ALBA beamline proposal

LOREA

A beamline for *Low-Energy Ultra-High-Resolution Angular Photoemission for Complex Materials* at ALBA

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1.-Summary

A beamline providing ultraviolet radiation with variable polarisation in the photon energy range 7 – 50 eV is proposed. It will be optimised for angle-resolved photoemission spectroscopy measurements of the electronic structure of solids, surfaces, interfaces, and nanostructures. The proposed beamline will deliver ultraviolet light with state-of-the-art resolution including an experimental end station with specific features for ultra-high (< 1 meV) energy resolution and very-low temperature (T < 1 K). The beamline will provide a versatile and competitive instrument to those scientists in the national and international research communities performing experiments on surface and bulk electronic structure and in the study of the low energy electronic properties of novel complex materials.

Summary of beamline specifications

.- Photon energy: from 7 to 50 eV
.- High flux: > 10^{13} ph/s/b.w. on sample
.- Spot size (H) < 20 μm on sample
.- Monochromator for very high energy resolution (E/ΔE > 20000@20 eV, 50000@50 eV): NIM, PGM or a combination of both
.- High purity and stability of the beam at source and experimental station
.- Electromagnetic quasi-periodic undulator providing variable polarization free from high energy harmonics
.- End-station equipped with:

1. Analysis chamber with

   • an ultra-high-resolution electron analyzer with sub meV energy resolution and angle multidetection.
   • two high-precision manipulators: one of them with sub 1 K cooling (4 degrees of freedom), the other one with sub 10 K cooling (5 degrees of freedom).

2. Pre-chamber equipped with standard preparation and characterization tools

2.-Introduction

The development of high (in the range of meV) and ultra high (below 1 meV) resolution electron analyzers with multichannel angular detection has recently stirred the interest in angle-resolved photoemission spectroscopy (ARPES). Ultra-high-resolution (UHR) analyzers represent a major breakthrough that has allowed ARPES to mature in power and simplicity, reaching the same level as 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 precision[1].

UHR-ARPES has enormous potential in most of the fields of solid state physics. Nominally[2], the energy resolution can be as low as 1 meV and the angular resolution of the order of 0.1º, i.e. $\Delta k \sim 0.001 \times (E\text{-}5)^{1/2} \sim 0.01$ Å^{-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 (E_F) in the whole Brillouin zone. High and ultra-high-resolution 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 as well as self-organized systems.

The impact of UHR-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 UHR-ARPES as well, although it must go beyond a standard system to a more specialized setup. Most of the UHR-ARPES experiments are connected to undulator beam lines that are effectively limited to photon energies beyond 20 eV. **This Outline Proposal describes a UHR-ARPES setup exclusively dedicated to ultra-high-resolution band structure measurements using synchrotron radiation in the 7-50 eV range.** This photon energy range enlarges angular resolution and increases the probing depth range, which is especially attractive for the study of emerging complex systems with large unit cells.

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

[1] See for instance an overview of S. Borisenko's work at http://www.ifw-dresden.de/institutes/iff/research/SC/arpes

[2] T. Kiss, T. Yokoya, and S. Shin, ISSP, Tokyo University, see VG Scienta web page at http://www.vgscienta.com/productlist.aspx?MID=22

experience as frequent users of HR-ARPES in different synchrotron facilities around the world, is not being adequately addressed in most cases. Thus, we plan a flexible but powerful preparation chamber comprising different MBE sources, Scanning Tunnelling Microscopy (STM) characterization and a broad sample temperature range.

3.-Scientific Cases

3.1 Preceding considerations, current status and perspectives

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

A large number of advanced materials have been developed over the last years, able to satisfy specific industrial needs, due to their mechanic or electronic properties. Their new physical and chemical properties provide a basis for promising applications and challenging scientific research. Concerning mechanical properties, 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 fulfil 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 solids[3]. 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.

[3] R. M. Martin, "Electronic Structure", Cambridge, 2004.

In the complex electron systems, the valence electrons self-organize into novel ground states substantially different from those of conventional metals and insulators. Strong electron-electron correlations, in concert with electron-phonon interactions, can give rise to a large variety of fascinating phenomena, the most spectacular being probably Mott-Hubbard insulating behaviour, unconventional and high-temperature superconductivity, and colossal magneto-resistance. From a fundamental point of view, the aim is to understand the underlying microscopic mechanisms responsible for the physical properties of these systems. From the point of view of applications, an active control of those mechanisms would define alternative pathways for the design of new materials and functional devices. The challenge of the experimental research is then to determine the suitability of the current approaches in the quantum theory of solids. This requires investigation of the elementary excitations as they reflect the interplay between the low-energy degrees of freedom and determine macroscopic physical properties such as electrical resistivity, magnetic susceptibility and specific heat.

Based on the photoelectric effect, ARPES measures the energy distribution of photoelectrons at different emission angles with respect to the sample surface normal, thus directly measuring two fundamental quantities for describing the electronic state of a solid, i.e. the energy (E) and the momentum (k). In the language of theoretical physics, ARPES measures the single-particle spectral function, a quantity that describes all the complex interactions of the electron with other electrons, spins and the lattice in a solid. The reader can find a complete description of the technique and its applications in many excellent reviews and textbooks[4].

The ARPES technique has matured in the last twenty years into what is arguably the most powerful probe of the quantum-mechanical state of the elementary electronic excitations within a solid. It provides direct insights on the single-particle spectral function which describes the propagation of an electron in a many-body system. Nowadays, the ARPES technique is essential in elucidating the connection between electronic, magnetic, and chemical structure of solids, in particular for those complex systems which cannot be described within the independent-particle picture. For that reason, considerable efforts have been devoted to improve the technique in terms of energy and momentum resolution. A first instrumental revolution came with the development of very high angle and energy resolution analysers, and their use at synchrotron beamlines. These technical breakthroughs allowed the mapping of the low energy excitations in the reciprocal space and in energy. A new technical development is the achievement of sub meV resolution in the radiation, as for instance in 1^3 beamline at BESSY or Merlin beamline at the ALS. Also the use of laser-like photon sources obtained from the high harmonic generation presents several interesting features, resulting in an important gain in energy and momentum resolution and in the bulk

[4] S. Hüfner, "Photoelectron Spectroscopy", Springer, 1995; "High resolution photoemission", Springer, 2007.

sensitivity with a high photon flux. We envisage laser photoemission as complementary to synchrotron based photoemission: detailed arguments are summarized in an Annex to this proposal.

The goal of this 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 as a flexible sample environment makes it possible to obtain experimental information on electronic properties with unprecedented precision.

3.1.2 Low-Energy High-Resolution ARPES: state of the art of a tool to study complex systems and phenomena

Physics in the 21st century is going 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 behaviour.

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, exhibit 1-2 nm 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 10-1000 nm range and involve excitations in the sub meV range. UHR-ARPES and low-energy (7-50 eV) photons provide the key approach to study electronic states with sub-meV energy resolution and interactions with length scales up to $1/\Delta k \sim 50$ nm (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 behaviour. One good example is high T_c superconductivity, which is now being disentangled with accurate Fermi surface measurements using single crystals and HR and UHR-ARPES.[5,6] The latter is particularly ideal since, despite that the ultimate electron pairing mechanism remains unknown, it is generally agreed that only a minor portion of the Fermi level (E_F) electrons are involved, and that these need to be identified within a generally 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 2 nm for 30 eV photons, but up to 5 nm for 8 eV photons. These limits are crucial for superstructures with relatively large "building blocks", like quantum dots, which are expected to play a role in future molecular electronics[7] and high density recording media[8]. They are now currently achieved by self-assembly on solid surfaces[9,10]. 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 $Å^{-1}$ 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 50 nm. For electron coupling between nano-objects in 50 nm periodic arrays, one can map accurate superlattice bands. For electron confinement within 50 nm 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 intensity[11].

It is known that ARPES is unique to probe all quantum numbers of the electrons in crystalline solid[4]. Thus, as far as crystalline systems are concerned, 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 > 30 eV electrons, where the escape depth has its minimum value of ~ 0.5-0.8 nm. 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 E_F, where the electron escape depth rises to

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approximately 3-4 nm. Furthermore, the extreme high surface sensitivity of the technique in the range 20-30 eV limits ARPES to few materials. In high T_c, the main part of the ARPES studies concerns the BSCO family which has a natural cleavage plane, with minimal charge transfer. But in YBCO (T_c = 93 K), the "surface state" is known to hinder the bulk electronic structure[12] because the surface state of the first CuO_2 bilayer is excessively overdoped[13,14.] In the case of heavy fermions, a typical manifestation of these surface-related changes in the electronic structure of rare earth compounds is the lowering of the core level binding energies, the so-called surface core level shift. However, the surface changes are not only driven by the surface core level shift but also by a decrease at the surface of the 4f hybridisation with the delocalised conduction band[15,16].

In summary, HR and UHR-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 UHR-ARPES is expected to provide, and it is already providing, new insights and fundamental knowledge in hot topics in physics.

