Project Summary

Title: **Surface Diffraction beamline**

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Principal characteristics of the beamline

<table>
<tr><th>Source</th><th>Energy range (keV)</th><th>Optics</th><th>Spectral resolution (E/ΔE) and flux (F) on the sample (HxV)</th><th>Experimental facilities</th></tr>
<tr><td rowspan="2">U20 Undulator On a short section</td><td rowspan="2">5-20</td><td rowspan="2">Double Crystal monochromator Si(111)

Vertically focusing mirror

Mirror tilted at 45° to invert the beam dimensions

Phase plate device for adjustable polarisation</td><td>E/ΔE = 10^4, F = 10^{14} ph/s at 5 keV

E/ΔE = $2x10^4$, F = $2x10^{12}$ ph/s at 20 keV

Beam size: (125x1750) μm^2</td><td>N-axis UHV Diffractometer for
- In-situ growth (by MBE, Laser Ablation…)
- GISAXS
- Magnetic Surface Diffraction</td></tr>
<tr><td>E/ΔE = 10^4, F = 10^{14} ph/s at 5 keV

E/ΔE = $2x10^4$, F = $2x10^{12}$ ph/s at 20 keV

Beam size: (1500x50) μm^2</td><td>Multi-purpose Diffractometer for
- Buried Soft Interfaces
- Electrochemical cells
-Reactivity chambers</td></tr>
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1 - INTRODUCTION

The Surface Diffraction beamline will be devoted to the study of surfaces, interfaces and nanostructures of different materials in various environments, exploiting the grazing incidence diffusion and diffraction of X rays. The undulator source gives a beam with high flux and low divergence, allowing one to well-define the grazing incidence angle, which is essential for the optimisation of the signal/noise ratio, being the surface signals very weak.

The beamline has an experimental configuration, which offers a rich combination of X-ray scattering techniques: Grazing Incidence X-Ray Diffraction (GIXD) in vertical or horizontal geometries, Grazing Incidence Small Angle X-ray Scattering (GISAXS) and X-ray reflectivity. Two instruments will be devoted to the techniques: a diffractometer in Ultra High Vacuum (UHV) that will allow the **in-situ** study of solid surfaces, interfaces, nanometric objects and growth mechanisms; a second diffractometer will be able to host different sample environments, like electrochemical cells, Langmuir trough, catalytic chambers… for the study of interfaces (liquid-liquid, liquid-solid, solid-gas).

The beamline project has been written with contributions from the following people:

- **Groupe de Physique des Solides (GPS) –** Bernard Croset
- **Matériaux et Phénomènes Quantiques (MPQ – Paris VII)** – Sylvie Rousset
- **CEA Saclay** – Antoine Barbier, Jean Daillant
- **(CRMD – CNRS – Université d'Orleans)** – Pascal Andreazza
- **Laboratoire de Cristallographie de Grenoble (LdC – CNRS)** – Marie Claire Saint-Lager
- **Laboratoire de Minéralogie Cristallographie de Paris (LMCP – Paris VI)** – Victor Etgens, Cécile Malgrange
- **Unité mixte CNRS – THALES** – Jean Pierre Contour
- **Synchrotron Soleil (St- Aubin)** – Thierry Moreno, Mourad Idir
- **Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE – Université Paris XI)** – Yves Garreau, Alessandro Coati, Michel Goldmann, Philippe Fontaine

2 – OUTLINE OF THE BEAMLINE

The beamline has been designed in order to satisfy a large users community, and will present a very original set-up. The main investigation tools, which are planned on the beamline, are the following:

