

NEEDS AND REQUIREMENTS FOR HARD X-RAY ABSORPTION SPECTROSCOPY BEAMLINE(S) IN “ALBA”

Working party*

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* Apart from the working party listed above, this document has been the result of the contribution of several other scientists from the Spanish user community and from abroad. Their suggestions and corrections have been invaluable and this note would like to be recognition to their work

Executive Summary

This report contains a short summary of the scientific cases that are intended for investigation by X-ray absorption Spectroscopy (XAS) in the synchrotron ALBA. This project is the result of the contribution of the very large scientific community making use of this technique in Spain. At present, more than 40 scientific groups (30 of them with reported publications) with four permanent scientists on average are currently using this spectroscopy, while several other have expressed their interest in becoming users in a near future. Very likely, this constitutes the largest scientific community of SR users in Spain. The scientific problems that are dealt with XAS define a large span of cases in the fields of materials, chemistry, environmental and earth science, biological sciences, magnetism and high pressure behaviour.

Depending on the scientific case, different detection systems and sample environments are required for recording high energy XAS spectra. This imposes different beam requirements and experimental conditions. The most usual measuring conditions and beam requirements are discussed and compared with those of similar facilities in Europe and, in particular, in relation with the SPLINE beamline to be in operation at the ESRF in a near future. Based on this analysis and on the interests of the scientific community, their present activities and, particularly, the most advanced and interesting developments envisaged for the future, the construction of three different beamlines is proposed. These beamlines, ordered according to their priority in time, are the following: (a) *high resolution chemical and magnetic spectroscopy*, (b) *microfocus* and (c) *time resolved*.

A description of approximate beam parameters and other specific features is made for each one of these beamlines. The *high resolution chemical and magnetic spectroscopy* beamline should provide service to the large scientific community making use of standard XAS (though with the most advanced designs for sample environments and detection systems) and, simultaneously, enable the implementation of innovative techniques to perform XES (X-ray emission spectroscopy) and XMD (X-ray magnetic dichroism) at the highest level. These two later techniques will be key features of the proposed line enabling experiments at the frontier of the knowledge within this topic. A *microfocus* X-ray beamline will provide a tool element specific with a high spatial resolution to study complex multicomponent systems. The energy dispersive set-ups of the *time resolved* beamline will allow studies of fast chemical reactions and structural characterization under extreme conditions. These three beamlines, as a whole, will provide the X-ray spectroscopy community in Spain an optimum framework to apply the expertise already acquired by using foreign SR sources.

1. Introduction

Over the past decades the Spanish scientific community has been developing a great activity in the field of X-ray absorption spectroscopy (XAS) in the hard X-ray energy region¹. Since the early eighties Spanish researchers began to exploit the X-ray absorption spectroscopy at the synchrotron sources available at the time, like FRASCATI (Italy) and DCI (France). Since then, the number of research groups active in the area has been continuously increasing. Each of these new teams of researchers contributes to the ever increasing range of applications of XAS. Nowadays the profile of this community is very wide and covers a large span of research topics. Very likely, the Spanish XAS user community constitutes the most numerous and diverse group among all the researchers interested in Synchrotron radiation (SR). A clear example of both the tradition and size of this community is the *Annex 1* of this report, where the active research groups, their area of research and their current interest in the use of XAS are listed. Similarly, in *Annex 2* a selection of published work has been included.

Data in *Annex 1* and *2* evidence the maturity of the XAS community as well as its capacity to undertake more ambitious projects in the future. The proposal of beamlines made in this report is the result of several discussions held within this community. These have shown a clear commitment of all the scientists interested in these topics to support the construction of several beamline(s) in ALBA for XAS experiments. An important number of these researchers and groups would be also interested in actively participating in the construction of beamlines and/or the final experimental stations. The meetings in Malaga (5-6th Feb 2004) and Sevilla (1st October 2004) have been important milestones for the elaboration and discussion of this document. The proposal is, at the same time, realistic and ambitious. It is realistic because it is the result of a combination of the present interests and topics of existing XAS users. However, it is also ambitious because it has considered the future developments and tendencies that, even if they are in some cases at the beginning of their development, will be able of generating significant¹²⁰ scientific interest in the near/medium future.

This report outlines the scientific cases that will be addressed in ALBA by means of XAS. It contains a general description of the technical requirements that are needed to perform the corresponding experiments. These requirements refer to different aspects of the experiments: beam characteristics, detection systems and sample environments. Although the most critical one for the aim of constructing a XAS beamline is the beam characteristics, the two others are also of outstanding importance to exploit at maximum the capacity of innovation of the research to be conducted in the beam line. Therefore, the description of the scientific cases presented in this document is accompanied by a general enumeration and, when pertinent, description of beam parameters (e.g., available photon energies or flux), detection systems and sample environments. Since the realization of all scientific cases with the optimum conditions will require beamlines with different characteristics, schemes for more than one beam line are proposed and a priority order is given. Priorities are established after considering the best options for the proposed

¹ Note that the proposal here addresses only the hard (or mildly hard) X-rays range. The softer X-rays range (e.g. below ca. 2000 eV) is as well undoubtedly of great interest for absorption spectroscopy, but since the physico-chemical systems and the instrumentation involved in this case are rather close to those of surface physics, separate proposals in that direction are being prepared by other group(s).

experiments and their compatibilities, as well as the future needs that will enable the community to perform new and more advanced research.

This report is organized as follows: first a description of the scientific cases that will be addressed in ALBA by the Spanish users, then a report on the user's community. Afterwards, a description of the required detection systems and sample environments needed to solve the proposed scientific cases. The alternative sources in Europe and a description of the proposed beamlines and their respective priorities are also extensively discussed. For the first beamline, that having the highest priority for the scientific community, a detailed description of its characteristics is accompanied by a description of the new and most advanced techniques that should be implemented. These techniques will bring this beamline to the frontier of knowledge and make it the most appealing for new developments.

2. Scientific cases of relevance for hard XAS from the perspective of the Spanish scientific community

X-ray spectroscopy (XAS) is one of the most versatile techniques based on synchrotron radiation. It provides a direct insight into the electronic structure and local environments at an atomic level around the target atoms. The work spans from magnetism to the description of the collective behavior of electrons, encompassing catalysis nucleation, materials science, environmental and earth science, trace analysis or biological systems.

A list of scientific topics where the use of hard XAS is of relevance and hence justified is listed below. This list is not necessarily complete but provides a clear view of the importance of this spectroscopy for a large variety of scientific topics. Since a full account of all of them is beyond the scope of this report, in the next section of this document only a selection of topics are discussed in some detail with the only purpose of stressing their importance and relevance for the scientific community.

Materials

Thin films and coatings

Ionic conducting oxides and materials for batteries

Biomaterials

Nanomaterials

Glasses and amorphous solids

Structure of the liquid state and molten salts

Optic and electronic materials

Ceramic and metallurgical materials

Chemistry

Solid state chemistry of novel compounds

Catalysis (homogeneous and heterogeneous)

Coordination compounds in solution

Electrochemistry and corrosion

Kinetics of fast chemical processes and photochemistry

Magnetism

Superconductors

Manganites and other magnetoresistance compounds

Magnetic alloys and metallic glasses

Rare earths ionic and semi-ionic compounds

Molecular magnets
Spintronics compounds

High pressure behaviour

Earth core simulation
Phase and metal-insulator transitions
Equation of state and atomistic parameterization studies

Environmental and earth science

Toxic ions speciation
Radionuclides

Biological science

Metalloenzymes and metalloproteines
DNA-metal complexation, anticancer drugs
Evolution of toxic heavy elements in living beings tissues

Fundamentals and new developments

Multielectron excitations
XANES computations
X-ray Emission Spectroscopy

Materials

The field of material science and technology is of the highest importance, both qualitatively and quantitatively, within the scientific community of Spain. A specific program is dedicated to this topic in the National Plan for Research. Around this subject there are also very active industrial sectors (e.g., ceramics, cement, metallurgy, etc.) that are potential users of a XAS beam station. Improvements in beam characteristics and in sample environments (i.e., “in situ” studies) will lead to a step change in this type of investigations. The generalization in the use of the XAS spectroscopy by the very large research community active in Materials is another strategic reason to support the construction of XAS beamlines in ALBA. There is a *large* variety of materials and/or processes which are being currently investigated by XAS. Nanomaterials, ion conducting oxides and materials for batteries and fuel cells, biomaterials, glasses and amorphous solids, porous materials, modified surfaces and interfaces, thin films, etc. are some of the research topics highly active in Spain.

Nanomaterials. These are recognized as one of the most tangible outcomes of the nanotechnology. In these materials it is critical to determine the exact crystalline/amorphous content, the ultimate crystal size, shape and size distribution of nanostructure and the role of dopants. Local order can be determined by XAS which, in this way, constitute an indispensable technique for this type of analysis.

Ion conducting oxides and materials for batteries. Studies of this type are intimately related to the energy sector, the hydrogen economy and, in general, the energetic problems of our modern societies. Virtually any research program all over the world has as a priority the investigation for the development of this type of materials. Characterization of the local order in the materials for batteries or cells (many of them vitreous or in the form of very small particles) constitutes the first outcome of the XAS spectroscopy within this topic. The research challenges in this field stem from the need of examining these materials under working conditions (that is “in situ”). The development of new experimental stations (e.g., electrochemical cells operating at high temperature) and the use of time resolved techniques are critical steps for the progress in this area. Thus, a high photon flux and time resolved systems of detection are required conditions for an updated beamline suited for this type of investigations.

Thin films and coatings. Thin films are incorporated in a large number of industrial materials and devices to improve their properties and performance. Thin films are required because of their optical, electrical, magnetic, hardness or tribological properties; wear resistance, etc. They form part of optical devices, hard disks, modified glasses, mirrors, protective layers and many others. Many of these thin films and coatings consist of inorganic oxides and metals or composites of them. XAS spectroscopy in the high energy X-ray range is required to get information about their structural properties, surface roughness and compactness and related micro structural characteristics. Detection of information in thin films is perhaps the key issue in any experiment based in SR. The peculiarities of this type of systems stem from the fact that thin films consist of a very little amount of material covering a substrate which typically is not transparent to the X-rays. This compels to use specific detection systems like total or conversion electron yield, TEY or CEY (with the requirement of vacuum conditions) or fluorescence detection. Alternatively, by working under conditions close to the total reflection (for incidence angles around the critical values), the detection of the reflected wave leads to an enhancement of the surface sensitivity. This working mode, REFLEXAS, requires a careful alignment of the sample that is accomplished by means of a two circle goniometer.

Biomaterials. Biomaterials will be the subject of one of the most intense developments in materials science during the next decade. Novel biocompatible materials are required for dentition, bone regeneration / replacement and other prosthetic materials. These are complex materials, derived from amorphous or sol-gel precursors in most cases. Its market is practically unlimited and only the biocompatibility and the long time stability in the human body are restricting its use at present. In Spain many research groups are joining this type of investigations, although the use that they make of XAS and, in general, of Synchrotron radiation, is still limited. This means that a big expansion in the use of SR for this type of investigations is foreseen in the future.

Glasses and Amorphous solids. XAS is one of the best suited techniques to study glasses and amorphous solids. The research topics covered here go from metal and vitreous glasses to studies of the historical heritage. The study of the chemical state and the structure around minor components and doping cations (e.g., color centers) in glasses is another topic of great interest in this field. In all these areas there are research groups which are already using or may become users of XAS in a synchrotron beamline. A challenging set of experiments for the future are the study the amorphisation/-crystallisation processes “in situ”, as they occur when a material or precursor is heated or cooled. This will require the development of specific furnaces and/or sample environments.

The majority of materials in current use have been developed by trial and error. The challenge now is to design a rational profile of materials with improved mechanical and biological characteristics. XAS in combination with SAXS / WAXS will be an important technique for new and successful developments in this area. The detection and analysis of trace elements, which are the subject of a specific point in this report, will also be of the utmost importance in this field. One can also imagine the implementation of studies where the materials are studied under biological conditions, particularly in relation with the determination of their biocompatibility. Owing to the particular characteristics of the matrix where these materials are typically integrated, it would be of interest for the XAS beamline to provide enough photon intensity with energies suited to investigate atoms such as Ca or K (i.e. 3500 E <math><4000\text{eV}</math>). The availability of special environments for the samples (e.g., vacuum conditions) will conceal the maximum attention. On the other hand,

the possibility of having spatial resolution while recording the XAS spectra would be of the utmost importance to perform a mapping of heterogeneous and composite materials.

In summary, besides the possibility to collect standard XAS spectra it is necessary to think about having a high photon flux for ultra dilute systems, the possibility to carry out time resolved experiments, or to have access to a high spatial resolution. As discussed below in detail, this multiple requirements are not compatible with a single beamline

Chemistry

Solid State Chemistry. XAS has played a key role in many fields of chemistry. Particularly, in the last few years it has been used to help in the development of new synthesis routes to prepare novel compounds with unusual properties. To name but a few, it has been successfully used to characterize new pyrochlores and oxyfluorides, novel perovskites, transition metal magnetic clusters, supramolecular entities, glass and mineral compounds capable of storing nuclear wastes, etc. It has become a standard tool in many chemical laboratories and it is envisaged that there will be a drastic increase in its use by the Spanish chemistry laboratories. The application of fluorescence detection in this field will allow the analysis of highly diluted species, while the detection of the spectra with high resolution would enable the analysis of mixtures of elements presenting interferences in their absorption edges.

Catalysis (Heterogeneous and homogeneous). X-ray absorption spectroscopy has been invaluable in the determination of the atomic architecture of many heterogeneous catalytic systems. Catalytic centers, generally metal sites, are present in low concentrations and, very frequently, as entities of nanometric size hardly amenable by X-ray diffraction characterization or electron microscopy. In many cases XAS studies have been capable to determine the structure of the active site, as well as its oxidation state. The challenges now are to analyze these systems under working conditions, which occasionally means high/medium temperature and/or medium pressure and, to improve time resolution for kinetic studies. On the other hand, there is a substantial activity in the area of open framework solids including micro- and mesoporous silicates, aluminosilicates (zeolites), aluminophosphates and metal ion substituted variants. Interest in these materials stems from their unique adsorption and catalytic properties. X-ray diffraction is used mostly to identify phases and to determine the framework structure of these crystalline solids. However, for heavy atom-exchanged zeolites, as in the case of other heterogeneous catalysts, the active phase is a low concentrated species and determination of its local structure requires the use of XAS.

Similarly, in homogenous catalysts, XAS is a unique tool for the study of the structure of dissolved active species. Moreover the selection of normal working catalyst concentrations can represent a severe challenge to XAS since they require to perform spectroscopy experiments in a beamline optimized for ultra-dilute samples and rapid detection (e.g., in stopped-flow apparatus). For both heterogeneous and homogeneous catalysts, the possibility of performing time resolved experiments would allow getting deeper information on reaction kinetics

Coordination compounds in solution. The usefulness of XAS in the study of coordination compounds and solvated species stems from its capability of providing “in solution” structure. In this way it is unique to trace structural changes induced by solution processes, as well as from solvent-ion interactions. Furthermore, since it is particularly sensitive to metal-metal contributions, it can yield information about polymerization and metal clustering processes.