3.1.3 ARPES: synergies and outlook

Modern ARPES presents unique features, as its capacity to provide us with direct k-space images of band dispersion as well as constant energy surfaces. As mentioned above, high resolution HR-ARPES has already a demonstrated record of successful results in many different scientific fields. Nowadays, there are two different approaches in the quest for an always better resolution. The first involves the use of synchrotron radiation sources of high brilliance to achieve actual resolutions in the range of 1 meV with photon energy tunability. A second approach is based in using new photon table-top ultraviolet (UV) laser sources, which are already able to reach energies in the range of 7 eV with superb resolution. While lasers of this kind are limited by the quality and availability of energy doubling crystals[17], they offer a compact and efficient source (see also Annex to this proposal). The sub-meV resolution range is changing the ARPES technique and offers new dimensions and possibilities in the investigation of the electronic properties of materials. In parallel, the development of a sub-K cryogenic ARPES setup will open the technique to the world of low temperature physics.

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3.2 The scientific goals: understanding complexity

3.2.1 High energy resolution in cooperative phenomena: superconductivity, metal-insulator 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 (CDWs) 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[18,19.] Detection of these changes requires the advanced capabilities of a beamline like LOREA.

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[20] or RE-FeAs oxides[21.] 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 gap[22]. Indeed, research on superconducting materials using ARPES has provided some of the most important advances on our comprehension of these complex materials. This research has also prompted many technical developments in the field.[23].

Metal-insulator transitions are a particularly fascinating phenomenon, being a type of quantum phase transition that is not yet completely understood. Usually metallicity is determined in an indirect way, for example by studying the density of states at E_F with photoemission, core levels or by measuring the local conductivity with inelastic electrons, non linear optics or scanning probe tecnhiques, although a precise distinction can only be made at 0 K. Conceptually, it is possible to make a distinction between phase transitions of non-interacting electrons (due exclusively to lattice effects), and phase transitions that involve interacting electrons. In the first group the most important examples are the Peierls transition and the Anderson transition due to disorder. In the second group, the Mott transition is the most important case. It is difficult to find out the

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nature of a particular transition unless the band structure and/or Fermi surface of the material is analyzed using HR- or UHR-ARPES:

- Peierls transition gives rise to the formation of charge density waves. The CDW state is a well known collective state in the bulk[24], and it has been observed on surfaces only recently[25]. The stabilization of a charge density wave state by the Peierls mechanism is due to the opening of a band gap in the Fermi surface for some reciprocal space regions that are coupled efficiently by a phonon. When this happens, it is commonly said that nesting is present in the Fermi surface. Electron-phonon interaction is more important in low dimensional systems because in this case it is easier that enough nesting between two Fermi surface portions occurs. This is a critical condition for the stabilization of a charge density wave phase. This feature and the interest in observing new collective two-dimensional states have motivated a lot of studies in this area. The search of CDW systems at surfaces is providing a lot of new information on the properties of the CDW state. LOREA capabilities are optimally suited to cope with this kind of problems, as it will provide photons of high quality on a temperature controlled sample.

- Anderson transition, where charge diffusion becomes zero due to the presence of disorder. It is a localization transition because the disorder caused by impurities is able to change the nature of the electronic states, from spatially extended to localized, even for non-interacting electrons. Its properties are relatively well understood[26].

- Mott transition, due to electron-electron interactions. The Mott state is a unifying concept of great relevance in modern Condensed Matter Physics. It can be defined as an insulating state induced by electronic correlations[27]. Its relevance is due to the fact that physical properties of many interesting materials are controlled by the proximity to a Mott insulator, including organic conductors[28], giant magnetorresistance manganites[29], actinides like Ce or Pu[30] and many transition metal oxides[31]. A question of great importance is how Mott state properties are affected by the dimensionality, since most of these materials are quasi two-dimensional. A good example is the Sn/Ge(111) interface considered in the expression of interest of Section 3.3.6. This surface is metallic

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for temperatures above 30 K and becomes a Mott insulator below 30 K. This transition is characterized by a loss of intensity at the E_F region, detected in the ARPES spectra. The opening of this Mott-Hubbard band gap is acompanied by some renormalization of the valence band.

In summary, electron-phonon or electron-electron interactions generate a broad range of phenomena of large fundamental interest and with potential technological applications. The corresponding energy scales necessary for the electron-phonon interaction and for the electronic correlations are below 100 meV[32] and 10 meV[33], respectively. The increased resolution associated to the use of two-dimensional detectors has enabled access to the range of phenomena related to these transitions. Other accesible properties include interactions with impurities[34] or magnons[35]. All these kinds of interactions can be experimentally analyzed from a careful study of the resulting UHR- ARPES spectra, in particular by comparing them with the situation in which interactions do not show up. As an example, electronic correlation effects are related to localization and modification of the effective mass, while electron-phonon interaction can be studied from the dependence of the surface states width as a function of temperature[36] and/or from the modifications of the dispersion near E_F (appearance of "kinks"). The advanced energy resolution expected from LOREA combined with a low-temperature (sub-K) sample manipulator, is the ideal tool to investigate the new Physics behind these effects.

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Electronic structure and Fermi surface of Sn/Cu(100)-(3√2x√2)R45º
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R. Cortés, A. Tejeda, J. Lobo, C. Didiot, B. Kierren, D. Malterre, E.G. Michel, A. Mascaraque
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3.2.2 Nanoscale systems: electron confinement

Low-dimensional, nanoscale systems are characterized by one or more dimensions (film thickness, surface array periodicity, nanostripe and quantum wire length) that are comparable to the electron wavelength. As a consequence, many relevant properties of these materials are directly affected by quantum phenomena. These include not only microscopic but also macroscopic properties. Metallic quantum wells are among the first nanoscale systems that have been investigated. They are model low-dimensional systems that have demonstrated the big potential of low energy, HR-ARPES to explore electron confinement and its influence in macroscopic properties. In fact, ultrathin metallic films are the simplest realization of a quantum box, and ARPES the most straightforward technique to probe the corresponding spectrum of quantum well levels[37]. On the other hand, it is noteworthy to mention that metallic quantum well states, in particular those at E_F, generally have *s,p*-like nature, and therefore the low-energy photon excitation for ARPES experiments is particularly desirable[37].

The energy spectrum of quantum well levels in a thin film is basically dependent on the thickness. At a fixed energy, e.g., E_F, the thin film behaves as an electron interferometer of atomic dimensions, where the density of states oscillates as a function of the thickness. Such oscillations at E_F, which are best tracked with ARPES[38], are at the basis of the exotic phenomena that have led to novel applications. One good example is the magnetic coupling across non-magnetic spacers[39], at the basis of antiferromagnetically coupled recording media. On the other hand, the presence of quantum well states at E_F is found to interfere in thin film growth in many systems. This is the so-called "electronic growth" phenomenon[40], now being applied to the development of ultra-smooth metallic mirrors[41]. In fact, the oscillations of the density of electrons at E_F due to the presence of quantum well states is reflected in the total electronic energy, which plays an important role in determining the crystalline structure. For a maximum in the electron density at E_F, the electronic energy is higher, and for electron density minima, the electronic energy is lower. During crystal growth, this may give rise to preferred thicknesses, with minimum electronic energy, or avoided thicknesses, with electronic energy maxima. Many other properties of the film are also affected by the reduced dimensionality and the subsequent changes in the electronic density of states at E_F, such as surface reactivity[42] or superconductivity[43]. In general, the electron properties of metals, such as collective states, can always be varied, and even tuned at will, in

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ultrathin film materials. This defines a vast field of research that can be appropriately investigated with low-energy, UHR-ARPES in LOREA.

Research in metallic quantum wells has been lately focused on the role of the interfacial scattering that shapes the quantum well spectrum[44]. It is observed that the electronic properties of the substrate influence the spectra via the energy-dependent reflection coefficient and scattering phase shift of the electron waves at the interface. The most striking example is that of magnetic substrates, which can polarize the spin in non-magnetic metallic quantum wells. The phase shift is actually determined by the substrate band structure, such that the band topology of the substrate is mirrored in quantum well spectra[45]. Interface scattering can also give rise to wave mixing and hybridization of quantum well bands[46]. Interfacial engineering emerges as a way of fine tuning metallic quantum wells, for example by inserting buffer layers[47], or with controlled interfacial roughness (see expression of interest by F. Schiller, section 3.3.10). However, most of these ideas, at the forefront of materials research, remain largely unexplored, since they require both an appropriate low energy ARPES setup and a fine sample and in-situ growth environment, such as the one planned at LOREA.

Beyond thin films, electron confinement in lower dimensions can be realized in nanostripes, atom chains and quantum corrals grown on crystal surfaces [48,49,50,51]. One big advantage of these surface nanostructures is that they can be manipulated and readily visualized by STM, which is also able of mapping the pattern of electron standing waves. ARPES can also map electron wave functions in surface nanostructures[52], while giving a much better description of electronic bands and excitation phenomena[4]. However, ARPES requires arrays of nanostructures with homogeneous size distributions. This can be achieved by vacuum deposition on previously patterned substrates that act as templates. LOREA will feature the appropriate sample preparation environment, including STM characterization, to fabricate fine nano-object arrays. Among the different surface templates, one may use single-domain reconstructed surfaces, dislocation patterns or arrays of steps in vicinal surfaces. One-dimensional nanowire arrays can be obtained on single crystals using (110) oriented surfaces (see expression of interest in section 3.3.7). For one-dimensional systems step lattices are particularly handy, since one can tune the chain spacing via the step lattice constant, i.e., the surface orientation (see F. Schiller's expression of interest, section 3.3.10). For example, one-dimensional metallic chains that exhibit exotic

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electronic properties have been grown using stepped semiconductor surfaces as substrates[53,54,55,56]. Here the substrate type and the lattice constant is chosen to minimize chain to chain coupling, in order to approach the truly one-dimensional behaviour of individual atomic chains. One-dimensional electron confinement by scattering at surface steps is readily achieved in bare noble metal vicinal surfaces[57], which are text-book examples of one-dimensional superlattices being probed with ARPES. Besides the exotic properties found, such as the smooth variation of the confining potential at the steps[57], these surfaces have served to demonstrate the big potential of HR-ARPES to map, with a high accuracy, the electron wave function in a low dimensional object[52].

