

# **Spanish X-Ray Beamline for Absorption and Diffraction**

## **Spanish CRG**

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### **1. ABSTRACT**

The present document concerns the Spanish beamline project. This beamline is planned to cover the needs of the Spanish Synchrotron Radiation Users Community with broad scientific fields and interests covering Physics, Chemistry, Materials Science and Biology.

The project is aimed at designing and building a multidisciplinary and multipurpose beamline. It is planned to use a wide front end (9 mrad) to split the beamline into two branches: **A** and **B**. Both branches will be equipped with focusing optics and experimental stations. Thus each branch can be operated simultaneously and independently from each other. One branch will have facilities for high resolution powder diffraction and X-ray absorption experiments including X-ray standing waves, while the other will have a macromolecular crystallography station, a multipurpose diffractometer for single crystal, thin film and surface diffraction and a small angle camera detector.

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## 2. INTRODUCTION

The main goal of the Spanish CRG X-ray beamline is to satisfy the needs of the Spanish Scientific Community with a broad range of interests crossing very different research areas. Due to this, it was decided almost one year ago by the CICYT to conceive the beamline as interdisciplinary and multipurpose, being conscious that this would imply a price to be paid in terms of performances compared to a specialized one-technique beamlines. There are many research groups in Spain in physics, chemistry, and biology using X-ray as their main experimental tool. Most of these groups employ X-ray emitted by sealed tube or rotating anode generators. At the present time, an increasing number is using synchrotron radiation (SR) facilities around the world. Most of the experiments have been carried out as visitors in foreign institutions which have some natural limitations. In this sense, the Spanish CRG beamline will contribute to increase long term research projects using SR and will provide competitive facilities to the Spanish Scientific Community interested in the use of X-ray radiation. The beamline has been designed to give the Spanish Scientific Community access to a third generation synchrotron radiation facility to perform X-ray absorption and diffraction experiments in a broad energy range. The Spanish SR necessities and interests may be served providing a beamline with experimental facilities for X-ray absorption spectroscopy (XAS), high resolution powder diffraction (HRPD), macromolecular crystallography (MC), Single crystal and interface diffraction (SCD) and Small/wide angle X-ray scattering (SAXS/WAXS).

Most of the beamlines built by the ESRF have been installed in insertion devices. These lines are meant to be specialized and fulfill only specific user requirements. The Spanish beamline, as other CGR beamlines, will be installed to a bending magnet. The beamline components are, of course, constrained by the space availability and source characteristics. Nevertheless, the specifications of the planned multipurpose beamline should be better than those obtained in second generation synchrotron sources. By using the advantages of a wide Front End (9 mrad) the Spanish beamline will be split into two lines. Both branches will be fully equipped with its focusing optics and experimental stations. This design will permit measurements on either branch to proceed independently from the other. Each branch will have allocated two experimental stations with similar technical constraints and will use 2 mrad of the available radiation fan. One branch will be allocated on the soft edge (A) and the other on the hard edge

(B). In accordance with the Spanish scientific necessities as well as the technical constraints of the different techniques branch **A** will allocate the following facilities:

- High resolution powder diffraction (HRPD) including anomalous dispersion.
- X-ray absorption Spectroscopy (XAS).
- X-Ray Standing Waves (XSW).

while branch **B**:

- Macromolecular crystallography including MAD
- Single crystal diffraction and diffraction from interfaces
- X-ray diffraction/scattering camera for non-crystalline specimens

Extensive consultations with the Spanish Users Community have been carried out during the last few months. In addition, the global beamline design has been approved by the Spanish National Synchrotron Radiation Committee (Comisión Nacional de Radiación Sincrotrón) after several presentations and discussions. Moreover, very recently a meeting of Spanish synchrotron radiation users has taken place in Madrid to present the concept of the beamline. Representative scientists of different user disciplines have been designed to help in the coordination and definition of the different facilities in accordance with the requirements on each field. Additionally, they have the major responsibility in the elaboration of the scientific cases of their corresponding works areas. The area coordinators are:

High resolution powder diffraction	Dr. Miguel Angel García Aranda
X-ray absorption Spectroscopy	Dra. Asunción Fernadez Camacho and Dr. Joaquin García Ruiz
Single crystal diffraction	Dr. Enrique Gutierrez Puebla
Interface diffraction	Dr. Enrique García Michel and Dr. Agustin Rodríguez Gonzalez-Elipse

Macromolecular crystallography

Dr. Inagcio Fita

Small angle X-ray scattering

Dr. Tiberio A. Ezquera and

Dr. José Manuel Andreu

The above scientists have contributed to the elaboration of the scientific cases that are presented in section 3. In section 4 the conceptual description of the beamline is explained. Section 4.5 deals with the experimental stations, section 5 with budget and finally section 6 with the time schedule.