Magnetism

In the recent years, the X-ray magnetic dichroism (XMD) has experienced a notorious success, thanks to the tremendous brilliance delivered by 3rd generation synchrotron light sources and the possibility to create a well defined incident polarization state, either circular or linear, as well as to analyze the polarization state of the scattered photons. Of particular relevance in the hard X-ray energy range are both X-ray magnetic circular dichroism (XMCD) and X-ray magnetic linear dichroism (XMLD) techniques. XMCD is the difference between the absorption cross sections for parallel and antiparallel orientation of the magnetization of the sample and the helicity of the incoming photons. XMLD is the difference in absorption for parallel versus perpendicular orientation of the electric field vector and the magnetic axis of the sample. The advantages of these techniques as compared to other magnetic characterization procedures lay in the fact that they provide information at a local level and as a function of the valence state of the atoms. The metals are usually ferromagnetic and their magnetic properties are best studied with XMCD spectroscopy, while the oxides are usually antiferromagnetic and are studied with XMLD spectroscopy. These experimental techniques enable, among others, the selective detection of the orbital and spin components of the magnetic moment of the magnetic elements, to perform hysteresis cycles specific for such elements, to prove the generation of induced magnetic moments and to study the spin-orbit coupling or determine the magnetic anisotropy.

These techniques can be applied to the study of numerous magnetic materials and magnetic phenomena: magnetic impurities; strongly correlated materials; superconductors; Magneto-electronic Materials including Magnetoresistive Oxides (CMR) and Half-Metals; Soft Magnetic Materials as ferrites and garnets; Hard Magnetic Materials as Rare Earth-Transition Metal Intermetallics, etc. Growing interest is nowadays focused onto the study of amorphous and nanocrystalline materials, Nanostructured Hard Magnetic Materials and Nanoparticles; Thin Films, Multilayer Films and Superlattices. Despite the high number of potential users in the field of magnetism and in nano-science, the use of specialized tools like XMCD and XMLD in Spain is limited at present to six groups, probably due to the shortage of available beamlines in the operating SR sources. For this reason and because this field is envisaged as one with great potential, in this report it is proposed the building of an experimental setup for XMD measurements in one of the proposed XAS beamlines.

Typically, a X-ray Absorption Spectroscopy (XAS) station in the hard x-ray region covers the energy range corresponding to the following absorption edges: the K-edge of both the 3d and 4d transition metals and the L_{2,3}-edges of the lanthanides and 5d transition metals. A clear advantage of a hard X-ray line with respect to a soft X-ray equivalent is that, in the former, XMD and structural analysis by EXAFS can be carried out simultaneously. This opens the possibility to combine structural and magnetic information, something that would not be completely reliable if the sample has to be exposed to the air. Such a possibility would be of the utmost importance for materials such as perovskites and other air sensitive samples

Based on the standard arrangement for XAS measurements in the transmission mode, it is possible to design an experimental station to perform spin-dependent spectroscopy studies. This goal can be easily achieved by combining the linear polarized x-rays (coming from a simple bending magnet or from an insertion device ID) with a phase retarder. The phase retarder can function both as a quarter-wave plate, which converts from linear to circular polarization, and a half-wave plate, which generates vertical linear

polarization. This simple modification is the one that will allow the performance of the XMCD and XMLD experiments mentioned above. For additional description of the scientific cases and beamline design See *Annex 3*.

High Pressure Behaviour

The use of XAS to characterize systems under high pressure in solid and in liquid states has a high interest. In particular, the study of phenomena such as phase transitions (solid-solid, liquid-solid or liquid-liquid) and magnetism under pressure is currently of considerable importance. A current hot topic is the study of the structure of high pressure melts, mainly because it should contribute to the understanding of the evolution of the earth and other planet's core and their magnetic field, and also to the study of hydrothermal solutions in relation with mineral formation. On the other hand, high-pressure studies continue to provide data for the determination of accurate inter-atomic potentials used for condensed matter simulations.

In this topic, the information provided by XAS is complementary to that of XRD and the experiment requires a well controlled environment of sample with very demanding requirements, i. e. beam size, photon flux, etc. Thus, a minimum size of the beam ($<50 \times 100 \mu\text{m}$ HxV) and a maximum photon flux ($>10^{12}$ ph/sec) are conditions that will push forward the front line of these studies. Besides the development of new and more advanced experimental stations and the decrease of the beam size, future challenges in this research field include the combination of XAS (local order information) with XRD (long range structural order). Some research groups in Spain have long experience in this field, and been involved in the development of high pressure cells which enable the enlargement in the range of pressure and temperature to be investigated.

This type of experiments might be carried out either in a beamline with energy dispersive detection systems, as the one used for *time resolved experiments*, or in a *standard XAS beamline*, depending on the type of cells used.

Environmental and Earth Sciences

Toxic metal speciation. Large areas of contaminated land and waterways have been produced by man activities in all developed and developing countries as a consequence of industrial and domestic processes. XAS is proving an extremely important tool to identify the nature of toxic metals causing the contamination, thus enabling the development of remediation strategies. This is a unique tool to provide information on "heavy" metals such as Cd, Hg, As, Sb, Cu, Zn, Cr and Pb metals that are present in waste products of industrial processes. Crucial information concerning the speciation of the metals and their sorption on mineral surfaces has been provided by XAS, being these factors highly relevant for the toxicity, mobility and bioavailability of the contaminants. The application of fluorescence detection mode in this field enables the analysis of highly diluted species, as well as the analysis of mixtures of elements presenting interferences in their absorption edges. Since environmental legislation is becoming stricter and the maximum permitted amounts of toxic elements are decreasing down to sub-milimolar concentration, very sensitive detection systems have to be used to analyze these ultradispersed samples.

Radionuclides The use of synchrotron facilities in the radioactive field is becoming of paramount importance for a large variety of problems, such as evaluation of surface reactivity, influence of radionuclides retention or the study of coordination environments and complexation with humic substances or colloids. EXAFS studies of radioactive

elements present in the environment such as Tc, Pu, Np and U has solved several relevant problems in this field. This interest is fostered by the growing legacy on contamination and wastes. In this regard, XAS is used in the study of 'natural' and model systems, often being the only technique capable of providing structural information on the non-crystalline components. Beamline stations such as ROBL at ESRF are already dedicated to the analysis of medium and high activity radioactive samples. In Spain, the growing community interested in this topic will justify the implementation of means to analyze low activity samples not requiring highly demanding safety conditions.

Earth Sciences. XAS has also been very successful for the study of systems that are crucial for the understanding of fundamental Earth processes, particularly for both bulk and surface chemistry of rock-forming and economically important minerals. Such information is relevant to Earth and environmental studies.

In other European countries, particularly in those having national facilities, such as UK or France, there are mature research communities in both fields, environmental and earth sciences. In Spain this community has already been involved in the use of XAS and is foreseen that the use of this technique will increase substantially in the near future.

Biological Science

Biological XAS is a broad field where chemistry, materials and environmental sciences overlap. The systems of interest span from small therapeutic molecules (e.g. anticancer Pt drugs), to metalloproteins, biomineralisation processes or evolution of toxic heavy elements in tissues. The use of diffraction or scattering techniques is limited because most biological systems are disordered, even when they are in solid state. Moreover, despite the outstanding growth in protein crystallography over recent years, the bond length accuracy achieved at metal binding sites in metalloproteins (typically 0.1 Å) is still smaller than desired. All this, plus the ability of the XAS technique to determine with high accuracy oxidation states of the metal centres, make it a perfect complement of the most traditional techniques. A recent development is a consistent refinement of the structure of the metal site of a protein determined by PX with the more local information provided by XAS methods. XAS has the additional advantage of enabling the study of biological systems under physiological conditions, where pH, temperature and ionic strength can be controlled. Many of these applications require a high-flux station designed for ultra dilute systems.

XAS Fundamentals and new developments

The user community in Spain has contributed to the development of the basis of XAS spectroscopy. For instance, several groups have been actively involved in developments, concerning experimental conditions, such as design of special cells for measurements under extreme conditions. Some others have contributed with new advances in theory, such as the evaluation of multielectron excitations associated to the main ionization process. Among the other aspects which have received a special attention, it can be mentioned the basic description of the XANES spectra and its simulation or the implementation of procedures to take into account statistical effects in the computation of XAS spectra by combining them with results from molecular dynamics simulations.

The last years have also witnessed the development of the so called *X-ray emission spectroscopy*. X-ray emission spectroscopy (XES) is a subsequent optical process in which a core electron is excited by an incident x-ray photon and then this excited state decays by

emitting an x-ray photon to fill the core hole.² The energy of the emitted photon is the energy difference between the involved electronic levels. The analysis of the energy dependence of the emitted photons is the aim of the X-ray emission spectroscopy. This process has been mainly used as an analytical probe, being one of the most sensible techniques for the detection of low atomic concentrations. Recently, with the advent of more powerful X-ray sources as the third generation synchrotron radiation facilities, the study of the energy dependence of the emitted photons, i.e., of X-ray emission spectra, is becoming an important tool for the detailed study of the electronic structure in solids. Different XES techniques have emerged, depending on the information that can be obtained from the experiment and the energy of the incident photons: (i) If the core electron is resonantly excited to the absorption threshold by the incident photon (as in X-ray absorption spectroscopy), the resulting emission spectrum depends strongly on the incident photon energy; this technique is denoted as Resonant X-ray Emission spectroscopy (RXES). (ii) If the core electron is excited well above the absorption threshold, the XES spectroscopy is called NXES (Normal X-ray Emission Spectroscopy). In this case, the emission spectrum does not depend on the energy of the incident photons. The difference between RXES and NXES is that the intermediate state of RXES is the same than the final state of an X-ray absorption spectrum, where an electron is promoted to an empty bound level. Meanwhile that of NXES is the same as the final state of X-ray photoemission from the deep level. Sometimes RXES is denoted as RIXS (resonant inelastic X-ray scattering) or RXRS (Raman X-ray Scattering) because it can be described as an inelastic process due to the fact that the energy of the emitted photon is different from the energy of the incident photon. On the other hand, NXES is also called “x-ray fluorescence spectroscopy”.

These techniques can be easily installed in a XAS beamline with the only requirements of high flux ($>10^{12}$ ph/sec), high-energy resolution in the detection systems (>5 eV) and relatively good focalization. Two spectrometers can be considered: i) a conventional spectrometer as those used in classical X-ray fluorescence spectroscopy, used when the measurement of the total intensity of the fluorescence signal is the relevant parameter (high resolution is not required in this case). ii) A high-resolution spectrometer able to determine with high resolution the energy dependence of the emitted photons. For this purpose optics based on the Rowland circle geometry are generally used. The photons emitted by the sample are selected and focalized in the detector. The combined capability of scanning with the beam line monochromator the energy of the incident photons and with the XES spectrometer the energy of the emitted ones, would enable to carry out a large variety of new experiments of high-scientific interest from either the fundamentals or the application points of view, such as those listed below.

- X-ray absorption spectroscopy in diluted systems and in systems where the absorption thresholds interfere (e.g., in manganites the K edges of Mn and the L edges of rare earth elements)
- High resolution absorption spectroscopy. Measuring the emitted line with a narrow energy window (in combination with a high resolution also in the beam line monochromator) it is possible to resolve XAS structures, otherwise hidden in a conventional spectrum due to the core-hole lifetime. This is possible because in this case the lifetime governing the intrinsic line width is that of the shallower hole left after the fluorescence transition.
- X-ray absorption spectroscopy resolved in spin or in chemical state. Recent results looking at the fluorescence lines of metals and their compounds have shown their sensitivity to the spin or redox state of the absorbent atoms. Separation in an

²A. Kotani and S. Shin, Reviews on Modern Physics, **73**, 203 (2001) and references therein

EXAFS spectrum the contributions of different states is a new possibility open by this finding that has been already exploited in a few cases.

- X-ray emission spectroscopy. If the incident photon energy is fixed at an energy higher than that of the threshold, the emitted fluorescence provides an information similar to that of photoemission with the difference that the information would come from the bulk of the material and not from its surface.
- Resonant inelastic scattering. The study of the shape of the emitted fluorescence peaks for incident photon energies close to the threshold provides information about electronic states and symmetry of the resonant atom.

Among the experiments above, only the first three pertain strictly to X-ray absorption spectroscopy and are of direct interest to it. The other two would constitute an additional advantage of such a setup, of interest for other spectroscopic studies. Taking into account the new fields opened by this technique, the present document makes a quest for incorporating it into one of the lines whose construction is proposed in Section 6. (See additional description of scientific cases in *Annex 3*).

3. Spanish User community

Annex 1 includes a list of XAS users, defined as scientists who were awarded beamtime within a research project in any Synchrotron Radiation Sources in the last five years or who are known to have the intention to apply for it in the near future. The list also includes a reference to the permanent scientists who have taken part in such experiments. At present there are around 35 research groups in Spain who are using SR to perform XAS experiments, with more than 200 projects approved in the last four years. 175 permanent scientist have taken part in these experiments. From these 35 groups, more than twenty are current users visiting the sources periodically, on average more than once per year. Although many of them hold collaborations with foreign groups, the majority have enough expertise to lead their works personally.

The longest tradition in the use of XAS by Spanish scientists can be found in the fields of Material Science, Solid State Physics, Chemistry and Catalysis, but there are emerging communities in the field of High Pressure who are becoming very active. A significant development of researchers coming from the field of the Biological Sciences is also expected. The majority of the present users are carrying out their measurements at the ESRF, although depending on the technical requirements of the experiment or the beamtime availability at this source, they are also measuring in several other sources all over the world (see *Annex 1*). In the past, they also used ADONE (Frascati), LURE (Orsay) and SRS (Daresbury). It is important to indicate here that some of these groups have been already involved in the design and construction of the part of hutch A in SPLINE devoted to XAS. It is also important to stress the high commitment of many of these groups to collaborate in the construction of a XAS beamline in ALBA. The name of the researchers that have expressed their interest in participating in the building of the line, experimental stations or any other kind of support for the success of this project has been written in bold in *Annex 1* (groups 1-9, 21). All these researchers have participated actively in the elaboration of this document. Most of them are specialists in XAS, with a long experience in the technique, either as users or as developers.

Annex 2 includes some of the outcome of the Spanish user community, listed as published works. Although the number of papers included has been restricted for obvious reasons, it is clearly seen that the scientific production, in terms of both the high production and the quality of the published works, is of the topmost level, proving the maturity of the Spanish user community of XAS.

4. Detection systems and sample environment

The detection devices of the future XAS beamline(s) should be optimized for each type of measurements. As it will be discussed below, the first XAS beamline to be constructed in ALBA should comply with both, the possibility of performing high quality standard XAS experiments and with the incorporation of instruments to carry out XES and XMD experiments. The two latter techniques will be described with more detail in Section 6. Concerning the standard XAS experiments, its variety requires a wide range of *detectors* that should be available at the line. Among them we can quote the following:

- Incident/transmitted flux monitors (photodiode or ion chamber type) for conventional measurements in transmission.
- Cooled semiconductor fluorescence detector for other geometries of detection, study of trace elements, etc...
- Electron yield detection (total electron yield or conversion electron yield, requiring either vacuum or controlled atmosphere conditions) to study thin films and surface layers.

Concerning the magnetism experiments the special requirements should be:

- Diamond X-ray phase retarder.
- Magnetic field (electromagnet or superconducting magnet).