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Magnetic Nanostructures
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Measurement of electron wave functions and confining potentials via photoemission
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3.2.3 Weakly and strongly coupled molecular networks

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 structures[58]. Also in the field of solar cells the interest is focused on the charge transfer process at the atomic level, which in turn is prompting an increasing

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number of works on ultrathin donor-acceptor structures in intimate contact with metallic electrodes[59] (see expressions of interest in sections 3.3.3, 3.3.4 and 3.3.11). 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 (faceting[60]), co-operative self-assembly of surface atoms and molecules[61], and a host of molecular and supramolecular patterns on an unaltered substrate.

Electronic states in supramolecular structures are ideally investigated by means of HR-ARPES, which provides the accurate energy spectrum of occupied molecular levels. Low-energy, synchrotron radiation is necessary to enhance cross sections in molecular orbitals with atomic *s,p* nature. Molecular levels are thoroughly probed by tuning the photon energy and the light polarization in a synchrotron beam line. This allows the full characterization of molecule-molecule and molecule-substrate bonding in supramolecular structures, namely the geometry and the strength of molecular bonds for molecular units[62]. It is generally found that electronic states in weakly-bound networks are not extended states. They are rather single molecule electron levels, altered by the proximity of the substrate. In this context, ARPES is powerful as a high resolution electron spectroscopy that fully characterizes molecular levels. Nonetheless, ARPES appears particularly promising to investigate the novel phenomena of extended surface states that interact strongly with supramolecular structures, leading to hybrid surface-molecule electronic bands (see expression of interests 3.3.1, 3.3.8, and 3.3.11). Such phenomenon, which is expected to interfere the self-assembly process itself, has been observed in systems with a high technological interest, such as supramolecular nanoporous networks[63] (Section 3.3.8), or donor-acceptor molecular layers[64] (Section 3.3.11). In both cases the surface-molecule hybridization transforms the otherwise featureless surface electron density into a strongly patterned one, with the same motif and (2-3 nm) periodicity of the array. Surface-molecule hybrid superlattice bands are thus expected, and these should be ideally explored with HR- and UHR-ARPES.

In the last decade an extensive research work has been aimed to the exploration and characterization of molecular arrays with weak supramolecular coupling. Nowadays the field is moving rapidly towards molecular structures linked by strong covalent

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bonding[65]. Such interest is fuelled by the necessity of creating more sophisticated surface functionalities, such as molecular machines, by in-situ coupling the previously self-assembled motifs (see section 3.3.11). A variety of molecular precursors and coupling strategies are currently being tested, mainly the thermally activated coupling of supramolecular units, which can be carried out easily in vacuum. ARPES will be unique to explore the conducting electron bands expected for such low dimensional systems. Moreover, π-conjugated molecular structures are text book cases of low-dimensional systems exhibiting the full catalogue of electron correlation phenomena and excitations, such as Peierls instabilities, spinon-holon band splitting, Mott transitions, solitons, polarons and strong electron-phonon coupling[66], i.e., ideal scenarios for high resolution, low-energy ARPES. For example polyacetylene is the best example for a one-dimensional metal with a Peierls distortion, i.e., the single-double C bond. To date, the lack of properly assembled, homogeneous array systems has prevented ARPES to enter this field. Appropriate strategies, such as the use of nanostructured surfaces as templates, are being proposed. In any case, as for molecule/surface hybrid bands, covalently linked molecular arrays are expected to exhibit narrow bandwidths and large unit cells, and hence high energy (1-2 meV, He cryogenics) and angular resolution setups, such as the one proposed in this proposal, will be required

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Self-assembly of heterogeneous supramolecular structures with uniaxial anisotropy
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J. Phys. Chem. B **110**, 25573 (2006)

Spectroscopic fingerprints of amine and imide functional groups in self-assembled monolayers
M. Ruiz-Osés, Th. Kampen, N. González-Lakunza, I. Silanes, Ph. M. Schmidt-Weber, A. Gourdon, A. Arnau, K. Horn, and J. E. Ortega
Chem. Phys. Chem. **8**, 1722 (2007)

Self-assembly of diindenoperylene (DIP) on Au(111) single crystals: crystallographic and electronic structure
D. G. de Oteyza, E. Barrena, H. Dosch, M. Ruiz-Osés, J. E. Ortega, I. Silanes, A. Arnau, B. P. Doyle, and Y. Wakayama
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Tuning the non-covalent interactions relevant for supramolecular self-assembly
D. G. de Oteyza, I. Silanes, M. Ruiz-Osés, E. Barrena, B. P. Doyle, A. Arnau, H. Dosch, Y. Wakayama, J. E. Ortega
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3.2.4 Superlattice bands in surface arrays

The surface specificity and the high angular resolution in state of the art low-energy ARPES systems ($\Delta k \sim 0.01\text{-}0.001$ Å^{-1} for E between 30 eV and 7 eV photons), makes this technique unique to explore superlattice bands in nanostructured surfaces and arrays with extended states and 1-10 nm lattice constants. Such fine systems are characterized by relatively weak electron potentials, and hence relatively narrow superlattice gaps, which need high energy resolution and low temperature setups to be accurately determined. To date, only a few model cases have been explored, such as surface reconstruction patterns[67], strain dislocation networks[68], and step superlattices[69]. Yet, such model systems have demonstrated, on the one hand, a rich phenomenology, such as the likely interplay between electronic states and structures in dislocation patterns and step lattices, but also the clear need for fine ARPES and preparation chamber setups.

One of the big advantages of the in-situ grown systems is the vast number of materials, i.e., atoms, molecules and substrates that can be combined in a search for novel periodic nanostructures with exotic properties. This is a unique scenario for HR-ARPES. Of fundamental interest will be those systems that exhibit "nesting" of the Fermi surface, i.e., systems where the lattice constant matches the characteristic Fermi wavelength $\lambda_F/2$. Such coincidence is naturally expected to prompt structural/electronic energy instabilities in the array, in the same way as CDWs arise in atom chains with half-filled bands. We must note that CDWs systems are always difficult to realize, because the band filling is determined by the chemical potential of the supporting system, and hence the Fermi wavelength can have any value. The in-situ growth of surface nanostructures offers an interesting alternative to the structural/electronic instability problem in low-dimensional systems, namely the ability to smoothly tune the lattice constant in surface arrays, thereby matching the nesting conditions (see expression of interest in Section 3.3.10). A number of strategies are foreseen, such as the growth of surface alloys with smoothly variable stoichiometry, all of them requiring the highly refined sample preparation environment that is planned at the LOREA beam line.

One of the major challenges to the use of ARPES in the context of low-dimensional systems grown on surfaces is the inherent low intensity that characterizes the relevant photoemission peaks. For chain or nanodot arrays, substrate atoms are more abundant and hence the spectral features of the nanostructure are generally obscured by the much stronger substrate emission. So far, the intensity problem has not affected many of the ARPES studies of low dimensional surface nanostructures, since they were focused on atom chains or molecular assemblies decoupled from the substrate. Electronic

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decoupling requires the use of semiconducting or noble metal substrates, characterized by absolute or directional bulk band gaps around E_F, and hence by low background intensity at the relevant energy range. In other contexts, electronic coupling with the substrate may be sought, i.e. if one seeks substrate/adsorbate hybrid bands or magnetic behaviour induced by the substrate in non-magnetic chains. These fields remain completely unexplored. Also novel carbon-related nanostructures, such as fullerenes or graphene nanostripes with *s,p*-like electron levels, require the use of transition or refractory metal substrates, with strong *d*-band emission near E_F that kills the C emission from the nanostructure. In all such cases, the substrate *d*-band in the photoemission spectrum needs to be largely suppressed, compared to the *s,p*-emission from the surface nanostructure. Although this is generally done by tuning the Cooper minima at energies above 100 eV, high photon energies limit the overall resolution of the ARPES experiment. The alternative can be the very low photon energy range, below 8 eV, where the atomic *d*-like wave function cross section is observed to decrease dramatically[70], while energy and momentum resolution reach their maximum values.

