

Needs and requirements of the Spanish Users Community in the UV and Soft X-rays

A document prepared to summarize the current and future needs of the Spanish Surface Science community in connection with the construction of Beamlines at ALBA

This document was prepared by J.A. Martín-Gago (gago@icmm.csic.es) and Enrique G. Michel (enrique.garcia.michel@uam.es)

It contains contributions from the Spanish Users Community as described in the text

Table of Contents

1.-Summary

2.-The Spanish users community in the UV and soft x-rays

3.-Scientific Cases identified

4.-Beamlines proposed

5.-Time scale

1.-Summary

This report summarizes the conclusions of two meetings held by the Surface and Interface Science Spanish users community in the field of Electron Spectroscopies (Málaga, February 2004; Madrid, November 2004). The main goals of the meetings and of this report are the following:

- Identify the current and mid-term (5-years) needs of the Surface and Interface Science users community interested in Electron Spectroscopies.
- Identify the research groups in the field (both current and potential users), and their interest to get involved in the ALBA project.
- Summarize the scientific cases relevant to the field, and evaluate the potential role of ALBA in terms of Beamlines relevant to the scientific cases identified.
- Propose a well-defined strategy and a realistic time-scale to satisfy these needs in the short to mid-term.

2.-The Spanish users community in the UV and soft x-rays

We have identified approx. 25 groups of frequent synchrotron radiation users in this field, comprising around 95 experienced users. This includes on the one hand users from Surface and Interface Science, interested in using Electron (Photoemission) and Absorption Spectroscopies. On the other hand, there is also a significant number of groups coming from the fields of Chemistry, Geology, etc, interested in the application of Absorption Spectroscopies to polycrystalline samples. Finally, there is a group of users interested in the application of Photoemission in realistic environments (moderate pressures). All groups of users are very active and represent scientific communities with a significant tradition, based in a long-standing activity in their fields. Most of the users got involved in the use of synchrotron radiation in the early 80s, and by now they have reached a significant degree of expertise. A fraction of the users community in this area was developed in the course of the Spanish-French beamline at SuperAco, which was operational in the time period 1991-2003. Finally it is worth mentioning that many users have performed extended stays at synchrotron radiation laboratories, either as postdocs or beamline scientists, and have experience at all levels (users, experiment design, beamline construction, etc.)

The needs of this ample community are large. We may cite a few figures describing the current situation. In the period 1995-2000, the access of Spanish groups working in this field to many different synchrotrons world-wide was quite significant. The table below summarizes the number of groups *actually receiving beamtime* at the facilities (the number of groups *applying for beamtime* could be 2-3 times larger). Note the ESRF is excluded because there is no activity in the photon energy range relevant to this report. The access has been granted in European synchrotrons through EU support programs, and in other cases from the own budgets of the groups.

| FACILITY | Nr. GROUPS |
|------------------------|-------------------|
| BESSY (Germany) | 11 |
| HASYLAB (Germany) | 6 |
| ELETTRA (Italy) | 4 |
| LURE (France) | 17 |
| SRS (United Kingdom) | 15 |
| Max-Lab (Sweden) | 2 |
| ALS (USA) | 2 |
| SRC(USA) | 2 |
| NSLS (USA) | 2 |
| Spring8 (USA) | 1 |
| Photon Factory (Japan) | 2 |

Spanish Groups working in surface and interface science using synchrotrons worldwide

Besides being a large and well-represented community worldwide, Spanish users in the UV and Soft X-rays areas receive a significant number of shifts. Indeed, a few figures show that proposals coming from Spanish groups in this field represent a large percentage of all the proposals from foreign users in many facilities. For instance, at BESSY (18%), HASYLAB (15%), SRS (15%) and LURE (19%).

Following remarks describe well the current situation of the users community as identified by us:

1. There is a well-represented and experienced users community in Spain in the field of UV and Soft X-rays.
2. The growth of this community is mainly limited by the access difficulties to facilities abroad, and also by the concomitant lack of involvement in the latest technical advances in the field.
3. The access to SR sources abroad exhibits well-known problems and limitations, but it has been exploited in the past very efficiently by the users, both in scientific performance, and in terms of gaining experience and expertise.
4. The beamtime need of the users community is one of the largest in Spain, in part because of the technical complexity of ultra high vacuum experiments (common in this area), but also because of the size and strength of the community.
5. There is a large potential for further growth: let us remind that many applications for beamtime are rejected, in most cases not due to a lack of scientific quality, but rather to the enormous oversubscription of beamlines in this field (acceptance ratios of 15-20% are not rare).

3.-Scientific cases identified

The use of UV and Soft-X rays has a broad range of applications. It comprises methods like Photoemission, Absorption Spectroscopy, Photoelectron Diffraction, Band Mapping (Angle-resolved Photoemission), magnetic dichroism, etc. These techniques are suitable to provide information on a wide range of materials, like semiconductors, oxides, metals, artificial materials like heterostructures, etc, and have a profound impact in emerging areas like Nanoscience and Nanotechnology (because of the wavelengths involved), Biological Surface Science, Catalysis, Environmental Studies, etc. Absorption Spectroscopies are particularly well-suited for providing structural information of materials, independently on the aggregation state.

On the other hand, recent developments (in particular for Photoemission Spectroscopy) permit a much broader pressure range (up to a few mbars at least), paving the way to applications in what we may call “realistic conditions”. This is a crucial advancement for areas like Catalysis, Environmental Studies, etc. The Spanish users are well-represented in all these field. Thus, there are groups interested in nanostructured materials, colloids, thin films, diluted species in liquid phase, alloys, inorganic compounds, amorph alloys, magnetic materials, transition metal oxides (including ionic conductors, chalcogenides, high T_c superconductors, manganites), and of course the broad field of catalysis. There are also potential users in Chemistry in groups interested in the study of local environments in complex metals, enzymatic centers, etc.

Different scientific cases have been identified. They condense the activity of the users in the area of UV and Soft X-Rays in Spain and most of them are related to techniques like Photoemission and

Absorption Spectroscopy. In the following we summarize the scientific cases identified, more details are to be found in the specific beamline projects.

- 1.- Low energy photoemission (<100 eV)
- 2.- Core level photoemission and absorption (100-2000 eV)
- 3.- Photoemission under moderated pressures
- 4.- Dichroism in photoemission and absorption.

The case of Photoemission Microscopy is excluded, since it will be explicitly considered in other beamline.

1.-Low-energy photoemission (< 100 eV)

Motivation:

Nowadays, there are only a few beamlines working in the low energy range and offering a reasonable flux, in particular if we consider the lowest energies (7-20 eV). This is due in part to the fact that generic photoemission beamlines tend to favor a larger energetic range, due to the use of PGM or TGM monochromators. However, this is a range of huge future relevance because of several reasons. First, the ultrahigh energetic and angular resolutions of new analyzers (<3 meV and < 0.003 Å⁻¹), can only be adequately exploited using low photon energies. This opens the way to analyzing medium to large periodic structures, with unit cells in the range of nanometers, like those commonly found in Nanotechnology and Nanoscience applications. Second, in this low energy range there is a significant increase in the penetration depth, a critical point to probe reliably bulk properties (high energy photoemission is certainly not a solution if angular resolution is needed). Finally, this is the range able to probe a wide range of interesting physical phenomena, as described in the following.

Scientific cases:

1. Quantum confined systems: low dimensional systems, quantum-well states, surface phase transitions, collective states at surfaces (superconductivity, magnetic ordering, charge density waves), one dimensional systems at surfaces (quantum wires, electron confinement in stepped surfaces), nanostructured two-dimensional systems.
2. Bulk materials: gap opening in superconductors, highly correlated materials, manganites. Many-body effects, electron correlation, phonons, etc.
3. Reactive activity related to surface defects: origin of the reactivity in different surface sites (steps, kinks), electronic structure of reactive sites.
4. Valence band analysis with polarization: density of states, degree of carrier polarization as a function of temperature (structural, magnetic and electronic phase transitions) in bulk and thin films and polycrystalline heterostructures. Electronic properties of nanostructured materials with lateral sizes up to 100 Å.
5. Electronic structure of large unit cell materials (organic adsorbates) with unit cells in the range up to 5-7 nm, relevant for the process of surface self-assembling.

Technical requirements:

Beamline: low-energy monochromators (7-100 eV), high resolution (<3 meV). In some cases, polarization selectivity is interesting.

End station: high-resolution angle-resolved photoemission (Scienta), preparation facilities in UHV. Low temperature (< 10 K) in the sample environment with high precision positioning.

2.-Core-level photoemission and X-ray absorption (100-1500 eV)

Motivation:

Photoemission is one of the most versatile techniques in this energetic range. Those beamlines offering this energetic range and combining high flux and resolution are between the most demanded in synchrotron facilities, and as a consequence, they have a large oversubscription. This kind of beamlines is able to satisfy the needs of a broad, multidisciplinary community, active in the fields of materials science, physics, and chemistry. On the other hand, both the in situ and ex situ analysis of samples are required. This energetic range includes X-ray absorption spectroscopies, core-level photoemission, resonant photoemission and photoelectron diffraction.

Scientific cases:

Characterization of surfaces, interfaces and nanostructures from chemical, electronic, and structural points of view, both for materials, thin films, and atomic layers in situ deposited and/or ex situ prepared. This includes compounds of transition metals (oxides, nitrides), carbon materials (hard coatings like BCN or CN, carbon nanotubes, polymers, organic compounds).

Technical requirements:

Energetic range: 100-1500 eV to reach rare-earth 3d core levels. Resolving power: 10^4 , able to provide photons with a resolution better than 100 meV in the whole spectral range. Spot size at the sample below 100 μm . Sample temperatures down to 40 K and fast-entry lock.

3.-XPS at moderated pressures (10-100 mbar range in the sample environment)

Motivation:

The main motivation of this case is the need to analyze with chemical sensitivity processes with high technological relevance and occurring at moderated pressures. There are only two beamlines in the world addressing this kind of problems, 9.3.2 at ALS and U49.2 at BESSY, and there is a third beamline in construction. This is a multidisciplinary scientific case, with special impact in the areas of catalysis, surface chemistry, and environment. The particular features of ALBA (high brilliance and microfocus), make it possible to further reduce the pinhole size at the analyzer entrance slit, and thus to further improve the efficiency and working pressure.

Scientific cases:

1. Description at atomic level of surface reactions under realistic pressure and temperature conditions. In particular, corrosion processes and environment analysis, e.g. analysis of gas sensors under real operating conditions.
2. Interaction of molecules with surfaces. In particular, separation of the surface atoms contribution and analysis of their modifications after adsorption or thermal treatments in UHV.
3. Chemical state of adsorbed species (CO, NO, H₂O, light hydrocarbons) over polycrystalline catalysts (including powder pellets).
4. In both cases, it is interesting to perform analysis in equilibrium with gas phase at controlled temperature.

5. Studies under wet conditions: biological processes, membranes, surface wetting.

Technical requirements:

Energetic range from 80 to 1500 eV, resolving power around 10^4 at the monochromators, at least 50 meV resolution at the analyzer. Focusing at the sample up to the level needed to maintain the analyzer resolution (10-100 μm). This application requires a very specific instrumentation: the sample chamber must be able to reach a pressure of mbars during measurement, and the analyzer should have differential pumping stages to maintain it under UHV.

4.- Dichroism in photoemission and absorption

Motivation:

The analysis of magnetic phenomena using the photoemission and absorption techniques has experienced an enormous development over the last years. On the one hand, UHV provides an environment suitable for controlled and careful sample preparation, and it combines it with a full analysis of electronic properties and magnetic ordering. On the other hand, it offers the high sensitivity and specificity typical of photoemission and absorption techniques.

Scientific case:

Chemical characterization of surfaces, interfaces, thin layers, multilayers/superlattices, nanostructured arrays, etc., including the depth profile, in combination with electronic and magnetic characterization.

Study of “soft” disordered and/or polycrystalline magnetic materials, grown as thin layers, multilayers, nanoparticles, and as lithography patterns.

Technical requirements:

High photon-flux at the sample. Resolving power $>10^4$ in the whole energetic range. The beam size should be at least 50 μm . The monochromators should cover the $L_{2,3}$ adsorption edges of most 3d transition metals, thus the 100 to 2000 eV range is ideal. A large beam stability is required both at the entrance of the end station and at the sample position. Fast change from circularly polarized to linearly polarized light. Experimental station with a sample preparation chamber, provision for user own chambers.

4.-Beamlines proposed

An analysis of the technical requirements outlined above shows that the whole photon energy range demanded is approximately 7-100 for Case 1 and 100-1500 eV for Cases 2, 3 and 4. On the other hand, Cases 1, 2 and 4 could share a more or less complex UHV end station, while case 3 requires a very specific end station with a differentially pumped electron analyzer. The energetic ranges demanded are too broad to be covered with a single source (undulator). Indeed, an analysis of the technical solutions so far available suggest that keeping such a broad range should result in a significant decrease of performance in both lowest and highest energies. On the other hand, the low energy application requires a fairly long undulator source. Due to the specific ring design of ALBA, this means that it could be accommodated only at one of the three longest straight sections. Due to this complex combination of requirements and limitations, we find and the most sensible solution to split the scientific cases in two different beamlines, with two well defined energetic ranges:

Beamline 1: (Electron and X-ray absorption Spectroscopies, EXES), covering scientific cases 2, 3 and 4 with two independent end stations in a single beamline. The first end station is devoted to electron spectroscopies in UHV, the second end station to photoemission at moderated pressures.

Beamline 2: (High-Resolution Low-Energy Photoemission, UV-PES), covering scientific case 1 in a single dedicated end station, devoted to ultrahigh resolution photoemission at low energies.

A more detailed analysis of each beamline is to be found in the attached documents, called EXES and LOREA

5.-Time scale

The operation of two beamlines with the features described above is certainly required in view of the current and prospective needs of the Spanish community. However, the construction and efficient exploitation of each of the beamlines is certainly a demanding task for the users community. On the other hand, only five beamlines are to be funded at the first phase of ALBA. Taking into account these boundary conditions, we propose that only one of the two Beamlines is included in the first phase of ALBA. We have selected for this Beamline 1, because it covers a broader range of applications, and thus also a larger users community. At the same time it offers a challenging scientific case, beyond the current state of the art (case 3), but also more conventional applications in a well-known setup, able to be operational in the short term.

In summary, the following time scale for the implementation of the two Beamlines at ALBA is proposed:

1. We propose the funding of **Beamline 1** (Detailed proposal attached: **EXES.pdf**) as one of the five first phase beamlines of ALBA.
2. We propose the funding of **Beamline 2** (to be presented to the SAC at a later date, outline project attached: **LOREA.pdf**) in the second phase of beamlines at ALBA.

ALBA BEAMLIN PROPOSAL

Electron and Soft X-ray Emission Spectroscopies (EXES)

Proposal coordinated by

Jose A. Martín-Gago (gago@icmm.csic.es) and

Enrique G. Michel (enrique.garcia.michel@uam.es)

It contains contributions from the whole

surface and interface science community.

December- 2004

Table of Contents

1.-Introduction

2.-Experimental techniques

3.-Scientific Case

2.1.-surfaces in equilibrium with high pressure gases

2.2.-wet-chemistry

2.3.-surface and interface science

4.-Complementarity and relationship with other beamlines

3.1.-In other European synchrotrons

3.2.-In ALBA

3.3.-Interaction with SOLEIL

5.-Spanish scientific community

6.-Beamline layout and requirements

5.1.-Insertion device and optics

5.2.-Experimental end-stations

7.-Estimated budget

8.-Annexes:

Annex I: Most relevant publications of the research groups since 1999 (2 per group)

Annex II: European research groups explicitly supporting this project.

1.-INTRODUCTION: preceding considerations, perspectives of the field for the next 5 years, and objectives of the proposal.

During the past 20 years several technologies based on surface and interface properties have become the basis of major industries. These include, among others, microelectronic devices, magnetic information-storage materials, industrial and environmental catalysis, coatings, optical fibers, biocompatible materials, chemical sensors and bio-sensors. Requirements of miniaturization and of improved device performances have made these technologies to become ever more sophisticated, and as a consequence, new advances are driven by surface and interface science. Thus, surface and interface science is a valuable piece of contemporary physics, chemistry and materials science.