### 3. SCIENTIFIC CASES

#### 3.1. POWDER DIFFRACTION

##### 3.1.1. Introduction

Powder diffraction has been used for more than half a century for phase identification, determination of accurate unit cell parameters and for the analysis of structural imperfections. There was a dramatic increase of interest in powder methods during the 1970s following the Rietveld's proposal to use the full profile as data for structure refinement.

Rietveld technique has boosted the interest in powder diffraction as it is possible to undertake many studies resulting in a better characterisation/understanding of polycrystalline materials. For example it is possible (a) to solve crystal structures "ab initio" without a prior knowledge of the structure, (b) to determine quantitatively the amounts of crystalline phases even in very complex composite materials, (c) to refine a crystal structure in multi-phases systems, (d) to analyse the size and shape of microparticules, (e) to study residual stress and strains, etc. All these applications have been extended to the broad range of temperatures, pressures and chemical gradient, that can be easily attained in a powder diffraction experiment.

However, as the problems to be tackled with powder diffraction are becoming more complex, higher resolution data are needed. Alternatively, for time and temperature resolved experiments, more intensity is essential to collect data in shorter time scales. Synchrotron powder diffraction is playing a key role as it provides the highest resolution diffraction data and the shortest overall collecting time. These leading characteristics of powder synchrotron diffraction result in invaluable information for several branches of science. Hence, scientists working in Solid State and Materials Science are increasingly demanding more synchrotron beam time to solve their problems.

The synchrotron powder diffraction domains of excellence are small angle scattering, phase identification in transient solid state reactions, transformations under pressure, and very high resolution powder diffraction. Due to the extremely high Q-resolution, this technique is ideal for *ab initio* structure determination and microstructural analysis.

Most of the Spanish powder-diffraction users have already experience in synchrotron powder diffraction. We can underline works in resonant diffraction<sup>(1,2,5)</sup>, time-resolved transformations<sup>(3,4,8)</sup>, pressure and temperature dependent studies<sup>(7,9)</sup>, and complex structure determinations<sup>(6,10)</sup>. This will be the core seed that will encourage other groups to start relevant studies with synchrotron powder diffraction.

### 3.1.2. Scientific cases

#### **High precision powder crystallography.**

The high resolution data will allow to study the structures of interesting compounds such us drugs and pharmaceutical compounds, superconducting samples, alloys, catalysts, zeolites, ionic conductors, magnetic materials, etc. Many industrially and technologically important materials are not single phases, and in this diffractometer it will also be possible to carry out the phase analysis of these mixtures and eventually to study the structures of some phases. There is always a compromise between resolution and intensity and, below an approximated instrumental resolution limit ( $\Delta d/d \sim 0.04\%$ ) sample broadening is so important that more resolution does not help very much to the structural investigation. There is state-of-the-art software that allows combined structural studies using several powder data sets which results in a very detailed structural picture. Some representative examples are indicated below :

*Ab initio structure determination of metal organo-inorganic materials.* The structure of complex metal phosphonates with unit cell volumes bigger than  $2000 \text{ \AA}^3$  may be solved by powder diffraction.

M.A.G. Aranda. Dept. Química Inorgánica, Cristalografía y Mineralogía. Universidad de Málaga.

*Ab initio structure determination of metal organo metallic compounds and ion exchanger inorganic materials.*

S. García-Granda. Dept. de Química Física y Analítica. Universidad de Oviedo.

*Quantitative phase analysis of heat-resistant coatings in contact with metal melts.* The high resolution powder data will allow to identify and analyse the complex mixture of compounds formed in the outer part of the coating after the reaction with melts.

S. García-Granda. Dept. de Química Física y Analítica. Universidad de Oviedo.

*Crystal structures of Spin-Ladder materials.* These compounds are obtained by the assembly of spin-1/2 chains next to one another to form quasi-one-dimensional "ladders" of increasing width that are interesting as low-dimensional quantum magnets. Cuprates of the series  $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ , with  $n = 3, 7, 11, \dots$  (prepared as tiny

amounts under high pressures) show complex crystal structures, with large lattice parameters. Hence, the high resolution data from a high intensity radiation source is necessary to study the structural details and their evolution with temperature.

J.A. Alonso. Instituto de Ciencia de Materiales. CSIC. Madrid

D. Beltrán. Institut de Ciencia dels Materials. Universidad de Valencia.

### **Resonant diffraction.**

Resonant diffraction, based on the anomalous dispersion, is a technique that provides new information making possible site and chemical selective diffraction enhancement. High resolution resonant diffraction will allow to understand the cation and oxidation states distribution in complex materials, generally of high industrial interest, such as electro-optic materials or superconductors. Some examples of the interest in the Spanish Powder Diffraction Community are :

*High-resolution resonant diffraction study of the Lithium ionic conductor  $La_{2/3-x}Li_{3x}TiO_3$  and related materials.* This very fast Lithium conductor has a perovskite-type structure with cation deficiencies that will be analysed by anomalous dispersion.