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Fermi gap stabilization of an incommensurate two-dimensional superstructure
F. Schiller, J. Cordón, D. Vyalikh, A. Rubio, and J. E. Ortega
Phys. Rev. Lett. **94**, 016103 (2005)

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J. E. Ortega and F. J. García de Abajo
Nature Nanotechnology **2**, 601 (2007)

3.2.5 Fermi surfaces of low-dimensional metallic organic salts

Quasi-one-dimensional and two-dimensional organic salts based on the π-donors TTF (tetrathiafulvalene) and TSF (tetraselenafulvalene) exhibit complex and extremely rich phase diagrams with a variety of ground states (metallic, Mott-Hubbard, spin-Peierls, antiferromagnetic, spin and CDW, superconducting, etc.). Such unusual wealth of competing electronic and structural instabilities, which gives rise to a fascinating low-dimensional physics, continues to attract materials chemists and physicists after more than 25 years. Among the host of synthesized salts, the mostly studied systems have been the quasi-one-dimensional mixed-valence radical cation salts, known as the Bechgaard-Fabre salts, of general formula $(TMTXF)_2Y$, where TM stands for tetramethyl, X = S or Se and Y represents a monovalent anion, and the superconductors based on the BEDT-TTF [bis-ethylene-dithio-TTF] donor.[71]

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Only recently, the surface science community has become interested on such materials and in general on molecular organic materials based on conjugated molecules as linear and non-linear acenes (i.e. pentacene and perylene), thiophenes, phthalocyanines, etc. as well as in supramolecular structures.[72] Very few ARPES studies have been performed up to date and mainly devoted to the quasi-one-dimensional metal TTF-TCNQ [TCNQ = tetracyanoquinodimethane] and to Bechgaard-Fabre salts, with the objective to better understand the breakdown of the Fermi liquid scenario in favour of the Luttinger liquid scenario.[73] However, no experimental determination of their Fermi surfaces has been undertaken.

The LOREA beamline would ideally allow the characterization of the electronic band structure of single crystals of organic salts with unprecedented energy resolution as well as to study the physics of the different phase transitions with characteristic signatures at E_F. The relatively large unit cells, with lattice parameters of about 2 nm, calls for the use of low energy photons. A first example is superconductivity. The highest critical temperature reached so far on BEDT-TTF-based compounds is about 12 K at ambient pressure corresponding to the κ-phase configuration. However, most of transition temperatures are below 8 K. Reaching sample temperatures down to 1 K is thus mandatory. Another example is the characterization of metal-insulator transitions (Peierls, anion ordering, charge ordering) associated to the formation of superstructures. The transition temperatures range from room temperature, for the β-phase of (BEDT-TTF)$_2$PF$_6$, down to few K. In the case of the Bechgaard-Fabre salts the monovalent anions can be either centrosymmetric or non-centrosymmetric. Those salts with non-centrosymmetric anions exhibit anion ordering below a given temperature. Above the transition temperature the anions exhibit random orientations but for sufficiently low temperatures they become ordered. Those salts with centrosymmetric anions exhibit charge-ordering phase transitions. Upon charge ordering the electronic equivalence of the donor molecules is removed below a critical temperature, making the charge disproportionate. In this case no structural modifications have been observed for these salts along the transition, hence deserving the term structureless. A further example of interest is single component molecular metals, as Ni(tmdt)$_2$. The possibility of obtaining such metals was predicted by theoretical work on the so-called two-bands systems by showing that electron transfer could be induced internally between two types of bands of the same component.[74] Internal doping has never been explored with ARPES.

The small size of the single crystals, usually below 1 mm, together with the difficulty of their handling calls for the use of collimated beams. An aspect that has to be taken into

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account is the damage that the beam might cause on such systems and how could be reduced, i.e. by beam defocusing.

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Characterization of the unoccupied and partially occupied states of TTF-TCNQ by XANES and first-principles DFT calculations
J. Fraxedas, Y. J. Lee, I. Jiménez, R. Gago, R. M. Nieminen, P. Ordejón, E. Canadell
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Characterization of the anion-ordering transition in $(TMTTF)_2ReO_4$ by X-ray absorption and photoemission spectroscopies
G. Subías, T. Abbaz, J. M. Fabre, J. Fraxedas
Phys. Rev. B **76**, 085103 (2007)

Long-range repulsive interaction between molecules on a metal surface induced by charge transfer
I. Fernández-Torrente, S. Monturet, K. J. Franke, J. Fraxedas, N. Lorente, J. I. Pascual
Phys. Rev. Lett. **99**, 176103 (2007)

3.3 Expressions of Interest

We present next a list of Spanish research groups supporting the LOREA initiative and a summary of their scientific activities and interests

3.3.1 Electronic and magnetic properties of surface-confined nanosystems

The focus of our research is controlling the interplay of the structural, electronic, and magnetic properties of nanosized systems such as nanoparticles, layered heterostructures, and functional metal-organic materials synthesized in one- and two-dimensional surface-confined environments. We combine STM and spectroscopy with synchrotron radiation spectroscopy in order to link microscopic phenomena to macroscopic observables that are relevant for the understanding and design of new materials and devices. Different spectroscopic techniques are combined in order to obtain a complete picture of the electronic and magnetic properties of the systems under study: magnetic properties are studied by X-ray Magnetic Circular Dichroism (XMCD) whereas a detailed picture of the electronic properties is obtained by ARPES. In particular, ARPES studies can be combined with the local electron spectroscopy performed at the lab with the STM. Due to the increasing interest on metal-organic materials on our group, the high-flux/variable-energy and polarized photon source of the synchrotron is extremely interesting in order to explore the symmetry and hybridization of metallic and molecular states by photoemission, and to observe fine electronic structures derived from the high correlation of electron in these systems such as the formation of Kondo lattices of small band gap openings. The diversity of systems under study, containing both organic and metallic compounds, requires a typical photon energy range from 10 to 170 eV, but focusing more on the low energy side (< 80eV), with a resolution of a few meV. The very low energy limit, below 10 eV, would allow us to maximize the energy and angular resolution near E_F in order to study the fine details described above. Cryogenic temperatures are required in order to measure temperature-dependent phenomena and maximize energy resolution. Spin resolution would also be highly desirable in order to study the spin polarization of the electronic states and correlate it with XMCD measurements.

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Publications:

Supramolecular control of the magnetic anisotropy in two-dimensional high-spin Fe arrays at a metal interface
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Modelling nanostructures with vicinal surfaces
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J. E. Ortega, M. Ruiz-Osés, J. Cordón, A. Mugarza, J. Kuntze and F. Schiller
New J. of Phys, **7**, 101 (2005)

3.3.2 Spin dynamics and electronics in nanomaterials

Our research interests are focused on nanostructures, including nanoclusters and nanoparticulated films, surface nanostructuring by artificial (lithography) and self-organized processes (by homo and hetero-epitaxial growth), ultra-thin films, multilayers and superlattices grown by PLD (pulsed laser deposition) and MBE (molecular beam epitaxy).

Our group has a long tradition (about 20 years) in the use of synchrotron radiation at several European and American facilities (BESSY, LURE, ELETTRA, Max-lab, ESRF and ALS), employing very different photon energy ranges and techniques (photoemission, absorption, dichroism, X-ray diffraction and Microscopy, etc.). Photoelectron spectroscopy with synchrotron radiation in the low energy range (also in the ARPES mode) has been used as a primary technique in our research. Future projects will greatly benefit of the LOREA beam line implementation at ALBA, i.e. allowing studies of low dimensional effects related to electronic properties. In fact, UPS, XPS and their related angle-resolved techniques are available in our group at the ICMM-CSIC.

The desired LOREA technical specifications are: (i) low photon energy range (up to 140 eV, if possible, to include Si 2p core level), (ii) high photon flux and ARPES detector (Scienta-type) with meV energy resolution, (iii) spin detection, (iv) high precision manipulator including LN2-cooling and heating (1300 K) facilities.

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Publications:

Electronic states in arsenic-decapped MnAs (1-100) films grown on GaAs(001): A photoemission spectroscopy study
M. Moreno ,A. Kumar, M. Tallarida, K. Horn, A. Ney and K. H. Ploog
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Observation of a Ferromagnetic-to-Paramagnetic Phase Transition on a Ferromagnetic Surface Using Spin-Polarized Photoelectron Diffraction: Gd(0001)
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Interface Structures of Ordered Fe and Gd Overlayers on W(110) from Photoelectron Diffraction, E. D. Tober, RX. Ynzunza, F J. Palomares, Z Wang, Z. Hussain, MA Van Hove, and CS Fadley Phys. Rev. Lett. **79**, 2085 (1997)

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Surface Photovoltage Effects in Photoemission from Metal-GaP(110) interfaces: importance for band-bending evaluation
M. Alonso, R. Cimino and K. Horn
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3.3.3 Electronic structure of self-assembled monolayers of organic and bio molecules on single crystal surfaces

The determination of the structure of nanometric systems, particularly those related with self assembled monolayers of organic and biomolecules on single crystal surfaces, is an area of continuous growth due to the huge possibilities provided by a control of organic superstructures. Our aim is to relate both structure and electronic properties and our strategy is to combine techniques as DFT or STM, which include atomic and electronic information. ARPES is used by our group to study the evolution of the electronic states at an epitaxially grown thin film interfaces. We study the Fermi surface evolution and how these electronic features are transferred to the STM images. LOREA appears as an excellent tool able to feed-up calculations to elucidate the electronic structure.