In addition, high precision mechanic stages for sample holders or chambers will be required in some cases. Thus, for REFLEXAFS a high precision goniometer (angular resolution better than 0.001° is needed to control accurately grazing incidence angle on planar samples; for XES, a sample translation stage is needed able to align the position of the on-sample spot with respect to the fluorescence analyzer crystal to ca. $\pm 10 \mu$.

Some groups are interested in experiments that would require specific beamlines that are not compatible with the beam characteristics required by the first beamline proposed. Thus, with a lower priority, this document also proposes the construction of two additional beamlines to cover the specific demands of some research groups. These beamlines would require other ways of detection such as

- Dispersive setup for time resolved experiments. The detectors needed for energy dispersive EXAFS (EDE) are position sensitive detectors. These can be based on CCD cameras with an associated scintillating screen that transform the X-ray photons to visible light, or on more modern technology such as silicon micro-strip detectors, where the X-ray photons are directly measured. In both cases the main limitation is the lack of a suitable detector to measure the incident beam without damaging the energy spread in position. Considerable efforts are currently being made to address this problem by different groups such as those the ESRF and at the CCLRC.
- μ -focus setup for chemical “mapping” with high spatial resolution. In this case, fluorescence detectors with exceptionally good energy resolution are needed. In addition to standard Ge or Si fluorescence detectors, multilayer analyzer array detectors or Bent crystal Laue detectors would be needed to achieve higher energy resolutions, especially at low energies.

A new line at the frontier of the state of the art should not consist of just a simple setup aiming at the “ex-situ” characterization of samples. Additional instrumentation around the sample stage must be implemented to enable more elaborated experiments “in-situ” according to the needs of the users. In some cases, this would lead to the

Proposal for the construction of XAS beam lines in ALBA

implementation in the beamline(s) of novel facilities which are state-of-the-art (and maybe unique). Certainly, a wide variety of sample environments will be also required and should be developed in collaboration with user groups. These include cells capable of operating at high and low temperatures and pressures, process monitoring and gas or liquid mixing control equipments for reacting systems, etc. A (certainly incomplete) list of sample environments and experimental conditions that, according to the groups of interested users, will be utilized in the line is the following:

- Reaction cells for catalysis (control of gases, temperature, etc.)
- High pressure cells.
- Low temperature equipments such as cryostats.
- Furnaces for “in-situ” studies of materials.
- Stopped flow systems for liquids.

In general, the previous experimental devices will be provided by the users, since they constitute a central part of their experiments. However, the planning of the beamline should consider the needs of space and of basic infrastructure (e.g. supply lines for liquid He or reacting gases, electric power for electromagnets, etc.) needed to run these devices; otherwise the line could have important limitations for their installation on place.

Since each specific experiment or group of experiments requires certain beam conditions mainly linked with the type of detection, in Table 1 we have summarized the parameters of the line(s) required to perform the experiments relying on a particular detection procedure. The included detection systems have been selected in relation with the scientific cases outlined before, while the values of the optic parameters are those that fit better for both the present requirements of the research community and the possibility of implementing new and more advanced facilities in the future. The specified values in this table are just orders of magnitude that refer to the *minimum conditions* required to perform a series of experiments in a reasonable way. Obviously, a given experiment could be done for shorter measuring times if conditions are specifically optimized for it.

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Table 1- *Approximate values of some beam parameters in the XAS beamline(s) of ALBA According to the detection system required for a given experiment.*

	Energy range (keV)	Energy resolution $\Delta E/E$	Flux	Spot size	Time resolution	X-ray Polarization
XAS ¹	2.5 - 30	10^{-4}	High	¹⁶	medium ¹³ high ¹⁷	-
Fluorescence ²	4.5 - 30	10^{-4}	High ⁸	¹⁶	-	-
Electron detection ³	4.5 - 20	10^{-4}	-	-	-	H-V linear polarization ¹⁴
XES ⁴	4.5 - 30	$>10^{-4}$	High ⁸	small ¹⁰	-	-
XMD ⁵	4.5 - 20	10^{-4}	High ⁸	-	-	$\lambda/4$, $\lambda/2$ plate ¹⁵
High Pressure ⁶	5.5 – 12 >15	10^{-4}	High ⁸	small ¹¹	Medium ¹³ -	$\lambda/4$, $\lambda/2$ plate
Mapping ⁷	4.5 - 30	10^{-4}	very high ⁹	very small ¹²	-	-

1. Includes conventional EXAFS and XANES in systems to be measured in the transmission mode.
2. Fluorescence detection is needed for the study of highly diluted systems.
3. Total and converted electron yield detection modes are needed to study coatings and thin films.
4. XES has to be treated separately from the conventional fluorescence detection because it requires a high energy resolution in the detection system, to monitor the emitted photon in the fluorescence decay process.
5. XMD permits to obtain unique information of magnetic materials
6. “High pressure” refers to the study of samples under extreme conditions obtained in diamond anvil cells (DAC) or large volume cells. Depending upon the type of used cells, different energy windows are available.
7. “Mapping” refers to sample homogeneity measurements.
8. The flux should be as high as possible in order to obtain realistic detection times.
9. Particularly high brightness: A high flux is needed because of the small concentration of absorber in the small area probed by the beam. This usually requires focussing of the beam.
10. This will depend largely on the fluorescence analyzer setup which would be finally decided. Note that this is a relatively new technique, and specific X-ray optics simulations may be needed to decide the appropriate parameters.
11. A spot size of 80x30 μm (HxV) will assure measurements in a DAC sample environment.
12. The spot size will determine the resolution of this type of microscopy. Typical values are 5x5 μm .
13. Time resolution is needed, for instance, in the recording of a chemical reaction. In a conventional XAS experiment a time lower than the minute should be achieved. To do quickexafs, a high flux is needed since the spectra have to be collected with very low integration times. Time resolution (less than a minute) is also needed to orientate the DAC in order to avoid diamond glitches. The quality of the spectrum must allow glitches identification in all the spectral range.
14. Linear polarization in both horizontal and vertical planes is needed to study epitaxial thin films.
15. Circular polarization can be obtained in a conventional beamline by using a quarter wave plate.
16. Some measurements on damage-sensitive samples (biological, etc.) may mandate a not too small spot size, i.e., in the range of several mm^2 .
17. A sub-second time scale (down to millisecond or below), is also necessary for studies of fast dynamics processes, and gives rise to the demand of a time-resolved dispersive beamline as discussed below.

5.- Alternative Sources in Europe

Table 1 defines the limits in parameter values that would be required to perform a series of experiments using XAS. Taking these data into account, three beamlines are proposed in section 6 to cover at the highest possible level most of the requirements needed to develop the “scientific cases” outlined previously. However, before doing such an exercise it is convenient to recall the beam characteristics of other lines available in other 3rd generation synchrotrons in Europe, either available or under construction. Table 2 summarizes the working parameters of some of these beamlines, including those working at the ESRF, even if the critical energy of this synchrotron is higher than that expected for ALBA.

A quick comparison of the values in Table 1 with those in Table 2 below shows that the available beamlines in Europe would hardly comply with all the requirements summarized in the first Table.

Table 2.- Relevant parameters in other sources in Europe and beamlines at the European Synchrotron Radiation Source (ESRF). The unique CRG line considered is the Spanish Beamline (SPLINE).

SR	BEAMLINES	TECHNIQUES	ENERGY RANGE E(keV)	FLUX (ph/sec)	$\Delta E/E$	Spot SIZE	POLARIZATION	TIME RESOLUTION
DIAMOND (3 GeV – 300 mA)	I18 UNDULATOR	Microfocus Spectroscopy	2 - 20 5 – 13	5×10^{12}	1.4×10^{-4} – 3×10^{-5}	$< 1 \mu\text{m}^2$	-	-
	XAS3	XAS Dispersive	6-35	3×10^{13}	10^{-4}	50 (v) \times 30 μm (h)		
	I20 Wiggler	EXAFS XES	4-35	1×10^{14}	10^{-4}	50 \times 1700 μm		
SLS (2.4 GeV)	MicroXAS UNDULATOR	MicroXAS XRF-mapping GI-XAFS	5 - 20	2×10^{12} ph/s/400m A	2×10^{-4}	1 x 1 μm^2	Linear Circular	Femto second
SOLEIL (2.75 GeV)	D13 BENDING MAGNET	DIFFRACTION- ABSORPTION	3 - 25	6×10^{12}		250 \times 50 μm^2	-	-
	D9 SAMBA BENDING MAGNET	XAS (transmission, fluorescence, total electron yield)	4 - 40	2×10^{10} to 5×10^{12}		80 x 30 μm^2	-	-
	D1 ODE DIPOLE	DISPERSIVE XMCD	3.5 - 23	1×10^{11} to 3×10^{12}		40 x 40 μm^2	Quarter wave plates	ms
ANKA (2.5 GeV – 180mA)	ANKA-XAS BENDING MAGNET	XAS (EXAFS, XANES, XMCD)	2.4 – 25	2×10^{11}	2×10^{-4}	10 x 1 mm^2	Quarter wave plates	-
ELETTRA (2 GeV – 300mA)	BI 11.1 BENDING MAGNET	XAFS	2.3 - 25		2×10^{-4}	-	.	-

Table 2 (cont).- Relevant parameters in other sources in Europe and Beamlines at the European Synchrotron Radiation Source (ESRF). The unique CRG line considered is the Spanish Beamline (SPLINE).

BEAMLINES	TECHNIQUES	ENERGY RANGE E(keV)	FLUX (ph/sec)	$\Delta E/E$	Spot SIZE	POLARIZATION	TIME RESOLUTION
BM29	XAS	4 – 74	10^{11} - 10^9	10^{-4} - 10^{-5}			
ID 24	DISPERSIVE EXAFS XMCD	5 – 28	10^{12}		20 x 20 μm^2 60 x 20 μm^2	Quarter wave plates	μsec
ID 26	HIGH BRILLIANCE	3.2 - 30	$> 10^{13}$	1.4×10^{-4} 5.1×10^{-5}	200 x 80 μm^2	-	-
BM 25 SPLINE	XAS	5 – 35	10^{11}		0.2 x 0.1 mm^2	-	-

For the purposes of this document, it is particularly relevant to highlight the conditions of SPLINE AT the ESRF synchrotron. This Spanish beamline will likely be in operation when this document will be discussed and therefore its working conditions must be very carefully discussed. The design of this line is relatively complex. In fact, the radiation is provided by a bending magnet through a port that has been split to provide photons to two hutches, A and B. Moreover, the available beamtime in hutch A has to be shared between XAS and X-ray powder diffraction. This means that 100% of its time will not be devoted to XAS experiments. As a consequence, SPLINE is not foreseen to be capable of coping with all users demands. It is also important to stress here that the part of hutch A devoted to XAS in SPLINE has been designed to fulfill the basic requirements of standard, not highly demanding XAS experiments. In particular, it is well designed for analysis at high energy (range between 5 and 35 keV), but it does not cover the low energy range (2-5 keV) nor has the possibility of a high brilliance focusing like that desired in the beamline which is proposed in this document as a first choice. Another limitation is that in its initial design no special detection systems were planned, and that other devices to control sample environment will not have much space available for installation. Because all these reasons, this station, although expected to be very useful to the user's community, will not meet the special requirements demanded to perform outstanding experiments within 7-8 years.

6. Proposal of Beamline(s)

As stated in the previous sections, it appears that no single beamline comply with all the requirements to perform all the experiments related with the scientific cases described above. Therefore, a conclusion of the different discussions which are reflected in the present report is that three beamlines with different characteristics should be constructed to give service to the XAS Spanish community at the "highest" level. The basic characteristics of these beamlines are specified below. In addition, another important agreement of these discussions is a decision about priority criteria to order the time scale of construction of these beamlines. In relation with that it is important to state that the order

in which the beamlines are described in this document reflects the priority given to them by the Spanish XAS scientific community.

An important issue that should be mentioned is the large number of scientific cases and researchers that rely on the use of conventional XAS. It was evident for attendees to the workshop in Sevilla that the next commissioning of the SPLINE beamline at the ESRF is an unavoidable reference for any proposal to construct a new beamline to perform XAS experiments. This situation has been taken into account, particularly when discussing and proposing *Beamline 1* which is conceived under different premises from those of the Spanish line at the European synchrotron. In this respect, it is important to comment that the existing (SPLINE) and the here proposed lines are by no means equivalents and that each of them are optimized to meet the requirements of different experiments. Another important issue is that although the scientific excellence of *Beamline 1* does not rely on conventional XAS but in more advanced experiments as described below, its use for conventional XAS within the available limits should be also possible. This option is justified because SPLINE would hardly satisfy the wide demand of the Spanish community doing XAS and because *Beamline 1* will be born from quite different premises and conditions.

Therefore, *Beamline 1* tries to make compatible the service to a wide community carrying out standard experiments, with the implementation of one of the most advanced detection system (i.e., XES) and sample environment for magnetic studies (XMD). To comply with these two requirements a robust optic will be needed, as well as space and versatility at the experimental station site to incorporate different detectors and sample environments. A basic characteristic of this beamline is that it should be able to provide a high brilliance within a small spot size. This is required, for example, for XES and fulfills the needs of some experiments which hardly would be possible to be performed in SPLINE (e.g., high pressure studies, detection of trace elements, etc.)

Beamlines 2 and 3 are more specific since their basic requirements, very small beam size in the microfocus and energy dispersive set-ups, limit their use for conventional XAS. Nevertheless, they constitute an investment for the future since they will open areas of great impact at the frontier of knowledge. Their need is justified because some of the experiments from the above described scientific cases could not be carried out without these special designs.

Beamline 1: High resolution chemical and magnetic spectroscopy

Key features of this beamline are a high flux and a reduced beam size. From the conventional scientific cases described in the previous sections, this beamline would be particularly suited to examine very diluted samples (e.g. in the field of environmental and earth sciences or biological samples), high pressure studies and the possibility to study absorption edges at medium energy ranges, in the order of 2.5 keV (i.e., to be able to look at atoms like Ca or S and at the L edges of second row transition elements). Moreover, this beamline should be capable of implementing new capabilities that would render it unique in its gender and, as such, internationally competitive within a few years. Also, it would allow to use of large volume (up to ca. 1 mm³) high pressure EXAFS cells, to carry out experiments under extreme conditions. The incorporation of XES detection and the possibility of performing XMD measurements on magnetic materials are the two distinct features that have been considered. A brief description of the implications of these two experiments is described below.

Some basic characteristics of the beam requirements should be the following:

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Photon Energy: Covering the most ample range of energies, i.e. from 2.5 eV to the highest possible values (approaching 30 keV). Although the definition of the insertion devices is not a task of the present document, it is clear that the type of the insertion device providing a beam of high brilliance and a small size in the range needed for high resolution XES, might impose some restrictions to cover the high energy range with enough flux. Nevertheless, to comply with the objectives of the line and the requirement of the users, it is expected that the beam may have a high flux up to 20 keV.

Resolution: $\Delta E/E = 1.4 \times 10^{-4}$ in collimated incident beam. This value should be approached also in the high energy range. For XES work, energy resolution should be even lower.

Beam size: It should have a small size to be capable of affording many of the proposed experiments. As an orientate figure, the beam should have a size of about $100 \times 60 \mu\text{m}$ at the sample position with a high brilliance. The exact requirements will also depend on the constrains imposed by the XES analyzer optics that will be finally chosen and designed.