1. Grazing Incidence X-ray Diffraction (GIXD): it allows the study of the structural properties of surfaces and interfaces. This information is a key step for a complete understanding of the physical and chemical properties of ultra thin heterostructures involved in modern materials science and technology. The high counting rate obtained with third generation synchrotron sources allows to perform studies in-situ, in real time and in extremely stringent experimental conditions (high temperature, magnetic field, gas atmosphere…), enabling to follow growth kinetics and surface structure transitions.
2. Grazing Incidence Small Angle X-ray Scattering (GISAXS): it combines the potentiality of small angle X-ray scattering with the surface sensitivity of grazing off-specular reflectivity: GISAXS will allow the study of the distribution and shape of nanometric objects on a sample surface during their in-situ growth.
3. Reflectivity measurements: they give access to the electronic density variations normal to the surface. In order to perform reflectivity measurements on liquid-solid, liquid-liquid or gas-liquid interfaces the beamline will offer a horizontal scattering geometry with a vertical beam deflecting device.
4. Magnetic diffraction measurements in grazing incidence condition will be possible thanks to a phase plate device, which will control the polarisation of the incoming beam on the sample surface. A polarisation analyser is needed to this aim.
5. The tuneable photon energy in the 5-20 keV range allows one to perform anomalous scattering measurements. Moreover, the beamline is optimised for magnetic measurements at the K absorption edges of transition elements (Cr, Mn, Fe, Co, Ni), which are in the 6-9 keV range, where the phase plate device will provide a full tunability of the beam polarisation. Obviously, in this energy range X ray magnetic dichroism measurements will be possible.
6. The beamline will offer a series of methods for the sample elaboration. An UHV chamber will be dedicated to the study of in-situ and real time growth and formation of nanostructures. Apart the classical evaporation tools, the chamber will present a facility for laser ablation which will permit the growth of complex materials, like oxides. Molecular Beam Epitaxy of hybrid heterostructures will be performed in dedicated chambers, which can be connected with the beamline.

7. A flexible multipurpose diffractometer will be able to host different apparatus, for the study of different materials in various environments: electrochemical cells, Langmuir trough, catalytic cells…

3 – SCIENTIFIC CASE

Nano-structured surfaces and nano-objects

There is a great interest, nowadays, in the surface community and in industry for the self-organised surfaces. This interest is mainly due to the potentiality of such systems to be used as templates for further growth of nano-objects. The template should provide a good periodicity in the position of the objects, furthermore it should lead to control their size distribution. To obtain optimised series of templates, it is important to understand the phenomenon of self-organisation itself. While the elastic relaxation of the substrate is widely considered as the self-organisation driving force, several questions are still open: which part does the thermal disorder play? What are the mechanisms controlling the kinetics of self-ordering? Moreover, in spite of their practical interest, both the period control and the ability to predict which systems self-organise are far to be reached. For these studies on self-organised surfaces and on clusters grown on templates, GIXD is complementary to near-field microscopy (AFM or STM) and to theoretical calculations, and will allow the comprehension of the mechanisms and the control of the self-organization, the cluster growth on self-organized templates, the physical properties of self-organized clusters. Moreover, the coupling of GIXD with GISAXS (possibly in anomalous conditions) gives a powerful tool for the investigation of in-situ and in real time system organisation.

Surface magnetic X-ray diffraction

A substantial progress has been accomplished today mainly thanks to the high photon flux now available at third generation synchrotrons. The polarization analysis has become essential for hard X-rays magnetic diffraction since only the photon interaction with the magnetic moment of the sample can change the polarization of the light. The use of horizontal and vertical linearly polarized light coupled with a polarization sensitive analyser is thus mandatory for an experiment to be carried out efficiently on magnetic scattering. The understanding of the magnetic and antiferromagnetic domain structure in the surface region, the Néel transition as well as the interaction with other materials are almost unexplored topics. They became recently very important to understand the operation of new devices based on the magnetic exchange coupling, extensively used in GMR (Giant Magneto-Resistance) spin valve sensors. Another important development concerns an internal magnetic field surrounding the sample, allowing switching the magnetic field from parallel to perpendicular with respect to the surface plane. This is not trivial but its implementation can open the way for resonant magnetic surface diffraction experiments, thanks to the asymmetry ratio of the surface scattering both for in-plane and out-of-plane magnetization. Working at high X-ray energies has another important advantage: the surface atomic structure as well as its magnetic properties can be both determined.