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Publications:

A NEXAFS study of nitric oxide layers adsorbed from a nitrite solution onto a Pt(111) surface
M. Pedio, E. Casero, , S. Nannarone, A. Giglia, N. Mahne, K. Hayakawa, M. Benfatto, K. Hatada, R. Felici , J.I. Cerdá, C. Alonso, J. A. Martin-Gago
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J. Mendez, R. Caillard,G. Otero, N. Nicoara, J.A. Martin-Gago,
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Structure of rutile TiO2 (110)-1x2: Formation of Ti2O3 quasi-1D metallic chains
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3.3.4 New materials for organic solar cells

Organic Solar Cells are attracting increasing interest both from the scientific community and the energy markets. The benefits that can be obtained from the fabrication of photovoltaic devices with organic materials come from their inherently low-cost, flexibility, light weight and easy scale up for large area processing that would allow their integration into virtually any kind of surface (roofs, windows, clothing, small electronic gadgets, etc.). However, the main challenges for this kind of devices are the increase of efficiency with respect to silicon solar cells, and the stability or lifetime improvement. Focused in these two points (efficiency and lifetime), one of the main research lines of our group is the development and improvement of organic solar cells. For these goals some conducting polymers are tested: P3OT, P3HT, PCBM, carbon nanotubes, etc, as well as small new molecules. The main tool that we use is scanning probe microscopy (SPM) and related techniques such as Kelvin probe microscopy (KPM), electrostatic force microscopy (EFM) and capacitance force microscopy (CFM). These methods give a detailed picture about not only the morphology but also the electrical properties of the conducting polymers. Besides, our group is capable to perform traditional macroscopic IV measurements with the aim to relate the macroscopic electrical properties with the nanomorphology and the nanoscale electrical properties. However, for the improvement of the actual devices and for the development of new devices with new molecules a complete understanding of the electronic band structure (HOMO, LUMO, bandgap, work function, etc) is necessary, where low energy photoemission plays a fundamental role. Another branch of our research lines is the study of the interaction of semiconductors (Si), metals (Co, Fe) and small molecules (NO, O_2) with metal oxide surfaces, mainly TiO_2. The use of angle resolved photoemission is fundamental to understand the electronic interactions between these adsorbates and the substrate. With regard to the technical conditions of the experiments a photon energy regime between 5 and 100 eV would be desirable, with an energy resolution in the range of meV. In addition, the possibility to cool the samples at cryogenic temperatures at least 4 K would be very interesting for our investigations.

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A. Urbina, *et al*
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3.3.5 Ultra thin alloy and oxide films

We have two research lines that would benefit greatly from the LOREA beamline. One of them is centred on the study of surface bimetallic alloys, and the most recent one is centred on the growth and characterization of ultra-thin oxide films. In both cases, the focus is on the magnetic and chemical activity of the nanostructured materials. In particular, ultra-thin oxide films are a promising field of the study of model catalytic behaviour, where the oxide films can be grown by MBE and characterized by surface science techniques. Magnetic applications of ultra-thin oxides are also a field of extreme interest. On the other hand, in the field of bimetallic alloys we sought to understand the detailed interplay of reactivity/magnetism and film strain state (including the presence of dislocation networks).

We have both a molecular beam epitaxy system and a magnetron sputtering deposition chamber, allowing us to learn the growth procedure for each ultra-thin film. Our main tools are STM, low energy electron microscopy (through collaborations, both spin-polarized and non-spin polarized), X-ray photoelectron spectroscopy, low energy electron diffraction, and Mössbauer spectroscopy. In particular we are extending our Mössbauer experience to UHV in-situ systems.

To complete the characterization of our systems we require angle resolved photoemission spectroscopy. In particular, we want to detect the band-gap opening due to band folding in antiferromagnetic bimetallic alloys, and to be able to follow such opening as a function of composition and thickness down to the atomic level. The same level of understanding will be required in the area of ultra-thin oxide films, where we furthermore expect novel phenomena in adequately characterize films.

With regard to the technical conditions of the experiments a photon energy regime between 5 and 300 eV would be desirable, with an energy resolution in the range of meV. In addition, we would greatly benefit from the possibility to cool the samples at least to 100K, and preferably down to 4 K. Finally, the possibility of selecting the light polarization would be a clear advantage to both our magnetism and our reactivity studies.

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S. Stewart, J.F. Marco, P. Crespo, J.J. Romero, F.J. Palomares, A. Hernando, J.M. González,
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Benito Santos, Juan M. Puerta, Jorge I. Cerda, Roland Stumpf, Kirsten von Bergmann, Roland Wiesendanger, Matthias Bode, Kevin F. McCarty, Juan de la Figuera
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Adv. Mater. **20**, 1760 (2008)

3.3.6 Structural and electronic properties of low-dimensional materials

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 Tc superconductors, colossal magnetoresistance compounds, related compounds (like nickelates or cobaltites), 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 UHR-ARPES. This technique is sensitive to the spectral function and provides information on the properties of the relevant quasi particles. Indeed, an ARPES spectrum is a direct visualization of the spectral function, and its line shape reflects the electron correlation and dimensionality of the system.

The main scientific interest of our group is to investigate the structural and electronic properties of low-dimensional materials. First, we would like to analyze metal/insulator transitions due to electron correlation phenomena in metal/semiconductor interfaces. As second objective, we are interested in investigating laterally nanostructured materials (as vicinal metal surfaces and metal surfaces self-organized by ion bombardment) exhibiting lateral electronic confinement. Both types of systems are suitable to model many other advanced materials, and exhibit complex electronic and structural properties. In order to understand their complex behaviour, the electronic states closest to E_F will be studied. By using ultra high resolution angle resolved photoemission we can gain deep understanding in their spectral density, localized vs. delocalized character, possible correlation effects, etc. Understanding the electronic properties of such complex systems implies in our particular case the study of electronic states close to E_F, and the characterisation of the electrons living there.

Due to the subtle variations we expect to observe in the electronic structure of the systems of our interests, we need to have access to experimental facilities that can provide us with ultra high energy and momentum resolution, as LOREA beamline. This implies both the use of a last generation electron spectrometer (Scienta-type) and of synchrotron radiation light. We have to point out that we would need a photon energy regime between 5 and 100 eV, with an energy resolution in the range of meV. In addition, the possibility of cooling the samples at cryogenic temperatures (at least 10 K) would be crucial too for our investigations.

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3.3.7 Silicon nanowires and nanoribbons

In the quest for electronics on the nanoscale, one-dimensional quantum structures are expected to play a key role[75,76]. Systems that might act as nanowires (NWs) are of major importance, but are rather difficult to prepare experimentally[77]. Such NWs bear great potential to exhibit exotic and attractive physical phenomena[78]. In recent years, several self-organized quantum wire arrays have been grown upon depositing metals on semiconductor[77,78, 79,80,81,82,83] or on metallic surfaces exhibiting regularly spaced steps [84,85]. Given the central role of silicon in microelectronics and the potential occurrence of quantum size effects in silicon-based devices, silicon NWs have attracted considerable interest[86]. However, with respect to procedures used, producing Si NWs with controlled sizes is far from being trivial and aligning them in a well-ordered fashion, a crucial issue, is another problem.

Our group has been involved in the last years in the preparation of massively parallel arrays of one-dimensional, individual, metallic silicon nanowires (Si-NWs) on silver (110) single crystal surfaces. Such NWs exhibit parallel alignment across the entire sample surface with a x 2 periodicity along their lengths (reaching several hundreds of Å along the Ag [1-10] direction) but varying separations in the orthogonal [001] direction when prepared at room temperature. Most of them have the same "magic" width of 1.6 nm. Previous valence band spectra reveal striking quantized states that disperse only along the length of the NWs, confirming their one-dimensional character, while extremely sharp, two-component Si 2p core level spectra are observed. This demonstrates that in the large ensemble each individual NW is a well-defined quantum object comprising only two distinct silicon atomic environments.

One of the main objectives of the group includes a detailed, high-resolution study of the valence band and quantized states of Si NWs that might be ideally performed in the LOREA beamline.

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Physics of Silicene Stripes
A. Kara, C. Léandri, M. E. Dávila, P. De Padova, B. Ealet, H. Oughaddou, B. Aufray and G. Le Lay
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3.3.8 Tailoring quantum well states and the resulting band formation by means of periodic supramolecular porous networks

Complex molecular layers on surfaces with engineered architectures and properties are expected to play an important role in the development of future devices at the nanoscale. A remarkable research effort focused in understanding the molecule-surface and intermolecular interactions involved is currently taking place with the final goal of controlling the self-assembly processes on the surface. But many other issues, such as the electronic interaction of the surface states with the molecular adlayer, need to be addressed to achieve a full control of the self-assembly processes.

The recent finding of electronic confinement of the Shockley state of a noble metal imposed by a self-assembled supramolecular porous network is an experimental demonstration of a textbook quantum mechanical effect which might play a crucial role in engineering future molecular devices. The confinement observed occurs within the molecular network pores. But this confinement has proven to be imperfect, leading to an interaction between neighbouring pores which, due to the periodicity imposed by the supramolecular network, results in an artificial electronic band structure.

The established and prospective possibilities to control the structures of porous networks, together with its characteristic degree of coupling between ad-molecules and the surface state, will be the starting point for the fabrication and investigation of coupled confined electronic systems with tailored band structures. With these studies, one can engineer '2D electronic metamaterials', in analogy to the well-established optical metamaterials. This might provide new insight into the behaviour of molecular guests within porous host networks on surfaces, and the expected influence of the guests on the electronic band structure, which may even induce long-range effects in their host-guest behaviour. Moreover, the resulting electronic bands might play a decisive role in the stabilization of the porous networks themselves.