Therefore, atomic- and molecular-scale studies at the interfaces solid/vacuum, solid/high-pressure gas, solid/liquid, as well as solid/solid are required to progress to the state of the art. Until nowadays surface science has developed a powerful battery of experimental techniques that allow us to find out the atomic structure of surfaces with hundredths of an Å of precision and electronic features accurately reproduced by first principle simulations. However, the price you usually pay for such a precision is ultra high vacuum environment. The so-called 'pressure gap' has shown itself as a barrier for the transferring of the results obtained in UHV to technology. Consequently, understanding processes of technological relevance will require studies at higher pressures, higher spatial resolutions and shorter time scales. *One of the challenges of modern surface science is thus to expand its range of investigations to all these types of interfaces and to develop a thorough understanding of the relationships between molecular-scale surface properties and parameters relevant to potential applications and devices.*¹

The comprehension of the structure, electronic properties, kind of bonding, reactivity of surfaces and interfaces at an atomic- and molecular-level and at higher pressures (and even in wet environments) is a current frontier of research. Such studies are becoming more valuable because the increasing importance of the nanometer-scale structures in almost every technological application, from heterogeneous catalysis to sensor fabrication. As the scale of devices continues to be reduced, the distinction between bulk and surface properties is not so well defined, and interfaces play an ever increasingly important role in technology. Currently the trend of the surface and interface community is to move from ideal surfaces towards more realistic surfaces and interfaces, closer to applications.

These ideas are in the basis of this proposal. The aim of this beamline is to provide a set of surface and interface characterization techniques, particularly x-ray photoemission, which could be applied on different sample environments and in an interdisciplinary context. Fundamental questions, at the cutting edge of knowledge, would be specifically addressed by this beamline. A new science is emerging from this interdisciplinary approach. The fact that the proposed beamline will be operational in 2009, suggests that we have to be ready for this demand. Currently there exist just two BLs in the world with such a capability. These experimental stations are BL 11.0.2 at the Advanced light source (ALS) in Berkeley and U49.2 at Bessy II. The ALS has first built beamline 9 to test a prototype of electron analyzer able to work at pressures of about 1 mbar. After the great success and evaluating the huge

¹ Workshop on scientific directions at the advanced light source. July-1988

potentiality of the technique, they decided to create beamline 11.0, which is currently in a commissioning stage. It can be anticipated that these beamlines will be oversubscribed in the next years. Therefore, it makes sense to build up a new one specifically designed for this purpose, profiting from the experience gained through the construction of the previous beamlines.

To achieve this goal, we propose a beamline where X-ray Photoemission Spectroscopy (XPS), X-ray absorption and X-ray Emission Spectroscopy (XES) could be performed in a wide variety of environments (moderated pressures, wet-surfaces, buried interfaces, ultra high vacuum...) for applications covering many different fields. There are two specific features that make this beamline unique. On the one hand, it covers a pressure range from the ultra-high vacuum (10^{-10} mbar) up to at least tens of mbar. On the other hand, the simultaneous use of photoelectron, absorption and soft x-ray fluorescence spectroscopies makes it possible a full characterization of the electronic and atomic structure of a wide range of materials and scientific cases, extending from fundamental to applied studies. Each area considered is well represented in the Spanish users community by a significant number of experienced groups. This broad community will gain access to state-of-the-art instrumentation, generating a multidisciplinary scientific environment for the experiments.

One of the main experimental techniques of the beamline is XPS. Photoemission is one of the most significant and well established techniques in every 2-3 GeV synchrotron radiation facility, due to the large demand and the suitable photon spectrum provided by the machine. However, XPS at high pressures is still susceptible of many improvements and further designs. A beamline able to fulfill these expectations *is not another standard beamline for performing a particular technique, but rather involves a strong experimental development, that should be performed in the home laboratories of the involved groups from the beginning of the project.* This is particularly true for the design of the high pressure XPS spectrometer and a possible in-situ liquid cell. Therefore this project will implicate to the whole users community to develop these kinds of techniques.

Summary of beamline specifications

Photon energy : from 150 to 1500 eV

Undulator period: around 50 mm (energy of maximum brilliance: 900 eV)

High flux : 2×10^{19} ph/s/mm²/mrad²/0.1%b.w on undulator

Very high energy resolution $E/\Delta E \geq 10000$ over whole energy range

High purity and stability of the beam at source and experimental station

Variable polarization

2 endstations:

2 separate analysis chambers, linked by a platform.

Moderated pressures chamber: equipped with high-pressure XPS (up to 1 mbar), reaction chamber, liquid-cell, XES spectrometer. Possibility for total and partial auger yield for absorption.

Ultra high vacuum chamber: XPS spectrometer and XES detector operating in UHV, 2 High precision manipulators, one of them with helium cooling, possibility of high temperatures and magnetic fields. The second one especially designed for introducing series of samples. Efficient Gas admission system.

Pre-chambers equipped with all standard preparation and characterization tools

Broad range of sample environments

2.- Experimental techniques

Introduction

Soft x-rays spectroscopies represent a set of powerful analytical tools providing compositional, chemical and electronic information for the study of materials, films, interfaces and surfaces. We consider in particular x-ray photoemission spectroscopy (XPS), x-ray absorption spectroscopy (XAS) and soft x-ray fluorescence spectroscopy (also called x-ray emission spectroscopy, XES).

In order to describe the scientific cases relevant to soft x-ray spectroscopies, it is convenient to restrict ourselves to the photon energy range 100-1500 eV. A large number of elements can be studied with at least one of the three techniques mentioned above (XPS, XAS, XES). The different shells that can be excited with 100-1500 eV photons are:

| | |
|----------|---------|
| K-shell: | Z= 4/12 |
| L-shell: | Z=13/34 |
| M-shell: | Z=26/69 |
| N-shell: | Z=41/92 |

We will describe briefly the experimental techniques that could be performed in the proposed beamline, and which information will provide for defining the scientific cases.

X-ray Photoelectron Spectroscopy (XPS), is a common technique in laboratory-based XPS apparatus, although it reaches its ultimate performance (resolution limited by the core hole lifetime, low noise spectra, fast acquisition times) using synchrotron radiation sources. This technique provides information about the elements present on a sample and their chemical state. Due to the nanometric length of the photoelectron escape depth, the sample characterization is always limited to the surface region. This is an advantage for Surface Science research, but it might be undesired in Thin Films and Materials Science research. Also, charging in non-conductive materials has limited its application to metals and semiconductors. The experimental setup proposed supports different specific configurations, suitable to obtain complementary information. In particular, these methods are:

X-ray photoelectron diffraction (PhD): this technique provides information on the structure of surfaces, molecules and thin-overlayers. PhD samples local ordering, and therefore is also suitable for polycrystalline systems, which do not present extended ordered areas. It is based in a diffraction process experienced by the outgoing photoelectron, and therefore it can be performed either by scanning the photon energy or the sample orientation with respect to the electron analyzer.

Resonant photoemission: it is a Fano-like intensity modulation for a valence band peak observed as a function of photon energy near an absorption threshold of a particular element. This phenomenon is mainly found in photoemission from transition-metal and rare-earth compounds. It is very useful to determine the chemical structure of polycrystalline metals exhibiting this feature.

Fast-XPS: the high brilliance of the beamline, in combination with a multichannel electron analyzer makes it possible the recording of very fast sequential XPS spectra, in order to follow surface reactions. The typical scanning time for a single XPS spectrum could be reduced to the order of 1 second by adjusting the number of points to the number of channels

in the detector. In any case, fast scans will monitor real-time adsorption and desorption kinetics.

X-ray emission (XES), also known as soft x-ray fluorescence, is a photon-in photon-out technique providing information on the partial (atom projected) density of occupied states. XES provides information on the electronic structure from the bulk of a material, without any charging problems, making it an ideal tool for Materials Science studies. In addition, the vacuum requirements are not as stringent as for XPS, permitting the analysis in relatively high pressures or liquid environment.

X-ray absorption (XAS) provides geometrical information when studying the extended region (EXAFS and SEXAFS) and electronic information at the near-edge (NEXAFS). The photoelectron and fluorescence spectrometers required for XPS and XES, will provide the Partial Electron Yield (PEY) and Partial Fluorescence Yield (PFY) signals, respectively, that can be recorded simultaneously to the Total Electron Yield (TEY) from the sample photocurrent, and Total Fluorescence Yield (TFY) from a simple photodiode. In this way, a very complete description of the photoabsorption process at different sampling depths can be obtained.

Without further considerations, the combination of XAS, XES and XPS allows one to perform a very detailed study of the electronic and atomic structure of a sample. XAS provides the partial density of unoccupied states, XES the partial density of occupied states, and XPS the total density of occupied states. On the other hand, structural information can be gathered by analysing core-level shifted components, PhD or EXAFS. This means that, by using this combination, it is possible to investigate, in a single apparatus, the chemical, electronic and structural properties of materials with surface and bulk sensitivity, in conductive and non-conductive samples.

3.- SCIENTIFIC CASES

Many important technologies and areas of knowledge hold well-established principles based in empiric rules, lacking of a complete description of the processes that undergoes at the molecular level. This beamline will provide an experimental setting where many important fundamental questions, at the frontier of knowledge, could be addressed. Hereafter, in this section, we present some of them.

Particularly it will make possible to investigate surfaces in equilibrium with high pressure gasses, achieving the study of wetting and de-wetting processes, catalysis, chemical vapor deposition, electrochemistry, atmospheric chemistry, and biosurfaces among many others fields. An important remark is that the selected scientific cases have been, up to now, gathering its fundamental knowledge via an ex-situ characterization. *This beamline could provide, for the first time, in-situ characterization of many fundamental and technological fields.*

On the other hand, this beamline will provide to the large scientific community of surfaces and interfaces, with a high-quality tool for studying high resolution in-situ core-levels, combining both high –flux and high-resolution

This is the aim of the scientific cases that we are going to detail next. Although we have classified them, this sorting is somehow arbitrary, because the same scientific problem could be investigated in different environments.

3.1.- Surfaces in a moderated pressure environment.

Nowadays it is clear that surface science has failed in extrapolating many of the results obtained in UHV to the real world, beyond the pressure gap. For instance, it is known that surfaces in thermodynamic equilibrium with gasses at reaction temperatures are not fairly reproduced in standard UHV experiments. There are many important topics in which we do not have in-situ information about the chemical reactions taking place at surfaces exposed to moderated pressure gases (≈ 1 mbar). We may mention the following examples:

Thin-film growth: Which are the molecular mechanisms of the chemical vapor deposition (CVD)?

Chemical Vapor Deposition (CVD) is a thin-film deposition technique based on chemical reactions, which transform gaseous molecules, called precursor, into a solid material, in the form of thin film or powder, on the surface of a substrate. Most films can be deposited from several different precursor systems. The process is widely used to fabricate semiconductor devices and coating materials. Typical pressures for reaction ranges between 1 and 10^{-3} mbars, and therefore, they are in the range accessible to our proposed experimental set-up.

Although the technique is extensively used, many fundamental questions about the initial stages of the formation, that is, about the interface of the surface with the film are not completely clear. *Nowadays, the mechanisms and the chemical reactions taking place at the film surface are unknown and just hypothetically proposed.* As an example, silicon oxides

films deposited from thermally activated SiH_4/O_2 are commonly used as intermetal insulator, passivation layer, and diffusion barrier in the manufacture of Silicon based electronic devices. This layer incorporates hydrogenated species, which degrade the film quality. Many surface reactions have been proposed for this process, and the mechanisms for hydrogen elimination in silica deposition strongly depend on the oxidation reaction. The possibility of studying in-situ and in-real time all the intermediate species that are formed in the process is of both technological and fundamental relevance.

These ideas have been already explored in pioneering experiments performed by P.H. Fuoss et al. using surface X-Ray diffraction for studying in-situ the growth of GaAs and ZnSe. These experiments have shown that albeit with difficulty, the information that one can obtain is very important, and a photoemission technique seems more appropriate for a detailed chemical description of the process. Therefore, a technique offering chemical detection of the residual and secondary species incorporated in the film from the gas phase in every stage of the growth will suppose a real break-through in the field.

This kind of experiments will be of interest not exclusively for the CVD community, but also to all scientist and technologies of PVD growth, a very large community in Spain who has explicitly expressed its interest.

Further information: Dr. J.M. Albella, albella@icmm.csic.es

A reference: F.Ojeda, F. Abel and J.M. Albella hydrogen elimination kinetics during chemical vapor deposition of silica films. J. Phys. Chem. B 2002, 106, 6258.

P.H.Fuoss, D.W. Kisker, G. Renaud, K.L. Tokuda, S. Brennan and J.L. Kahn. Atomic Nature of organometallic-vapor-Phase-Epitaxial growth. Phys. Rev. Lett. 63,2389 (1989)

Planetology: which are the surface reactions at the Mars surface rocks?

One of the most important areas of astronomy is the field of planetology. By studying planets and other large bodies in the solar system, we learn about the history and possible future of Earth. Some of the large planets, such as Mars, Mercury or our satellite the Moon, have preserved a record of the history of the solar system in their craters. On the other hand, Venus could offer us a glimpse into a possible future for the Earth, in the case the "greenhouse effect" become as important here as in Venus. Recently, the scientific community has access to more accurate data from the orbiting satellites, Rovers and telescopes, which have update and contrasted information about the atmosphere composition of the planets and large bodies of the solar system. Many geologists have drawn their attention towards the chemistry that could drive processes in these conditions of pressure and temperatures, and their possible relationship with the generation of organic molecules and therefore, of life.

Mars surface atmospheric pressure is about 1 mbar, being the major gasses (percentage by moles): Carbon Dioxide (CO_2) - 95.32% and Nitrogen (N_2) - 2.7%. therefore, one could generate this atmosphere to study in situ, for instance, chemical and structural transformations induced in Pyrite-type surface or soil after irradiation or temperature cycling.

On the other hand, the satellites of the outer solar system are also geologically interesting. The satellite of Jupiter, Europa, for instance, is currently a NASA priority for exploration

because of the possible existence of harbor oceans below the icy surface. Its interior salty water might be connected with the surface by faults, as some observations indicate. These materials are re-processed exogenically due to the exposure to vacuum and high radiation environment. These pressure-temperature conditions could be reproduced in the beamline experimental station proposed in this project. The final spectral signature obtained by XPS and XANES of the materials at the surface are the consequence of the involved geological processes.

Studies on particular ices as clathrate hydrates might be remarkable. They are in many places of the solar system, from the Earth to the comets. They have been involved in many geological processes in Mars and probably Europa, and might play a role in planetary cycles of carbon of the planets.

Further information: Dr. Olga Prieto: prietobo@inta.es

References: Kargel, J. S., et al. (2000). Europa's crust and ocean : origin, composition, and prospects for life. *Icarus* 148, 226-265.

Prieto-Ballesteros, O. and Kargel, J. S. (in press). Thermal state and complex geology of a heterogeneous salty crust of Jupiter's satellite, Europa. *Icarus* in press

Catalysis: understanding catalysis under real conditions

The importance of heterogeneous catalysis is evidenced from the fact that the production of more than 90% of all industrial chemicals relies in the use of catalysts. This includes the production of gasoline, plastics, food, reactants and drugs. The industrial production using heterogeneous catalysis involves the adsorption of one of the reactants on the catalyst surface, which determines the kind of reaction taking place.

It is a common situation that the surface adsorption site is of nanometer size (atomic cluster), and thus its electronic properties are modified by the adsorption of the reactant itself. XPS is widely used to characterize catalysts, but the need of UHV is a strong limitation for its applicability. The possibility of having XPS working at pressures of about 1 mbar would open the way to in situ characterization of catalysts. This possibility would certainly mean a critical step forward in our understanding of the role played by the different features of the catalyst in the catalysis process, like e.g. atomic structure and nature of the adsorption sites as a function of temperature, partial pressure, etc. Previous pioneering experiments in this field, by using X-Ray diffraction techniques, have shown the viability and relevance of this kind of studies². This analysis could be extended to both single crystalline mode catalysts and real polycrystalline catalysts³. An analysis of all the different catalytic processes would certainly involve the design of different reaction cells, adapted e.g. to the relevant reaction in decontamination processes, fine chemistry, gasoline production, fuel cells, etc.