Solid-gas interfaces in catalytic environment

To understand the microscopic mechanism involved in heterogeneous catalysis, one needs to precisely determine the reactive site and the reaction pathway thus identifying the intermediary steps of reaction. Surface studies help to characterize the chemically adsorbed species participating in the surface reaction. These studies required however techniques adapted to ultra high vacuum or at least to very low pressures (low energy electron diffraction-LEED, near field microscopies-

STM, electron spectroscopies-XPS/AES, vibrational spectroscopies like HREELS, infra-red-IRRAS), which are far from the real conditions of a catalytic reaction. The results obtained under these extreme conditions can hardly be extrapolated to the real conditions of reactions, which occur in ranges of pressures 8 to 10 orders of magnitude higher. Indeed the reorganisation of a surface in the presence of a gas and the real nature of the intermediate phases produced during the catalytic reaction can be very different from those observed in ultra-high vacuum or at low pressures. Only the most strongly bonded species are expected to remain under ultra-high vacuum whereas the weakly bonded states may be desorbed very quickly. We know that these weakly interacting species, referred to as precursors, are precisely the ones supposed to guide the reaction towards its final product. The identification of these species as well as the characterization of the active sites are thus essential for a further comprehension of the reaction mechanisms. The development of new techniques to study the surfaces in reactive environment is thus an essential point to attain such information. X-ray diffraction is non-destructive and can be used to probe any type of gas environment in a large range of pressure, from the ultra-high vacuum up to very high pressures. With the high brilliance of the new synchrotrons, it becomes also possible to study these reactions in real time.

The study of electrified interfaces in liquid environment

Electrochemical interfaces are important for catalysis, energy production, chemical synthesis, corrosion or even for crystal growth. Electrochemistry strongly contributes to new nanotechnologies in different domains like nanomagnetism. The chemical properties and the reactivity of the electrochemical interface strongly depend on the atomic surface structure of the electrode. Among the various surface sensitive techniques, surface X-ray diffraction provides an *in-situ* probe for the atomic arrangement of the electrode surface but also for the interfacial ordered layers surrounding it. The weak interaction between X-rays and matter means that only the surface and the interfacial region diffract a small fraction of the incoming beam. This can be overcome if one takes the advantage of bright synchrotron radiation sources. Substantial progress has been made in the determination of the structure of the electrochemical interface at an atomic level. GIXD allows quantitative studies on several fundamental interfacial phenomena, such as the reconstruction at the electrochemical interface, the underpotential deposition (UPD) of metal monolayers on foreign substrate, the phase transitions in adsorbed films…

Buried soft interfaces

Soft interfaces are created when at least one of the two media is a liquid, liquid crystal, polymer etc. Since the cohesive energies between molecules in these media are of the order of k_BT, the properties of such interfaces can be strongly modified, for example by intercalating surfactant molecules soluble in only one of the two media. In some cases, these molecules will form a monolayer at the interface, reduce the interfacial tension and more generally modify its properties. Such systems are relevant in many fields of physics, chemistry and biology. In the case of the liquid-air interface, and when the surfactant molecules are insoluble in the liquid phase, they form films called Langmuir films. Moreover, surface interactions at solid-liquid and liquid-liquid interfaces also provide a unique way to orient and manipulate fragile membranes or colloidal particles, which can then be studied in great detail. Finally, they are of fundamental importance in processes of technological relevance like adsorption, corrosion or liquid extraction. During the last decade, the application of the Grazing Incidence X-ray Diffraction (GIXD) to the study of Langmuir films has been responsible for major breakthroughs in this field, giving access to the microscopic structures. Such experiments of course take over technical challenges. In most of them a macroscopically thick upper liquid phase is used and the X-ray penetration in the liquid has to be large enough which can be achieved using high-energy beams (18-20 keV). In addition to scattering techniques, the possibility of performing grazing incidence fluorescence experiments will provide a very powerful tool combining the depth sensitivity of the evanescent wave with the chemical sensitivity of fluorescence in order to precisely locate atoms across a complex interface.