Flux on sample: 1×10^{13} Photons/sec/0.1% bandwidth (minimum) with Si(111) @10 keV

Detectors: For *conventional experiments* ionization chambers and/or electron detection systems should be implemented in the line. *Diluted systems* would require the use of fluorescence detectors. Compact multielement solid state detectors based upon either Ge or Si with digital signal processing will be valuable for low scattering matrices. For *ultradilute samples* with a strongly scattering matrix it is likely that multilayer Bragg filters developed at the APS will emerge as the only viable route to collect good data. For XES measurements more complex setups should be required, as described in *Annex 4*.

Others: Integration of a polarization stage for XMD and easy implementation of a XES detector.³ In this respect, Figure 1 shows the additional elements which are specific for magnetic measurements. These elements (magnet and phase retarder) would be easily removable from the sample environment, allowing other instrumentation to be set in place.

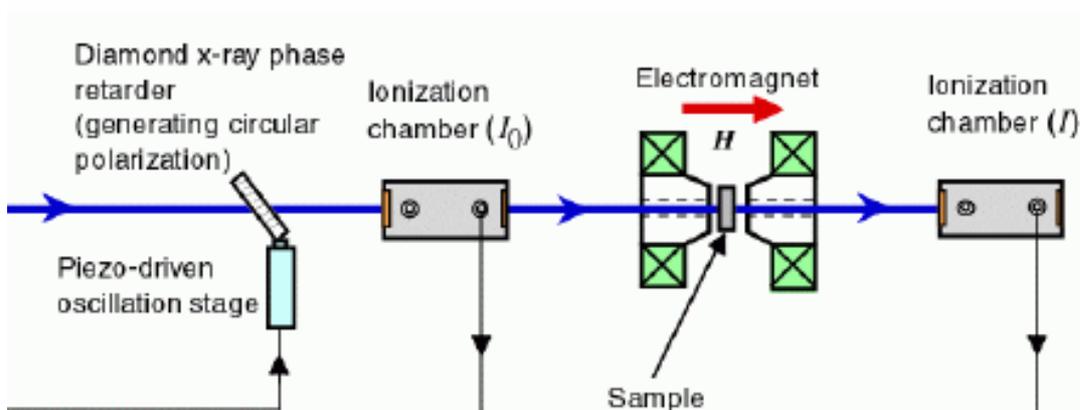


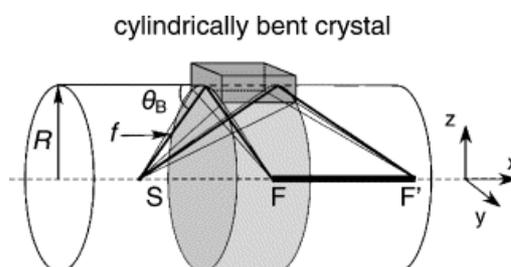
Figure 1.- Scheme of XMD setup for a XAS-1 beamline in ALBA.

Another proposed additional instrumentation is a fluorescence monochromator analyzer (possibly with a Rowland circle-based dispersive configuration, as in the example

³ A simple arrangement makes it also possible to perform x-ray magnetic dichroism experiments under extreme conditions. For example, by using a conventional cryostat it is possible to perform experiments through the temperature range between 1.7 and 300 K under the action of an applied magnetic field of 10T. It is also possible to use a diamond anvil cell (DAC) to study magnetic phenomena under conditions of low temperature (5 K), high magnetic field (6–7 T) and high pressure (20–50 GPa).

of Figure 2 below, although other setups might be considered) which could be inserted over the sample stage to resolve line shapes of emitted X-rays. This will give access to 2D X-ray spectroscopy (i.e. with both absorption and fluorescence energy dimensions) and consequently to resolve different redox or spin states as well as to increase of spectrum resolution beyond the core hole intrinsic line width value. This would enable the recording of high resolution XES spectra, one of the most ambitious experiments that will be carried out in this line (note however, that the final detector should be decided in due time and new alternatives might have been developed by then). In fact, imaginative solutions would be desired here. This will represent an appealing challenge for obtaining a state-of-the-art facility in ALBA.

The incorporation of a polarization stage and a XES detecting system as described above would open its use to magnetism and final state related studies. These types of studies would put this beamline in a frontier position with respect to the developments in CXAS. In this way, the beamline, besides serving the XAS community making use of the more traditional instrument of detection, would foster more advanced studies in fields of greater innovative character. Since these two techniques constitute the highest novelty of the line, a more detailed description of their requirements and of the science that can be done with them are included in *Annexes 3 and 4*.



*Fig. 2 - Scheme of a cylindrical monochromator in a Rowland circle configuration of radius R with additional energy resolution due to small variation of diffracting angle θ_B in the axial direction, suited to use in XES (H. Hayashi et al., *J. El. Spectr. Rel. Phen.* 136 (2004) 191).*

Beamline 2: Microfocus

Focusing below the range of some tenths of microns to make a mapping of samples would not be possible in the previous beamline. A wide range of experiments in environmental, earth sciences and heterogeneous catalysis would not be possible without a beam size within the range of microns. On the other hand, micron beams will open up the study of reactions at solid/solid and solid/liquid interfaces, such as those involved in high temperature fuel cells, hydrothermal synthesis of materials and corrosion processes. In general, this type of beamline would allow the study of real systems in the fields of environmental earth and materials sciences. The interest of such a line would be centered, among others, in the following experiments:

- XRF mapping:
 - Spatial heterogeneities in materials.
 - Phase associations (combined with cluster analysis)
 - Element distribution in composite materials.
 - Cross-sectional analysis of thin films and multilayered materials and devices.

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- Micro-XAS:
 - Reduction of detection limits. Analysis of enriched particles. Removal of interferences.
 - Identification of small particles sources (anthropogenic, natural) and assessment of their environmental impact.
 - Study of depleted uranium (DU). Identification among particles from uranium-rich samples.
- μ -tomography:

Acquire information about the structure of slices of a sample with a good spatial resolution given by the small beam, independently of the resolution of the detector

Some basic characteristics of this beamline should be as follow:

Photon Energy: 4.5- 20 keV.

Resolution: $\Delta E/E = 10^{-4}$.

Beam size: The minimum possible, but at least smaller than $10 \times 10 \mu\text{m}$

Flux: The maximum possible, but in any case higher than 10^{11} - 10^{12} ph/s with Si(111) at 10keV.

Several focusing devices could be used to achieve the small focal spot that will provide a good spatial resolution, such as zone plates, compound refractive lenses or mirrors in Kirkpatrick-Baez geometry (KB). The preferred option for a spectroscopic beamline is usually KB mirrors, due to their achromatic character, i.e. the focal distance is independent of the wavelength of the incident beam. The main limitation of this device is the space constraints that its use imposes at the sample position. The space available to the sample is typically restricted to 10-12 cm maximum in the direction of the beam. This constraint reinforces the need for a careful design of sample environment and incident beam detectors.

A schematic layout of such a beamline incorporating a KB mirror setup is presented in Figure 3.

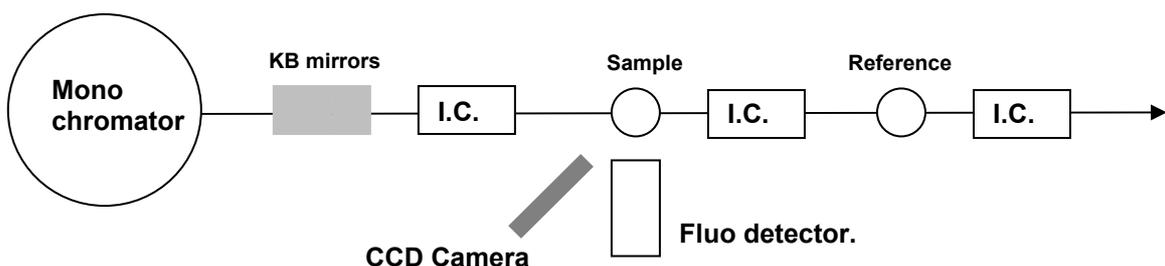


Figure 3.- Scheme of a microfocusing beamline base on KB mirrors

Other: It would be of interest to have the possibility of analyzing radionuclides at this beamline. However, the safety requirements for such studies have not been considered when making this proposal and it is an open question to be addressed in case this beamline is approved.

Detectors.

Due to the various techniques proposed for this beamline, a range of detectors is required. These include:

- Solid state fluorescence detector, based on silicon or germanium technology, depending on the energy range of the beamline.
- Multilayer array detector for high resolution spectroscopy (60eV). Especially suitable for low energies (<10keV).
- Ion chambers for I_0 and transmission measurements. A special design of I_0 ion chamber is needed due to the limited space available in the vicinity of the sample.

Beamline 3: Time resolved XAS

Time resolved experiments are of paramount importance for many scientific issues. In fields like catalysis it is a common practice to carry out experiments where the evolution of the samples is followed as a function of time. These experiments can be carried out in a conventional beamline where recording of spectra can be done in a short time, in the order of minutes, even seconds in the QuickEXAFS mode. By contrast, time resolved XAS refers here to time resolutions of the order of msec or below. This time scale combined with additional techniques such as stopped flow, irradiation or heat pulses or establishment of sudden changes in voltage (e.g. in electrochemistry or electroactive devices) or pressure (e.g. in studies of phase transitions or shock waves) opens the possibility of studying other series of phenomena. These include the identification of chemical transients in a wide range of chemical reactions in liquid or solid media, provided that they are homogeneous. A beamline where these studies could be performed would require that the XAS spectra are recorded in *dispersive mode* with a *position sensitive detector*. Moreover, this configuration is particularly appropriate to carry out measurements under high pressure with small volume (10^{-4} mm³) diamond anvil cells.

Some approximate parameters of such beamline would be as follow:

Photon Energy: 4 -30 keV

Beam size: 60 x 60 μ m

Flux at sample: 1×10^{12} - 1×10^{11} ph/s with Si(111) @ 10keV.

Energy Dispersive EXAFS (EDE) uses a bent crystal polychromator to focus an energy dispersed X-ray beam onto the sample. Due to the curvature of the crystal, the energy components within the beam are spatially distributed. After passing through the sample, the beam is collected by a position sensitive detector. This allows the absorption over a range of energies, given by the bandwidth, the curvature of the crystal and the divergence of the beam, to be collected simultaneously. A schematic representation of a dispersive setup is shown in Figure 4.

The main limitation of this technique is the need to record the incident beam intensity at a different time of the collection of the transmitted beam intensity. This imposes stringent requirements of beam stability.

Detectors

As mentioned previously, several detector options can be considered for the dispersive setup. The state of the art of the technology in this area is the silicon micro-strip detector, XSTRIP, developed by CCLRC. This device consists on 1024 channel PSD operating with a 10 μ s minimum integration time. To fulfill the maximum potential for time resolved XAS the development of a suitable I_0 detector should be given a high priority.

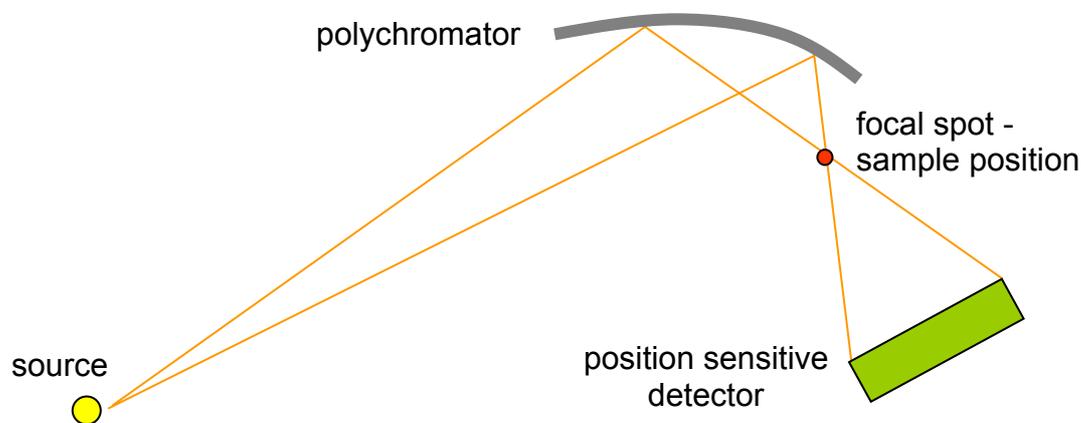


Figure 4.- Schematic representation of a dispersive setup to carry out time-resolved-XAS measurements

ANNEX 1.

List of SR actual (or potential) users in Spain that would benefit of the XAS line(s) in ALBA

Groups 1-9, 21: Long experienced users. They would participate in the construction of XAS beamlines.

Groups 10-29: Using XAS currently. With reported publications, included in *ANNEX 2*.

Groups 30-41: Recent XAS users, without reported publications yet.

Groups 42-48: Without experience but interested in the development of XAS beamlines in ALBA.

Group/researchers	Affiliation	R&D field(s) of activity	Technique/Special requirements	SR sources used
¹ Joaquin García Ruiz jgr@unizar.es 5 staff members	ICMA. CSIC- Universidad de Zaragoza	Materials, Chemistry, Magnetism,	EXAFS, XANES, XES, RXS, DAFS, XRPD, XRD. Ultrahigh diluted samples, XMCD, XES,.	Adone(Frascati), SRS (Daresbury), LURE (Orsay), NSLS (Brookhaven), Elettra (Trieste), ESRF (Grenoble).
² José C. Conesa Cegarra (jcconesa@icp.csic.es), M. Fernández García (mfg@icp.csic.es), Arturo Martínez Arias	Instituto de Catálisis y Petroleoquímica, CSIC, Madrid	Chemistry, Materials	EXAFS/XANES, XES, <i>In situ</i> (T and gas control) time-resolved work, XES,	Adone(Frascati), SRS (Daresbury), LURE-DCI (Orsay), BESSY I (Berlín), ESRF (Grenoble), NSLS (Brookhaven), CHESS (Cornell)
³ M.Luisa Fdez-Gubieda malu@we.lc.ehu.es J.M. Barandiarán, A. García Arribas, J. Gutierrez, A. García Prieto	Universidad del País Vasco	Materials, Chemistry, Magnetism,	EXAFS, XANES, XMCD, XRD, High magnetic field, Low temperature	Adone (Frascati) SRS (Daresbury) ESRF(Grenoble) Spring-8(Japon)
⁴ Jesús Chaboy jchaboy@unizar.es + 3 staff members	ICMA. CSIC- Universidad de Zaragoza	Materials, Chemistry, Magnetism	XAS (EXAFS + XANES), XMCD Polarized-RS High magnetic field (5-10 T) Low temperature (4.2 K) High pressure (20-50 GPa)	Adone (Frascati), LURE-DCI (Orsay),SRS (Daresbury), ESRF(Grenoble) ARNE (KEK-Japón), Photon Factory (Tsukuba, Japón) Spring-8(Japon) DAFNE (Frascati,Italia)
⁵ Carlos Prieto de Castro cprieto@icmma.csic.es +5 staff	Instituto de Ciencia de Materiales de Madrid, CSIC	Materials.	EXAFS/XANES of thin films, TEY detection.	LURE-DCI (Orsay), ESRF (Grenoble).
⁶ Agustin R. Gonzalez-Elipe (arge@icmse.csic.es) A. Caballero Caballero@us.es J. P. Holgado, J. P. Espinos, F. Yubero	ICMSE- CSIC/Universidad de Sevilla	Chemistry, Materials	EXAFS/XANES, XES, TEY detection, thin films, <i>in-situ</i>	LURE-DCI (Orsay), ESRF (Grenoble)