M.A.G. Aranda. Dept. Química Inorgánica, Cristalografía y Mineralogía.. Universidad de Málaga.

*Cation distribution and structural analysis of Rare-earth nickelates,  $Ln_{1-x}A_xNiO_3$ .* Small changes in the Ni valence, due to the  $A^{2+}$  cations replacing the lanthanides, result in dramatic changes in the transport and magnetic properties of these materials. The replacement of Ni by other transition metals, such as Mn, leads to interesting dismutation effects associated to subtle lattice distortions. The structure and cation distribution will be studied from high resolution synchrotron powder data by using anomalous dispersion.

J.A. Alonso. Instituto de Ciencia de Materiales. CSIC. Madrid.

*Anomalous diffraction study on Fe-Co-Cu nanocrystalline alloys*

C. Prieto A. de Andres, A. Bernabe and F. Monpean, Instituto de Ciencia de Materiales. CSIC. Madrid.

*Cation distribution analysis of the  $A_{1-y}B_yC_2X_4$  series ( $A = Zn$  or  $Cd$ ;  $B = Mn, Co, Ni$  or  $Fe$ ;  $C = Ga, In$  or  $Cr$  and  $X = S, Se$  or  $Te$ ) studied by resonant powder diffraction.* To determine the metal distribution it is vital to understand the magnetic, spectroscopic and magneto-optical properties of these materials.

F. Palacio. Instituto de Ciencia de Materiales de Aragón. CSIC. Zaragoza

### **Real crystals: defects, microparticles and microstrains.**

Because the instrumental broadening will be very small, it will be possible to study the line broadening due to the material either from fabrication or use. Then, the technological implications will be analysed to understand, and if possible to improve, the properties of the

studied materials. Thermal and mechanical treatments of super-alloys is a good example where the microstructural characteristics play a key role that governs the practical applications. As an example the following project can be used :

*Temperature and time resolved studies of the evolution of domains in metal alloys.*  
The growth of domains after a phase transition of alloys such as  $\text{Cu}_3\text{Al}$ ,  $\text{Fe}_3\text{Al}$ ,  $\text{Fe}_3\text{Pt}$ , will be analysed following the changes in several diffraction peaks.  
A. Planes. Dept. d'Estructura i Constituents de la Matèria. Universitat de Barcelona.

### **Studies of phase transitions and transformations.**

Structural phase transitions in solids is one of the most exciting areas of condensed matter. The very high resolution will allow to measure even very subtle distortions making possible to analyse the order parameter(s) as a function of temperature, chemical gradients, and eventually pressure. Melting and crystallization processes of a very wide range of materials such as polymers or advanced alloys will be analysed. Thermal expansion characterization will also be undertaken. Some examples are given below :

*Subtle structural transitions in Lithium ionic conductors,  $\text{LiM}_2(\text{PO}_4)_3$  ( $M = \text{Sn}, \text{Hf}, \text{Zr}$ ).* Some Lithium ionic conductors undergo very subtle structural transitions that strongly affect to the conductivity properties. Very high resolution data is vital to understand the transitions although neutron data is also necessary to locate the mobile cations precisely.  
J.E. Iglesias. Instituto de Ciencias de Materiales. CSIC. Madrid.

*Influence of hydrostatic high pressure on the structural arrangement of the  $\text{A}_{1-y}\text{B}_y\text{C}_2\text{X}_4$  series with  $A = \text{Zn}$  or  $\text{Cd}$ ,  $B = \text{Mn}, \text{Co}, \text{Ni}$  or  $\text{Fe}$ ,  $C = \text{Ga}, \text{In}$  or  $\text{Cr}$  and  $X = \text{S}, \text{Se}$  or  $\text{Te}$*   
Palacio. Instituto de Ciencia de Materiales de Aragón. CSIC. Zaragoza.

*An in-situ investigation of the nanocrystallization process in  $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_1\text{Cu}_1\text{X}_2$  ( $X = \text{Zr}, \text{Nb}, \text{Mo}$  and  $\text{V}$ ) Alloys*  
A. Conde-Amiano , C. Conde-Amiano and J. Borrego, Dpto. Fisica de la Materia Condensada, Universidad de Sevilla.

### **Time-dependent phenomena: in situ powder synchrotron diffraction.**

Time resolved experiments allow to follow chemical reaction. It is vital to identify the phases in transient solid state chemical reactions and to characterize structurally crystalline materials under relevant industrial conditions if improvements in chemical processes have to be carried

out. New bidimensional detectors will allow to access to short time scales. Two projects related with the accessible part of the crystallization processes of cements are proposed:

*Effects of Cement on Clay Barrier Performance.* In the framework of the EU program Nuclear Fission Safety, under a financed EU Project with the industries ENRESA (Spain) and ANDRA (France).

