (XAFS) techniques and enabled to link both synchrotron radiation techniques by rescaling both time-resolved experiments. The monitoring by XAFS allowed to determine the proportion of Zn-based phases present as a function of time (herein ZnO Qdots and unreacted zinc oxy-acetate precursors) and to reveal stepped transformations i) with fast increase of ZnO Qdots (~47%) at the expense of precursors, ii) then a steady state with no increase of the amount of ZnO Qdots but with increasing radii as revealed by UV-Vis and iii) a new increase of the quantity of ZnO Qdots up to ~82% in a time period where UV-Vis revealed aggregation or huge particle growth.
Regarding the analysis of SAXS in the context of the conclusions drawn from XAFS and UV-Vis, it has been evidenced that the stepped processes occurring during the formation of colloidal ZnO nanocrystals are: i) ZnO Qdot nucleation and growth; ii) growth of compact ZnO Qdot aggregates followed by the growth of fractal aggregates described by a cluster-cluster diffusion limited growth; iii) and finally secondary nucleation and fractal aggregation.

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The NeXus format, one more step towards homogeneity

> NeXus is a good candidate to harmonize data formats

Stéphane Poirier,
SOLEIL Computing division – "control, order and acquisition" group

What is the NeXus format, what are its advantages?
The NeXus format was not invented for the SOLEIL synchrotron. It was created in about 1996 in research institutes that were using neutron sources to analyze matter. Laboratories needed a format for recording larger volumes and a greater variety of data, for storing both experimental data and data describing the context of the experiment. They based it on an existing format developed in U.S laboratories, the Hierarchical Data Format (HDF), which is extremely powerful but rather complex to use. The NeXus format is an approach that makes HDF simpler to use and also specifies the contents of the files. The most important added value of NeXus is that it does not impose constraints in terms of number and volume of datasets that can be stored in the file, unlike most of the formats used until now.

Why is the NeXus format of interest to SOLEIL?
I arrived at SOLEIL in 2004 and my mission was to define a way of recording the data: what format and with which tools. I spent my first few months searching the "ideal" format and I then came across NeXus. Neutron sources and synchrotron radiation allow research which is relatively similar, so the specifications I found with the NeXus format were applicable without modification. Today, more and more of the measurements recorded on the beamlines represent large volumes of information that will always grow in size. Thus, the classic text formats that people used previously have proved unsuitable. On the other hand, one of the constraints imposed on the site was to use the same format on all beamlines. What was needed was a generic format to meet these diverse needs. There has also been an effort at the European level to try to harmonize data formats and NeXus is a good candidate. But it is not alone.
Now, at SOLEIL, in collaboration with an Australian Institute (ANSTO), we are trying to go beyond NeXus and free ourselves completely from the data format.
Having standardized the format of data files produced by the beamlines allows SOLEIL to have a "library" of its experimental data, a library the content of which can be explored computationally using, for example, the Web application TWIST. SOLEIL thus possesses the scientific memory of experiments that have taken place on its beamlines.

Managing on a large-scale basis, our experimental data is new in the synchrotron world and puts us in a very favorable position for different European projects (PANDATA, PNI…) related to this issue. Today, we are taking advantage of this position trying to convince IT personnel of partner institutes (ESRF, DESY, etc.) to join us in the "CommonDataModel" approach, an ambitious project that aims to unify access to scientific data for the data analysis software. So stay tuned…

Have you encountered problems in getting NeXus accepted at SOLEIL?
It took time convincing SOLEIL scientists, so it was quite a slow process. The biggest barrier is that in order to use an HDF file, you need software that can read it. The development of data reduction applications able to read NeXus files started one year ago, three years after the production of our first Nexus file. In the meantime, so that people can work, we have developed a "conversion tool" that allows NeXus files content to be read by existing analysis applications. For the SWING beamline, we developed an application called FOXTROT which can analyze experiments that have been stored in NeXus files. This application is heavily used on that beamline and we are starting to deploy it on other beamlines.

→ **For further information** www.synchrotron-soleil.fr/Soleil ToutesActualites/2009/TWIST

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IN BRIEF

SOLEIL INVOLVED IN THE PARIS-SACLAY-INNOVATION NETWORK

SOLEIL is one of 18 participants forming part of the Paris-Saclay-Innovation network set up for research development and the creation and development of innovative technology companies in order to give the business community access to experimental facilities, research skills and the scientific and technical know how of the laboratories on the Saclay campus and in the Yvette valley. The network runs a bilingual website presenting its offer (www.paris-Saclay-innovation.fr) and had a stand at the Orly TechInnov on February, 11th, 2011.