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⁷ Adela Muñoz Paez (adela@us.es) E. Sanchez Marcos, R.R. Pappalardo, J.M.Martinez	ICMSE-CSIC- Universidad de Sevilla	Chemistry, Materials	Ultradiluted systems, Reflexafs measurements	SRS (Daresbury), LURE(Francia Photon Factory (Tsukuba, Japón) ESRF(Grenoble) Spring-8(Japon)
⁸ Julio Pellicer Porres julio.pellicer@uv.es A. Segura; D. Martinez Garcia; Ch. Ferrer Roca; J. F. Sanchez Royo, D. Errandonea	Universidad de Valencia	Materials, High pressure studies	EXAFS, XANES, XRD, Extreme pressure and temperature conditions	LURE (Orsay) ESRF (Grenoble) APS(Argonne)
⁹ L. Fernández Barquín, Barquinl@unican.es J. Rodriguez, J. I. Espeso	Universidad de Cantabria	Materials, magnetism, high pressure studies	EXAFS, XANES, XMCD, XRD, Low temperature, High Pressure	Adone (Frascati) SRS (Daresbury) ESRF(Grenoble)
¹⁰ Asunción Fernández Camacho asuncion@icmse.csic.es J. C. Sánchez López; T. Cristina Rojas Ruíz	ICMSE-CSIC- Universidad de Sevilla	Materials, Chemistry	EXAFS, XANES, XCMD	LURE (Orsay) ESRF (Grenoble)
¹¹ José Antonio Alonso Alonso, ja.alonso@icmm.csic.es M.J. Martínez Lope; M.T. Casais	ICMM-CSIC	Chemistry, Materials	EXAFS, XANES, XMCD	Campinas (Brasil)
¹² Diego Cazorla Amorós cazorla@ua.es .+ 7	Universidad de Alicante. Alicante	Catálisis, Envirmental Sciences	EXAFS/XANES, Time resolved,	Photon Factory, Spring-8 ESRF, BESSY
¹³ Elena Casero Junquera elena.casero@uam.e ; E. Lorenzo Abad; F. Pariente Alonso	Universidad Autonoma de Madrid	Chemistry, Biological systems	EXAFS/XANES, very diluted systems	Four runs in RS sources
¹⁴ María Hernando, marher@quim.ucm.es . M. Parras; J. M. González-Calbet	Universidad Complutense de Madrid	Materials	EXAFS/XANES, microXANES	LURE (Orsay)
¹⁵ Vicente Rives-Arnau vrives@usal.es M. del Arco, C. Martín, Ma. J. Holgado, S. R González Carrazán, F. Martín Labajos	Universidad de Salamanca	Materials, Chemistry	EXAFS/XANES, <i>insitu</i> control of temperature and atmosphere	Daresbury, ESRF
¹⁶ Teresa Blasco tblasco@itq.upv.es A. Corma, F. Rey, J. M. López Nieto	ITQ, Valencia	Chemistry, Materials	EXAFS/XANES, <i>in situ</i> control of temperature and atmosphere	LURE (Orsay)
¹⁷ Carmen N. Afonso;	Instituto de Optica-	Materials	EXAFS/XANES, GISAXS	LURE (Orsay)

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cnafonso@io.cfmac.csic.es J. Gonzalo, F. J. Gordillo-Vázquez, M.I Jiménez de Castro, Angel Perea, R. Serna, J. Siegel, J. Solís	CSIC			
¹⁸ S. Valencia	BESSY	Magnetism	XAS	BESSY
¹⁹ Fernando Bartolome bartolom@unizar.es L. M. Garcia Vinuesa	ICMA- CSIC/Uni. Zaragoza	Magnetism, Materials	EXAFS, XANES, XMCD, RIXS, high magnetic field, low temperature	LURE (Orsay), SRS(Daresbury), ESRF(Grenoble), ARNE (KEK-Japon), Photon Factory (Tsukuba, Japon), Spring-8 (Japon), ALS (Berkeley), NSLS(Brookhaven)
²⁰ Enrique Rodriguez Castellon castellon@uma.es A. Jimenez, P. Maireles Torres, J. Santamaria, J. Merida, J. Jimenez Jimenez, P. Braos	Universidad de Malaga	Chemistry	EXAFS/XANES, <i>in situ</i> control of temperature and atmosphée	LURE (Orsay), ESRF
²¹ Sofia Diaz-Moreno sofia.diaz-moreno@diamond.ac.uk	DIAMOND	Chemistry, Catalysis	EXAFS/XANES, Time resolved, microfocus	SRS (Daresbury), ESRF(Grenoble) Photon Factory (Tsukuba, Japon) Spring-8 (Japon) DIAMOND
²² Leonardo Soriano, lsoriano@uam.es , J.M.Sanz Martinez, P. Prieto, A. Gutierrez,	U. Autonoma Madrid	Materials	EXAFS, XANES, REFLEXAS, XES, micro- XANES	LURE, BESSYII, Max-Lab, ESRF
²³ Jose E. Prieto de Castro Joseemilio.prieto@uam.es 3 permanent staff	U. Autonoma Madrid	Magnetism, Materials	EXAFS, XANES, XMCD	BESSY, ESRF, Max-Lab, ALS
²⁴ Pedro Gorria, pgk@pinon.ccu.uniovi.es 3 permanent staff	U. Oviedo	Materials, magnetism	EXAFS/XANES, XMCD	ESRF
²⁵ Arantxa Fraile Rodriguez Arantxa.fraile-rodriguez@psi.ch	Swis Light Source	Materials	EXAFS/XANES, XMCD, very diluted samples	MAX-lab, ELETTRA (Italy), BESSY (Berlin), SLS
²⁶ Isabel Castro, Isabel.castro@uv.es M. Julve, F. Lloret, J. Faus, J. Cano, M. Luisa Calatayud, J. A. Real, M. C. Muñoz,	Dpt. Quimica INorganica, Universidad de Valencia	Chemistry, Magnetism	EXAFS, XANES, XMCD, coordination chemcistry	LURE (Orsay),
²⁷ Miguel Camblor macamblor@icmm.csic.es 4 more permanent staff	ICMM-CSIC	Chemistry, Materials	EXAFS/XANES	DARESBURY (U.K.)
²⁸ Joan de Pablo Joan.de.pablo@upc.es , M. Grive mgrive@enviros.biz , L. Duro Lduro@enviros.biz 5 more permanent staff	U. Politecnica Cataluña ENVIROS Spain	Materials, Enviromental Sciences, Chemistry	EXAFS, XANES, microXANES	ESRF

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²⁹ Silvia Ramos sramos@bham.ac.uk	U. Birmingham U.K.	Materials, Chemistry	EXAFS/XANES Micro XAS	ESRF
³⁰ Emilio Moran Miguelez emoran@quim.ucm.es M.A. Alario Franco, M. M. Aguirre, S. Garcia-Martin	U. Complutense Madrid	Materials	EXAFS/XANES	LURE (Orsay)
³¹ Manuel Valiente Manuel.valiente@uab.es A. Bernaus Anna.bernaus@uab.es X. Gaona, Xavi.gaona@uab.es	U. Autonoma Barcelona	Environmental sciences	EXAFS, XANES, very diluted samples, microXANES, solid/liquid reactions	ESRF
³² Maria E. Davila mdavila@icmm.csic.es J. Avila, J. F. Sanchez,	ICMM-CSIC	Materials	EXAFS/XANES, XMCD	LURE (Orsay), ELETTRA (Italia), MAX-LAB(Suecia)
³³ Fernando J. Lahoz Díaz, lahoz@unizar.es J. A. López Calvo, L. A. Oro Giral, J. Pérez Torrente, D. Carmona Gascón, E. Sola Larraga, M. P. García Clemente	ICMA. CSIC- Universidad de Zaragoza	Chemistry, Catalysis	EXAFS/XANES, very diluted samples	Daresbury (UK)
³⁴ Marta Castellote Armero	IETcc-CSIC	EXAFS, XRD	T and gas control; time- resolved work	ESRF(Grenoble)
³⁵ Mercedes Suarez msuarez@usal.es , M. Sanchez del Rio, E.Gracia Romero	Universidad de Salamanca	Materials	EXAFS, XANES, surface sensitive detection	ESRF, ELLETRA
³⁶ Elena Arroyo c.arroyo@ceu.es +4 permanent members		Materials	EXAFS/XANES	DESY (Alemania)
³⁷ Diego Cazorla, cazorla@ua.es 7 permanent staff	Dpt. Q.Inorganica, U. Alicante	Materials, Chemistry	EXAFS, XANES	Photon Factory, Spring-8, ESRF, BESSY
³⁸ Eugenio Coronado Eugenio.coronado@uv.es C.J. Gomez-Garcia, J.J. Borrás Almenar	Universidad de Valencia	Materials, Chemistry, Magnetism	EXAFS, XANES, XMCD	LURE (Orsay), ESRF
³⁹ Santiago Garcia Granda sgg@fq.uniovi.es 12 permanent staff	Q. Fisica, U Oviedo	Materials	EXAFS/XANES	ESRF
⁴⁰ Javier Diaz javidiaz@condmat01.geol.uniovi.es C. Quiros	U. Oviedo	Materials, Magnetism	EXAFS, XANES, TFY and TEY detection, XMD, EXRD, low magnetic fields	ESRF, Elettra, Bessy, ALS (Berkeley), SSRL (Stanford)
⁴¹ Joaquin Pérez Pariente jperez@icp.csic.es C. Márquez Álvarez	Instituto de Catálisis y Petroleoquímica, CSIC	Chemistry, Materials	EXAFS/XANES, in situ (T and atmosphere control	LURE-DCI (Orsay), LNLS (Campinas, Brazil)
⁴² Hermas Jiménez García,	Univ. Valencia	Chemistry, biological	EXAFS, XANES, very diluted	

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Hermas.Jimenez@uv.es 2 more permanent staff		systems	samples	
⁴³ Teresa Cuberes	Universidad Castilla-La Mancha	Materials, biological systems	EXAFS/XANES	
⁴⁴ Vicente Esteve Cano esteve@qio.uji.es J. M. Delgado, M. Querol	U. Jaume I Castellon	Environmental Sciences	EXAFS/XANES	Without previous experinece
⁴⁵ Javier Quiñones Diez Javier.quiñones@ciemat.es	CIEMAT	Chemistry	EXAFS/XANES, very diluted samples	Without previous experience
⁴⁶ Ana I. Ruiz anairuiz@quim.ucm.es C. Pico, M ^a Luisa Veiga, M ^a Luisa Lopez	U. Complutense Madrid	Materials	EXAFS/XANES	Without previous experience
⁴⁷ M ^a Antonia Señaris Rodríguez tonasr@udc.es S. Castro Garcia suqui@udc.es	U. de A Coruña	Materials, Magnetism	EXAFS, XANES, XMCD, time resolved	Without previous experience
⁴⁸ M ^a Angeles Tena tena@qio.uji.es Five permanent staff	U. Jaume I Castellon	Materials	EXAFS/XANES	Without previous experience

ANNEX 2

List of selected relevant publications (last five years, no more than five per group) of Spanish users of XAS according to scientific cases. (Superscript on the left refer to group number in ANNEX 1)

Materials

⁵C. Prieto, A. de Bernabé, R. Castañer, A. Muñoz-Martín, R.J. Jiménez-Rioboó, M. García-Hernández and A. de Andrés, "Influence of the Short Range Structural Properties on the Elastic Constants of Si/Ge Superlattices", J. Phys.: Condens. Matt., 12, (2000). 2931-2943.

⁵M.L. Ruiz- González, C. Prieto, J. Alonso, J. Ramírez-Castellanos and J.M. González-Calbet, "Stabilization of Cu^(III) under high pressure in the new phase Sr₂CuGaO₅", Chem. Mat. 14, 2055-2062 (2002).

⁵F. Jiménez-Villacorta, A. Muñoz and C. Prieto, "XRD and EXAFS structural characterization of non-spherical crystallographic grains in iron thin films", J. Appl. Phys. (in press, Dec. 2004).

⁶E. Lopez-Navarrete, A. Caballero, A.R. González-Elipe, M. Ocaña Chemical state and distribution of Mn ions in Mn-doped α -Al₂O₃ solid solutions prepared in the absence and the presence of luxes J. Eur. Ceramic Soc. 24 (2004) 3057-3062

⁶E. López-Navarrete, A. Caballero, A.R. González-Elipe, M. Ocaña. Low-temperature preparation and structural characterization of Pr-doped ceria solid solution. J. Mater. Res. 17 (2002) 797-804

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⁶A.R. González-Elipe, F. Yubero, J.P. Espinós, A. Caballero, M. Ocaña, J.P. Holgado, J. Morales. Amorphisation and related structural effects in thin films prepared by ion beam assisted methods. Surface Coatings Technol. 125 (2000) 116-123

⁶V.M. Jiménez, J.P. Espinós, A. Caballero, L. Contreras, A. Fernández, A. Justo, A.R.González-Elipe. SnO₂ thin films prepared by ion beam induced CVD: preparation and characterization by X-ray absorption spectroscopy. Thin Sol. Films 353 (1999) 113-123

⁷ A. Muñoz-Páez, J. I. F. Peruchena, J. P. Espinós, A. Justo, F. Castañeda, S. Díaz -Moreno, D. T. Bowron, Experimental evidences of new nitrogen containing phases of alloyed elements in hardened ferritic steels. Chemistry of Materials 14, (2002). 3220

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⁸J. Pellicer-Porres, A. Polian, A. Segura, A. Di Cicco, A. Traverse. X-ray-absorption fine-structure study of ZnSexTe1-x alloys. Journal of Applied Physics 96, 1491-1498 (2004).

¹⁰T. C. Rojas, J.C. Sánchez-López, M.J. Sayagués, E.P. Reddy, A. Caballero and A. Fernández. Preparation, characterization and thermal evolution of oxygen passivated nanocrystalline cobalt. J.Mat.Chem., 9, 1999, 1011-1017.

¹⁰V.M. Jiménez, G. Lassaletta, A. Fernández, J.P. Espinós, F. Yubero, A.R. González-Elipe, L. Soriano, J.M. Sanz, D.A. Papaconstantopoulos. Resonant Photoemission Characterization of SnO. Phys. Rev.B 60, 1999, 11171-11179.