X. Turrillas. Instituto de Ciencias de la Construcción Eduardo Torroja. CSIC. Madrid.

*In situ hydration of calcium aluminate cements by synchrotron radiation and its effect on mechanical properties.*

X. Turrillas. Instituto de Ciencias de la Construcción Eduardo Torroja. CSIC. Madrid.

A summary of subfields of current interest for the Spanish Scientific Community is given below. It is important to underline that our dynamic Community will answer rapidly in case of the appearance of new systems of industrial importance.

### **Transition Metal and Rare Earth Mixed Oxides**

High  $T_c$  superconductors and related materials

Giant Magneto-Resistance materials

Ionic conductors, solid electrolytes.

### **Composite and technological materials: catalysts, zeolites, cement/concrete...**

#### **Molecular solids**

#### **Coordination and organo-metallic chemistry**

#### **Modulated structures and aperiodic materials: quasicrystals...**

#### **Diluted magnetic semiconductors.**

### **3.1.3. Final remarks**

It is very important to offer new opportunities to the Spanish Scientific Community to develop current and new ideas. This must be done not only to improve basic scientific knowledge, but mainly to get a better understanding of every day industrial, environmental and health problems that will help to develop solutions in these areas.

### **3.1.4. References**

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- (10) Aranda, M.A.G.; Losilla, E.R.; Cabeza, A.; Bruque, S. "Effective Correction of Peak Asymmetry: Rietveld Refinement of High Resolution Synchrotron Powder Data of  $Li_{1.8}(Hf_{1.2}Fe_{0.8})(PO_4)_3$ " *Journal of Applied Crystallography*, **1997**, submitted.

## 3.2. X-RAY ABSORPTION SPECTROSCOPY

### 3.2.1. Introduction

X-ray absorption spectroscopy is today a basic tool of research in Science. Its capability to supply, in an easy way, direct structural and electronic information of the matter independently of its aggregation state makes it useful in the different Science disciplines. XAS has demonstrated to be a suitable technique to solve problems in Solid State Physics, Materials Science, Surface Physics, Catalysts, Chemistry, Biology and Geology. Moreover, XAS is the technique most strongly linked to Synchrotron Radiation. It is well-known that almost the whole world research activity in XAS is made with SR.

These characteristics of XAS are probably the origin of the wide and intense activity of the Spanish Scientific Community in this field. Actually there is an important number of experienced users of XAS and related techniques with synchrotron radiation. At the present the most active XAS groups in Spain are:

**Grupo de Magnetismo. Universidad del País Vasco. (UPV).**

M. L. Fdez-Gubieda, J. M. Barandiaran, F. Plazaola, I. Orue, A. García-Arribas, P. Gorria, J. S. Garitaonandia, R. Lopez and J.C Gomez-Sal (Univ de Cantabria). Topics: *Structural and magnetic characterization of magnetic materials. Alloys, glasses, amorphous, nanocrystals and magnetic multilayers.*

**Departamento de Física de la Materia Condensada. Universidad de Cádiz: (CA).**

L. Esquivias, C. Barrera-Solano, M. Piñero.

Topics: *Semiconductors and sol-gel.*

**Departamento de Química Inorgánica. Universidad de Málaga: (MA)**

E. Rodriguez Castellón, M. A. Aranda, S. Bruque.

Topics: *Inorganic materials and layered structures.*

**Instituto de Catálisis y Petroleoquímica. CSIC-Madrid. (ICP)**

Fernández García, J. C. Conesa, M. Lopez-Granados, C. Marquez Alvarez and I. Rodriguez-Ramos.

Topic: *Catalysts.*

**Instituto de Ciencia de Materiales de Madrid (ICM).**

C. Prieto, A. de Andrés, J. L. Martínez, F. Agulló-Rueda, F. Mompeán, M. García-Hernandez, R. J. Jimenez Rioboó, R. Castañer and A. Bernabé.

Topics: *Dopants in solids, highTc superconductor related oxides, semiconductors, metallic thin films and inorganic materials.*

**Instituto de Ciencia de Materiales de Sevilla y Universidad de Sevilla (SEV).**

G. Munuera, A. Caballero, JP Holgado, R. Alvarez, A. Fernandez, AR Gonzalez Elipe, J.P Espinos, G.Lassaletta, JC Sanchez Lopez, F Yubero. P. Malet, C. Martin (Salamanca), V. Rives (Salamanca), MJ Capitan (ESRF), A. Muñoz-Paez, MD Alba, MA Castro, A. Becerro. A. Muñoz-Paez, S. Diaz Moreno, E. Sanchez Marcos, JM Martinez and RR Pappalardo..