The execution of this project is based on the use of a state-of-the art ARPES end-station comprising low photon energies (in the range of 15 eV to 100 eV) and high energy and momentum resolution detectors. In this way it will be possible to investigate the existence of higher order sub-bands (which are usually very close to E_F) as well as their dispersion, which is hampered by its smaller reciprocal unit cell related to the larger size of the supramolecular network compared to the underlying substrate.

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Rashba type spin-orbit splitting of Quantum well states in ultrathin Pb films
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Phys. Rev. B **77**, 165431 (2008)

3.3.9 Rashba spin splitting evolution in vicinal surfaces by ARPES

The rapidly growing field of spintronics introduces functionalities in electronic devices that are based on the electron spin. The spin field-effect transistor, as proposed by Datta and Das, is one of such proposed devices which relies on the Rashba–Bychkov effect to manipulate electron spins. Spin rotation is achieved by a field and momentum dependent spin splitting of bands in a two-dimensional electron gas (2DEG). While actual devices are currently realized in semiconductor heterostructures, fundamental issues can be more easily studied in two-dimensional metallic systems involving heavy metal atoms, where spin splittings are much larger.

Au(111) exhibits a so-called Shockley surface state that propagates almost freely within the surface plane and thus exemplifies a 2DEG of nearly-free electrons. Due to the high atomic number of Au, this 2DEG is subject to spin-dependent momentum shifts, induced by the Rashba effect that has its origin in the spin-orbit interaction. The resulting sub-bands have opposite spin directions, which are mainly contained in the surface plane and tangent to the circular constant energy surfaces in momentum space.

A question to be answered is how does the spin structure evolves by introducing defined structural defects on the surface, i.e. when the surface has a regular array of steps. This study would enable to address a more fundamental investigation: what are the mechanisms dominating the spin-dependent scattering processes at defects. These studies would eventually shine some light on spin-dependent transport properties that are at the heart of the new field of spintronics.

The first steps to achieve such goals have been taken by a preliminary investigation of several selected vicinal Au(111) surfaces. Even if high-resolution ARPES has failed to observe the surface state splitting, spin resolved photoemission (SR-ARPES) results obtained at the Swiss Light Source (SLS), shows this characteristic spin structure. The possibility of upgrading the ARPES station by including two orthogonal Mott detectors, in such a way that one would be capable of mapping the three dimensional spin polarization vector for any value of electron momentum, would allow the investigation of such spin-dependent scattering processes at defects. Furthermore, this experimental technique would also allow to study magnetic surface phenomena on more general magnetic systems, which are still not fully understood from the results obtained with other complementary synchrotron techniques such as XMCD or PEEM.

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Surface state confinement imposed by a molecular porous network: Band formation from coupled quantum wells
J. Lobo-Checa, M. Matena, K. Müller, J.H. Dil, F. Meier, L.H. Gade, T.A. Jung, M. Stöhr.
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3.3.10 Tuneable superlattices

The general objective of our research line is to provide an accurate description of the structural and electronic properties of nanostructured systems with atomic resolution. To this aim we utilize a combined STM+HR-ARPES system, especially designed to study complex self-assembled systems, i.e., periodic superstructures with 2-10 nm length scales, and characteristic energies below 10 meV. Such systems are prepared in-situ within the standard surface science approach, i.e., sublimation on single-crystal surfaces in ultra-high vacuum, followed by rapid transfer to analysis chambers without breaking the vacuum. The experiments at our home Lab are complemented with low-energy, ARPES measurements using synchrotron radiation, currently performed at the Synchrotron Radiation Center (SRC) in Wisconsin. Therefore, many of our research projects will enormously profit from a low-energy, ARPES beam line with a state-of-the-art sample preparation environment in Barcelona, which will take over our current activity at the SRC.

Among the investigated systems, we have lately focused our attention on the band structure of metallic superlattices with tuneable lattice constant. In particular arrays of steps on noble metal surfaces (Au, Cu and Ag), smoothly tuned in cylindrical crystals, adlayers grown on such step lattices (Ag/Cu, Co/Au) and strain dislocation networks in metallic monolayers (Ag/Cu, Au/Ni). These systems exhibit an interesting interplay between structural and electronic properties when the lattice constant matches the Fermi wavelength, either in one or two dimensions (the so-called nesting of the 1D and 2D Fermi surface, see recent publications in our group). We plan to extend these studies towards more sophisticated systems, such as oxide layers on stepped surfaces, and generalize the structural/electronic interplay problem in two-dimensional strain dislocation lattices by tuning the stoichiometry in surface alloys. In summary, our potential scientific activity in LOREA will comprise the following topics:

1.- Non-metallic templates for one dimensional conducting wires. These comprise very thin layers (and ultimately, monolayers) of oxides of technological interest, such as rare earth oxides and rutiles, and insulators, such as alkali halides and nitrides, on vicinal metal surfaces, such as noble metals and platinum. Using curved crystals we will explore different crystal planes to tune substrate/template lattice matching, with the aim of obtaining atomically sharp oxide interfaces and smooth, flat surfaces.

2.- Metallic templates for magnetic quantum dot and wire structures. Here we plan to produce strain dislocation lattices by growing surface alloys, with smoothly varying stoichiometry and thickness to tune the superlattice constant. Such dislocation networks are then utilized as nanostructured templates for further growth of magnetic dot lattices (2D networks) and wires (uniaxially strained templates).

3.- Interplay of electronic states and structures in tunable, self-assembled metallic superlattices. In this topic, our two strategies are:

a) One-dimensional Fermi surface nesting of surface electron bands via step lattices in noble metal surfaces and noble metal adlayers grown on top, using curved crystals.

b) Two-dimensional Fermi surface nesting in noble-metal-based surface alloys with strain dislocation lattices, such as those obtained in binary noble metal mixtures, as well as in ferromagnetic/noble metal and rare earth/noble metal alloys, using wedges with smoothly varying stoichiometry.

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J. Phys. Cond. Matt. (submitted).

3.3.11 Coupled and hybridized molecular networks

We investigate supramolecular monolayer assemblies using STM and photoelectron spectroscopies, namely XPS, NEXAFS and ARPES. The latter are carried out in synchrotron radiation laboratories, such as ELETTRA, ALS and BESSY. In the context of supramolecular structures, our electron spectroscopy studies provide us the fundamental electronic fingerprints of the systems. Our objective in the future is double. First, we will go beyond the weak molecule/molecule interaction towards the formation of strong covalent bonds. Second, we will extend (see publications) our studies to molecules with potential interest in solar energy applications, such as mixtures of donors and acceptors.

The creation of surface-based molecular machines and devices is a fledgling area and, to date, only single-function components, ranging from individual switches, rotors and linear drives, have been successfully positioned at surfaces. To go further and fabricate a sophisticated "molecular machine" it is imperative to couple different blocks that exhibit specific functions. The major route forward is to interconnect all these molecules in a controlled way directly on a surface. Studies of covalent interlinking of molecules adsorbed on a substrate have been scarce, but in the past year an increasing number of works have been published, all reporting the successful covalent linking of molecules at surfaces to create robust nanostructures. Some of them show that aromatic or benzylic radicals, namely the type of structures we have been investigated in the past (see publications below), can be prepared directly at a surface by thermal activation of starting functional blocks, which subsequently couple via single or double C-C bonds, without any substrate-C bonding. In collaboration with Gourdon's Synthetic Chemistry group in Toulouse, we plan to synthesize and utilize molecules specific functional groups, which are likely to form covalent bonds upon annealing in-situ. Using the low-energy, UHR-ARPES in LOREA, as well as the advanced preparation setup (sample transfer, cryogenics), we plan to look into delocalized bands of such in-situ polymerized molecular networks, where we expect exotic phenomena, such as strong electron correlation effects.

The efficiency of charge carrier separation from photogenerated excitons in organic solar cells is determined by the interface of the organic p-n junction. However, little is known on the electronic structure at such interfaces. We intend to fill this gap studying binary donor/acceptor monolayers with electron spectroscopies. The general aim is to study electronic states and their dependence on the crystalline structure and on the composition of the donor/acceptor interfaces, as a way to understand interface energetics, intermolecular interactions and charge transfer processes. In particular we will study structured mixtures exhibiting strong interaction with the metallic substrate. For them we expect the appearance of new hybrid surface bands and fine effects, such as minigaps and exotic excitations, which can only be investigated with HR-ARPES.

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4.-Spanish users' community: requirements, opportunity and need of a low energy photoemission beamline at ALBA

The Spanish community interested in low-energy ARPES is very active, with significant performance records, broad experience in using synchrotron radiation facilities and a demonstrated expertise in the field. 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.

We show in the following a list of expert users, 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, whose main research interest is related to ARPES. A second table includes a list of occasional or potentially interested users, together with former users of the Spanish-French ARPES beamline at LURE, which operated between 1990 and the shutdown of the facility in 2002.

Selected recent publications of the groups supporting this proposal are quoted along the scientific cases and expressions of interest

4.1 Impact of LOREA in the Spanish scientific community

An important argument for the construction of LOREA is its expected impact in the users community, and the capacity of this community to efficiently exploit in first instance the features of LOREA. We think that the users 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. Furthermore, a complete picture of the proposed experimental systems to be studied can hardly be obtained without a complementary theoretical study. The users community will indeed benefit from the close proximity to reputed Spanish theory groups with broad experience in the analysis of the electronic structure of solids.