Further information: Dr. Alfonso Caballero: caballero@us.es, Dr. J.C. Conesa: jconesa@icp.csic.es

Publications: D.F.Ogletree, H.Bluhm, G.Lebedev, C.S.Fadley, Z.Hussain, M.Salmeron, *Rev.Sci.Instr.*, 73, 3872 (2002).

² Adsorption of Carbon monoxide above atmospheric pressure investigated with surface x-ray diffraction, K.F. Peters, C.J.Walker, P. Steadman, O. Robach, H.Isern and S. Ferrer *Phys. Rev. Lett.* **86**, 5325 (2001)

³ F.G.Requejo, E.L.D.Hebenstreit, D.F.Ogletree, M.Salmeron; *J.Catal.*, 226, 83 (2004).

Hydrogenation of carbon monoxide on Ni(111) investigated with surface x-ray diffraction at atmospheric pressure , M. Ackerman, O. Robach, C. Walker, C. Quiros , H. Iern and S. Ferrer. Surf. Sci. 557, 21 (2004)

3.2.-Wet chemistry

A major breakthrough in this field has been the study with XES techniques of the electronic structure of liquid water, by using a 100 nm Si₃N₄ window to separate a static liquid cell containing water from the UHV chamber containing the XES spectrometer⁴. Static liquid cells permit the study of liquid mixtures, like water and alcohol⁵ opening a new research field. The scientific possibilities are enormous in the case of dynamic liquid cells with flows of reacting liquids, in order *to study real wet chemistry using Surface Science tools*.

The possibility of analyzing liquids by using a combination of XPS, XES and XANES will provide information so long unavailable using a UHV photoemission apparatus. The importance of liquids, and in particular water, is obvious in many different areas, like Biology, Chemistry, electrochemistry, Physics, and Environmental studies. Also the study of liquid water in contact with vapor is a good example of the possibilities of the technique⁶. These studies are relevant for such important fields like the dynamics of biological systems and physiology of cell membranes, and will provide crucial information in all of them.

Currently, this is one of the most important topics of the 11.0.2 beamline of the ALS, where the group of Miquel Salmeron (pre-reviewer of the outline proposal) has recently performed pioneering experiments to determine, for instance, the ion segregation to the surface of salt solution or to study whether or not the melting of ice is driven by a surface pre-melting phenomenon and the influence of the contaminants in the pre-melting.

Biophysics: bonding, dynamics, kinetics and interactions of biomolecules in a liquid environment

Biotechnology is a very vital research field since new developments in molecular biology and biophysics are easily transferred into technological applications, rising to important consequences in our *every day life* throughout medicine, food technology and environmental control. A growing number of biotechnological applications are based in the immobilization of molecules onto surfaces, allowing the establishment of new interdisciplinary areas such as Biological Surface Science and Bionanotechnology.

Although most of the methods of surface science can be applied to biomaterials, there is a need to develop new methodologies for the study of bio-interfaces in the native, liquid state. Therefore, the possibility of having quantitative and chemical sensitivity via XES and NEXAFS in a liquid environment (small drop) on a surface could be a major advance in

⁴ J.-H. Guo, Y. Luo, A. Augustsson, J.-E. Rubensson, C. S  the, H.   gren, H. Siegbahn, J. Nordgren: Phys. Rev. Lett. 89, 137 402 (2002).

⁵ J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D.K. Shuh, H. Agren, and J. Nordgren, Phys. Rev. Lett. 91, 157401 (2003).

⁶ D.F.Ogletree, H.Blum, G.Lebedev, C.S.Fadley, Z.Hussain, M.Salmeron, Rev.Sci.Instr., 73, 3872 (2002).

H.Blum, D.F.Ogletree, C.S.Fadley, Z.Hussain, M.Salmeron; J.Phys. Cond.Matter 14, L227 (2002).

these relevant fields of applied research. Also, basic science can benefit from the possibility of exploring the mutual interaction among biomolecules as well as between biomolecules and surfaces.

Several examples can be identified where properties and processes at interfaces between surfaces and biological environments can be investigated via XES and NEXAFS:

Biosensors and microarrays development. A biosensor can be defined as an analytical device containing a biological component and a signal transducer. In conventional biosensors, the detector biomolecules or “probes” are attached on a solid surface in such a way that a specific signal is obtained from the sensor when the biomolecules selectively react with the “target” molecules they are designed to detect. The biorecognition events that are monitorized by the biosensor are a combination of 3D structure of the biomolecules and their dynamic properties. There are three main kinds of biosensors currently used, which are based in bio-catalytic, metabolic and bio-affinity processes. All of them may involve proteins (antibody-antigen, enzyme-substrate, receptor-ligand), nucleic acids (interactions between complementary strands of DNA, RNA or peptide nucleic acid, PNA) or both (interactions of DNA or RNA with proteins such as polymerases, transcription factors, etc). Also whole-cells and tissue biosensors have been developed. Regarding transduction systems, they can be electrochemical, opto-electronic, optical, acoustic or thermal.

Among the biosensors, a rapid advance has been produced in the so called “**microarrays**” or “**biochips**”, which are based in the covalent immobilization of thousands of probe molecules on a substrate, in arrays of points of about 100 micron of diameter. Target protein or DNA molecules present in a natural sample are generally detected by means of a previous fluorescent labeling of the sample analyzed, allowing the detection of its interaction point with a high resolution scanner. Protein microarrays have been used to miniaturize some of the above mentioned kind of biosensors. Examples of the use of DNA microarrays include the detection of microorganisms by species-specific DNA probes, the expression profiling in diseases and metabolic alterations, the optimized detection of mutations and polymorphisms in genes and the determination of RNA structure in viral genomes.

Biosensors and microarrays routinely work in many laboratories. Nevertheless, a lack of knowledge exists at the molecular level, and many fundamental questions and process remain unclear. For instance few is known about the molecular recognition events that allow the interaction between protein or nucleic acid strains in solution. Recently, a Spanish group has reported on the molecular behavior of peptide nucleic acids for DNA biosensing studied by XPS and NEXAFS. These experiments were performed ex-situ, and it would be really valuable to repeat all this characterization in the real working conditions of a biochip⁷. Regarding applied aspects, a limited sensitivity is reached in some of the cases, a perfect sensitivity probe-target is not always obtained, and the need of fluorescent labeling of the sample to be analyzed decreases the performance of conventional microarrays. The use of XES and NEXAFS in solution could open new avenues of research for biosensor development.

Other relevant biophysical and biotechnological applications of XES and NEXAFS in solution can include the following:

⁷ C. Briones, E. Mateo-Martí, C. Gómez-Navarro, V. Parro, E. Román, J.A. Martín-Gago, Ordered self-assembled monolayers of peptide nucleic acids with DNA recognition capability, *Physical Review Letters* 93: (2004) 208103.

- Study of the electronic alterations that occur in the active center of an (immobilized) enzyme during the catalytic process. Advantage: most enzymes have metals at their active centers. Inconvenient: typical reaction times of ns to ps.
- Formation/dynamics of lipid bilayers and micelles. Bipolar fatty acids spontaneously assemble into micelles in aqueous solutions. This process could be studied, together to the influence of different buffer composition and pH, as well as the encapsidation events of substances within the micelle from the aqueous solution.
- Interactions between membrane proteins and proteins in solution. Applications for metabolic processes, receptor activation and cellular signal transduction.
- Interactions among nucleic acids and proteins in macromolecular assemblies such as ribosomes or chromatin.
- Dynamics of monomolecular reactions between biological molecules.
- Study of engineered biomaterials.

Further information: Dr. Carlos Briones: brioneslc@inta.es

References: J. Cheng, E.L. Sheldon, L. Wu, A. Uribe, L.O. Gerrue, J. Carrino, M.J. Heller, J.P. O'Connell, 1998. Preparation and hybridization analysis of DNA/RNA from E. coli on microfabricated bioelectronic chips. *Nature Biotechnol.* 16: 541-546.

M. Martell, C. Briones, A. de Vicente, M. Piron, J.I. Esteban, R. Esteban, J. Guardia, J. Gómez, 2004. Structural analysis of hepatitis C RNA genome using DNA microarrays. *Nucleic Acids Res.* 32: e90-104.

Electrochemistry: how does it change the electronic structure of an electrode during work?

The application of XPS to the study of liquid-phase systems has been hampered by the experimental difficulties of handling liquid samples under UHV conditions. Several approaches have been proposed to overcome these difficulties⁸. Electrochemistry of hard-matter can be performed in the so-called thin-layer experimental configuration. For instance electrochemically grown clusters of Pd-Pt have been reported to present enhanced catalytic properties. The combination of XPS, NEXAFS and XES will allow us to understand the electronic structure of those clusters. On the other hand, many fundamental questions about how the electronic density of states at the electrode surface changes during an electrochemically-induced reaction remains unclear up to now due to the lack of adequate techniques for studying this problem. Voltammetry is the main technique used in electrochemistry. The voltammogram gives integrated information about charge-transfer processes at a glimpse. For the last years, many works have tried to combine electrochemistry to structural characterization techniques (as surface x-Ray diffraction or infra-red spectroscopy), in order to associate charge transfer processes, obtained via voltammetry, to structural changes at the surface. This beamline will make possible to go one step beyond. *A combination with these techniques will make possible to analyze, for the first time, the surface of an electrochemical electrode during operation*

Other interesting points are related to electrochemical bio-sensors. Interaction of proteins and enzymes on surfaces, and how they recognize a complementary molecule. The importance of

⁸ ELECTRON-SPECTROSCOPY FOR CHEMICAL-ANALYSIS OF LIQUIDS AND SOLUTIONS. H. Siegbahn *J. Phys. Chem.* **89**, 897-909 (1985)

the structural deformation associated to de-wetting or environment for the biological function. Peptides that change their structure whether water or alcohol is used as solvent. These are *hot-topics* in electrochemical biosensing that will be accessible in this beamline.

This part of the scientific case has the drawback of constructing an electrochemical cell compatible with such experimental configuration. If this proposal is going ahead, several actions will be taken to design the experimental apparatus in parallel to the beamline construction. Several groups have expressed their interest in participating.

Further information: Dr. Fausto Sanz: sanz@qf.ub.es. Jose A. Martín-Gago: gago@icmm.csic.es, Victor Fernández: vmfernandez@icp.csic.es

First stages of corrosion and high temperature oxidation: complex surface reactions that determine materials lifetime.

The variety and complexity of physical and chemical processes involved in corrosion is such that our current understanding of corrosion is rather limited. Corrosion produces materials damage with very important economical and environmental effects. The corrosion is a surface process that progress inwards from the most external layers of a material. Actually, the corrosion behavior of materials is often controlled by the presence or absence of a protective surface film, named passive layer. The exposure of a technological material to a corrosive environment produces modifications in the structure and composition of this passive layer. Thus, it is of high interest to follow these modifications by the experimental techniques proposed in this project on the materials surface upon exposition to different environments (air, salts, soils, CO₂, H₂O, sea water, gases that contain corrosive agents like sulphur-containing molecules). Among these environments, one can distinguish between liquids and gases. In the former case the chemical reactions involved in corrosion are electrochemical, so the use of an in-situ electrochemical cell is essential to follow the changes of the surface produced by corrosion.

A special case of corrosion by exposure to a gas atmosphere is high temperature corrosion, which affects the chemical and the aerospace industry as well as the metal production processes among other real problems. This process may have important detrimental effects, which can even lead to catastrophic failures. Therefore, it is also of concern to study the surface of a material when it is exposed to corrosive environments combined with high temperatures. All these studies could be easily performed in the beamline proposed

Since technological efforts are driven to prevent, or at least diminishing, corrosion attack, it is becoming essential to apply different surface modifications to materials with the aim of generating a barrier against corrosion. In this way, coatings produced by CVD, PVD, as well as controlled surface oxidation are also important from a technological point of view.

The proposed EXES beamline is highly interesting for this research topic, since, on the one hand, it offers the possibility of performing advanced spectroscopic experiments (XAS, PES, RPES, etc) to determine surface composition and structure, and, on the

other hand, it will have the necessary equipment to carry out in-situ experiments by exposing materials to different environments (high-pressure cell, electrochemical cell). This will permit to investigate the dynamics of the corrosion process, especially the first stages, in real-time and in realistic (or close to realistic) working conditions. Also the possibility of in-situ creating protective coatings and of studying them from the first stages is crucial to understand their protecting properties.

This scientific case include all metallic technological materials, which can be subject of corrosion, and also some semiconductors and ceramics. But, due to the large economical repercussions it is of particular importance for stainless steels, titanium alloys (aerospace, biomaterials,...), and aluminium alloys (aircraft industry, building applications, packaging) or from a fundametal point of view, the first stages of the oxidation of a pure Si surface. The combination of these technological materials, their possible coatings deposited to improve their corrosion properties and the exposure to liquids or to corrosive gases, represent an important amount of unique experiments.

Further information: Dra. Paqui López: mflopez@icmm.csic.es, Dr. Alejandro Gutierrez: a.gutierrez@uam.es, Dr. Jose María Sanz: josem.sanz@uam.es
Publication: M. F. López, A. Gutiérrez, F. J. Pérez Trujillo, M. P. Hierro y F. Pedraza “Applications of soft x-ray absorption spectroscopy to the study of passive and oxide layers on stainless steels: influence of ion implantation”, J. Electron Spectrosc., **115** (2001) 825.

3.3.- Surface and interface science

As stated in the introduction, Surface science of ordered overlayers is evolving towards the study of more complex systems. We may mention the study of large surface reconstructions, oxides surfaces and molecular reactions. The study of surfaces has provided a lot of understanding to the condensed matter field. The approach followed was modeling throughout the use of surfaces with long-range order. Nowadays, more realistic situations suggest a picture with broken translation symmetry, which requires new experimental and theoretical approaches to deal with amorphous or poorly ordered materials and structures.

Due to the limited escape depth of photoelectrons, XPS has become the dominant technique for the chemical characterization of all types of surface problems and the alignment of energy levels at surfaces and interfaces. During the last decade, a very active area has been the study of surface core level shifts (SCLS), corresponding to the interatomic charge transferred in the surface and interface structures due to surface reconstructions, and the photoelectron diffraction effects from the different components. At present, there is a good understanding of SCLS from simple metallic surfaces. However, more complex surfaces and interfaces remain an open research field. As an example, only recently the SiO₂/Si(111) interface has been analyzed in detail⁹. The current challenge in XPS is reaching an experimental resolution below the intrinsic lifetime broadening, that will permit the study of complex surface reconstructions, and new problems like the influence on core level shifts of electron-electron interactions in highly correlated systems or vibrational (electron-phonon interaction) effects

⁹ S. Dreiner, M. Schurmann, C. Westphal, and H. Zacharias, Phys Rev Lett. 86, 4068 (2001).

¹⁰ S.G. Urquhart, H.Ade, M. Rafailovich, J.S. Sokolov, and Y. Zhang, Chem. Phys. Lett. 322, 412 (2000).

Regarding the partial density of electronic occupied and unoccupied states mapped by XES and XAS techniques, respectively, they provide a complete picture of the chemical bonding between surface and adsorbates, which is only accessible with the proposed experimental setup¹¹. Moreover, both techniques are used to probe insulating materials, thus opening the vast new field of surface-adsorbate interactions in insulators, including such challenging areas like the research of water-surface interaction¹².

During the last decade, there have been important studies regarding the monitoring of interface formation during the growth of multilayers and superlattices. This required in-situ interface growth, and hence the use of a preparation chamber connected to the analysis chamber. However, due to the limited analysis depth of photoemission, one cannot assure that the formed interface has the same crystalline and electronic features as a buried interface in a real device.

The challenge in the next future is to study the electronic and geometrical characteristics of **buried interfaces**. Regarding XPS, the route is to analyze with good resolution (~100 meV) photoelectrons with increased escape depth, i.e. either with kinetic energy below 10 eV or with energy exceeding 1000 eV to analyze a depth above 2 nm. A different and better approach is to use XES techniques, with an analysis depth about 1 μm , an energy resolution similar to XPS and no charging in insulating samples. The potential of the technique is so high, that beamlines devoted to a single physical problem are projected. As an example, the CISSY collaboration (Hahn–Meitner Institute, University of Würzburg, BESSY, and Shell Solar) is designing a XES-XAS-XPS setup at BESSY II to study in detail the interfaces of the most promising material for the next generation of Solar Cells, $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CIGSSe), in particular the $\text{ZnO}/\text{CdS}/\text{CIGSSe}$ structure^{13,14,15}.