Topics: *Catalysts, Thin films, Nanostructured materials, Layered structures and Ionic solutions*

**Instituto de Tecnología Química. Universidad Politécnica de Valencia.(VAL)**

Blasco, A. Corma,. J. Perez-Pariente.

Topics: *Catalysts.*

**Instituto de Ciencia de Materiales de Aragón. CSIC-Universidad de Zaragoza. (ZAR)**

Joaquin García Ruiz, Jesus Chaboy Nalda, Luis Miguel Garcia, M. Grazia Proietti, Javier Blasco Carral, M. Concepción Sanchez Sierra, Gloria Subias Peruga, Alfonso Solera, Jorge Perez, F. Bartolomé, J. Bartolomé.

Topics: *Fundamentals, magnetic materials, transition metal oxides, heterostructures and superlattices, catalysts and inorganic materials.*

The Spanish scientific production in XAS of the last five years is about 250 international publications. It has been pointed out indeed, that Spain is the country without own Synchrotron Radiation Facility that has the highest scientific production in the field of XAS<sup>(1)</sup>.

**3.2.2. Scientific Cases.**

The scientific activity of the Spanish Community in the field of X-ray Absorption Spectroscopy covers a wide area which, in addition to its application to specific problems, includes studies on Fundamentals of XAS, Developing and optimization of new experimental chambers and detectors, experiments in the different modes of the technique as: Transmission, Fluorescence detection for dilute samples, Electron yield detection to be sensitive to the surface, Glancing angle EXAFS, Surface EXAFS and experiences in related techniques as DAFS, XRMS or XCMD.

The applicative activity of our Community extends to Materials Science, Chemistry, Solid State Physics, Surface Physics and Biology. In particular, catalysts, sol-gel materials, thin films and coatings, nanostructured materials, layered and pillared structures, metallic glasses, alloys, magnetic materials, magnetic oxides and high Tc superconductors, semiconductor superlattices and metalloproteins, etc are some of the systems under investigation. The electronic and structural local information obtained from XAFS has allowed to resolve fundamental problems. In the following, an overview is given of the actual situation of some typical topics of interest in the Spanish Community and its previsible evolution.

### **Fundamentals of XAS.**

The richness of the electronic and structural information supplied by XAS is sometimes not well exploited due to the lack of an appropriate theoretical frame. EXAFS is today a well established technique and it is generally accepted that a further development is not necessary, but for a correct interpretation of the data it is necessary sometimes to take into account multiple scattering effects and many body effects as multielectron excitations. In spite of the success of the multiple scattering description of the XANES spectra that have allowed to interpret it in a unique theoretical frame and to get information on geometry (three particle correlation function) and electronic state of the absorber atom, there are still some problems associated essentially to the approximations included in the theoretical calculations, probably due to the use of the muffin tin approximation.

The ZAR group has collaborated since 1985 with the theoretical group of Frascati. The comparison of theory and experiment in very simple systems allowed to establish the significance of the multiple scattering events in the XANES region. Since then, a lot of theory-experiment works have been published by the group. Some important results that should be mentioned are: detection of multielectron transitions in the L spectra of rare earth atoms<sup>(2-4)</sup>, developing of an exact method of comparison of the L<sub>3</sub> and L<sub>1</sub> spectra<sup>(5,6)</sup>. Besides that, the SEV group, in collaboration with the theoretical group of the University of Nancy, has studied the cluster size effects in the XANES and EXAFS spectra of titanium oxides<sup>(7)</sup>. It should be mentioned as well the contribution “on request” to the Encyclopedia of Analytical Science of two members of the SEV group with an article devoted to EXAFS technique<sup>(8)</sup>.

At the present, the ZAR group participates in a European Network on “Interpretation and simulation of core spectroscopy”, the main objective of which is to avoid the use of the muffin-tin approximation. The comparison theory-experience with these new codes and the interpretation of the XANES spectrum in the frame of this theory will be part of the future work of the ZAR group. On the other hand, the SEV group has settled down a collaboration with J. Rehr, author of one of the most used codes to calculate theoretical references, FEFF, to simulate the EXAFS spectra of coordination complexes and solvates showing an aligned distribution of absorbing and backscattering atoms. High quality XANES spectra would be necessary to carry out this investigation.

### **Catalysis.**

X-ray Absorption spectroscopy is a technique particularly appropriate for the study of homogeneous and heterogeneous catalysts. The selectivity of the technique to determine the electronic and geometric structure around the active atom is particularly useful to determine the mechanisms responsible for the catalytic activity. Several Spanish groups have used this technique to study catalytic systems, as SEV, ZAR, ICP, VAL. From these investigations only some important works will be cited: ZAR group studied ruthenium based bimetallic catalysts showing that in the most dispersed catalysts only clusters of 12 to 16 atoms were formed<sup>(9,10)</sup>. In the field of homogeneous catalyst they characterize the intermediate  $TiCl_4$ -filodiene in the asymmetric Diels Alder reaction<sup>(11)</sup>. SEV group has been very active in this field<sup>(12-16)</sup> and some important works would be cited as: study of lanthanide oxides supported on  $\gamma Al_2O_3$ , study of alkaline-metal doped  $V_2O_5/TiO_2$  and  $MoO_3/TiO_2$  systems<sup>(14-15)</sup> and a study of the species appearing at the initial stages of the preparation of a  $Pt/Al_2O_3$  catalysts<sup>(14)</sup>. VAL and ICP also has studied some other catalytic systems<sup>(17-21)</sup>.