ICM HAS CHOSEN THE SAME NEW DATA STORAGE SOLUTION AS SOLEIL

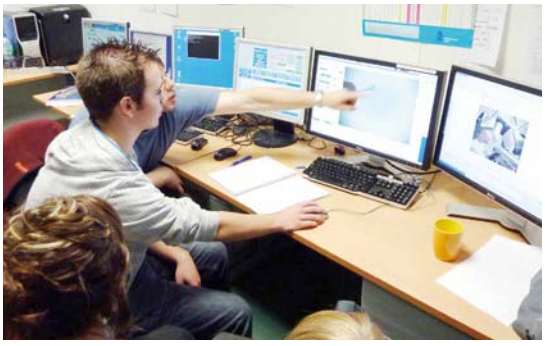
The Brain and Spinal Cord Disorders Institute (ICM) has just adopted the innovative scientific data storage solution Active Circle, already installed at SOLEIL.
A visit of SOLEIL, followed by discussions with experts in the Computing Division at SOLEIL, helped ICM decide on the Active Circle solution, proposed by a French company with its headquarters in Jouy-en-Josas, in close proximity to the Saclay campus.

EVERYTHING IS CHEMICAL... ESPECIALLY THIS YEAR

The year 2011 has been designated International Year of Chemistry by the United Nations. SOLEIL has chosen, as it often does, the experimental approach to mark this special year: included in the program will be, notably, a crystal garden, luminescence and phosphorescence, superabsorbent polymers... a new educational workshop tested and acclaimed by the public at the last Science Festival in October 2010

THE CENTRE REGION

Budding researchers



Eight young people and two teachers from the Centre region set up an experimental workshop in 2009 called "Protein experts: from the purification of lysozyme to solving its structure" on the PROXIMA1 beamline. SOLEIL made an exception and agreed to assign a few hours of beamtime to these highly motivated future young scientists.

→ **For further information** http://www.synchrotron-soleil.fr/Presse/Videos/Graines-de-Chercheurs

10

Ten years since the decision was made in September 2000 to build SOLEIL. This was a key year for SOLEIL, with a book published by Le POMMIER to record the intervening years.

→ http://www.editions-lepommier.fr

Ile de Science

Association, reflection, mediation

Created in 1992, the Ile de Science Association has involved, over the years, scientific and industrial partners in reflecting on science and technology. The next meeting is planned for the 12th May 2011 at HEC for a day devoted to open innovation. Ile de Science is also organizing "neighborhood science", a multidisciplinary science village that attracts over 2,500 people per year on the Saclay Plateau.

→ www.iledescience.org

"In a synchrotron, the latest cutting-edge instruments can also be used to study the objects and technologies of past societies. It's fascinating."

Solenn Reguer,
scientist on the DIFFABS beamline.

ISDSB 2010 Conference

At Lehmann conference centre (from left to right): M. Van der Rest, J.J. Girerd, J. Janin, G. Bricogne et V. Ramakrishnan.

201 PARTICIPANTS FROM 18 COUNTRIES, including a substantial number of young scientists, attended the 3rd International Symposium on Diffraction Structural Biology (ISDSB 2010) that was held May 25th to 28th 2010 near Paris, at Paris-Sud University and SOLEIL. It was organised by SOLEIL. The Executive Committee included N. Sakabe and N. Yasuoka (Japan), J.E. Johnson (USA), J. Helliwell (UK) and R. Fourme (France), with the advice of an international scientific committee. This conference was the third in the series of ISDSBs initiated in 2003 by the Japan Society for the Promotion of Science (JSPS), and specifically by the University-Industry Cooperative Research Committee (#169) chaired by N. Sakabe. It was the first to be held out of Japan.
The historical concept of the ISDSB Symposia is to bring together researchers using diffraction, crystallography, and more generally interactions of X-rays, electrons and neutrons with matter in the study of structural biology and, secondly, within this domain, to facilitate the interaction between academic and industrial researchers. The eight scientific sessions were: Electron microscopy, X-ray imaging, tomography; Drug and vaccine design; Protonation states; Large bio molecules; Membrane proteins; Protein structure/function; X-ray technologies; Structural genomics. The 33 invited talks included a conference by V. Ramakrihsnan, 2009 Nobel Prizewinner, and six Plenary Lectures (W. Baumeister, T. Blundell, G. Bricogne, W. Hendrickson, C. Luchinat, D. Svergun and I. Tanaka). There were two Poster sessions (structural results, methods and instrumentation) and also a Commercial and Industrial Companies Exhibition as well as a visit to the SOLEIL Facility. The Conference dinner was a relaxing moment held during a boat trip on the river Seine. A special feature was a 'Meet the Public' event hosted by SOLEIL and the Director General, M van der Rest, involving a panel comprising the Nobel Speaker and the plenary lecturers. The panel emphasized the prime importance of basic science, whilst recognising the need for applied science, as well as the crucial role of synchrotron and neutron sources. The importance of a better public information was also discussed.
The conference closed with an invitation from Japan to host the 4th ISDSB, probably sometime in 2013.