Another interesting possibility for this beamline will be to perform **fast-XPS** (faster than 1 spectra per second) to monitor in real-time structural phase diagrams for different molecules on surfaces. New third generation machines allow for a fast recording of the spectra for elucidating possible surface reactions coverage induced. The advantage of high flux is a faster data acquisition, eventually able to follow the dynamics of some of the processes.

Magnetic materials and spintronics: surfaces and interfaces of thin films, nanostructures and clusters.

¹¹ A. Föhlisch, M. Nyberg, J. Hasselström, O. Karis, L.G.M. Pettersson, A. Nilsson, Phys. Rev. Lett. 85, 3309 (2000).

¹² H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelenschikov, L.G.M. Pettersson, and A. Nilsson, Phys. Rev. Lett. 89, 276102 (2002).

¹³ C. Heske, U. Groh, L. Weinhardt, O. Fuchs, B. Holder, E. Umbach, C. Bostedt, L.J. Terminello, S. Zweigart, T.P. Niesen, F. Karg: Appl. Phys. Lett. 81, 4550 (2002).

¹⁴ C. Heske, D. Eich, R. Fink, E. Umbach, T. van Buuren, C. Bostedt, L.J. Terminello, S. Kakar, M.M. Grush, T.A. Callcott, F.J. Himpsel, D.L. Ederer, R.C.C. Perera, W. Riedl, F. Karg: Appl. Phys. Lett. 74, 1451 (1999).

¹⁵ M. Morkel, L. Weinhardt, B. Lohmüller, C. Heske, E. Umbach, W. Riedl, S. Zweigart, F. Karg: Appl. Phys. Lett. 79, 4482 (2001).

Soft x-rays are well suited for studies in the field of magnetic and magnetoelectronic materials, thus there is an accordingly growing demand for beamtime in this area. Understanding magnetic properties and magnetotransport in materials is a field of large technological impact in areas like data storage and magnetic and magnetoresistive sensors.

Surface and interface effects play an important role in determining the magnetic properties of thin films, nanostructures and clusters. Relevant information is obtained from temperature dependent measurements of spin and orbital moments of epilayers grown in-situ, from dichroism studies probing anisotropies in ultrathin films and nanoclusters; from an analysis of interface coupling using element specific vector magnetometry; etc.

Colossal magnetoresistive (CMR) oxides are an example of strongly correlated materials that have attracted much attention in recent years¹⁶. In this class of compounds, electrical resistance is strongly dependent on magnetic order, an effect with potential applications in high-density read heads. In particular, hole-doped manganese oxides with the perovskite structure and the general formula $R_{1-x}A_xMnO_3$, with R being a trivalent rare earth (La) and A a divalent cation (Ca, Sr), have recently been found to exhibit changes in electrical resistance in magnetic fields that are orders of magnitude greater than those achieved in magnetic multilayer structures of the giant magnetoresistive (GMR) type¹⁷. Hole doping causes an insulator-metal transition with a simultaneous onset of metallicity and ferromagnetism. Another peculiar aspect of the CMR materials is the half-metallic nature of the electronic structure, including strong spin polarization of states near the Fermi level¹⁸. Many properties are explained by the DE (double exchange) model, but the emerging theoretical picture is that DE model alone cannot account for the large magnetoresistance observed in the CMR compounds. It has recently been suggested that a strong coupling of the electrons to the lattice supplements the DE, resulting in lattice distortions and polaron formation¹⁹, and a substantial degree of $3d^4-3d^4$ ($Mn^{3+}-Mn^{3+}$) charge disproportionation into more stable $3d^5-3d^3$ ($Mn^{2+}-Mn^{4+}$) pairs. Therefore, many unanswered questions remain concerning the physics of these materials, which appear as a promising field for core and valence photoemission measurements.

Further information: Yves Hutel: yves@imm.cnm.csic.es, J. Palomares: fjp@icmm.csic.es, Javier Díaz: javidiaz@condmat01.geol.uniovi.es

Publications: Magnetic V embedded in copper evidenced by X-ray Magnetic Circular Dichroism, Y. Huttel et al., Phys. Rev. B **67**, Brief Report 052408 (2003).

Ratio of orbital-to-spin magnetic moment in Co core-shell nanoparticles, U. Wiedwald et al., Phys. Rev. B **68**, 064424 (2003).

Oxide surfaces, interfaces and nanostructures

In nowadays high-tech world, understanding the physics and chemistry of metal oxide surfaces is immensely valuable. There are numerous industries which can potentially benefit from such detailed knowledge, including heterogeneous catalysis, corrosion control, electronic component manufacture, gas sensing, and the emerging fields of nano- and bio-

¹⁶ R. von Helmolt et al., Phys. Rev. Lett. **71**, 2331 (1993); Y. Tokura, N. Nagaosa, Science **288**, 462 (2000);

¹⁷ S. Jin et al., Appl. Phys. Lett. **76**, 6929 (1994).

¹⁸ J. H. Park et al., Nature **392**, 794 (1998).

¹⁹ A. J. Millis et al., Phys. Rev. Lett. **75**, 5144 (1995).

technology. Such significance is reflected by the increasing volume of research in this area, extending from applied studies of engineering oxide materials to fundamental work on *model* oxide surfaces under highly controlled conditions. Given the strategic importance of oxide surfaces and the continuing drive towards forging nanoscale structure–function relationships to improve application performance, it is envisaged that this effort will continue to expand rapidly for the foreseeable future. We may expect that much on elucidating surface properties at the nanoscale from *model* oxide systems of increasing complexity (e.g. organic/metal oxide interfaces, metal oxide nanostructures, oxide supported metal clusters).

In the case of oxide nanoparticles, due to the larger surface/bulk ratio, there is a dramatic change in the electronic, chemical and even structural properties in comparison with bulk oxides. These modified properties are a function of the particle size. Nanoparticle size effects are also of high interest in fundamental research, since matter at this scale has an intermediate behaviour between solid state and single atoms or molecules. Oxide-oxide and oxide-metal interfaces are also related with this topic. Ultra-thin films of atomic and sub-atomic coverages are a special case of nanostructures where only one of the dimensions (the thickness) is in the nanometer scale. At these so low coverages, the adlayer has different properties than the bulk oxide, although in this case the interaction with the substrate plays a crucial role. Not only size effects are important for these kind of materials, also the addition of impurities (cations) or defects allows one to finely tune functionality to increase application performance.

This kind of research will greatly benefit from a facility like EXES, where one can make use of advanced spectroscopic techniques, like resonant-photoemission or x-ray absorption spectroscopy, very sensitive to changes in chemical and electronic properties, and also surface sensitive. Concerning the structural properties, photoelectron diffraction can be exploited to determine the structure of metal oxide nanostructures, which will almost certainly be key components of future sensors and high-density display devices. The size of the nanostructures (typically 1-5 nm in diameter) rules out most diffraction techniques for structure determination, but not photoelectron diffraction, which relies only on short range order.

Further information: Alejandro Gutierrez: a.gutierrez@uam.es, Rob Lindsay: rlindsay@icmab.es

Self-assembled monolayers (SAMs): chirality and molecular orientation

SAMs are organic layers spontaneously formed on inorganic substrates via a covalent bond. SAMs provide a unique link between the science of organic surfaces and technologies seeking to exploit their adaptable character. Research in this area began in the early 80s and since then has experienced a rapid increase motivated by their appealing technological properties. SAMs are model systems for the study of organic and biological interfaces with applications for the fabrication of sensors, transducers, protective layers, for lubrication, and as materials for patterning. Most of the work performed in SAMs is related to alkanethiol monolayers self-assembled on gold surfaces. They are anchored through the thiol head group to the surface and form reproducibly densely-packed, robust and often crystalline monolayer films. These ideas are exploited nowadays to create functional bio-layers on surfaces, which can be effectively studied by XPS and XANES techniques.

This beamline will permit to study the structure of a molecular layer, which is directly related to its functionality. The possibility of having access to *variable polarization* allows one to perform experiments where the polarization vector can enhance or inhibit a particular transition, and therefore, to study chemical interaction and bonding with the surface, molecule-molecule interaction and molecular orientation.

Surface chirality studies could be of a particular relevance. Nature has chosen left-handed forms (L) for aminoacids to construct proteins and right-handed (D) sugars to form structures. Human proteins are exclusively built from L-aminoacids. The origin of this fundamental dissymmetry is still mysterious. Although both forms present a similar chemical activity, when interacting, molecules recognize each other just as your right hand distinguishes another right hand from a left when you shake hands. The possibility of studying high-resolution core-levels combined with NEXAFS will allow experiments to evidenced differences in L,D or racemic mixtures of chiral-SAMs deposited on surfaces. All this important molecular layers supported on surfaces could be structurally studied in this beamline.

Further information: Jordi Fraxedas: fraxedas@icmab.es, Jose A. Martín-Gago gago@icmm.csic.es

Publication: C. Briones, E. Mateo-Martí, C. Gómez-Navarro, V. Parro, E. Román, J.A. Martín-Gago, Ordered self-assembled monolayers of peptide nucleic acids with DNA recognition capability, *Physical Review Letters* 93: (2004) 208103.

Materials Science

Materials Science comprises both a wide range of scientific cases and of different users. The use of these techniques for advanced characterizations is becoming more and more demanded and therefore the combination of electron spectroscopies with a flexible working environment will be a valuable help to design experiments that cannot be done in a home laboratory, A few relevant examples are detailed in the following.

Polymers

Polymers have become the most used materials for a wide range of applications, from simple plastic bags to sophisticated heart valves or high-strength fibers. Except for the most recent conductive polymers, these materials are insulators, making photoemission studies very complicated. The combination of XPS with XAS and XES techniques provides a new approach to study the electronic structure of polymers. Moreover, in combination with environmental setups, it will be possible to study their reactivity, melting and crystallization from the electronic structure standpoint. Regarding polymer blends, a relevant technique is photoemission microscopy (PEEM)²⁰, suitable to analyze problems like the miscibility and segregation of polymers^{21,22}. The potential of these spectroscopies on carbon-based materials is so important that an optimal photon flux and resolution should be guaranteed at the C K-edge.

²⁰ A PEEM apparatus could be shared with other beamlines. See experimental end-station section.

²¹ S. Zhu, Y. Liu, M. H. Rafailovich, J. Sokolov, D. Gersappe, D. A. Winesett and H. Ade, *Nature* 400, 49 (1999).

²² S. Minko, M. Müller, D. Usov, A. Scholl, C. Froeck, and M. Stamm, *Phys. Rev. Lett.* 88, 035502 (2002).

Organic molecules and materials

Organic molecules and organometallic complexes can exhibit a great variety of physicochemical properties, including dielectric strength, high conductivity, low dimensional conductivity, superconductivity, electroluminescence, liquid crystal behavior, catalytic activity or even molecular magnetism. These complex organic molecules include tetrathiafulvalenes, porphyrazines, phthalocyanines or porphyrins. They are receiving a great attention, not only because of the electronic molecular structure, but also due to the way they are deposited on metal, semiconductor and insulating substrates to form organic thin films. One of the key questions is the bonding and alignment of the molecules, a problem that is commonly faced with angle resolved XAS and XPS techniques, essential in any complete study of these materials²³.

Biomaterials

Biocompatible materials require a carefully balanced interaction between body fluids and proteins with the surface of prosthetic materials. Therefore, there is a vast field of research regarding the chemistry of body fluids in contact with solid surfaces, in particular the chemistry of water (oxygen) and proteins (carbon, nitrogen, sulfur), an area sensitive to the soft x-ray energy range, in particular the 200-600 eV region.

Thin films and coatings

Although the variety of problems in Thin Film Science is as large as the type of materials that form the coating, some specific scientific problems appear for Thin Films. In particular, the bonding structure may differ from the stable bulk material due to subtle changes in the bonding distances that originate an internal stress, or by the stabilization of metastable phases. The structural study of the interatomic distances can be difficult in the case of films composed of nanometric grains, being XAS the most powerful tool. The scientific problem is even more challenging in the case of amorphous films with mixed coordination numbers and a poorly defined bonding structure²⁴.

Nanoclusters

In nanoscience and nanotechnology the study of clusters has become an important issue. A molecular beam or a cluster source for clustering production and characterization can be mounted exploiting the flexible environment planned. The research tools offered makes it possible to determine in-situ the electronic and crystalline properties of nanoclusters simultaneously.

Further information: Ignacio Jimenez, Ijimenez@ictp.csic.es

Final considerations:

²³ S. M. Barlow and R. Raval, Surf. Sci. Reports 50, 201 (2003).

²⁴ J. M. Ripalda, N. Díaz, E. Roman, L. Galan, I. Montero, A. Goldoni, A. Baraldi, S. Lizzit, G. Comelli, and G. Paolucci, Phys. Rev. Lett. 85, 2132 (2000).

This proposal involves many different research fields at the cutting edge of knowledge. Each of these research lines is supported by well established groups. It is true that in some of the cases they do not have previous experience in this kind of studies, but nowadays almost nobody has it, because there are just two recent beamlines operating. On the other hand, this project will give access to a wide community to develop the required instrumentation for every specific case during the construction phase.

This project is well suited for a source with the ALBA technical characteristics. The experimental constraints of the proposed end-station require high flux at energies up to 1500 eV, and low beam divergence, two features which can be easily fulfilled by the ALBA undulators.

We are aware of the damage induced by radiation. This is a problem inherent to most synchrotron radiation experiments. Nevertheless in the case of gases in thermodynamical equilibrium our set-up presents the advantage of a continuous recovering of the desorbed molecules.

4.-Complementarity and relationship with other beamlines

4.1-Similar beamlines in other European synchrotrons

Table I summarizes the main features of other electron spectroscopies beamlines in European synchrotron radiation facilities with technical features similar to ALBA. We would like to remark that we are comparing beamline characteristics, no possibilities of the end-station. If the latter is considered, there exist just two BLs in the world with such a capability. These experimental stations are BL 11.0.2 at the Advanced light source (ALS) in Berkeley and U49.2 at Bessy II. Both of them use undulators and PGM monochromators. Their resolving power is better than 10^4 and the spot size at sample position is of the order of $6 \times 11 \mu\text{m}$.

Two main insights can be made for the table. First, there is a strong motivation from the facilities to build this kind of BL already from the foundation phase. The reason behind is a strong need of electron spectroscopies as characterization techniques and their widespread use by a broad users community. Second, just eight beamlines are available in Europe, and the number of beamtime applications received by each of them is about four times the allocated beamtime, thus describing a large oversubscription scenario. On the other hand, the technical improvements in the field have broadened significantly the users community. While a few years ago most electron spectroscopy beamlines were used by the surface science community, nowadays “materials science” would be a better description of the research area of most users.

| Facility | Beamline | Experiment. Techniques | Monochrom. | Energy range (eV) | Polariz. | Status | E/ Δ E | Spot size(μ m) | detector |
|-----------------|------------|--|--------------------------|--------------------|-----------|--------------|------------------|---------------------|----------------------------------|
| Diamond | SISA | XPS,XAS, PhD, Resonant ph. | | 200-1000 (2-10keV) | Linear | Planned | $1.5 \cdot 10^4$ | 27x100 | TEARES |
| | SIS | ARUPS,XPS, PhD, FSM, XAS,XES, Resonant ph. | NIM (10-30) PGM (20-800) | 10-800 | Variable. | In operation | 10^4 | 50x100 | Mott and hemisph- Scienta |
| ELETTRA | SuperESCA | XPS, PhD, FSM, XAS,, Resonant Ph | SX-700 | 80-1500 | Linear | In operation | 10^4 | 5x100 | Double pass hemisph 96 channels. |
| | VUV | ARUPS,XPS, PhD | 5 gratings | 17-900 | Linear | In operation | 10^4 | | Omicron EA125 |
| | APE | ARUPS,XPS, XAS, Dichroic PES | 4 PGM | 10-100 100-2000 | Variable | | 10^4 | 50x100 | Mott and Scienta |
| SOLEIL | CASSIOPEE | ARUPS,XPS, XAS,FSM Dichroic PES | 4 PGM | 10-1000 | Variable | Planned | 10^4 | 50x50 | Mott and Scienta |
| | TEMPO | XPS,XAS time resolved, Dichroism | 5 PGM | 100-1500 | Variable | Planned | | | Mott and Scienta |
| | ANTARES | ARUPS,XPS, XAS,FSM Dichroic PES | | 10-1000 | Variable | Planned | 10^4 | | Mott and Scienta |
| | I311 | XPS,XAS | SX-700 | 30-1500 | Linear | In operation | 10^4 | | Scienta SES200 |
| MAXII | I411 | XPS,XAS | SX-700 | 50-1500 | Linear | In operation | 10^4 | | Scienta SES200 |
| | I511 | XPS,XAS, XES | SX-700 | 100-1500 | Linear | In operation | 5×10^3 | | Scienta SES200 |
| | PGM1 and 2 | | 2 PGM | 90-1300 | Linear | In operation | | 20x900 | |
| BESSY II | RGBL | | 2 PGM | 30-1500 | Linear | In operation | 10^4 | | |
| | WERA | XPS,PEEM, XAS | | 80-1400 | Variable | Planned | | | |
| ANKA | | | | | | | | | |
| ALBA | EXES | ARUPS,XPS, PhD, FSM, XAS, XES, Res. PES MPPS | PGM | 150-1500 | variable | | 10^4 | | Scienta |

Table 1.- Main figures of merits of some of the similar beamlines devoted to electron spectroscopies in other European 3rd generation synchrotron radiation facilities. Information provided by the facilities.