The evolution of the XAS in catalysts from the point of view of the Spanish Community follows the general evolution of this topic in the world. The “in situ” studies carried out in adequate cells by heating under controlled gas pressure allow the characterization of the catalysts in the different steps of preparation. Moreover, an important goal to is study the catalyst in its reaction media in order to get information on the mechanisms responsible for the catalytic activity. The structure of the support (zeolites, alumina, silica, etc) is also very important. In the field of homogeneous catalysts the objective is to characterize structurally the intermediates during the reaction which give us information on its evolution mechanisms.

### **Nanostructured materials.**

Nanostructured materials and nanocomposites, characterized by an ultrafine grain size ( $50 < \text{nm}$ ), have attracted interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. The UPV group has studied these kinds of materials due to their magnetic properties<sup>(22)</sup>. Also the SEV group has studied by XAS the effect of small particle size in the electronic structure of nanometric oxide particles<sup>(23)</sup>. X-ray absorption spectroscopy combined with diffraction studies on such materials will provide valuable information on the local structure, lattice distances, degree of oxidation, structure of grain boundaries or formation of alloys or segregated phases.

### **Thin films and coatings.**

The synthesis and characterization of thin films and coatings is of fundamental interest due to the high number of technological applications. Coatings are used as protection against corrosion or erosion, as hard coatings for cutting tools, in optical applications, as sensors, dielectric or ferroelectric layers, etc. Some groups of the Spanish Community, as SEV and ICM have been very active in the use of XAS to characterize thin films and coatings. Examples of the studies carried out in this field are: Surface modification of metals by ion implantation, oxide films growth by ion beam induced chemical vapor deposition or amorphous thin films of magnetic materials<sup>(24, 25)</sup>. The structural information obtained in these systems by XAS has been very useful and cannot be obtained by other methods, specially in the case of amorphous films. In particular, the use of total electron yield detection methods in small vacuum chambers allows the study of growing mechanism and surface modification of thin films by ion beams.

### **Highly diluted species.**

The determination of the local structure of dopants in single crystals, glasses, and semiconductors is one of the main topics in which the Spanish Community is interested. Groups of ICM, ZAR have used XAS to determine the localization site of transition metal dopants in MgO, LiNbO<sub>3</sub> or fluorine glasses<sup>(26)</sup>. This information has been fundamental to understand their optical and electronic properties.

Another field of interest is the solvation structure of ionic solutions. The knowledge of the structure of such systems is interesting from the point of view of basic and applied research,

since many economically important reactions take place in aqueous solution. From the point of view of basic research, transition metal water solutions have been used by the ZAR group as reference models to “ab initio” simulations of the XANES spectra. The SEV group has a long tradition in the theoretical study of the solvation processes, having developed a new model including the continuum-discrete approximations. They have extended recently these works performing experimental measurements using XAS techniques. To carry out these studies, they designed and built a new liquid EXAFS cell<sup>(27)</sup> useful in highly corrosive media, and using it, they have determined the structure of first and second solvation shells in aqueous solutions containing transition metal cations in a wide range of concentrations<sup>(28)</sup>. The existence of ordering beyond the first coordination sphere affects not only to solvent molecules, but to counter-ions, Cl<sup>-</sup>, in solutions containing chromium (III) chloroaquocomplexes<sup>(29)</sup>.

Another classical high diluted species are the metalloproteins. Some experience in this systems was gained lately by the Community<sup>(30)</sup> and its growing is previsible in the future.

### **Heterostructures and Superlattices.**

The study of semiconductor and metallic superlattices and heterostructures has a growing interest because the artificial modulation at atomic level shows very interesting electronic, optical, magnetic and mechanical properties. Actually, the group at ICM works in the structural characterization of multilayers by means of XAFS and related techniques<sup>(31,32)</sup>. The structural properties of superlattices is normally studied by X-ray diffraction techniques. The complementarity of the EXAFS spectroscopy for the determination of the local order around an absorber atom makes it particularly useful in the cases of reduced number of periods of the superlattice where the long range order is very difficult to be observed. Concerning semiconductors, the ZAR group has been carrying out a study on the structural properties of strained materials, either ternary III-V semiconductor epitaxial samples (GaAs, InGaAs, GaAsP, InP/GaAs, InAs/GaAs) have been studied by glancing angle EXAFS, SEXAFS, DAFS and PD obtaining information about strain accommodation and interface characteristics<sup>(33-35)</sup>.