The Spanish ARPES community has a significant number of potential users, including both scientist who frequently make use of laboratory-based photoemission apparatus, but who have not yet been introduced in synchrotron radiation facilities, and also groups

able to grow complex, single-crystalline materials, who are interested in understanding their electronic properties. A national facility will have a strong impact in both communities. This has been the case in many other countries and it is also our own experience during the years of operation of the French-Spanish ARPES beamline at LURE, which promoted a lot the use of ARPES in Spain and helped to create nowadays' well established users community.

List of experienced users of ARPES explicitly supporting this proposal

Name and email	**Number of experienced researchers**	**Domain of research**	**Affiliation**
J.E. Ortega ortega@sq.ehu.es	4	Electronic states in nanostructures	Nanophysics lab-San Sebastián
E.G. Michel enrique.garcia.michel @uam.es	2	Electronic structure of surfaces and interfaces	Dto. Fís. Mat. Cond. Univ. Autónoma de Madrid
J. Fraxedas jfraxedas@cin2.es	2	Molecular organic materials	CIN2 (CSIC-ICN)
A. Mugarza aitor.mugarza.icn@uab.es	2	Electronic and magnetic properties of surface-confined nanosystems	CIN2 (CSIC-ICN)
M. Alonso malonso@icmm.csic.es	4	Electronic and magnetic properties of surface-confined nanosystems	Instituto Ciencia de Materiales de Madrid-CSIC
J.A. Martín Gago Gago@icmm.csic.es	4	Electronic structure of self-assembled organic and biomolecules	Instituto Ciencia de Materiales de Madrid-CSIC
José Abad jabad@um.es	3	Organic solar cells Interaction of small molecules with oxide surfaces	Universidad de Murcia
A. Mascaraque arantzazu.mascaraque @fis.ucm.es	5	Electronic structure of low-dimensional materials	Universidad Complutense de Madrid
M.E. Dávila mdavila@icmm.csic.es	1	Surface electronic structure	Instituto de Ciencia de Materiales de Madrid-CSIC
Jorge Lobo Jorge.lobo@unibas.ch	1	Supramolecular porous networks Rashba splitting	CIN2 (starting April, 2009, now at Univ. of Basel, Switzerland)

List of occasional users of ARPES and of former users of the French-Spanish ARPES beamline at LURE (excluding those already listed above)

Name and email	Domain of research	Affiliation
Inmaculada Colera icolera@fis.uc3m.es	Oxide surfaces	Universidad Carlos III de Madrid
A. Gutiérrez a.gutierrez@uam.es	Nanoparticles of oxides	Dto. Física Aplicada, Univ. Autonoma de Madrid
I .Jimenez ijimenez@ictp.csic.es	Band structure of light element materials	Instituto de Ciencia y Tecnologia de Polímeros-CSIC
Y. Huttel yves@imm.cnm.csic.es	UPS of magnetic nanoclusters	ICMM-CSIC
L. Galán luis.galan@uam.es	Secondary electron emission	Dto. De Física Aplicada, Univ. Autónoma de Madrid
J.F. Sánchez juan.f.sanchez@uv.es	2D systems, II-IV valence band	Univ. de Valencia
J.Fontcuberta fontcuberta@icmab.es	Electronic properties of manganites	ICMAB-CSIC, Barcelona
A. de Andrés ada@icmm.csic.es	Electronic properties of magnetoresistive oxides	ICMM-CSIC, Madrid
C. Palacio carlos.palacio@uam.es	Valence band of transition metal oxides	Fac. Ciencias, Univ. Autónoma de Madrid
L. Soriano l.soriano@uam.es	Electronic properties of NiO	Fac. Ciencias, Univ. Autónoma de Madrid
J.R. Ramos Barrado barrado@uma.es	Oxide thin films	Univ. de Málaga

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

ARPES beamlines are found in almost all third generation synchrotrons. Table I summarizes the main features of other ARPES beamlines in European synchrotron radiation facilities with technical features similar to ALBA. An inspection of the Table immediately revels that most current ARPES beamlines try to access an energetic range as broad as possible, in general reaching photon energies above 800 eV, except for the BaD ElPh at ELETTRA. This offers a larger spectral range, and it opens the possibility of probing core levels. However, the broad photon energy range decreases the efficiency of these beamlines in the extreme (lowest and highest) photon energies, and in practice none of this beamlines is really competitive in the whole nominal spectral range. Very few BLs offer competitive experimental conditions in terms of photon energies below 40 eV, and competitive ancillary facilities, like cryogenic sample manipulators with several degrees of freedom, sample preparation facilities, etc. The consequence is a large oversubscription of these beamlines. One beamline in Europe (1^3 at BESSY) is addressing the goal of sub-meV resolution below 100 eV combined with cryogenic facilities. The combination of these features in a single scientific instrument, as argued above, is opening new areas of physics, as demonstrated by the success of both the 1^3 beamline and by the similar setup at the ALS (Merlin beamline).

In view of these considerations we conclude that the specific technical features of LOREA represent an area of research of growing impact and with a high present and future demand. Furthermore, in terms of opportunity, this area has not been sufficiently developed due to different reasons, but mainly because most PES beamlines try access a too broad spectral range. Due to this fact, we foresee that LOREA beamline will have a strong impact in a rapidly developing area of current and future importance.

5.1 Impact of LOREA in the European scientific community

LOREA is intended to be a complement to similar experimental stations conceived for low photon energy photoemission, as 1^3 at BESSY, SIS at SLS, MERLIN at ALS and BaD ElPh at ELETTRA, and as such should be a reference at the international level due to its optimization in the 7-50 eV range, encouraging external users to perform their experiments. As already mentioned, high quality ARPES beamlines in European synchrotrons are heavily oversubscribed. There is a growing demand for instruments providing state-of-the-art resolution with enough flux for the investigation of an always increasing range of novel materials. This proposal collects Expressions of Interest of Spanish colleagues only due to the fact that ALBA is a national facility and we

preferred to provide a detailed view on the interests and needs of the Spanish community. However, there is a large community of European users who will move to any instrument offering better features in terms of flux or resolution, as demonstrated recently by the successful operation of SIS beamline at the SLS, for instance. We foresee that as soon as LOREA provides its expected specifications, it will be one of the instruments of choice for the large European community working in low-energy high-resolution ARPES. LOREA and the few beamlines providing an environment of comparable quality will become the home for breakthrough experiments in the variety of physical problems described before.

Facility	**Beamline**	**Techniques**	**Monochrm.**	**Energy range (eV)**	**Polariz.**	**Status**	**E/ΔE**	**Spot size(μm)**	**detector**
ALBA	**LOREA**	**ARPES**	**NIM/PGM**	**7-50**	**Variable**	**This proposal**	**10^4**	<20	**Scienta**
SLS	SIS	ARPES,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	VUV	ARPES,XPS, PhD	PGM	17-900	Linear	In operation	10^4		Scienta R4000
	BaD ElPh	ARPES	NIM	4.6-40	Linear	In operation	10^4		Phoibos 150
	BEAR	ARPES, PES, PhD	NIM (4-40) PGM (40-1400)	4-1400	Bending magnet source	In operation	$5x10^3$	30x100	Hemisph. on goniometer
	APE	ARPES,XPS, XAS, Dichroic PES	4 PGM	10-100 100-2000	Variable	In operation	10^4	50x100	Mott and Scienta
SOLEIL	CASSIOPE E	ARPES,XPS, XAS,FSM Dichroic PES	4 PGM	10-1000	Variable	In operation	10^4	50x50	Mott and Scienta
	ANTARES		4 PGM		Variable	Planned	10^4		
MAXIII	I4	ARPES	SGM	15-200	Linear	In operation	10^4	25x100	Scienta SES200
		ARPES, spin resolved	NIM	5-50	Variable	In operation	10^5	200x300	Scienta, spin detector
BESSY II	U112/PGM2a	ARPES, 1cubed	PGM	4-200	Variable	In operation	10^5		Scienta

Table1.- Main figures of merits of undulator beamlines in other European 3rd generation synchrotron radiation facilities. Information provided by the facilities

6.- Beamline layout and requirements

We present in this Section the most relevant parameters to be considered in the final design. The detailed design will have to be decided, if the proposal is approved, taking into account several parameters not know at the moment, as the length of the straight section available (either 4m or 8m).

The scientific cases mentioned above require a beamline with ultra-high photon energy resolution and able to provide a high flux in the low photon energy range (7-50 eV for most applications). The main chamber should be equipped with a high-resolution electron spectrometer (Scienta R4000 or similar), with a demonstrated resolution in the meV and sub-meV range. The standard manipulator to be equipped with a He flow cryostat and a high precision sample rotation stage will be mounted on the experimental station. The standard manipulator should allow angle resolved measurements over 2π stereo radian down to $T < 10$ 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 equipped with a commercial STM for structural analysis.