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- ¹¹C. Piamonteze, H.C. Tolentino, A.Y. Ramos, N.E. Massa, J.A. Alonso, M.J. Martínez-Lope, M.T. Casais, Physica B, **320**, 71-74 (2002)
- ¹¹N.E. Massa, H.C. Tolentino, H. Salva, J.A. Alonso, M.J. Martínez-Lope, M.T. Casais, J. Mag. Mat. **233**, 91-95 (2001)
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- ¹²D. Lozano, E. Raymundo, D. Cazorla-Amorós, A. Linares-Solano, M. Müller y C. Riekel, *Characterization of pore distribution in activated carbon fibers by microbeam small angle X-ray scattering*. Carbon, **40**, (2002). 2727-2735.
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- ¹⁵ M del Arco, P Malet, R Trujillano, V Rives *Synthesis and characterisation of hydrotalcites containing Ni(II) and Fe(III) and their calcination products*, , Chem. Mat., **11** (1999) 624.
- ¹⁵C Barriga, W Jones, P Malet, V Rives, MA Ulibarri *Synthesis and Characterization of Polyoxovanadate-pillared Zn,Al Layered Double Hydroxides: An X-Ray Absorption and Diffraction Study*, ,Inorg. Chem., **37** (1998) 1812.
- ¹⁵C Martin, P Malet, G Solana, V Rives, *Structural Analysis of silica-supported Tungstates*, J Phys. Chem (B) **102** (1998) 2759.
- ²²L. Soriano, M. Abbate, A. Fernández, A. R. González-Elipe, F. Sirotti, J. M. Sanz *Oxidation state and size effects in CoO nano-particles*. Journal of Physical Chemistry B, **103**, (1999). 6676.
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²M. Fernández-García *XANES analysis of catalytic systems under reaction conditions* Catal. Rev.-Sci. Eng. 44 (1): (2002) 59

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²A. Iglesias-Juez, A. Martínez-Arias, A.B. Hungría, J.A. Anderson, J.C. Conesa, J. Soria, M. Fernández-García. *Influence of the nature of the Ce-promoter on the behavior of Pd and Pd-Cr TWC systems*, Appl. Catal. B 259 (2004) 207.

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⁷ P.J. Merklings, A. Muñoz-Páez E. Sánchez Marcos, *Exploring de Capabilities of X-ray Absorption Spectroscopy for determining the structure of electrolyte solutions: Computed spectra fro Cr³⁺ and Rh³⁺ in water based on molecular dynamics* J. Amer. Chem. Soc. 124, 10911 (2002).

¹⁶F. Rey, G. Sankar, T. Maschmeyer, J. M. Thomas and R. G. Bell, *Synthesis and characterisation by X-ray absorption spectroscopy of a suite of seven mesoporous catalysts containing metal ions in framework sites*, Topics in Catalysis 3 (1996) 121.

¹⁶C. Prieto, T. Blasco, M. Cambor and J. Pérez-Pariente, *Characterization of Ga-substituted zeolite beta by X-ray absorption spectroscopy*, J. Mater. Chem. 10 (2000) 1383.

²⁴T. Blasco, P. Botella, P. Concepción, J. M. López Nieto, A. Martínez-Arias, C. Prieto *Selective oxidation of propane to acrylic acid on k-doped MoVSbO catalysts. Catalyst characterization and catalytic performance*. J. Catal.(2004) in press

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²⁰E. Rodríguez-Castellón, A. Jiménez-López, P. Maireles-Torres, D.J. Jones, J. Rozière, M. Trombetta, G. Busca, M. Lenarda, and L. Storaro. *Textural and structural properties and surface acidity characterisation of mesoporous silica-zirconia molecular sieves*, J. Solid State Chemistry, 175 (2003) 159.

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²¹M. Basyaruddin, B. Abdul Rahmana, Peter R. Bolton, John Evans, Andrew J. Dent, Ian Harvey and Sofia Diaz-Moreno, 'Application of Stopped Flow Techniques and Energy Dispersive EXAFS for Investigation of the Reactions of Transition Metal Complexes in Solution: Activation of Nickel -Diketonates to Form Homogeneous Catalysts, Electron Transfer Reactions Involving Iron(III) and Oxidative Addition to Iridium(I)', *Faraday Discussions*, 122, p. 211 (2002).

²¹Sofia Díaz-Moreno and Daniel T. Bowron, 'Determination of the in-solution molecular structure of reactive osmium compounds involved in the synthesis of vicinal diols', *Organometallics*, 22, p. 390 (2003).

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²⁶R. Ruiz, C. Surville-Barland, Y. Journaux, J.C. Colin, I. Castro, B. Cervera, M. Julve, F. Lloret and F. Sapiña. *A Family of Oxamido-Bridged Mn^{II}Cu^{II} Bimetallic Molecular-Based Ferrimagnets: Synthesis, EXAFS Structural Characterization, and Magnetic Properties*. *Chem. Mater.* (1997), 9, 201-209.

²⁶A. Escuer, I. Castro, F. Mautner, M. Salah-El-Fallah and R. Vicente. *Magnetic Studies on the μ -Azido Polynuclear Nickel(II) Compounds with the 222-tet Ligand. Crystal Structure of $(\mu\text{-N}_3)_2[\text{Ni}(222\text{-tet})]_2(\text{BPh}_4)_2$, (222-tet = triethylenetetramine) and EXAFS Structural Characterization of the Triangular Compounds $(\mu\text{-N}_3)_2[\text{Ni}(222\text{-tet})]_3(\text{X})_2$, X = PF₆⁻ and ClO₄⁻*. *Inorg. Chem.*, 36, (1997) 4633-4640.

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Annex 3. X-ray Magnetic Dichroism

List of supporters and their scientific cases for a XMD station

1. Half Metallic Magnetic Compounds. (ICMA, J. García & J. Blasco)

The emerging field of magnetoelectronics has spurred up interest in studying the spin-polarized transport properties of metallic ferromagnetic materials [1]. In a ferromagnetic metal (Fe or Co), the exchange energy splits the conduction band into majority and minority carrier bands, resulting in a spin imbalance at the Fermi level. The transition metal ferromagnets and their alloys are found to be partially spin polarized and have polarization values typically in the range of 25-40%. In the ultimate limit of complete spin polarization of the conduction electrons at the Fermi level, one electron spin has a band gap at the Fermi level whereas the Fermi level intersects the band for the other electron spin. Magnetic materials with such band characteristics are termed half-metallic [2].

Half-metallic compounds provide conduction electrons with only one-spin directions at the Fermi level, which normally optimizes the output of spintronic devices. In most cases, ideal half-metallic behavior is expected only at low temperature where thermal excitation of magnons is weak and a significant gap exists for one electron spin. Therefore, the polarization magnitude decreases as temperature increases. This is the reason to search half-metallic compounds with high Curie temperature in order to build devices operational at room temperature. To this respect, a great deal of attention was focused on perovskites, manganites and ordered double-perovskites.

Doped manganese perovskites $RE_{1-x}A_xMnO_3$ (RE = trivalent rare-earth, A = divalent alkaline-earth element) show magnetoresistance values of unprecedented magnitude. In most cases, the large resistance changes are achieved around room temperature but only in a strong field, thus severely limiting their practical utility. On the other hand, ordered double perovskites are very promising among the metallic compounds since Sr_2FeMoO_6 was reported to show half-metallicity and Curie temperature of 420 K [4]. The tailoring of Curie temperature (T_c) and metallic properties is not well understood so far. For example, the decrease of A-size lead to materials with similar T_c and lower conductivity in the A_2FeMoO_6 system. However, the same kind of substitution in the A_2FeReO_6 system produces samples with higher T_c but very poor conductivity. Nowadays the maximum recorded T_c is reported for Sr_2CrReO_6 (620 K) that can be grown in metallic thin films by sputtering techniques [5].

A number of techniques have been employed for measuring the degree of spin polarization in a material. Among them, XCMD is a powerful tool due to the atomic specification. We hope that XCMD would provide new insights to understand the electronic states of the transition metals and the type of magnetic interactions. Finally, it is worth mentioning that the study of both families of compounds could shed light in the basic properties of mixed oxides. The strong interplay among orbital, magnetic and structural degrees of freedom gave rise to new 'exotic' properties explained in terms of charge and/or orbital ordering. A deep study of these properties is casting doubts on the naive ionic approximation of the oxides so that the use of new techniques such as XCMD could give rise to new ideas to understand the basic phenomena in this field.

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2. Magnetism in Nanostructured materials (UPV, M.L. Fernández-Gubieda, F. Fernandez Barquin, U. Cantabria).

Magnetic nanostructured materials have fostered an intense research activity in the last years because of the potential applications in magnetic recording, sensing and biomedical applications as cell labeling, drug delivery, hyperthermia [Nalwa 2002, O'Handley 2000].

The nanostructures exhibit a rich variety of interesting magnetic phenomena. Their novel properties emerge as the sample size becomes comparable to or smaller than certain characteristic length scales, such as spin diffusion length, carrier mean free path, magnetic domain wall width, exchange length etc. As a consequence, new magnetic phenomena appear: superparamagnetism [Néel 1949, Dormann 1997], exchange coupling between different magnetic phases [Nogués 1999], induced magnetic moment [Crespo 2004]. XMCD experiments can be of enormous interest to study the new magnetic phenomena associated to these systems since this technique incorporates magnetic selectivity on the atomic species and can provide information on spin and orbital magnetic moment.

The *magnetic nanoparticles* are among those nanostructured materials that present the highest interest because they offer attractive possibilities in biomedicine [Pankhurst 2003] and in magnetic recording [Puntes 2001]. Most of these systems present two magnetic phases in a core/shell structure. The core (2-10nm) can be a crystalline ferromagnet (Fe, Co, Ni) or an amorphous ferromagnet (FeCoNiB), and the shell (2-3nm) can be a diamagnetic (Au, Ag, Pt, Cu) or an antiferromagnet (Fe-Co oxide). XMCD experiments will ensure the study of the magnetic behavior of phases, the core and the shell. Different magnetic aspects will be explored: a) the induced magnetic moments on the diamagnetic shell (Ag, Au, Cu), b) the interface effects on the magnetic anisotropy, c) the influence of particle size on the orbital and spin magnetic moment, d) exchange coupling between ferro and antiferro magnetic phases.

Other interesting nanostructured materials are *the nanogranular films*. The nanogranular films are made of magnetic nanoparticles (Fe, Co) embedded in a nonmagnetic metallic matrix (Au, Ag, Cu). These systems present giant magnetoresistance: a huge decrease of the electrical resistance when a magnetic field is applied. This phenomena has a paramount relevance in the spintronic field [Baibich 1988; Berkowitch 1992, Xiao 1992]. The magnetic and magneto transport properties of the nanogranular films are strongly influenced by particle size and interface. The influence of the interface increases as the cluster size diminishes. This situation corresponds to a high surface to volume ratio, i.e, for a cluster size of 3 nm the number of atoms at the interface is at least 60% of the total atoms in the cluster. In this case, the influence of the interface on the magnetic behavior is determinant. X-ray magnetic circular dichroism will provide us direct information about the effect of the interface on the magnetic and magneto transport response.

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3 Amorphous Ferromagnets (UPV, M.L. Fernández-Gubieda).

Metal-metalloid Fe based amorphous alloys have been the subject of considerable research activity for the last two decades due to the interest of their outstanding magnetic properties. A great amount of experimental data has been gathered [Luborsky 1983; Hasegawa 1983] and some elaborate theoretical investigations have been accomplished [B.W. Corb 1983; Malozemoff 1984]. However, the magnetism of 3d amorphous alloys is still far from being understood.

Two basic frameworks, localized and itinerant magnetism, have been specifically applied to develop theories that explain the magnetic behavior of the amorphous ferromagnetic alloys, but none of them is capable to offer a complete explanation of the composition dependence of the magnetic properties.

A special handicap is the knowledge of the ferromagnetic nature (weak or strong) and its concomitant implications on the magnetic behavior [Fdez-Gubieda 2000]. X-ray magnetic circular dichroism (XMCD) at the Fe K-edge offers a unique possibility to determine without ambiguities the ferromagnetic nature and the 3d magnetism of amorphous ferromagnets.

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4. Granular Ferromagnets (Un. Oviedo, J. Blanco & P. Gorria).

The study of FeTM (TM=transition metal) granular systems constitutes itself a very broad field within the 3d Magnetism research. In particular, solid solutions of the type $\text{Fe}_x\text{Cu}_{100-x}$, obtained by mechanical alloying, show important magnetovolumic effects [1-2], which are at the origin of both the Invar and anti-Invar behaviours observed in these materials. These magnetovolume instabilities have been experimentally determined from both magnetization and neutron diffraction experiments. Therefore, it is necessary to study, from the microscopic level, the mechanisms responsible for these magnetic instabilities. To this aim XMCD can be an invaluable tool as it allows us to disentangle both Fe and Cu magnetism. In particular, the study of the XMCD at the Fe and Cu K-edge should provide information concerning the Fe magnetic moment, the hybridization between Fe 3d and the Cu sp-band and the possible magnetic polarization of this Cu sp-band induced by the Fe magnetic moments.

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5. Rare-earth Transition Metal Intermetallic Compounds. (ICMA, J. Chaboy)

The Magnetism of rare-earth-transition-metal (R-M) systems concentrates a large body of research. It relies on a combination of 4 *f* localized and 3*d* itinerant magnetism giving rise to a wide range of magnetic properties, some of them well suited for technical applications, as for example hard-magnet devices [Buschow1988, Herbst 1991].

The magnetic coupling of the magnetic moments in R-M intermetallic compounds is not well modeled by any theoretical model. However, there is a general phenomenological consensus regarding the role played by the rare-earth 5*d* electrons to determine the magnetic behaviour through the hybridization with 3*d* states of the transition-metal (M) [Campbell,1972]. Therefore, it is of paramount interest to characterize magnetically the R(5*d*) states. However, this characterization is a hard task because the response of the 5*d* states to the macroscopic magnetic probes is small and it is masked by the high R(4*f*) and M(3*d*) magnetic signals. To this respect, the capabilities of XMCD are very attractive as this technique incorporates magnetic selectivity on the atomic species and, therefore, it should be able to characterise both the transition metal and the rare-earth sublattices independently.

From the point of view of both basic and applied magnetism, there are many R-M systems in which the use of XMCD is of fundamental interest. A common open problem to these systems concerns the determination of the role played by the rare-earth 5*d* states for tuning the macroscopic magnetic properties. Beyond this common goal, XMCD can provide a deeper insight into different subjects of *classic* Magnetism that remain still open. Among them we can indicate: i) the study of the competition between localized (RKKY) and itinerant (Stoner's model) magnetism: role of the rare-earth 5*d* states [Laguna-Marco2004]; ii) study of the Co magnetic moment instability in RCo₂ systems [Gratz2001]; iii) order of the ferromagnetic-paramagnetic transitions and its relationship with the collective metamagnetic behaviour of the 3*d* electrons in RCo₂ systems [Duc]; iv) triggering of ferromagnetic order in paramagnetic systems as YCo₂ driven by substitution of non-magnetic Al for Co [Yokoyama2001]; v) effect of applied pressure on the collapse of R and M magnetic moments [Hauser2000]; etc.

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6 Single-molecule magnets (ICMA, F. Luis)

Molecular crystals made of large magnetic molecules, such as Mn₁₂ [1], have attracted a great deal of scientific interest in the last few years. These molecular clusters have a net spin $S = 10$ at sufficiently low temperatures and are therefore intermediate between paramagnetic ions and bulk magnets. Furthermore, the magnetization of Mn₁₂O₁₂ becomes hysteretic below approximately $T = 3$ K [2]. This property makes these materials potential candidates for information storage at the molecular scale. Hysteresis is caused by the superparamagnetic blocking of the molecular spins along the direction (*z*) favoured by the uniaxial magnetic anisotropy. The anisotropy is related to

the strong Jahn-Teller distortion of the oxygen octahedron surrounding the eight Mn³⁺ ions located in the outer ring of the molecular core. These molecules are also the first mesoscopic materials for which quantum tunnelling of the magnetic moment has been convincingly observed [3].