4.2.- Other beamlines in ALBA

Most beamline projects are still being defined, but a first comparison is already possible. The only beamline with some degree of coincidence is the project called “Beamline for magnetism and polarization dependence spectroscopies”, in particular in what concerns energy range, undulator with variable polarization and use of absorption techniques. However, the users community of magnetism is very different, and large enough to cover most of the beamtime. Therefore, as it already happens in other facilities, this BL will most probably exclude all proposals not making use of light polarization. A PEEM instrument is considered in this beamline. Indeed, the flexibility of the branch line of EXES beamline would allow us to transfer this end station to EXES whenever light polarization is not needed.

On the other hand, most of the beamline features are specific of EXES, as the broad range of pressures for the sample environment.

4.3.- Interaction with SOLEIL

A collaboration agreement of partnership between SOLEIL and ALBA has been recently signed. It could be important to take into account the beamlines in SOLEIL to avoid duplication between both institutions. As shown in table 1, the most similar BL to EXES could be CASSIOPEE and ANTARES. However, although both of them are photoemission beamlines, there are several differences between them and EXES.

Two are the main differences. The first one is related to the energy range, and the second, and most important, to the scientific case. We could have some overlapping in the case of photoemission in UHV. However, both, CASSIOPEE and ANTARES, have a strong dedication to magnetic studies²⁵ (variable polarization, Mott detector, dichroic photoemission) and particularly, ANTARES²⁶ will have a strong commitment to Fermi surface mapping with spin polarization and PhD. In any case it is clear that the amount of beamtime involved in the agreement with SOLEIL (around 2-3% in total, to be distributed between all beamlines in SOLEIL) is much below the needs of the Spanish community of users in the electron spectroscopies area, which on the other hand has a strong demand for a setup available at the national synchrotron radiation laboratory ALBA. Therefore CASSIOPEE (and ANTARES) and EXES are not overlapping but rather complementing to each other.

²⁵ “APS for a Condensed Matter High Resolution Spectroscopy Beamline at SOLEIL in the 10 to 1000eV range”, A. Taleb-Ibrahimi, F. Bertran, P. Le Fèvre.

²⁶ “SU8 beamline transfer from super-ACO to Soleil. M.C. Asensio, J. Avila, M.E.de Avila

5.- Spanish Users Community

The Spanish community using synchrotron radiation based electron spectroscopies is large. Almost all relevant areas are represented, with a demonstrated expertise in the field. We have identified nearly 25 groups, representing 95 PhDs. This strong community is also particularly active and **it has regular access to SR laboratories** around Europe, USA and Japan. Most of the groups include young researchers with postdoctoral experience working in synchrotron radiation facilities. Also, most of the groups use ultra-high vacuum and are familiar with BL design and construction.

This project will give to a wide community the *opportunity to come into scene, developing new instrumentation* adapted to every one of the scientific cases. This will be certainly of a great importance for Spanish scientific community, since in rare occasion we have had the opportunity of contributing collectively to a large project.

We show in the following **a list of real users of soft X-rays spectroscopies**, who have explicitly expressed their support to the construction of this beamline and discussed this proposal. In this list we exclusively count experimented and well-defined groups of users. A much broader list would include less-frequent or potentially interested users. Annex I lists the most important publications of the groups in this area during the last five years, restricted to a maximum of two publications per group.

| Name of group leader | Number of experienced researchers | Domains of research | Affiliation |
|--|-----------------------------------|--|--|
| J.E. Ortega ortega@sq.ehu.es | 4 | Electronic states in nanostructures | Nanophysics lab-S. Sebastian |
| E.G. Michel enrique.garcia.michel@uam.es | 2 | Electronic structure of surfaces and interfaces | Dto. Fis. Mat. Cond. Univ. Autonoma de Madrid |
| J.A. Martín Gago Gago@icmm.csic.es | 4 | Core level and XANES of molecular layers and surfaces | Instituto ciencia de Materiales de Madrid-CSIC |
| Inmaculada Colera icolera@fis.uc3m.es | 3 | Oxide surfaces | Universidad Carlos III de Madrid |
| M. Alonso malonso@icmm.csic.es | 3 | PES, XANES,.. from MBE grown (magnetic) metal and semiconductor hetero and nanostructures. | Instituto Ciencia de Materiales de Madrid-CSIC |
| L. Aballe lucia.aballe@elettra.trieste.it | 4 | X-ray microscopy, LEEM and PEEM of nanostructures | ELETTRA- Trieste |
| J. Palomares fjpalomares@icmm.csic.es | 2 | Electron spectroscopies on Magnetic structures | Instituto Ciencia de Materiales de Madrid-CSIC |

| | | | |
|--|---|--|---|
| J. Avila avila@lure.u-psud.fr | 5 | XPS and Fermi surface mapping. | Instituto Ciencia de Materiales de Madrid-CSIC |
| I. Jimenez ijimenez@ictp.csic.es | 6 | XPS, XES and XAS of light element materials | Instituto de Ciencia y Tecnologia de Polimeros-CSIC |
| Y. Huttel yves@imm.cnm.csic.es | 3 | XPS, UPS and NEXAFS of magnetic nanoclusters | Instituto ciencia de Materiales de Madrid-CSIC |
| L. Galán luis.galan@uam.es | 2 | Secondary electron emission | Fac. Ciencias, C-XII Univ. Autonoma de Madrid |
| Germán Castro castro@esrf.fr | 3 | X-Ray photoemission at high photon energy, oxide surfaces. | ESRF- Grenoble |
| Alfonso Caballero caballero@us.es | 6 | Absorption and XPs on thin layers. | Universidad de Sevilla, ICMS-CSIC |
| T. Cuberes tcuberes@maip-al.uclm.es | 2 | Surface characterization | Universidad de Castilla-La Mancha |
| A. Gutierrez a.gutierrez@uam.es | 7 | Nanoparticles of oxides | Fac. Ciencias, C-XII Univ. Autonoma de Madrid |
| X. Torrelles xavier@icmab.es | 4 | Structural studies of overlayers and molecular layers | Instituto ciencia de Materiales de Barcelona-CSIC |
| J.C. Conesa jcconesa@icp.csic.es | 3 | XPS and absorption spectroscopy of catalysts | Inst. De catálisis y petroquímica-CSIC |
| A. Mascaraque arantzazu.mascaraque@fis.ucm.es | 2 | Surface structure: electronic and atomic | Universidad Complutense de Madrid |
| J. Fraxedas fraxedas@icmab.es | 3 | Molecular layers | Instituto Ciencia de Materiales de Barcelona-CSIC |
| J. Díaz javidiaz@condmat01.geol.uniovi.es | 7 | XPS of magnetic layers | Universidad de Oviedo |
| J.M. Sánchez- Royo rolo@uma.es | 3 | | Universidad de Valencia |

Impact of ALBA/EXES in the Spanish scientific community

The soft X-ray electron spectroscopies community has a large number of potential users, i.e. scientist that frequently make use of laboratory based photoemission apparatus, but who have

not yet been introduced in synchrotron radiation facilities. A national facility would have a strong impact in this community. We would like to remark, that every conventional XPS machine working in Spain receive many research groups from different areas, mostly chemist, that perform an ex-situ characterization of the samples, and that are potential users.

6.- Beamline layout and requirements

6.1.- Insertion device and optics:

As several significant parameters of ALBA are not yet defined, we can just make an outline proposal, presenting together some of the details that should be taken into account for a final design. On the other hand, we have been informed that the detailed design will be undertaken by the staff of ALBA. The beamline is required to deliver monochromatic photons ranging from 150 to 1500 eV, both flux and small divergence are to be optimized in the design.

The source: there is a clear need of an undulator insertion device, Apple II type, able to cover the wide range of energies from 150 eV to 1500 eV with maximum brilliance. This undulator makes it possible to use variable polarization without substantial increase of the price.

The insertion device should be computer-controlled by the user, allowing energy scans, as needed in absorption spectroscopies.

After discussing with the machine staff of ALBA, we propose to use an undulator PPM, with a period of 50 mm and a minimum gap of 11 mm. With these parameters the estimated minimum energy will be 160 eV at the first harmonic and the total power delivered 2.8 kW, what is easily handled. The minimum energy could be further lowered by using hybrids magnets to about 100 eV without losing flux.

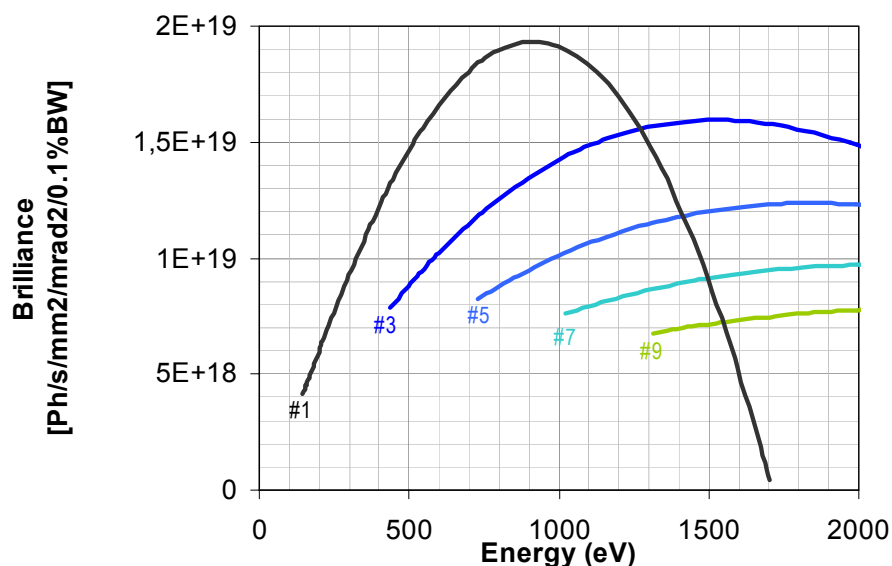


Fig. 1 Brilliance for a 50 mm undulator with a total length of 200 mm

Optics: the low emittance of the machine allows one to use the source as a diffraction limited object for the monochromator. No entrance slit is thus necessary, maximizing flux and reducing the optical path. The first optical element of the beamline would have to absorb the

major part of the beam power. A proper cooling system, ensuring maximum stability of the beam is needed. The energy resolution should be $E/\Delta E \geq 10000$ over whole energy range

We propose a monochromator setup with plane grating monochromator (PGM) to provide an efficient harmonic rejection at low photon energies.

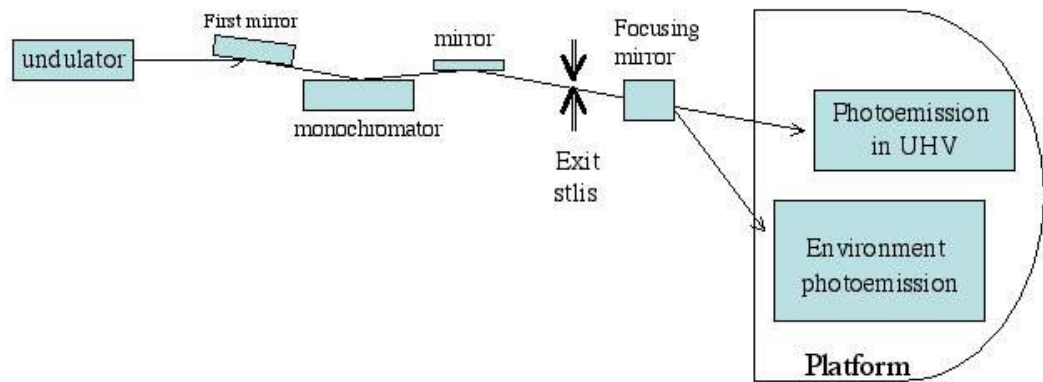


Fig.2.- Block diagram of EXES

6.2.- Experimental end-stations

Obviously two different and fully independent end-stations are required. The first will be devoted to electron spectroscopies in ultra high vacuum and the second one to photoemission and absorption at moderated pressures. The change from one to the other would be performed using a platform, and moving chambers with a bellow. Experience from ALS beamlines guarantees a time for switching the configuration of around 1 hour, with minor alignments.

Using this configuration, one experiment can be prepared and optimized, while working on the other station, which is a very interesting situation from the point of view of an optimal use of the beamtime

The main components and characteristics of the stations are described in the following:

Electron spectroscopies in UHV:

We propose an experimental set-up composed of three interconnected vacuum chambers: (1) Analysis chamber containing the XPS and XES spectrometers, plus a free port with the suited geometry for the eventual incorporation of other techniques (for instance a PEEM instrument is considered in the magnetism beamline. It could be easily transferred to this end station whenever light polarization is not needed). (2) A central preparation chamber under UHV conditions, with at least two ports for the connection of dedicated preparation modules under “dirty” conditions, (3) Load lock system for fast entry of external samples.

Two main detectors are to be mounted in this station:

Hemispherical electron analyser combining both high-transmittance and resolution required for experiments of core level XPS (Scienta type or Phoibos with multichannel detection).

Soft x-ray fluorescence analyzer covering the range 50 eV- 1 kV (Gammadata XES-350 type), providing a resolution of 80 meV at the Si L_{2,3} edge, 110 meV at the C K edge, and 200 meV at the N K edge.

Taking advantage of the experience of several beamlines at ELETTRA, we propose the use of two different sample manipulators. The first one would be specific for low temperatures studies, including He cooling and possibility of sample alignment for polarization and photoelectron diffraction studies. The second manipulator will be specially conceived for studying several samples *in situ* at the same time. Both manipulators should allow heating up 1200° C.

A user-friendly preparation chamber will be connected to the main chamber through a flexible transfer system. The prep-chamber has fast load-lock of MBE evaporators and *in situ* calibration via a quartz microbalance mounted at the same sample stage, as well as LEED and an Ar ion gun pointing to the focus of the electron analyzer. Also an efficient gas admission system and mass spectrometer will be required. Scanning/atomic probe microscopy should be available for *in situ* surface characterization. This tool will enable researchers to ensure that surface phases prepared elsewhere are reproduced accurately, increasing the consistency and veracity of data.

Photoemission at moderated pressures:

The maximum pressure limit in a photoemission experiment is limited by the scattering of photoelectrons with the residual gas molecules. The first approach to increase the pressure during a measurement is to reduce as much as possible the distance between the sample and the analyzer. Due to the small electron mean free paths, and taking into account that electron analyzers need ultra-high vacuum in any case, this approach must be complemented by the use of one or several differential pumping stages. Thus, the high-pressure sample environment is connected to the electron analyzer by a small aperture allowing a substantially higher pressure difference between both places. This approach has been used to develop photoemission equipments able to operate up to 1 mbar^{27,28}. This method could be in principle further applied to attain a larger pressure difference, but the amount of collected electrons decreases too much. Better performances can be obtained from the use of synchrotron radiation, due to the higher flux of incident photons. A second improvement comes from the use of electrostatic electron lenses in the stages of differential pumping, to focalize electrons along the detection direction. Using a high-brilliance photon source and electron focalization, useful working pressures above 1 mbar can be reached.