A very important feature related to meV photon/electron energy resolution is the sample temperature. Thermal broadening at 10 K is approx. 1 meV. This means that when this level of energy resolution is reached, an equivalent level of sample temperatures below 5 K must be achieved. This range means an important step forward in ARPES, since most experimental setups worldwide are limited to 10 K, and only a few (1^3 beamline in BESSY, Merlin in the ALS) are reaching sub-K temperatures. This is due to the fact that achieving lower temperatures poses significant experimental problems, i.e. an excellent thermal contact must be guaranteed after sample transfer, thermal radiation shielding is needed to reach temperatures below 10 K, and a He^3 dilution cryostat is required for the sub-K range. This is a proven technology in Low Temperatures Laboratories, but its combination with the ultra-high vacuum as well as the photoemission requirements of an ARPES beamline has been achieved only very recently. Using the expertise in the field of several of the groups involved in this project, we propose the construction of a specific sample manipulator designed to reach sample temperatures below 1 K and suitable for UHR measurements. Beside this, commercial solutions are nowadays available for such sample cryostats, if required.

6.1 Source and optics

The beamline is required to deliver monochromatic photons from at least 7 to 50 eV. Both photon flux and energy resolution are to be optimized in the design of the source and the beamline.

The source: the UHR requirements demand a high brilliance source, so that the use of a bending magnet is discarded vs. an undulator, the latter being able to cover the range of energies with maximum brilliance. The features required for the source can be summarized in the following points:

1.- Photon energy range : 7 eV - 50 eV using the 1st harmonic
2.- High harmonic rejection to have very good spectral purity, i.e., using a quasi-periodic undulator
3.- Variable polarization (vertically/horizontally linear polarization; circular polarization with left/right-handed helicity; all polarization rates >90%)
4.- Helicity switching. The speed of the switching does not seem to be critical, but similar Soleil devices (e.g., HU640 undulator) flip at 1 Hz.
5.- Photon flux in the range of 10^{14}-10^{15} photons/sec./0.1% b.w.

In view of the ALBA storage ring energy (3 GeV, somewhat above the values in similar 3rd generation sources, but typical for a medium-energy storage ring), a long electromagnetic undulator will probably be the best option due to the large magnetic period length required for the above rather low photon energy range. The medium straight section (4 m long) or the long straight section (8 m long) of the storage ring would be the possible choices. One of the three still available 8 m straight sections will certainly be a more attractive location due to the larger number of magnetic periods and thus enhanced brilliance of the insertion device, as required for such a high-performance beamline. As mentioned above, a quasi-periodic undulator magnet structure would be of importance for achieving high spectral purity from the source side (see below).
As a comparison, the HU640 undulator of Soleil (storage ring energy 2.75 GeV) of electromagnetic type provides photons in the 5-100 eV range using the first harmonic, circular as well as full linear polarization (at any orientation), and has a length of 10 m. Keeping circular polarization and full linear polarization for the horizontal/vertical direction *only* will allow reducing the period length and thus facilitate the accommodation of such a device with more magnetic periods at a given length in one of the straight sections. While details will have to be defined later, the device is clearly feasible.

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 ensure sub-meV resolution below 50 eV, i.e. $E/\Delta E > 20000$ (50000) for 20 eV (50 eV) photons. The simplest monochromators setup covering the targeted photon energy range (7-50 eV) with good resolution is a normal incidence monochromator (NIM). The use of an quasi-periodic undulator will help to eliminate higher order harmonics, which are particularly inconvenient at low photon energies. The NIM setup has significant advantages, as a demonstrated design and very high resolution at low photon energies. In turn, it has a rather low upper cut-off energy (50 eV maximum).

On the other hand, combined NIM-PGM setups reaching an extended photon energy ranges of about 4-200 eV and 10-800 eV, respectively, have been successfully installed at the 1^3 beamline at BESSY II and at the SIS beamline of the SLS. Thus, there are several design options that can fit with the target technical specifications. A final decision will be made taking into account the actual energy range provided by the undulator and the fact that the primary interest of the beamline is focused in the low energy range (7-50 eV). The sample spot size (H) should be <20 μm. As the analyzer acceptance is approx. 100 μm, bendable defocusing optics should be included in order to allow a continuous increase of the spot size up to ca. 100 μm. Defocusing, as made possible by bendable refocusing mirrors, will be mandatory when working with organic molecules in order to reduce beam damage.

6.2 Experimental end-station

The end station will be designed to obtain maximum performance for ARPES. We propose an 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 (i.e. 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 1 K. This manipulator would be specific for band dispersion studies, with ultrahigh angular and energetic resolution and will use a commercial He^3 cryostat adapted to UHV environment. A second manipulator is expected to provide a more versatile environment in terms of degrees of freedom at the sample, with a higher sample temperature, but still in the < 10 K range.

A user-friendly preparation chamber will be connected to the main chamber through a flexible transfer system. The prep-chamber will have a fast load-lock of MBE evaporators and in situ calibration via a quartz microbalance, as well as LEED and an Ar ion gun. Also an efficient gas admission system and mass spectrometer will be required. An important point is the presence of an STM stage at the preparation chamber. The STM can be chosen to be robust and stable for variable temperature measurements in the synchrotron environment (for instance, Omicron type or Aarhus 150 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.

6.3 Estimated budget

The part of the budget concerning the undulator, front end and valves will strongly depend on the final straight section used and the technical solution adopted, and thus it should be fixed by ALBA in due time.

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

Undulator + front-end valves and all UHV:	to de defined
Beamline: First mirror, entrance and exit slits, monochromator, refocusing optics, and all UHV accessories:	1500
Electron energy analyzer:	350
He^3 cryostat	200
First UHV manipulator	100
Second UHV manipulator	200
Chamber and UHV ancillary equipment	150
Prep-chamber and ancillary equipment	150
STM prep chamber	200
Support frame, bakeout system	50
Total estimation:	2900 k€

Annex: Laser-based *vs.* synchrotron-based photoemission

In recent years, a new tool for UHR photoemission has been developed. As mentioned above, in order to extract physically meaningful information from an ARPES experiment, the energy resolution must be lower than the relevant excitation energies. A novel UV high flux high-resolution photon source is being used since several years, namely UV laser radiation using higher harmonic generation. The field of high harmonic generation (HHG) is a method for generating laser-like light from the ultraviolet down to the extreme ultraviolet[87], and new UV photon sources are arising from its fast development. Already several groups have developed a laser-based angle resolved experiment by using a quasi-CW VUV laser at 6-7eV [88,89,90,91]. The use of a laser light source certainly has many advantages with respect to other sources:

- UV laser light provides an overall energy resolution better than 1 meV with a photon flux per second of about 10^{15} which is nearly one order of magnitude higher than that available from undulators at third-generation synchrotrons. At the same time, the laser has a great advantage in the small natural width of light (~0.260 meV) without sacrifying total photon flux numbers.

- Due the low photon energy, the gain in momentum resolution is also very significant. To get an idea, the momentum resolution at 6 eV is roughly a factor of 8 better than at 52 eV. For this low energy the enhancement of bulk sensitivity is also very significant. These two features are not specific of the laser light, but of the low photon energy. Finally, laser-based photoemission is a laboratory technique, i.e. it does not require beamtime application and, though expensive, it offers good features.

The 6-7eV laser-based ARPES instrumentation has significant limitations:

- From the momentum conservation law, the part of the k-space accessible decreases at low photon energy. This means that materials with a large Brillouin zone can hardly be investigated and even for materials with a small Brillouin zone, only the central part is accessible.

- The energy of the photon can not be tuned like in the synchrotron. This is a severe limitation, especially below 10 eV, where cross section effects can

[87] R. L. Sutherland *et al.,* Handbook of nonlinear optics (2nd ed.). New York: Marcel Dekker (2003)
[88] J. Korolek *et al.*,. Rev. Sci. Instrum. **78**: 053905 (2007)
[89] Guodong Liu *et al.*,. Rev. Sci. Instrum. **79**: 023105 (2008)
[90] T. Kiss *et al.*, , Rev. Sci. Instrum. **79**, 023106 (2008)
[91] S. Matthias *et al.*, Rev. Sci. Instrum. **78**, 083105 (2007)

completely change the distribution of intensity between valence band states. There are already some examples showing the importance of energy tunability in the sub 10 eV range.

In view of these advantages and disadvantages, it is clear that lasers are becoming the source of choice for laboratory based experiments, but still have too many limitations to overcome the possibilities of synchrotron-based photoemission at 3rd generation sources. In fact, the most important problem of many photoemission beamlines in operation is not derived from an intrinsic limitation of synchrotron photoemission, but rather by the fact that the beamline was asked to provide a too large range of photon energies (from 15 to 1500 eV in some cases), thus decreasing the overall performance both at low and high photon energies. On the contrary, more specialized beamlines focussing only the low photon energy range are not only competitive with laser photoemission, but much more powerful due to the broader range of photon energies available as compared with laser-driven HHG sources. Nevertheless, an additional laser-based photon source may be considered as a future additional and complementary photon source on the same ARPES setup once that the required HHG crystals will become widely available.

List of frequently used Acronyms

- **ARPES:** Angle Resolved Photoelectron Spectroscopy
- **CDW:** Charge Density Wave
- **E_F:** Fermi Energy
- **HR-ARPES.** High-Resolution ARPES
- **NIM:** Normal Incidence Monochromator
- **PGM:** Plane Grating Monochromator
- **STM:** Scanning Tunnelling Microscopy
- **UHR-ARPES:** Ultra High Resolution ARPES