Their unusual properties make these materials very promising for applications in both high-density recording and quantum computation. However, this requires that the molecules can be processed by e.g. depositing them onto metallic surfaces or inside nanoporous materials or by connecting them to other compounds (paramagnetic spins, optically active molecules, etc) that enable addressing a single molecule. In the last few years, some Chemistry groups, in Valencia, Barcelona, Florence, and other places have carried out a strong research along these directions [4-6]. The investigation of the magnetic properties of these processed materials faces however two main difficulties. The magnetic signal is usually too low for conventional magnetometers and it is difficult to disentangle the response of the molecules from that of other magnetic components that might be present in the sample. For these two reasons, XMCD experiments can be of enormous interest in this field, since this technique has shown to be capable of measuring the response of minute amounts of a magnetic material and it is element specific.

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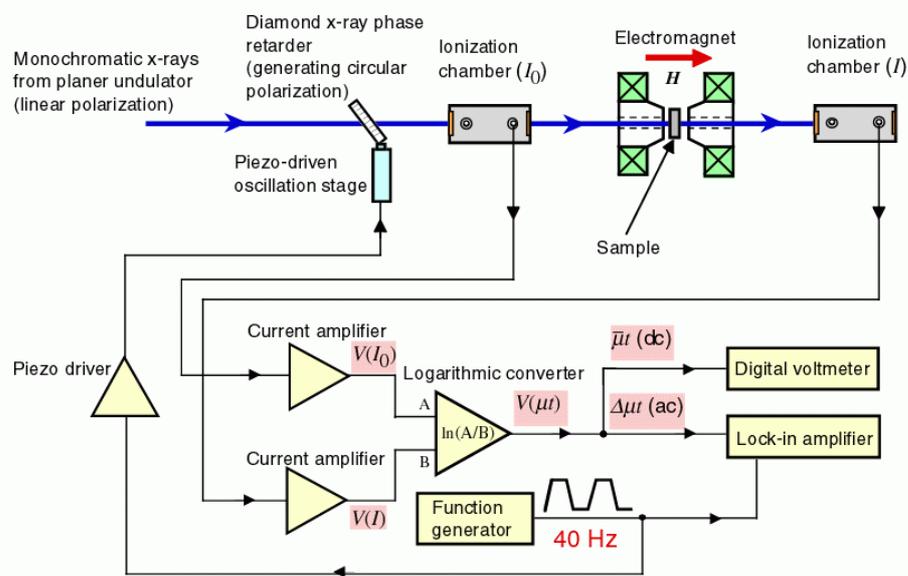
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7. Description of a XMCD Station.

The proposed setup for XMCD experiments is based on the standard arrangement for XAS measurements. It combines the linear polarized x-rays coming from the insertion device with a phase retarder (XPR) [1]. The phase retarder can function as both a quarter-wave plate, which converts from linear to circular polarization, and a half-wave plate, which generates vertical linear polarization. This setup enables the use of two standard methods for recording the XMCD spectrum: magnetic field-reversal and helicity-reversal. Because reversing of the magnetic field can affect the sample by inducing noise due to sample vibration, grain movement, etc., helicity-reversal mode (HM) should be preferred [2]. Therefore, XMCD experiments will be performed in the helicity-modulation mode, by combining an XPR with a phase-sensitive (lock-in) detection system. This technique provides extremely high quality XMCD spectra in short measurement times. Typically, a dichroism signal in the order of 10⁻⁴ is obtainable with a good signal-to-noise ratio for 10 seconds integration time at each energy point.

In order to install the HM technique for XMCD measurements, it is necessary to incorporate a piezo-driven oscillation stage. This system is mounted on a ω -2 θ rotation stage which is used to adjust the Bragg condition of the retarder crystal. Fast switching of photon helicities is performed by flipping the phase retarder around the Bragg angle using the oscillation stage. The x-rays linearly polarized in the orbital plane are alternatively converted to right-handed (RHC) and left-handed circular (LHC) polarization at 40 Hz. The piezo-driven oscillation stage can be installed either at the

end of the optic hutch (highly recommended & easy removal) or at the entrance of the experimental one.



Scheme of the experimental setup for the XMCD measurements with helicity-modulation technique. It shows also the electronics for phase-sensitive detection.

Covered Energy Range.

Typically, a X-ray absorption spectroscopy (XAS) station in the hard X-rays region covers the energy range corresponding to the following absorption edges: the K-edge of both the 3d and 4d transition metals and the L_{2,3}-edges of the lanthanides and 5d transition metals. The setup needs for a XMCD experiment does not affect the optics of the XAS station and therefore, the available energy range would be the same as for XAS experiments. However, it should be noted that the energy range for XMCD measurements is restricted by the absorption of the phase plate. Therefore, by using diamond crystals of different thickness it is possible to cover the energy range from 5 to 16 keV. This energy range covers the L_{2,3}-edges of the lanthanides, the K-edge of 3d elements and the L_{2,3}-edges of the 5d elements up to Au.

Thickness (mm)	Orientation	Geometry	Energy range (keV)	Transmittance (%)
0.34	(111)	111 Bragg	5 – 5.8	3 – 7
		220 Laue	5.8 – 7.5	7 – 41
0.45	(111)	220 Laue	6 - 9	5 – 53
0.73	(111)	220 Laue	8 - 12	22 – 65
2.7	(001)	220 Laue	11 - 16	13 - 47

Detection Mode.

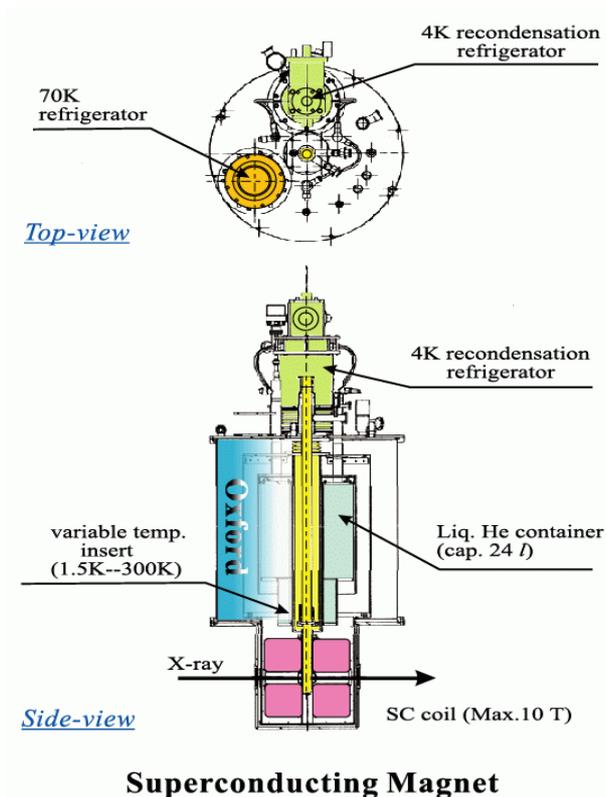
The advantage of the proposed XMCD setup is that it is completely compatible with that used for standard XAS measurements. The only difference resides in the polarization conversion stage that is performed before the beam enters the experimental hutch. The preferred detection modes will be transmission, by using ionization

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chambers, and fluorescence, by using solid state or fluorescence ionization chamber (Lytle) detectors.

Sample Environment.

As for XAS measurements sample environment is highly flexible. XMCD measurements needs of an applied magnetic field that can be supplied by a simple electromagnet (typical fields $H = 0.6, 1.1, 2.0$ T with a 45, 20, 10 mm-poles gap, respectively) or by using a superconducting magnet with variable temperature insert ($H = 0 \rightarrow 10$ T ; Temperature range: $1.7 \rightarrow 300$ K).

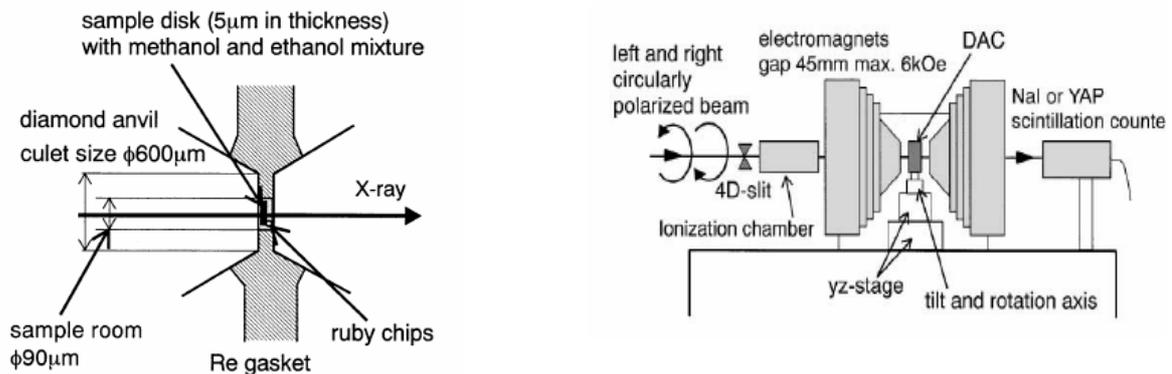


Other Developments: XMCD under extreme conditions.

The proposed XMCD setup, a simple modification of the XAS setup in the transmission geometry, makes it possible to observe different magnetic effects such as: X-ray resonant magnetic scattering (XRMS), X-ray scattering caused by anisotropy of the tensor of susceptibility (ATS), X-ray magnetic linear dichroism (XMCD) and X-ray magnetic diffraction (XMD) [3]. At the initial stage of operation of the line, none of these experiments are proposed. However, it should be underlined that this flexible setup would allow performing such a class of experiments in future.

In particular, the simple arrangement proposed for the XMCD station makes possible to use a diamond anvil cell (DAC) to study magnetic phenomena under conditions of low temperature, high magnetic field and high pressure (from ambient up to a maximum of 50 GPa) [4,5]. At present, several diamond-anvils of 400 μm , 600 μm and 1000 μm with 1 mm or 0.5 mm thicknesses are available for performing XMCD experiments. Typical size of sample disk may be about 400-600 μm and both fluorinate

or a methanol+ethanol mixture can be used as the pressure medium. For the measurement of the applied pressure the ruby-fluorescent method should be used. In a near future it would be possible to perform XMCD experiments using DACs with applied pressure and magnetic fields up to 50 GPa and 7 T, respectively. However, the most important restriction for these experiments comes from the absorption of the pair of diamond anvils (total thickness ~ 3 mm.). For example, the transmitted beam intensity at Fe-K edge is about 0.1% of the incident beam intensity after the phase retarder. Consequently, the evaluation of the performance of installing the high-pressure XMCD setup should be done after the final construction of the Insertion Device. For this reason, it would be necessary to use YAP and NaI scintillation counters as detectors of the transmitted beam.



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ANNEX 4.-X-ray emission spectroscopy (XES)⁴

1.- Scientific case

Detection of emitted X-rays fluorescence in XAS has been used since almost the beginning of this latter spectroscopy as a means of working with opaque and/or diluted materials [Koningsberger 1988]. To isolate the relevant fluorescence from other background contributions, experimentalists initially used Soller slits and filters with gas ionization counters, and more recently solid state detectors with discriminating energy windows of widths ≥ 200 eV. Rather more recently, schemes in which the fluorescence signal is analysed in energy with much higher resolution⁵, of the order of a few eV or below, have opened for XAS a new dimension of work which provides possibilities not available in the earlier studies [de Groot 2001]. These possibilities are of different kinds:

Separation of fluorescence signal from background and interfering edges.

For very low concentration of the absorbing element, the total number of background photons may be, even within a 200 eV window, significantly higher than the relevant fluorescence, leading to a poor S/N ratio. If one is able to select for measurement an energy range having a smaller width, much closer to that of the fluorescence line, that ratio will be significantly increased. Thus by analyzing the SR-excited X-ray fluorescence with a monochromating crystal it has been possible, for example, to detect trace elements in the ppb range, or in the ppm range for samples of less than 0.1 mg [Sakurai 2001]. For a XAS spectrum (which requires higher S/N ratios for EXAFS, but not so much for XANES), correspondingly much higher sensitivities to diluted elements than with traditional fluorescence detectors can be also achieved in this way. Needless to say is the high applicability of this XES spectrometer usage to fields such as biology, nanoscience, ultrathin coatings and doped semiconductors. Apart from this application, the technique allows interfering absorption edges to be studied. For instance, the Mn K edge strongly interferes with the L_{III} and L_{II} edges of many rare earth elements, and the separation of their fluorescence signals, even with a solid state detector, is problematic. Neodymium, praseodymium, etc. manganites could be then studied rather conveniently by means of this type of set-up [García 2001].

High resolution XAS spectroscopy.

When the absorption spectrum is recorded using as detected signal the fluorescence intensity, and the latter is selected within an energy interval significantly narrower than its natural width (which is determined, as is also that of the normal absorption spectrum, by the lifetime of the core hole generated in the absorption event), the intrinsic resolution of the XAS measurement is markedly improved as it was shown by Hämäläinen *et al.* [Hämäläinen 1991]. In fact, this intrinsic resolution is governed rather by the lifetime of the hole formed after the fluorescence event, that is much

⁴ We refer here only to XES with hard x-rays. XES with soft x-rays has also a great interest, but is not the matter of this proposal.

⁵ High resolution X-ray emission spectroscopy, observing fluorescence excited with X-rays of energy ω , is an important technique by itself. Typically one records, at fixed ω , the emission intensity as a function of emitted photon energy ω' , $I(\omega')$; if ω is close to the energy of an absorption edge, producing intensity enhancement effects, it is called resonant XES, otherwise it is normal XES. When the attention is focused on the spectrum response as a function of the $(\omega-\omega')$ difference (where again resonant conditions may be used or not) it is called inelastic X-ray scattering (IXS), X-Ray energy loss spectroscopy or X-ray Raman scattering.

longer than that of the primary hole. This leads to a smaller width (it has even been claimed that, with high quality spectra, a proper mathematical deconvolution treatment can remove this smaller width, leaving only the experimental broadening [Hayashi 2003]). In this way it is possible to resolve structures which are badly resolved or even not visible in a conventional XAS spectrum (even if obtained with integral fluorescence detection), see Fig. A [de Groot 2000]. This provides much better detail in XANES spectra, and also improves the resolution of the EXAFS region closest to the edge. Thus, fast oscillations which decay quickly (e.g. those of light elements at long distances, or features due to multiple-scattering events) can be better analysed providing further detail on the coordination of the excited element (note, however, that the spectrum so recorded may display small differences with respect to a spectrum obtained by mathematically sharpening a normal XAS spectrum through deconvolution [Loeffen 1996]) Recently, this technique has been applied to show that in some manganites the manganese atom is in an intermediate valence state, thus contradicting the conventional belief that manganese in these systems is in a fluctuating mixed-valence state [García 2001]. Moreover, this increased energy-resolution can also be applied in XMCD spectroscopy, so that fine features in linear dichroism spectra coming from anisotropy can be measured.