The study of these materials needs techniques sensitive to the surface, particularly if the superlattice is grown in a substrate that is opaque to the X-rays. Detection of absorption by means of the fluorescence yield or the total electron yield is necessary. On the other hand,

techniques as DAFS have demonstrated their utility to separate the contribution coming from the substrate from the contribution of the superlattice. In some cases ultrahigh vacuum environment would be also necessary.

### **Intermetallic alloys, crystalline and amorphous.**

The study of intermetallic alloys is a field of interest in many Spanish groups. In the case of amorphous alloys the application of the XAFS technique to get information on the local structure is the most effective method to try to correlate the structure with its electronic or magnetic properties<sup>(36-39)</sup>. For crystalline systems, electronic information obtained from the XANES and modification of the local structure after adsorption of H<sub>2</sub>, N<sub>2</sub> or C obtained by EXAFS is the relevant information that can be obtained<sup>(40,41)</sup>.

### **Layered structures.**

A traditional field of research of the SEV group has been natural clays. Lately they have focused on such as these forming the smectite family, because of their applications as absorbents and catalysts supports. One of the most spectacular applications based on their absorbing capabilities, is its use as natural barriers in the storage of high activity nuclear wastes. Within this field the SEV group using EXAFS and XANES has determined the structural evolution of the intercalated ions, from the aquocomplexes to the oxide-like environments, detecting as well a new disilicate phase<sup>(42-44)</sup>.

### **Inorganic materials.**

This topic includes a wide spectra of materials that ranges from solid state materials, to solutions or liquid crystals. In general the properties of these materials come from the bulk and they can be amorphous, crystalline, ceramics, glasses etc. The experience in this wide topic is very large in the Spanish Community and its interest is shared by all the groups. As a matter of example, we can cite some works recently published<sup>(45-47)</sup>.

Generally, the study of these materials needs the complementary use of X-ray diffraction and XAFS. The requirements of the XAS experimental station are conventional for these kinds of studies.

### 3.2.3. Final remarks

The actual project for a Spanish Beamline at the ESRF in Grenoble is today a necessity for the Spanish XAS users. Moreover, the existence of experienced groups guarantees the competitive use of this high flux source. In particular, the combination in “branch A” of complementary techniques, i.e. two axis diffractometry and X-ray absorption spectroscopy, makes it of great interest in many problems of Science, in particular in Solid State Physics and Chemistry allowing the simultaneous or quasi-simultaneous use of diffraction and absorption detectors. It is proposed to open new possibilities with quasi-simultaneous absorption/diffraction analysis as well as to improve the station to carry out real time experiments as well as high resolution and anomalous diffraction studies. It will allow to apply the new emerging techniques as Diffraction Anomalous Fine Structure (DAFS) or X-ray Resonant Magnetic Scattering.

Although this beamline is not designed for polarization dependent absorption, the activity of some Spanish groups in the related technique of XCMD to study the local magnetism in hard magnetic materials<sup>(48-50)</sup> must be underlined. As a matter of future, the use of X-ray quarter-wave plate will allow to perform these kinds of experiments.

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### **3.3. MACROMOLECULAR CRYSTALLOGRAPHY**

#### **3.3.1. Introduction**

Crystallography of Macromolecules has developed consistently in Spain only during recent years. However, since the early seventies, there has been a few pioneering attempts to set up the necessary equipment and some research work has also been initiated. At present (April/1997) there are, to our knowledge, seven active protein crystallography groups: two are located in Madrid, one in Oviedo and four in Barcelona. The groups in Madrid are lead by Antonio Romero (CIB-CSIC) and Martin Martinez-Ripoll (Rocasolano-CSIC). The group leader in Oviedo is Santiago García-Granda. The group leaders in Barcelona are Miquel Coll (CID-CSIC), Josep Tormo (CID-CSIC), Ignacio Fita (CID-CSIC) and Juan A. Subirana (Ingeniería Química-UPC). The three independent groups situated in the CID in Barcelona belong to the department of “Biología Molecular y Celular” and share most of the heavy equipment and computing facilities. However, there are many other groups which are more related to sample preparation and the structural determination is made with the collaboration of all the above mentioned groups. A large number of international collaborations have also been established in particular with all the protein crystallography groups in Portugal.

As a whole, for the seven groups, the number of publications in international journals in structural biology is well above 60 since 1994. These figures reflect the rapid increment of research in the field during the nineties as, practically, there are no publications in protein crystallography before 1989 coming from Spanish laboratories. This accelerated trend is most likely to continue in the near future both due to the international interest in structural biology and to the research situation in Spain. This prediction, in the Spanish side, is based: a) on the quality of the biological research done in many Spanish laboratories (in particular in areas such as biochemistry and molecular biology now closely related with structural biology) and b) on the increasing number of highly qualified Spanish scientists in protein crystallography that would allow the creation of new structural laboratories or the enlargement of the existing ones.