Conference supported by SOLEIL, the Ile de France Region, CEA, CNRS, Paris-Sud University and industrial sponsors. IUCr and ECA funded bursary applications for students.

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→ www.synchrotron-soleil.fr/workshops/2010/ISDSB
www.synchrotron-soleil.fr/Presse/Videos/ISDSB2010

Proceedings: Journal of Synchrotron Radiation, January 2011 (Guest Editor: N. Yasuoka).

Combined techniques

THE SECOND SYMPOSIUM ON THE SIMULTANEOUS COMBINATION OF SPECTROSCOPIES with X-ray absorption, X-ray scattering and X-ray diffraction was held at SOLEIL on 24th and 25th June 2010. In recent years, synchrotron studies coupled with laboratory spectroscopic techniques, such as Raman and UV-Vis absorption, have multiplied on different synchrotron facilities (ESRF, SLS, SOLEIL) and this for different structural characterization techniques in the hard X-ray (X-ray absorption, scattering and diffraction). At SOLEIL, the beamlines that are developing this type of coupling include SAMBA, CRISTAL, SWING, LUCIA, DIFFABS, ODE and PROXIMA1.
These studies have shown how combining techniques could be beneficial to the understanding of systems thus characterized. The symposium was an opportunity for sharing experiences between beamline scientists and users that have carried out such studies.
The aims of the symposium were to show, through oral presentations and poster sessions, what is being done on different beamlines and also to organize a roundtable to discuss the technical aspects of implementing these couplings.
The symposium attracted over 80 participants from 12 different countries. Following two plenary lectures on UV-Visible absorption spectroscopy and the value of combining vibrational spectroscopy with synchrotron radiation techniques, 19 oral communications were presented in four sessions dedicated to various themes using this coupling approach, ie catalysis, biology, materials physics and the genesis of nanomaterials.
During a roundtable, participants, scientists and industrialists were able to discuss the state of the art and future developments.

The work presented at this conference will lead to publication in a special issue of "Phase Transitions".

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Sixth SOLEIL Users' Meeting

The sixth SOLEIL Users' Meeting was held on the 19th and 20th January 2011 at the Ecole Polytechnique (Palaiseau) and at SOLEIL.
This annual meeting for the community of synchrotron radiation users was a good opportunity to obtain the latest information on the machine and on the performance of the various beamlines, as well as summarize the outlook at SOLEIL.
It consisted of 3 plenary sessions covering the following research themes: use of STXM (soft-x-ray scanning transmission x-ray microscopy) in Earth and environmental sciences, by K. Benzerara (IMPMC and HERMES beamline, SOLEIL); molecular photoionization, by R. Doerner (Frankfort University); coherent diffraction and its use in condensed matter physics, by S. Ravy (SOLEIL).
After the success of parallel sessions found during the 2010 session, the Users Committee wished to devote a full half-day to these, while still holding round tables in each community, for exchanges between users and heads of beamlines.
A period for socializing was also organized at SOLEIL on the afternoon of January 19th with a poster session, business stands and visits to the synchrotron.

→ **www.synchrotron-soleil.fr/Workshops/2011/SUM11/**

Two satellite workshops to this Meeting were also organized on the 17th and 18th January 2011:
"RIXS - New prospects for Resonant Inelastic soft X-ray Scattering". The aim of this workshop was to initiate an exchange between the community of RIXS specialists and potential users interested in the great potential of this technique for research on the physical and chemical properties of materials in the solid state but also in liquid or gaseous phases. The advantages of a novel soft X-ray emission spectrometer, developed jointly by the Laboratory of Physical Chemistry-Matter and Radiation (UPMC-Paris) and SOLEIL, and soon available on the SEXTANTS beamline, were also highlighted.