This end-station will be equipped with a special chamber. This apparatus consists of three well-differentiated parts: reactor, differential pumping, and electron analyzer. The reaction area will be flexible enough for admitting different experimental cases. The reactor is isolated from the rest of the beamline through an Al window. Design of this chamber should take into account an horizontal geometry for the sample goniometer.

This technique will include XPS, XANES and XES. Therefore, the following detectors will be required.

- 1.-Hemispherical electron analyzer to be developed specifically for this project, profiting of the advantage of previous projects.
- 2.-Soft x-ray fluorescence analyzer covering the range 50 eV- 1 kV (Gammadata XES-350 type), providing a resolution of 80 meV at the Si L_{2,3} edge, 110 meV at the C K edge, and 200 meV at the N K edge.
- 3.-Absorption will be performed by measuring either partial auger-yield trough the electron analyzer and total electron yield by measuring the current signal at the front-tip of the analyzer.

In any case, at the moment of the beamline construction, the experience of the previously mentioned ALS and BESSYII groups will be very valuable for designing a new experimental station, where all the problems that have emerge from the use has been solved. We would like to outline that *Miquel Salmeron*, beamline scientist of the ALS beamline, has also reviewed an outline of this proposal, and therefore the contact will be very close. Also, this new station will be designed nearby the users, and some of the experiments proposed in the scientific case will need of an especial set-up, that will be fabricated and tested in the laboratories of the different groups during the beam line construction.

²⁷ H.Siegbahn, K.Siegbahn; J.Electron Spectrosc. Relat. Phenom. 2, 319 (1973).

²⁸ R.W.Joyner, M.W.Roberts, K.Yates; Surf. Sci. 87, 501 (1979).

H.J.Ruppender, M.Grunze, C.W.Kong, M.Wilmers; Surf.Interface Anal. 15, 245 (1990).

M.A:Kelly, M.L.Shek, P.Pianetta, T.M.Gur, M.R.Beasley; J.Vac.Sci.Tech. A 19, 2127 (2001).

7.- Estimated Budget

One clear advantage of this beamline is that the undulator and optics part use well established solutions, and therefore the cost of the beamline itself does not involve significant development work. The same applies to the end-station of photoemission in UHV. Most of the investment is coming from the photoemission in moderate pressures end-station.

We can roughly estimate the following numbers (in k€):

| | |
|---|-------------|
| Undulator + front-end valves and all UHV: | 850 |
| Beamline: First mirror, monochromator, focusing mirror, exit slit, switching mirror, and all UHV accessories: | 1500 |
| End-station for UHV: | 500 |
| Electron energy analyzer: | 120 |
| Analyzer XES-350 | 236. |
| End-station for moderate pressures: | 700 |
| Electron energy analyzer: | 500 |
| Analyzer XES-350 | 236. |
| <u>Roughly</u> total estimation: | 4642 |

Annex I: Most relevant and related publications of the Spanish research groups involved in this proposal since 1999 (2 per group)

1. *Adsorption and desorption of SO₂ on the TiO₂(110)-(1x1) surface: A photoemission study.* D.I. Sayago, P. Serrano, O. Bohme, A. Goldoni, G. Paolucci, E. Román and J.A. Martín-Gago. *Phys. Rev. B*, **64**, 205402 (2001)
2. *Self-assembled monolayers of peptide nucleic acids with DNA recognition capacity.* C. Briones, E. Mateo-Marti, C. Gómez-Navarro, V. Parro, E. Román and J.A. Martín-Gago. *Physical Review Letters* **93**: (2004) 208103
3. *Resonant photoemission and x-ray absorption study of the electronic structure of the TiO₂/Al₂O₃ interface.* M. Sánchez-Agudo, L. Soriano, C. Quirós, M. Abbate, L. Roca, J. Avila, J.M. Sanz. *Langmuir* **17** 7339 (2001)
4. *Resonant Photoemission Study Of TiN.* G.G. Fuentes, P. Prieto, C. Morant, C. Quiros, R. Nuñez, L. Soriano, E. Elizalde, J.M. Sanz. *Physical Review B* **63** (2001) 075403-1.
5. *Spectroscopy of π -bonding in hard graphitic carbon nitride films: superstructure of basal planes and hardening mechanisms.* I. Jiménez, R. Gago, J. M. Albella, D. Cáceres and I. Vergara, *Phys. Rev. B* **62**, 4261-4264 (2000).
6. *High Resolution Beamline 9.3.2 at the Advanced Light Source: Design and Performance Over 30-1500 eV.* Z. Hussain, W.R.A. Huff, S.A. Kellar, E.J. Moler, P.A. Heimann, W. McKinney, C. Cummings, T. Lauritzen, J.P. McKean, F.J. Palomares, H. Wu, Y. Zheng, A.T. Young, H.A. Padmore, C.S. Fadley and D.A. Shirley. *Review of Scientific Instruments* **67**, 3372- 3375(1996)
7. *Polarization Measurement and Vertical Aperture Optimization for Obtaining Circularly Polarized Bend-Magnet Radiation at the Advanced Light Source.* J.B. Kortright, M.E. Rice, Z. Hussain, H.A. Padmore, A.T. Young. A. Adamson, W.R.A. Huff, E.J. Moler, S.A. Kellar, R.X. Ynzunza, F.J. Palomares, H. Daimon, E.D. Tober and C.S. Fadley . *Review of Scientific Instruments* **67**, 3363 (1996).
8. *Soft X-Ray Absorption Spectroscopy Study of Electrochemically formed passive layers on AISI 304 and 316L Stainless Steels,* M. F. López, A. Gutiérrez, C. L. Torres y J. M. Bastidas, *J. Mater. Res.*, **14**, 763 (1999).
9. *Effects of Ce, Mo, and Si ion implantation on the passive layers of AISI 304 stainless steel studied by X-ray absorption spectroscopy,* A. Gutiérrez, M. F. López, F. J. Pérez Trujillo, M. P. Hierro y F. Pedraza, *Surf. Interface Anal.*, **30**, 134 (2000).
10. *Soft x-ray absorption spectroscopy study of passive and oxide layers of titanium alloys,* M. F. López, L. Soriano, F. J. Palomares, M. Agudo, M. Sánchez-Agudo, G. G. Fuentes, A. Gutiérrez y J. A. Jiménez, *Surf. Interface Anal.* **33**, 570 (2002).
11. *Induced V and reduced Co magnetic moments at the V/Co interface,* Y. Huttel et al. *Phys. Rev. B* **68**, 174405 (2003).
12. *Magnetic V embedded in copper evidenced by X-ray Magnetic Circular Dichroism,* Y. Huttel et al., *Phys. Rev. B* **67**, Brief Report 052408 (2003).
13. *Si and Be intralayers at GaAs/AlAs and GaAs/GaAs junctions: Low temperature photoemission measurements.* M. Moreno, M. Alonso, J.L. Sacedón, M. Hóricke, R. Hey, K.Horn and K.H. Ploog. *Phys. Rev. B* **61** 16060-16067 (2000) .
14. *Electron-beam-induced reactions at O₂/GaAs(100) interfaces.* F.J. Palomares, M. Alonso, I. Jiménez, J. Avila, J.L. Sacedón, F. Soria. *Surf. Sci.* **482-485**, 121-127 (2001)
15. *Understanding the magnetic anisotropy in Fe-Si amorphous alloys* J. Díaz, N. Hamdan, P. Jalil, Z. Hussain, S. M. Valvidares and J. M. Alameda. *IEEE Transactions on Magnetism* **38** (2002) 2811-2813

16. *Angle dependence of the O K edge absorption spectra of TiO₂ thin films with preferential texture.* S. R ath, F. Gracia, F. Yubero, J.P. Holgado, A.I. Martin, D. Batchelor, A.R.Gonz alez-Elipe Nucl. Instrum. Methods Phys. Res. B **200** (2003) 248-254
17. *Structure and chemistry of SiO_x (x<2) systems* A. Barranco, F. Yubero, J.P. Espin os, J.P. Holgado, A. Caballero, A.R. Gonz alez-Elipe, J.A. Mej as. Vacuum **67** (2002) 491-499
18. *Nature of the low-temperature 3x3 surface phase of Pb/Ge(111).*A. Mascaraque, J. Avila, M.C. Asensio, S. Ferrer, and E.G. Michel. Physical Review Letters **82** (1999) 2524.
19. *Symmetry breaking and atomic displacements in the 3x3 surface phase of Pb/Ge(111).*A. Mascaraque, J. Alvarez, J. Avila, M.C. Asensio, S. Ferrer, and E.G. Michel. Surface Science **454-456** (2000) 191.
20. *A novel Sb induced reconstruction of the (113) surface of Ge.* Hirnet, K. Schroeder, S. Bl ugel, X. Torrelles, M. Albrecht, B. Jenichen, M. Gierer and W. Moritz, Phys. Rev. Lett., **88**, (2002), 226102-1.
21. *Geometry of the valence transition induced surface reconstruction of Sm(0001).* E. Lundgren, J.N. Andersen, R. Nyholm, X. Torelles, J. Rius, A. Delin, A. Grechnev, O. Eriksson, C. Konvicka, A. Grechnev, M. Schmid and P.Varga, , Phys. Rev. Lett., **88**, (2002), 136102-1.
22. *Interfacial redox processes under CO/O₂ in a nanoceria-supported copper oxide catalyst,* A. Mart nez-Arias, A.B. Hungr a, M. Fern andez-Garc a, J.C. Conesa, G. Munuera, J. Phys. Chem. B **108**, 17983 (2004).
23. *The behavior of mixed-metal oxides: Physical and chemical properties of bulk Ce_{1-x}Tb_xO₂ and nanoparticles of Ce_{1-x}Tb_xO_y,* X.Q. Wang, J.C. Hanson, G. Liu, J.A. Rodr guez, A. Iglesias-Juez, M. Fern andez-Garc a, J. Chem. Phys. **121**, 5434 (2004).

Annex II: International research groups explicitly supporting this project.

Dra. Amina Taieb: Beam line responsible of CASSIOPEE at SOLEIL

Dra. Giorgio Paolucci: Scientific director of ELETTRA.

Prof. Dr. Karsten Horn: Scientist at the Fritz-Haber-Institut der Max-Planck-Gesellschaft

Prof Miquel Salmeron: Beam line scientist of BL 11.0.3 at the ALS.

Outline for a Beamline Proposal at ALBA

Low-energy High-Resolution Angular Photoemission for Complex Materials (LOREA)

This proposal outline was coordinated by J.A. Martín-Gago (gago@icmm.csic.es) and Enrique G. Michel (enrique.garcia.michel@uam.es)

It contains contributions from the whole Surface and Interface Science Community

Table of Contents

1.-Summary

2.-Scientific Cases

2.1. Preceding considerations, current status and perspectives

2.1.1 The role of Angle-Resolved Photoemission in previous and current research

2.1.2 Low-energy High-resolution ARPES: state of the art of a tool to study complex systems and phenomena

2.2.- The scientific goals: understanding complexity

2.2.1 High energy resolution in cooperative phenomena: superconductivity, phase transitions and charge density waves

2.2.2 High angular resolution: Emerging complex materials

2.2.3 Low-flux, low-energy, HR-ARPES: Supramolecular assemblies

2.2.4 New physics in low-dimensional and nanoscale systems

3.-Spanish scientific community: opportunity and need of a low energy photoemission beamline at ALBA

4.-Beamline layout and requirements

5.-Complementarity and relationship with other beamlines in European synchrotrons

6.-Annex:

Most relevant publications of the supporting research groups since 1999
(2 per group)

1.-Summary

The development of high-resolution (HR) electron analyzers with multichannel angular detection has recently stirred the interest in angle-resolved photoemission spectroscopy (ARPES). HR analyzers represent a major breakthrough that has allowed ARPES to mature in power and simplicity, reaching the same level of the most advanced electron microscopies. Indeed, in a similar way as real space is imaged in a microscope, now the band structure of solids, i.e., the Fourier space landscape of valence band electrons, is readily visualized on a screen with unprecedented precision¹.

HR-ARPES has enormous potential in most of the fields of solid state physics. Nominally², the energy resolution can be as low as 1 meV (12 K) and the angular resolution of the order of 0.1°, i.e. $\Delta k \sim 0.001 \times \sqrt{E-5} \sim 0.005 \text{ \AA}^{-1}$ for $E=30$ eV photons. Thus, extremely accurate band structure measurements are at hand, making it possible to track most phenomena affecting the electronic structure by studying electron bands close to the Fermi energy in the whole Brillouin zone. HR-ARPES is being already extended to research in a variety of novel systems and their underlying interactions: many-body interactions and cooperative phenomena in bulk materials, like superconductivity, magnetism and phase transitions, strongly correlated electron systems, nanoscale systems and emerging complex materials. The latter include novel unconventional superconductors, alloys, intermetallic compounds, magnetic semiconductors, f-electron systems and low-dimensional and self-organized systems.

The impact of HR-ARPES in current solid state physics explains the increasing number of setups in synchrotron radiation facilities around the world. We strongly believe that ALBA must feature HR-ARPES as well, although it must go beyond a standard system to a more specialized setup. Most of the HR-ARPES experiments (like those of Soleil) are connected to undulator beam lines that are effectively limited to photon energies beyond 30 eV. This Outline Proposal describes a HR-ARPES setup exclusively dedicated to high-resolution band structure measurements using low energy (LE) photons (8-50 eV). This photon energy range enlarges angular resolution and increases the probing depth, which is especially attractive for the study of emerging complex systems with large unit cells, as explained in the Scientific Case section. We propose an undulator beamline, but taking into account the features of the ring, and subject to further analysis, a beamline connected to a bending magnet is also possible. This would define a lower-flux, LE beam line, which would still be competitive in all the areas mentioned before, while becoming unique in the research of complex molecular structures.

It is also necessary to stress that research of complex materials requires careful in-situ sample preparation and characterization. This is a critical point that, based on our experience as frequent users of HR-ARPES in different synchrotron facilities around the world, is not being adequately addressed in most of the cases. Thus we plan a simple and flexible, and hence powerful measurement-chamber, that include varied capabilities

¹ For a graphic tutorial on state-of-the-art photoemission with display-type analyzers see <http://www-bl7.lbl.gov/BL7/who/eli/SRSchoolER.pdf>

² T. Kiss, T. Yokoya, and S. Shin, ISSP, Tokyo University, see Gammadata web page at http://www.gammadata.se/ULProductFiles/R4000_analyzer_family.pdf

for sample preparation and characterization (STM, MBE sources, broad temperature range), which make up a sophisticated prep-chamber.

Summary of beamline specifications

Photon energy : from 8 to 100 eV, high performance in 8-50 eV

High flux : $> 10^{13}$ ph/s/b.w. on sample

Very high energy resolution $E/\Delta E \geq 20000$.

High purity and stability of the beam at source and experimental station

Linear polarization

Endstation equipped with:

1. Analysis chamber equipped with
 - a high-resolution electron analyzer with energy and angle multidetection.
 - two high-precision manipulators, one of them with helium cooling, possibility of high temperatures and magnetic fields. Second manipulator with 5 degrees of freedom.
2. Pre-chamber equipped with all standard preparation and characterization tools

2.-Scientific Cases

2.1 Preceding considerations, current status and perspectives

2.1.1 The role of Angle-Resolved Photoemission in previous and current research

A large number of advanced materials has been developed over the last years. Their new physical and chemical properties provide a basis for promising applications and challenging scientific research. We are considering materials able to satisfy specific industrial needs, due to their mechanic or electronic properties. In the first group we may mention composite materials (widely used in the aircraft industry), polymers (with applications ranging from microelectronics to chemical industry), and ceramics (used for coatings). In the second group, we include materials developed because of their specific electronic features. In this case, the requirements of the microelectronics and optoelectronics industries are more and more complex, and thus new artificial materials, designed to fulfill specific needs, are being designed. Nowadays, the requirements have reached such a degree of complexity that we may talk about a true “materials engineering” to describe how specific properties are designed and modified. This is the case of most electronic and optoelectronic devices. These materials involve complex properties, whose understanding is at the edge of Solid State Physics. But without a deep comprehension of these properties no real step forward is possible. In particular, a thorough and precise knowledge of their electronic structure is of crucial importance for tailoring their various functionalities.