4 – POTENTIAL USERS COMMUNITY

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High Pressure Gas/Surface reactions

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Surfaces in electrochemical environment

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Soft Surfaces and Interfaces

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2-Recommendations of the Scientific Advisory Committee

SAC meeting 16-17 Mai 2002

- **Beamline proposal 17 (surface diffraction)**

This project describes a sound scientific case that reflects the interest of the researchers involved. Surface diffraction is a technique which remains important in UHV studies, but is increasingly being used in other areas, many of which are being described in the present proposal. A surface diffraction beamline has to be built at SOLEIL on the basis of the existing community which has reached a high level of scientific achievements and of the large number of interesting applications of the technique. However, the scientific case has to be more focused and the technical design has to be worked out in much more details that the one exposed in the APS document. SAC makes the following suggestions :

- a careful planning of the experiment should be done by studying the complementarity with the IF beamline at ESRF on the one hand, and **by considering possible merging of part of this beamline options with other proposed new beamlines at SOLEIL on the other hand;**

- the option of two end-stations, one for UHV experiments and the other one for non-UHV environments is a good and practical solution that should be adopted. Some technical choices are necessary for the UHV end station in order to avoid an unpractical instrument due to the excessive number of technical options. Laser ablation growth and surface magnetic studies could be the priorities of the UHV set-up;

- the emphasis that is put on “mobile additional preparation chambers” is valuable since the sample preparation is always one of the limiting steps;

- the technical description is rather vague. The nice idea of the 45° mirror has to be studied in details since it could be difficult to realise.

Given the fact that a successful research program is being continued at LURE, there is no doubt that the extra available beamtime will find very good use, in particular since new (non UHV) directions are becoming increasingly feasible. ***SAC gives a high priority for the construction of a surface diffraction beamline.***

- **Beamline proposal 20 (soft interfaces)**

The state of synchrotron radiation research in the field of soft matter interfaces on liquid substrates is described, mainly referring to the current work at LURE and ESRF. This is an exciting, growing field of research with strong activities also at NSLS-Brookhaven and APS-Argonne. The scientific case is convincing, and top level experiments are proposed in the APS. However, there are other fields in modern chemistry and polymer science that emerge and for which the proposed beamline should be suited. SAC is convinced that there is exciting sciences in this field and, in 5 years from now, such a facility could be at the centre of a large research field. The beamline defining goal could be time resolved studies of diffuse scattering from thin layers of soft matter at liquid or solid substrates, making use of resonance scattering contrast variation from light elements like S, P ,…

SAC makes the following recommendations :

a diffraction beamline in 2-4 keV range at SOLEIL could be unique; however, one has to find out if there is sufficient support for the beamline in France and abroad. It is suggested to organise an international workshop on a dedicated low energy diffraction beamline for soft (and maybe hard) condensed matter thin films and interfaces at SOLEIL. There is also a strong case for resonance scattering, including magnetic scattering, on solid samples in this “tender” wavelength range, i.e. energies from ~2-4 keV . The beamline should also allow for reflectivity measurements;
the development of time resolved experiments should be considered more precisely;
the new opportunities offered by the high degree of coherence in the tender wavelength range should be explored;

Besides this “tender” X-ray wavelength range, two additional energy windows for photons around 8 and 13 keV are considered in the proposal. SAC believes that it could be more suitable to implement a liquid surface diffractometer to another diffraction beamline optimised for the harder X-ray wavelength range;

SAC recommends to go further in the definition of this beamline, considering that the science proposed here is excellent.

SAC meeting 20-21 Nov. 2003

- **Updated Beamline proposal "X ray diffraction for hard and soft interfaces"**

SAC strongly supports the project and approves the proposed merging of previous BLP17 and BLP20 proposal. SAC is satisfied that the study of liquid interfaces in addition to hard surfaces and interfaces will not lead to any compromise on the ultimate performances. The proposed solution for the diffractometer rotation (through a rigid arm) to follow the monochromatic beam is satisfactory.

SAC approves the proposed beamline proposal which merges the previous BLP17 and BLP20 proposals

3- Propositions de la Direction de SOLEIL

La direction de SOLEIL demande l'aval du Conseil pour la construction de la ligne « Surface Diffraction on hard and soft interfaces ». pour une ouverture début 2008. Les possibilités offertes par une telle ligne sur un onduleur ouvriront des domaines d'expériences d'une grande importance en physico chimie de la matière condensée. La communauté scientifique concernée est en expansion, en particulier dans le domaine de la catalyse et l'accès à d'autres sources comme l'ESRF risque d'être réduit sur le long terme. La direction de Soleil, consciente du budget élevé correspondant aux dispositifs expérimentaux prévus, souhaite mettre en place avec les laboratoires concernés un programme d'accompagnement du développement de l'instrumentation qui permette d'atteindre les objectifs fixés.