→ **www.synchrotron-soleil.fr/Workshops/2011/SatelliteSoft-RIXS**

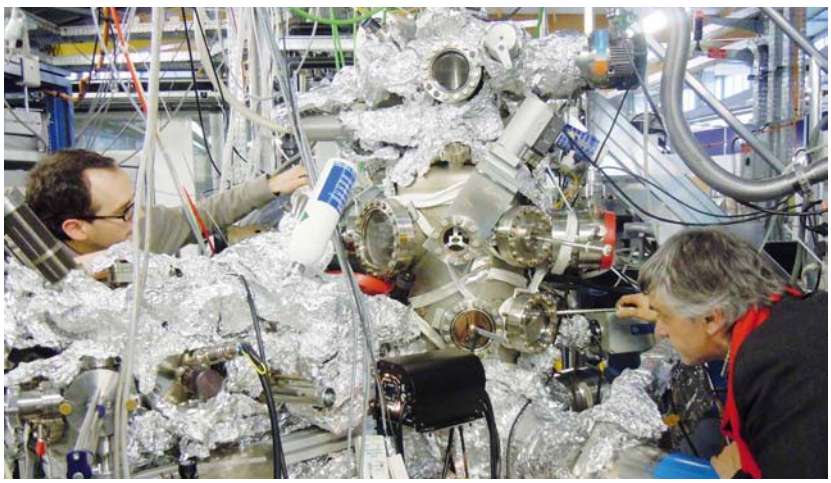
"IPANEMA 2011 – Synchrotron radiation for ancient materials". Continuing the defining work done by the IPANEMA working groups since 2008 (involving 100 scientists), this workshop was aimed at researchers in the fields of archeology, paleontology, conservation and ancient environments, already users of synchrotron techniques or wishing to familiarize themselves with them.

→ **www.synchrotron-soleil.fr/Workshops/2011/SatelliteIPANEMA11**

PHOTOVOLTAICS

TEMPO counts **on solar energy**

As the basic elements of solar panels, photovoltaic cells are electronic components that generate electricity when exposed to sunlight. Until now they were usually made of silicon semiconductors, but new generations of photovoltaic cells are now being studied, notably under TEMPO beamline X-rays



Mathieu Silly (on the left) and Fausto Sirotti (on the right) making soft X-ray photoelectron spectroscopy experiments on TEMPO.

"Classic" silicon photovoltaic cells produce a good yield (12-20%), but their cost is high and there is a risk that the basic material will run out. New hope has come from the development of organic photovoltaic cells based on polymers, which are less costly, both financially and in the energy required to manufacture them, and are biodegradable, flexible and lightweight. Unfortunately, their performance is poor (2-5%) because they do not absorb solar radiation efficiently in the low energy range (red and infrared) and they are unstable in the long term.
The inclusion of nanoparticles that absorb radiation in the near infrared would offset the disadvantage of the lack of sensitivity in this part of the solar spectrum. W. Flavell and her group (Manchester University) carried out experiments related to this on the TEMPO beamline in order to study the electronic structure of nanoparticles of lead sulfide (PbS) by soft X-ray photoelectron spectroscopy. The study aimed to correlate the electronic properties with the sizes of nanoparticles to ultimately control their sizes in order to optimize the extraction of energy from the solar spectrum throughout its range, from red to ultraviolet.
Studies are also underway to directly observe the phenomena of photon absorption by photovoltaic cells, through measurements combining synchrotron radiation and laser pulses.

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Three items of information on photovoltaics

1 The conversion of light into electricity, or the photovoltaic effect, was discovered by Antoine Becquerel in 1839. It was not until nearly a century later that scientists understood and exploited this physical phenomenon.

2 The main electronic property studied in the work cited above is the width of the "energy gap", on which depends the material's ability to conduct electricity. In conductive materials, this width is zero.

3 Standard methods of synthesizing PbS nanoparticles involve solvents or other highly toxic reagents. These researchers were interested in a new form of synthesis that was "greener" than its predecessors, the solvent being olive oil!

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