The development of advanced materials with specific electronic properties has been made possible thanks to a remarkable progress in the understanding of the electronic structure of solids³. In the case of simple solids, these properties are well known from a theoretical point of view since many years. In the case of more complex materials, a deeper understanding is difficult because of several features common in most of these systems. We may mention many body and electron correlation effects, dynamic and static disorder, cooperative and collective phenomena, which are in general difficult to treat theoretically.

From the experimental point of view, valence-band angle-resolved photoemission is the most important technique to determine the electron band structure of a solid⁴. It provides information on all the relevant aspects of the electron wave function (energy, symmetry, momentum, spin). An efficient combination of high resolution photoemission with an adequate sample preparation setup allows one to probe the various contributions to the complex valence band structure of novel materials in a very complete way.

The goal of this outline proposal is to describe the main features and the scientific case of a beamline devoted to the analysis of the electronic structure of a wide range of materials. The use of this technique with a state of the art detection system as well a flexible sample environment makes it possible to obtain experimental information on electronic properties with unprecedented precision.

³ R.M. Martin, “Electronic Structure”, Cambridge, 2004.

⁴ S. Kevan, “Angle Resolved Photoemission”, Elsevier, 1992.

2.1.2 Low-energy High-resolution ARPES: state of the art of a tool to study complex systems and phenomena

Physics in the 21st century will play a fundamental role in developing the new, sophisticated technologies needed to confront such big scientific and social issues as the search for new energy resources, the environmental protection or the human health. This explains the growing importance of interdisciplinary fields, like materials physics or biophysics, and the widespread of new emerging areas like low-dimensional physics and nanostructures. Most of them deal with complex systems that require powerful analytical and computational techniques, as well as developing the capability of engineering materials down to the atomic or molecular scale. The complexity is also inherent to many-body interactions, which lie at the frontier of knowledge in fundamental solid state physics. This comprises strong electron correlations, collective excitations, superconductivity, phase transitions and other exotic phenomena that characterize low-dimensional systems, such as charge density waves and non-Fermi liquid behavior.

As physical systems become more complex, their fundamental constituents scale up in size and their characteristic interactions scale down in energy. Electron energy levels in atoms and simple molecules range in the eV scale. Collective motions, such as phonons, or phase transitions that involve cooperative phenomena, such as Cooper pairs in superconductors, display 10-20 Å length scales and are triggered by energy excitations of the order of a few meV. Domain switching and percolation phenomena have length scales in the 100-10000 Å range and involve excitations in the sub meV range. HR-ARPES and low-energy (8-40 eV) synchrotron radiation provide the key instrument to study electronic states with 0.6 meV energy resolution and interactions with length scales up to $1/\Delta k \sim 500$ Å (at 8 eV), i.e. it covers the range of the electronic structure of molecules and atoms, a vast number of collective excitations and phase transitions, and tails into the physics of mesoscale domain interactions.

In recent years it has been proved that the physics of low dimensional and complex systems is better addressed in well-structured materials, i.e., solid crystals. Although final technology applications might not require crystal perfection, it is generally agreed that the crystallinity is best suited to understand the ultimate microscopic behavior. One good example is high T_c superconductivity, which is now being disentangled with accurate Fermi surface measurements using single crystals and HR-ARPES^{5,6}. The latter is particularly ideal since only a minor portion of the Fermi level electrons are involved, and these need to be identified within the complex Brillouin zone. However, the larger the unit cell becomes, the better the angular resolution needs to be. Assuming for instance band mapping with 10 points per surface Brillouin zone, the limiting size of the unit cell in a crystal structure that can be mapped is $0.1/\Delta k$, i.e. only 20 Å for 30 eV photons, but up to 50 Å for 8 eV photons.

⁵ A. Damascelli, Z. Hussain, Z.X. Shen, Rev. of Mod. Phys. 75, 473 (2003).

⁶ J.C. Campuzano, M. Norman, M. Randeria, Physics of Superconductors 2 (2003) 167.

It is known that ARPES is unique to probe all quantum numbers of the electrons in crystalline solids². Thus, as far as crystalline systems are involved, ARPES provides the most accurate, complete description of the electronic structure. In order to thoroughly explore the 3D band structure of solid crystals, photon energy tuning, light polarization, spin detection and angle and energy resolution are needed. For complex systems the finite sampling depth of photoelectrons limits (broadens) band structure measurements in the third dimension (in the bulk). This is critical in regular HR-ARPES set ups with 25-100 eV electrons, where the escape depth has its minimum value of $\sim 5-8$ Å. However, by using low photoelectron kinetic energies one can significantly increase the sampling depth, while maintaining wave vector resolution. Assuming 8 eV photons, the kinetic energy is lowered to 3 eV at the Fermi level, at which the electron escape depth rises to about 30-40 Å.

In summary, HR-ARPES is a powerful tool to investigate a vast number of emerging fields in solid state physics, with large scale lengths and complex interactions. In particular, by lowering the energy, one significantly increases wave vector resolution and bulk sampling depth, which become of key importance for band structure investigation of complex crystal structures. In the following we describe how HR-ARPES is expected to provide, and it is already providing, new insights and fundamental knowledge in hot topics in physics.

2.2 The scientific goals: understanding complexity

2.2.1 High energy resolution in cooperative phenomena: superconductivity, phase transitions and charge density waves

Phase transitions are an example of a broad range of cooperative phenomena where energetic resolution (combined with cryogenics) is critical to achieve sensitivity. Charge density waves and structural phase transitions in one-dimensional or two-dimensional systems, like atom chains, surface layers or low-dimensional bulk compounds are linked to a few meV gap opening at Brillouin zone edges^{7,8}.

Understanding the electronic structure of superconducting materials is a goal of photoemission spectroscopy, due to the stringent experimental conditions required in terms of energetic and angular resolution. This applies both to high T_c superconductors and to novel unconventional superconductor materials, like MgB_2 ⁹. Both are particularly attractive, due to their high superconducting transition temperature and its possible connection with structural changes. It is also interesting to explore quantum size effects in thin films and their connection to the transition temperature and the superconducting gap¹⁰.

One of the frontiers of solid state physics lies in the comprehension of the electronic properties of materials where the successful independent electron model fails. Interestingly, this kind of phenomena is relevant in most advanced materials, like high

⁷ T. Nakagawa, G. I. Boishin, H. Fujioka, H.W. Yeom, I. Matsuda, N. Takagi, N. Nishijima, and T. Aruga, Phys. Rev. Lett. **86**, 854 (2001).

⁸ F. Schiller, J. Cordon, D. Vyalikh, A. Rubio, and J. E. Ortega, Phys. Rev. Lett. **93**, (2004).

⁹ S. Tsuda, T. Yokoya, S. Shin, Y. Takano, H. Kito, A. Matsushita, F. Yin, J. Itoh, H. Harima, Physica C **412-414**, 36 (2004).

¹⁰ P. V. Komissinski and G. A. Ovsyannikov Phys. Rev. B **54**, 13184 (1986).

Tc superconductors, colossal magnetoresistance compounds, etc. In these materials, electron correlation induces novel ground states of valence electrons, giving rise to a wide range of exotic phenomena still poorly understood. An investigation on the elementary excitations of these systems is only possible by means of HR-ARPES. This technique is sensitive to the spectral function and provides information on the properties of the relevant quasi particles. Indeed, an angle-resolved photoemission spectrum is a direct visualization of the spectral function, and its line shape reflects the electron correlation and dimensionality of the system.

Obviously, a full exploitation of the energy resolution expected in LOREA is only feasible if a low-temperature (<5 K) sample manipulator is available, which means an step forward with respect to the lowest achievable temperatures at PES beamlines.

2.2.2 High angular resolution: Emerging complex materials

A host of emerging complex materials can be accurately probed only by accessing high angular resolution. A conspicuous example are one-dimensional atom chains, which are candidates to observe the physical realization of a Luttinger liquid, expected to display the characteristic spin-charge separation in the band structure^{11,12}. Characteristic properties of two-dimensional and one-dimensional magnetic systems, such as spin excitations^{13,14}, and other exotic predictions, like ferro-antiferro and order-disorder transitions in 2D and 1D organic molecular arrays¹⁶, can be traced back to minor changes in electron bands, which in turn can be located accurately in the Brillouin zone by means of HR-ARPES.

Superstructures with relatively large “building blocks”, like quantum dots, are expected to play a role in future molecular electronics¹⁵ and high density recording media¹⁶. They are now currently achieved by self-assembly on solid surfaces^{17,18}. Studying their electron states requires not only high energy resolution (and low temperature) but also high angular resolution, due to the size of the blocks and the superlattice unit cell. The resolution is better at the lowest energy, e.g. at 8 eV photon energy one might achieve 0.002 \AA^{-1} wave vector resolution that allows one to appropriately probe the Fourier space of the electron for nano-object sizes and superstructure periodicities of the order of 500 Å. For electron coupling between nano-objects in 500 Å periodic arrays, one can map accurate superlattice bands. For electron confinement within 500 Å size quantum dots or atomic aggregates, one can straightforwardly determine quantum levels from the ARPES data, and even probe electron wave functions from the spectral distribution of the photoemission intensity¹⁹.

¹¹ J. Voit, Rep. Prog. Phys. **58**, 977 (1995).

¹² J.N. Crain, J.L. McChesney, F. Zheng, M.C. Gallagher, P.C. Snijders, M. Bissen, C. Gundelach, S.C. Erwin, F.J. Himpsel, Phys. Rev. B **69**, 125401 (2004).

¹³ P. Segovia, D. Purdie, M. Hengsberger, and Y. Baer, Nature (London) **402**, 504 (1999).

¹⁴ G. Grüner, Rev. Mod. Phys. **66**, 1-24 (1994).

¹⁵ “Molecular Electronics: Science and Technology”, eds. A. Aviram and M. Ratner, Annals of the New York Academy of Sciences vol. **852**, New York 1998

¹⁶ See for instance the “Seagate” data storage future technology at <http://www.seagate.com/newsinfo/technology/research/D4b2.html>

¹⁷ S.M. Barlow, R. Raval, Surface Science Reports **50**, 201 (2003) 201.

¹⁸ J. Shen, J. and J. Kirschner, Surface Science **500**, 300 (2002).

¹⁹ A. Mugarza and J. E. Ortega, J. Phys. Cond. Mat. **15**, S3281 (2003).

2.2.3 Low-flux, low-energy, HR-ARPES: Supramolecular assemblies

The deposition of large functional molecules on surfaces is the single most important step in creating thin films of complex organic molecules for the emerging fields of molecular devices, such as optoelectronic and logic circuits, sensors, and molecular recognition structures²⁰. In order to use molecular layers in laterally structured arrangements, i.e. in device applications, self-organization of molecules on surfaces is of central importance. Molecular self-assembly is governed by intermolecular forces, the molecule-surface interactions and entropic effects. The range of structures that may result from these seemingly simple factors is immense and encompasses massive restructuring of the substrate (faceting²¹), co-operative self-assembly of surface atoms and molecules²², and a host of molecular and supramolecular patterns on an unaltered substrate.

Electronic states in such fine and complex structures are ideally investigated by means of HR-ARPES. This technique can provide a fresh look into the basic electronic properties. Synchrotron radiation is necessary to enhance cross sections and perform polarization and photon energy dependent measurements. This allows a full characterization of the molecule-molecule and the molecule-substrate bonding, i.e. geometry and strength²³. But HR-ARPES will be essential to explore the formation of conducting electron bands, which are important from the technological point of view, in the field of molecular electronics, but also from the fundamental point of view, where extreme electron correlations are expected, in particular in one-dimensional molecular wires.

Electronic structure studies of supramolecular arrays at surfaces are very scarce. The difficulty arises, on the one hand, in the complexity and the size of the building blocks, which requires very detailed structural analysis and LE-HR-ARPES to enhance wave vector resolution. The supramolecular structure should be preferably prepared and structurally analyzed in-situ, and this requires a well-equipped prep-chamber including STM. On the other hand, adsorbed molecules and arrays are frequently unstable upon exposure to high intensity beams, which induce desorption, modification or degradation. Thus, the best performance can be obtained at beam lines with low density of photons and relatively large spots, which are readily achieved with bending magnet sources. This area includes the formation of ordered layers of complex organic molecules like tetrathiafulvalenes, porphyrazines, phthalocyanines or porphyrins, which are receiving a great attention, not only because of the electronic molecular structure, but also due to the way they are deposited on metal, semiconductor and insulating substrates to form organic thin films. One of the key questions is the nature of the intermolecular forces and the role of the substrate in the assembling process, a problem which can be optimally analyzed by LOREA²⁴. This area includes also the investigation of alkanethiol

²⁰ "Molecular Electronics: Science and Technology", eds. A. Aviram and M. Ratner, Annals of the New York Academy of Sciences vol. **852**, New York 1998; Heath et al., Science **280**, 1716 (1998); Chen et al., Science **286**, 1550 (1999); Collier et al., Science **289**, 1172 (2000).

²¹ M. Böhringer, R. Berndt, and W. Schneider, Phys. Rev. B **55**, 1384-1387 (1997).

²² J. K. Gimzewski, S. Modesti, and R. R. Schlittler, Phys. Rev. Lett. **72**, 1036-1039 (1994).

²³ W. Widra et al., Phys. Rev. Lett. **80**, 4269 (1998); E. W. Plummer and W. Eberhardt, Adv. Chem. Phys. **49**, 533 (1982).

²⁴ S. M. Barlow and R. Raval, Surf. Sci. Reports **50**, 201 (2003).

monolayers self-assembled on gold surfaces. They are anchored through the thiol head group to the surface and form reproducibly densely-packed, robust and often crystalline monolayer films. These ideas are exploited nowadays to create functional bio-layers on surfaces. Their electronic structure can be effectively analyzed at LOREA.

2.2.4 New physics in low-dimensional and nanoscale systems

Low-dimensional and nanoscale systems exhibit a unique feature: their typical lateral size (thickness, periodicity, length, etc) is comparable to the electron wavelength. Thus, all relevant properties of these materials are directly determined by quantum phenomena. This includes not only microscopic properties, but also their overall macroscopic behavior. A few examples can help to understand the relevance of this situation. The first well-known phenomenon is the formation of quantum well states in thin films²⁵. When a thin metallic layer is deposited on top of a semiconductor or even a metal (provided that there is a partial band gap), electron confinement in the thin layer splits bulk bands in discrete quantum states, called quantum well states. Their energy location depends on the thickness of the layer. In turn, changing the thickness in a controlled way allows one to tune the position of a quantum well state, e.g. close to the Fermi energy or far away from it. Thus, two possible states are feasible, the first one with a high density of electrons at the Fermi energy, the second one with a much smaller electron density. The realization of each of these two states depends periodically on the film thickness. A wide variety of physical phenomena is affected by the density of states at the Fermi energy, and thus we may expect that they are also affected by the formation of quantum well states. The first observation of the involvement of quantum well states in a macroscopic property of technological relevance, was the relationship between quantum well states and the oscillatory magnetic coupling in magnetic multilayers²⁷, a phenomenon behind the Giant Magnetoresistance Effect. Later on, the phenomenon of “electronic growth” was observed. We speak of “electronic growth” when the electronic energy of a thin film plays a relevant role in determining the crystalline structure of the film²⁶. This is the case of a thin film with quantum well states, and indeed the state with high electron density at the Fermi level has a significantly higher energy than the state with a reduced electron density. Since the electron density depends on the film thickness (number of atomic layers), this gives rise to the observation of “magic” thicknesses and “forbidden” thicknesses during the growth of thin films²⁶.

One step beyond, we expect that many other properties of the film are also affected by the reduced dimensionality. This has been recently demonstrated for surface reactivity²⁷, a property also depending on the electronic density of states at the Fermi energy. Furthermore, collective states like BCS superconductivity are also strongly dependent of the electronic density at the Fermi energy, and thus they are also affected, as recently shown²⁸. A vast field is open for research in the electronic properties of nanoscale materials, where both single-electron, collective states, and macroscopic properties can be tuned and traced back to a typical size of the order of nanometers. LOREA is a unique tool to investigate this vast field of new phenomena describing a world far away from conventional 3D systems, and thus a large playground for forefront research.