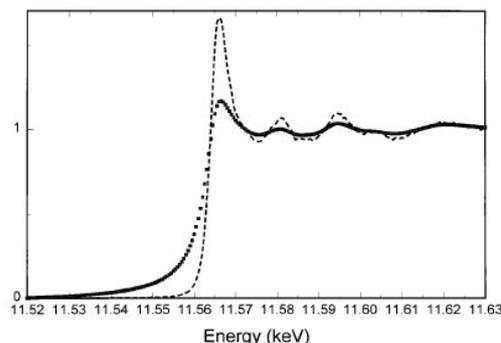


Fig. A XAS spectrum of Pt (L_{III} edge) recorded in normal mode (dots) and by high resolution selected fluorescence (dashed line).

Chemical state- and spin-resolved XAS.

By using XES it is possible to achieve site selectivity in XAS spectroscopy [de Groot 2000]. From recent experiments using X-ray emission spectrometers, it results that the position and shape of the K fluorescence of transition metals is sensitive to the spin and/or redox state of the photoabsorbing atom. Therefore, if the fluorescent

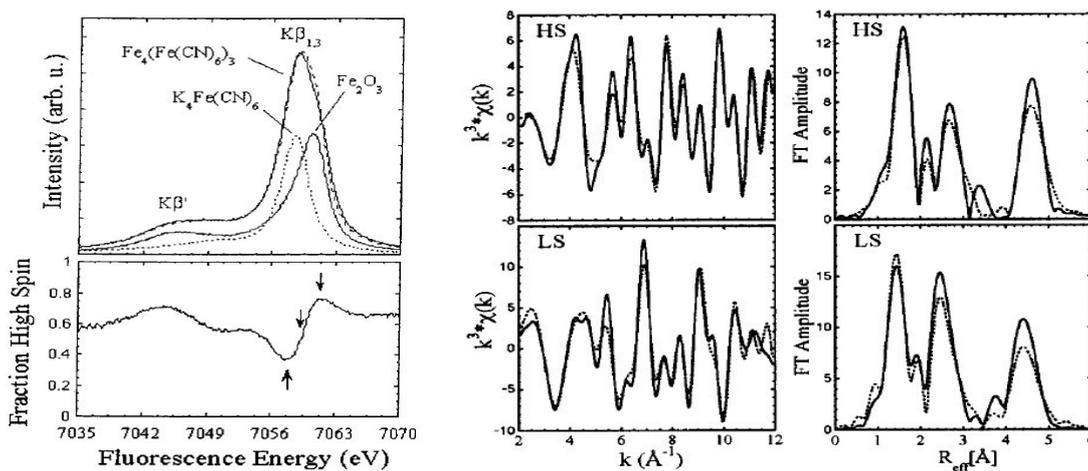


Fig. B (Left) resolution of Fe^{2+} and Fe^{3+} in the $Fe K_{\beta_{2,3}}$ fluorescence of Prussian Blue (energies used are indicated) (Right) EXAFS oscillations, and corresponding Fourier transforms, for both XES- Fe states.

emission is recorded with enough resolution at (suitably chosen) different energies which discriminate among these states, the contribution of these latter to a XANES or EXAFS spectrum can be discriminated as well. In the simplest case, just two energies

are sampled. This was enough to separate the contributions of Fe^{2+} and Fe^{3+} to the EXAFS spectrum of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (Prussian Blue). In this way the coordination data for both species was obtained separately (Fig. B) [Glatzel 2002].

Another possibility is to resolve separate XANES components, corresponding to the two (up and down) spin directions. For example, this has been done for the two peaks of the split $K\beta$ main line in Mn oxide and fluoride [Hämäläinen 1993] or in a magnetic (La, Ca)-Mn perovskite [Quian 2003]. This type of experiments should give another approach to the study of magnetism by X-rays that would complement the XMCD experiments. In another approach monitoring a satellite fluorescence peak is carried out. This peak includes transitions involving electronic levels of a different element which is present as next neighbour to the main excited one. In this case, the obtained XAFS spectrum corresponds to only those atoms which have this other element as close neighbour. Such an approach enables, for example, to probe in a metal/oxide or metal/semiconductor interface system (e.g. in microelectronics or catalysis applications) the environment and state of only two absorbing atoms which are in direct contact with atoms of the semiconductor or oxide phases. This analysis would be highly selective of the interface atoms, providing information about their electronic state and atomic environment.

Full use of XES: 2-D X-rays spectroscopy

Full spectroscopic analysis by X-ray fluorescence (normal or resonant XES) has an intrinsic interest and has been pursued for a number of years. Even effects of X-ray magnetic dichroism have been observed in XES [Krish 1996], although is still an open problem how to get effective magnetic information from the MCD of XES. One of the interests of this technique lies in the fact that the obtained spectra reflect an atom-projected density-of-states of the material and the information retrieved from it is very similar to that obtained from photoemission, but with a fundamental difference: the mean free path of the photons is longer than that of the electrons. With these experiments, an analogue of photoemission spectroscopy can be obtained which samples atoms from the bulk instead of only those close to the surface. When analysed

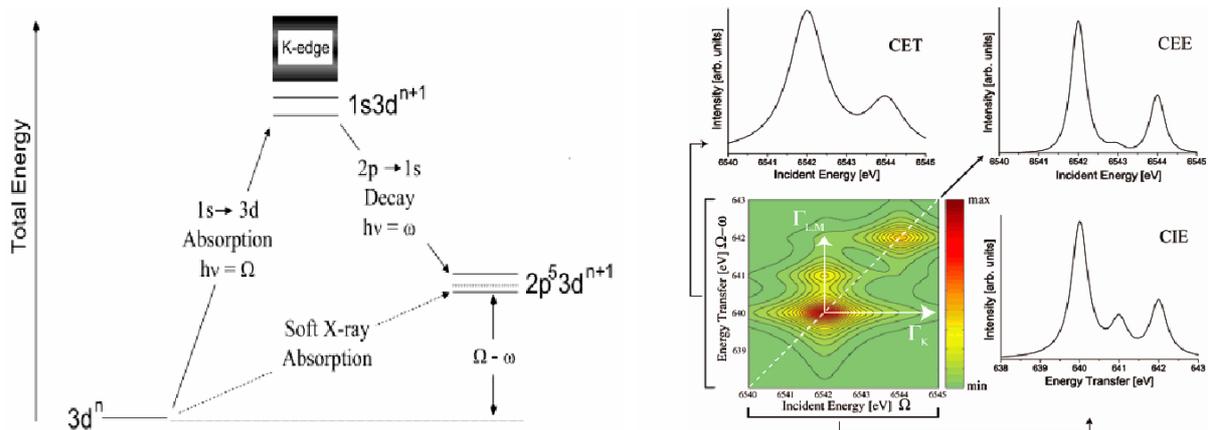


Fig. C Left: Scheme of states and transitions relevant for 2-D RIXS. Right: 2-D representation of data obtained for an hypothetical case such as that shown in the scheme. Right: plots at constant energy transfer, constant emitted energy or constant incident energy.

in detail, it can allow the study of resonant electronic states and local symmetries.

This way of operation does not pertain by itself to X-ray absorption spectroscopy, and therefore would be marginal to the objective of this proposal.

Nevertheless it could be of interest to carry out such measurements in the facility here proposed. However, one may think of recording a full spectrum of the emitted fluorescence (within a given energy window) for every point of an incident energy scan of the type carried out for a XAS (XANES and/or EXAFS) spectrum. Then, each fluorescence spectrum could be deconvoluted in the contributions of different transitions (possibly with principal component analysis using statistical methods and optimizing data utilization). In this way separate XANES or EXAFS spectra could be discriminated for different chemical or magnetic states in the spirit of case 3 above. More generally speaking, this gives rise to a *two-dimensional X-ray spectroscopy*, which is particularly useful in an IXS perspective. These data may then be handled in different manners as shown in the corresponding 2-D representation (Fig. C) [Glatzel 2004]. Note that the plot of intensity versus energy transfer (the IXS mode) is the analogous to a soft X-rays absorption spectrum, which in this way can be obtained with hard X-rays. These techniques, of great theoretical and practical interest, are now in their first steps of development and considerable improvements of them can be expected in the near future. Installation in ALBA of an optimized instrumentation of this kind would contribute to make it a facility of worldwide interest.

2. Relevance for the Spanish SR community.

As said above, the high resolution XES techniques described here are relatively new, significantly with respect to their application to XAS. This, coupled to the fact that the XAS stations to which Spanish groups have normally access do not offer in a regular basis the use of the special monochromator analyzers needed for HR-XES, explains the still scarce use and the relatively limited interest of Spanish groups in these techniques. It seems that only some work at line ID26 of ESRF has been done by Spanish researchers [García 2001]. However, it is expected that the spread of information will increase the knowledge on these techniques within the Spanish scientific community. In the coming years, this will certainly lead to a higher interest and experience in these methods, particularly among the groups most interested in the discrimination between chemical states and electronic levels. Therefore, there is no doubt that if, as proposed here, the HR-XES technique is implemented at a XAS beamline in ALBA, the Spanish scientists (and, for that matter, also many foreign ones) will be directly involved in the use of these new potentialities. This commitment will be especially true if the facility is able to achieve superior performance levels thanks to the main advantages (brilliance, focusing capabilities, etc.) offered by ALBA.

3. Instrumentation

Key elements for XES are a high resolution energy analyzer of the fluorescence radiation (which mandates a small size for the source of the latter) and a sensitive detector (extended or point like, this will depend on the configuration). There is not a single optimum analyzer setup, and different designs have been used. In most cases they are based on a curved focusing and monochromating crystal of Johann or Johansson type mounted in a Rowland circle setup; its position, as well as that of the detector, are moved to scan or select the fluorescent radiation energy. The resolution of this type of analyzer is maximized for near-normal incidence (it decreases with a decrease in the Bragg angle θ); the best results are thus obtained if a number of crystals and Bragg reflections with different $2d$ spacings are available so that one can match well the wavelength to be analysed. Resolution can be increased also (at the expense of sensitivity) by increasing the Rowland circle radius R and decreasing the sizes of both the emitting area and the detecting element. A rough estimate of the necessary sizes can be done with simple typical formulas [Georgopoulos 1981]. These show for example

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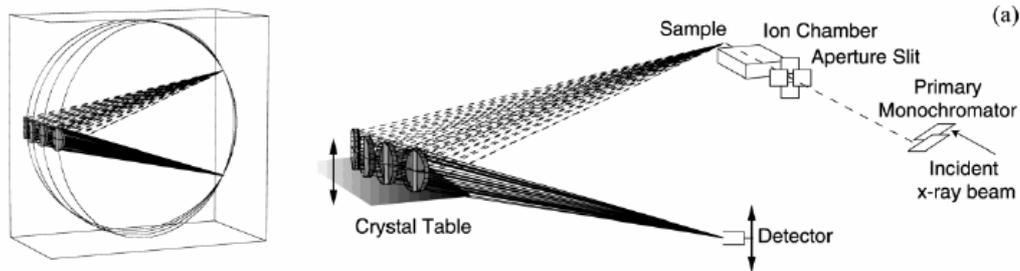


Fig. D Arrangement of several bent Ge crystals, set in a configuration of several Rowland circles which have same source and detector positions, used to increase photon count in XES experiments.

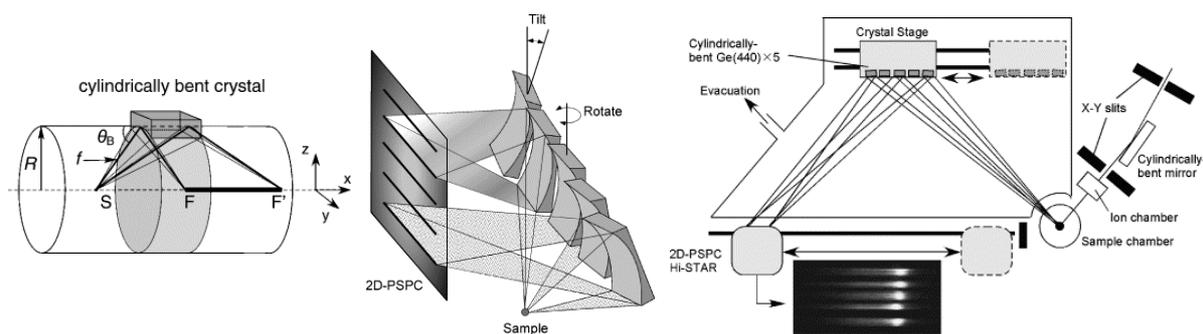


Fig. E Dispersive-focusing XES spectrometer setup described in [Hayashi 2004].

that, using as an analyzer a Johansson Ge(220) crystal in a Rowland circle setup with $R=40$ cm and having spot and detector area dimensions of $50 \mu\text{m}$, one can obtain appropriate resolutions.

For Bragg reflections of different crystals, the following resolutions can be expected: for the Ti $K\alpha_1$ radiation ($E=4.51$ keV, natural width=1.45 eV), ca. 0.22 eV through the (220) reflection; for Co $K\alpha_1$ ($E=6.93$ keV, natural width ≈ 2.7 eV) and with the (440) reflection, 0.12 eV; for Pt $L\alpha_1$ ($E=9.44$ keV, natural width ≈ 7.6 eV) with the same reflection, 0.5 eV; for U $L\alpha_1$ ($E=13.61$ keV, natural width ≈ 12.4 eV) and (660) reflection, 0.7 eV; for Pd $K\alpha_1$ ($E=21.18$ keV, natural width ≈ 8.8 eV) and with reflection (10 10 0), 0.9 eV. Note that these figures assume perfect optics; real conditions, i.e. imperfect crystals, and alignment will increase this figure, possibly by a factor of 2. Refined estimations and designs may be obtained with ray tracing methods; still, it is clear that the beam spot on the sample will need to have dimensions below $100 \mu\text{m}$ to reach the desired XES resolution levels (a fraction, not higher than e.g. 20%, of the natural line width).

Sensitivity is here always an important concern, and this has led in some places to try to increase the analyzer effective area by using several crystals, as for example in the setup of Fig. D, used in APS [Heijboer 2004]. These two concerns together imply that the beam line will need, besides a high monochromator resolution, a precise focusing optics. This is necessary to obtain on the sample a small and positionally stable emitting area without having to use pinholes which would decrease too much the signal intensity (conditions that, obviously, cannot be met by the SPLINE EXAFS facility in ESRF).

If a full 2-D spectrum measurement in the spirit of point 4 above is to be done, the need of repeated movement of such a monochromator (i.e. one scan for each incident energy) is a drawback and therefore dispersive setups have been designed. An example is shown in Fig. E, which has been used in Spring-8 [Hayashi 2004]. A similar spectrometer is used at ESRF [Hoszowska 2004]. In the former case, multiple crystals are used with the purpose of extending the analysed energy range. Other dispersive variations of the Rowland circle setup may be proposed. All these set-ups require position-sensitive counters, where a high spatial resolution (again, at least in the 50 μm range, much preferably lower) will be required.

The specific design of the overall setup to be implemented in a XAS-XES beamline and station in ALBA will depend on technical considerations; if a state-of-the-art facility is desired, this may constitute an interesting challenge calling for imaginative solutions. In any case, it will have to achieve resolution levels significantly below the natural width of the examined fluorescence lines in an energy interval as wide as possible.

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