²⁵ M Milun, P Pervan and D P Woodruff, *Rep. Prog. Phys.* **65**, 99 (2002).

²⁶ D.-A. Luh, T. Miller, J. J. Paggel, M. Y. Chou, T.-C. Chiang, *Science* **292**, 1131 (2001).

²⁷ L. Aballe, A. Barinov, A. Locatelli, S. Heun, and M. Kiskinova, *Phys. Rev. Lett.* **93**, 196103 (2004).

²⁸ Yang Guo et al, *Science* 306, 1915 (2004).

3.-Complementarity and relationship with other beamlines in European Synchrotrons

Angle-resolved photoemission beamlines are frequently found in third generation synchrotrons. Table I summarizes the main features of other ARUPS beamlines in European synchrotron radiation facilities with technical features similar to ALBA. An inspection of the Table immediately reveals that most (if not all) current ARUPS beamlines try to access an energetic range as broad as possible, in general reaching photon energies above 800 eV. This brings a larger spectral range, and it opens the possibility of probing core levels. However, the efficiency of these beamlines in the extreme (lowest and highest) photon energies is not outstanding, and in practice the flux below 20 eV is frequently too low to be used in most applications. Currently, just three operational BLs can reach photon energies below 20 eV, and none of them is particularly performing in the range 15-20 eV. The consequence is a large oversubscription of these beamlines.

The signature of a collaboration agreement of partnership between SOLEIL and ALBA makes it sensible to establish a comparison with BLs at SOLEIL. As shown in table 1, the most similar BLs to LE-HR could be CASSIOPEE and ANTARES. CASSIOPEE has a strong dedication to magnetic studies²⁹ (variable polarization, Mott detector, dichroic photoemission) and a much higher energy range. On the other hand, from the information available³⁰ ANTARES will have a strong commitment to Fermi surface mapping with spin polarization and photoelectron diffraction. We conclude that LOREA and these beamlines are not overlapping but rather complementing to each other. Furthermore, it is clear that the amount of beamtime involved in the agreement with SOLEIL (around 2-3% in total, to be distributed between all beamlines in SOLEIL) is much below the needs of the Spanish community of users, which on the other hand has a strong demand for a setup available at the national synchrotron radiation laboratory ALBA, which is the only way to guarantee not only access to beamtime, but also the possibility of staying at the forefront of research.

²⁹ “APS for a Condensed Matter High Resolution Spectroscopy Beamline at SOLEIL in the 10 to 1000eV range”, A. Taleb-Ibrahimi, F. Bertran, P. Le Fèvre.

³⁰ “SU8 beam-line transfer from Super-Aco to Soleil: A low-energy light source for electronic and structural studies in condensed matter”, M.C. Asensio, J. Avila, M.E. Dávila.

| Facility | Beamline | Experiment. Techniques | Monochrom. | Energy range (eV) | Polariz. | Status | $E/\Delta E$ | Spot size(μm) | detector |
|-----------------|------------|--|--------------------------|-------------------|-----------|--------------|--------------|----------------------------|--------------------------|
| SLS | SIS | ARUPS,XPS, PhD, FSM, XAS,XES, Resonant ph. | NIM (10-30) PGM (20-800) | 10-800 | Variable. | In operation | 10^4 | 50x100 | Mott and hemisp- Scienta |
| | VUV | ARUPS,XPS, PhD | 5 gratings | 17-900 | Linear | In operation | 10^4 | | Omicron EA125 |
| SOLEIL | APE | ARUPS,XPS, XAS, Dichroic PES | 4 PGM | 10-100 100-2000 | Variable | In operation | 10^4 | 50x100 | Mott and Scienta |
| | CASSIOPEE | ARUPS,XPS, XAS,FSM Dichroic PES | 4 PGM | 10-1000 | Variable | Planned | 10^4 | 50x50 | Mott and Scienta |
| MAXII | ANTARES | | 4 PGM | | Variable | Planned | 10^4 | | |
| | I311 | XPS,XAS | SX-700 | 30-1500 | Linear | In operation | 10^4 | | Scienta SES200 |
| BESSY II | U125/1-PGM | | 1-PGM | 8-700 | Linear | In operation | | | |
| ALBA | LE-HE | ARUPS, | NIM | 8-50 | Variable | | 10^4 | | Scienta |

Table I.- Main figures of merits of undulator beamlines in other European 3rd generation synchrotron radiation facilities. Information provided by the facilities.

4.-Spanish Users Community

The Spanish community interested in low-energy angle-resolved photoemission is very active, with significant performance records and broad experience in using synchrotron radiation facilities and a demonstrated expertise in the field. We have identified XX groups, representing XX PhDs. This community has gained regular access to SR laboratories around Europe, USA and Japan. Most of the groups include young researchers with postdoctoral experience working in synchrotron radiation facilities. An important argument for the construction of LOREA is the expected impact in the Users Community. We think that this community is mature enough, not only to make an efficient use of the beamtime (which is a very important argument), but also to make significant contributions to the field, and even to play a world-leading role in some areas, provided that a technically sound beamline is constructed. These arguments are clear both from the past record of the researchers involved in this proposal and by the impact of the research topics addressed.

We show in the following a list of users classified according to scientific case, who have explicitly expressed their support to the construction of this beamline. In this list we exclusively count experimented and well-defined groups of users. A much broader list would include less-frequent or potentially interested users, and will be presented together with the final proposal

Annex I lists the most important publications of the groups in this area during the last five years, classified according to scientific case.

| Group leader and email | Number of experienced researchers | Domains of research | Affiliation |
|--|--|--|--|
| J.E. Ortega ortega@sq.ehu.es | 4 | Electronic states in nanostructures | Nanophysics lab-S. Sebastian |
| E.G. Michel enrique.garcia.michel@uam.es | 2 | Electronic structure of surfaces and interfaces | Dto. Fis. Mat. Cond. Univ. Autonoma de Madrid |
| J.A. Martín Gago Gago@icmm.csic.es | 4 | Core level and XANES of molecular layers and surfaces | Instituto ciencia de Materiales de Madrid-CSIC |
| Inmaculada Colera icolera@fis.uc3m.es | 3 | Oxide surfaces | Universidad Carlos III de Madrid |
| M. Alonso malonso@icmm.csic.es | 3 | PES, XANES,.. from MBE grown (magnetic) metal and semiconductor hetero and nanostructures. | Instituto Ciencia de Materiales de Madrid-CSIC |
| L. Aballe lucia.aballe@elettra.trieste.it | 4 | X-ray microscopy, LEEM and PEEM of nanostructures | ELETTRA- Trieste |
| J. Avila avila@lure.u-psud.fr | 5 | XPS and Fermi surface mapping. | Instituto Ciencia de Materiales de Madrid-CSIC |

| | | | |
|--|---|--|---|
| A. Gutierrez a.gutierrez@uam.es | 7 | Nanoparticles of oxides | Fac. Ciencias, C-XII Univ. Autonoma de Madrid |
| I .Jimenez ijimenez@ictp.csic.es | 6 | Band structure of light element materials | Instituto de Ciencia y Tecnologia de Polimeros-CSIC |
| Y. Huttel yves@imm.cnm.csic.es | 3 | XPS, UPS and NEXAFS of magnetic nanoclusters | Instituto ciencia de Materiales de Madrid- CSIC |
| A. Mascaraque arantzazu.mascaraque @fis.ucm.es | 4 | Surface electronic structure | Universidad Complutense de Madrid |
| L. Galán luis.galan@uam.es | 2 | Secondary electron emission | Fac. Ciencias, C-XII Univ. Autonoma de Madrid |
| J. Fraxedas fraxedas@icmab.es | 3 | Molecular layers | Instituto Ciencia de Materiales de Barcelona-CSIC |

5.- Beamline layout and requirements

The scientific cases mentioned above require a beamline with high photon energy resolution and able to provide with a high flux in the lowest photon energies (around 8 eV). The main chamber should be equipped with a high-resolution electron spectrometer (Scienta R4000 or similar), with a demonstrated resolution in the meV range. A precision manipulator equipped with a He flow cryostat and high precision sample rotation stage will be mounted on the experimental station. The manipulator should allow angle resolved measurements over 2π steradian down to $T \sim 10\text{K}$. A user-friendly prep-chamber will be connected to the main chamber through a flexible transfer system. The prep-chamber will allow quick load-lock of MBE evaporators and in-situ calibration via a quartz microbalance mounted at the same sample stage, and will be featured with a commercial STM for structural analysis.

A very important feature related to meV energetic resolution is sample temperature. Thermal broadening at 10 K is approx. 1 meV. This means that when this level of energetic resolution is reached, an equivalent level of samples temperatures below 5-6 K must be achieved. This range means an important step forward in photoemission spectroscopy, since most experimental setups worldwide are limited to approx. 30 K. This is due to the fact that achieving lower temperatures poses significant experimental problems, e.g. an excellent thermal contact must be guaranteed after sample transfer, and thermal radiation shielding is needed to reach temperatures below 10 K. Using the expertise in the field of several of the groups involved in this project, we propose the construction of an specific sample manipulator designed to reach sample temperatures below 10 K, and suitable for ultra high resolution measurements.

5.1.- Source and optics:

We present in this outline proposal the most relevant parameters to be considered in the final design. The beamline is required to deliver monochromatic photons from 8 to 100 eV, with emphasis in the 8-50 eV range. Both flux and resolution are to be optimized in the design.

The source: the first option is an undulator insertion device, able to cover the range of energies with maximum brilliance. In view of the critical energy of ALBA (3 GeV, somewhat above the values in similar 3rd generation sources), a long electromagnetic undulator will have to be installed, probably in one of the three largest straight sections of the ring. A second choice is using a bending magnet source. In this case there will be obviously less flux, but we do not exclude this possibility, because it could be an advantage for some of the applications (e.g. study of organic molecular adsorbates).

Optics: the first optical element of the beamline would have to absorb the major part of the beam power. A proper cooling system, ensuring maximum stability of the beam is needed. The energy resolution should be $E/\Delta E \geq 20000$. The simplest monochromators setup covering the energetic range targeted with good resolution is a normal incidence monochromator (NIM). The use of an aperiodic undulator will help to eliminate higher order harmonics, which are particularly inconvenient at low photon energies.

5.2.- Experimental end-station

The end station will be designed to obtain maximum performance for angle-resolved photoemission. We propose a experimental setup composed of three interconnected vacuum chambers:

- (1) Analysis chamber containing the electron detector.
- (2) A central preparation chamber under UHV conditions, with the usual preparation and characterization techniques, plus STM
- (3) Load lock system for fast entry of external samples.

The electron detector should represent the state of the art in the field, combining high-transmittance and maximum angular resolution (Scienta R4000). In order to exploit the potential of the beamline in terms of energy and angle resolution, a crucial part is a reliable sample manipulator. As mentioned above, one original feature of the beamline is the project to build a UHV sample manipulator with a target sample temperature below 4 K. This manipulator would be specific for band dispersion studies, with ultrahigh angular and energetic resolution. A second manipulator is expected to provide a more versatile environment in terms of degrees of freedom at the sample, but with a higher sample temperature.

A user-friendly preparation chamber will be connected to the main chamber through a flexible transfer system. The prep-chamber has fast load-lock of MBE evaporators and in situ calibration via a quartz microbalance mounted at the same sample stage, as well as LEED and an Ar ion gun pointing to the focus of the electron analyzer. Also an efficient gas admission system and mass spectrometer will be required. An important point that would make the beamline unique is the presence of an STM stage at the prep chamber. The STM can be chosen to be robust and stable for variable temperature measurements in the synchrotron environment (for instance, Omicron type STM). It is a unique characterization tool for the preparation of well ordered overlayers of organic molecules, but also of many other systems of interest.

Annex I: Most relevant publications of the research groups in recent years (2 per group)

1. A. Mugarza, J. E. Ortega, F. J. Himpsel and F. J. García de Abajo, *Phys. Rev. B* **67**, 081404 (2003).
2. A. Mascaraque, L. Roca, J. Avila, S. Drouard, H. Guyot, M. C. Asensio. *Physical Review B* **66**, (2002) 115104
3. A. Mugarza, A. Mascaraque, V. Pérez-Dieste, V. Repain, S. Rousset, F. J. García de Abajo, and J. E. Ortega. *Physical Review Letters* **87** (2001) 107601
4. P. Segovia, D. Purdie, M. Hengsberger, and Y. Baer. *Nature* **402** (1999) 504.
5. C. Rogero, C. Koitzsch, M. E. Gonzalez, P. Aebi, J. Cerda y J. A. Martín-Gago. *Phys. Rev. B* **69**, 045312 (2004)
6. C. Rojas, J. Cerdá, I. Jiménez, M.G. Martín, J.A. Martín-Gago. *Surf. Sci.* **466**, 144-154. (2000)
7. J. E. Ortega, S. Speller, A. Bachmann, A. Mascaraque, E. G. Michel, A. Mugarza, A. Närmann, A. Rubio, and F. J. Himpsel. *Phys. Rev. Lett.* **84**, 6110 (2000).
8. A. Mugarza, A. Mascaraque, V. Pérez-Dieste, V. Repain, S. Rousset, F. J. García de Abajo y J. E. Ortega, *Phys. Rev. Lett* **87**, 107601 (2001)
9. D. Farías, W. Kaminski, J. Lobo, J. Ortega, E. Hulpke, R. Pérez, F. Flores, and E.G. Michel, *Phys. Rev. Lett.* **91**, 016103 (2003).
10. M. Moreno, M. Alonso, J.L. Sacedón, M. Höricke, R. Hey, K.Horn and K.H. Ploog. *Phys. Rev. B*, **61**, 16060 (2000).
11. F.J. Palomares, M. Alonso, I. Jiménez, J. Avila, J.L. Sacedón, F. Soria. *Surf. Sci.* **482-485**, 121 (2001).
12. A. Mascaraque, J. Avila, M.C. Asensio, S. Ferrer, and E.G. Michel, *Phy. Rev. Lett.* **82**, 2524 (1999).
13. M. F. López, A. Gutiérrez, F. J. Pérez Trujillo, M. P. Hierro y F. Pedraza, *J. Electron Spectrosc. Rel. Phen.* **115**, 825 (2001).
14. L. Aballe, A. Barinov, A. Locatelli, S. Heun, and M. Kiskinova, *Phys. Rev. Lett.* **93**, 196103 (2004).
15. L. Aballe, C. Rogero, P. Kratzer, S. Gokhale, and K. Horn, **87**, 156801 (2001).
16. J. M. Ripalda, N. Díaz, E. Roman, L. Galan, I. Montero, A. Goldoni, A. Baraldi, S. Lizzit, G. Comelli, and G. Paolucci, *Phys. Rev. Lett.* **85**, 2132 (2000).
17. J. M. Ripalda, E. Román, N. Díaz, L. Galán, I. Montero, G. Comelli, A. Baraldi, S. Lizzit, A. Goldoni, and G. Paolucci, *Phys. Rev. B* **60**, R3705-R3708 (1999).
18. Y. Huttel et al. *Phys. Rev. B* **68**, 174405 (2003).
19. Y. Huttel et al., *Phys. Rev. B* **67**, 052408 (2003).
20. R. Ramírez, I. Colera, R. González, Y. Chen, and M. R. Kokta, *Phys. Rev. B* **69**, 014302 (2004).
21. R. Ramírez, R. González, I. Colera, and Y. Chen, *Phys. Rev. B* **55**, 237-242 (1997).
22. A. Gutiérrez, M. F. López, A. Hernando, and J. M. Rojo, *Phys. Rev. B* **56**, 5039-5041 (1997).
23. A. Gutiérrez and M. F. López, *Phys. Rev. B* **56**, 1111-1113 (1997).
24. J. Fraxedas, Y. J. Lee, I. Jiménez, R. Gago, R. M. Nieminen, P. Ordejón, and E. Canadell, *Phys. Rev. B* **68**, 195115 (2003).
25. I. Jiménez, L. J. Terminello, D. G. J. Sutherland, J. A. Carlisle, E. L. Shirley, and F. J. Himpsel, *Phys. Rev. B* **56**, 7215-7221 (1997).
26. I. Jiménez, R. Gago, J. M. Albella, D. Cáceres, and I. Vergara, *Phys. Rev. B* **62**, 4261-4264 (2000)