#### **3.3.2. Scientific Cases.**

All the seven above-mentioned groups working in protein crystallography have used *Synchrotron Radiation* in the past. For some of those groups *Synchrotron Radiation* is

becoming the major source of data collection in spite of having the basic X-ray equipment at home. The Spanish requirements of *Synchrotron Radiation* for macromolecular crystallography are expected to rise sharply in the coming years due to the increase in research in structural biology (mentioned above) and to the type of structural studies that are now being initiated.

The Spanish projects now aiming to use *Synchrotron Radiation* are trying to benefit from all its peculiarities. However, most problems can be included in one of the following categories. Some representative examples are also indicated.

### **Crystals with large unit cells or long cell axis (>250Å).**

These types of crystals diffract weakly and present serious overlapping problems between adjacent spots. *Synchrotron Radiation* provides X-ray beams with both very low angular divergence and high brilliance. Therefore, *Synchrotron Radiation* is specially well suited to treat with these kinds of problems that are very common in studies of large biological aggregates. Some examples are given below:

#### *Structural analysis of the bacteriophage phi29 connector<sup>(1,2)</sup>.*

The connector particle from dsDNA bacteriophage has been crystallized in two crystal forms. Crystal form I is monoclinic space group C2 and unit cell dimensions  $a=416.9\text{Å}$ ,  $b=227.6\text{Å}$ ,  $c=236.7\text{Å}$  and  $\beta=96.3$ , with four connector particles in the asymmetric unit. Crystal form II belongs to space group P422 and has unit cell dimensions of  $a=168.7\text{Å}$ ,  $c=140.7\text{Å}$ . Electron microscopy reconstructions are being used as initial searching models. Heavy atom derivatives are also being analyzed.

#### *Structural analysis of large enzymes.*

Tetragonal crystals, space group P41212 or P43212 and unit cell parameters  $a=291.6\text{Å}$ ,  $c=189.4\text{Å}$ , have been obtained from Carbamoyl Phosphate Synthetase I (with 1450 residues per subunit which is one of the largest enzymes analyzed by crystallographically<sup>(3)</sup>).

Hexagonal crystals, space group P6122 and unit cell parameters  $a=184.3\text{Å}$  and  $c=305.5\text{Å}$  (more than 2000 aminoacids in the asymmetric unit) have been obtained from the tetrameric "Atypical Catalase" from *Saccharomyces cerevisiae*<sup>(4)</sup>.

### **Anomalous scattering and the solution of the phase problem.**

The possibility of collecting X-ray diffraction data at different wavelengths allows to optimize the anomalous signal according to the type of anomalous diffracting atoms in the sample. The

anomalous information can then be used in different ways contributing to the solution of the phase problem. *Synchrotron Radiation* offers a continuum X-ray spectrum allowing to choose almost any wavelength needed. Conventional X-ray sources, on the contrary, have most of the X-ray intensity concentrated on the wave lengths defined by the material of the anode. Some examples are shown below:

*MAD measurements at Se or Sm edge.*

For the regulator response protein phoB heavy atoms such as Pt, Hg or Os do not give any consistent derivative signal and are useless for phasing. On the other hand lanthanides (such as Samarium) yield strong anisomorphism. However, these derivatives and also the SeMet protein crystals prepared, can be used for anomalous phasing. Se-Met orthorhombic crystals of the leader proteinase of foot-and-mouth disease virus<sup>(5)</sup>.

*MAD measurements at the Ta edge of the enzyme Carbamate Kinase*

This enzyme appears to be a dimer with more than 350 residues per subunit. No consistent isomorphous heavy atoms derivatives have been obtained. Crystals of the enzyme complexed with Ta, that diffract close to atomic resolution, have been obtained and can be used for MAD<sup>(6)</sup>.

**Extending the resolution and improving the quality of the diffraction data available.**

Even crystals of macromolecules that can be determined and handled with conventional equipment would benefit enormously from having a final data set collected using *Synchrotron Radiation*. The higher quality and the extended resolution of the Synchrotron data allows to obtain a better refined and more complete molecular model, as in the case listed below:

*Catalase HP11 from Escherichia coli*<sup>(7,8)</sup>.

*Beta-glucoside glucohydrolase*<sup>(9)</sup>.

*Streptomices halstedii xylanase*<sup>(10)</sup>.

*Tripanosoma cruzi Macrophage Inhibitor Potentiator*<sup>(11)</sup>

*Complexes of viral epitopes with neutralizing antibodies*<sup>(12,13)</sup>.

Other projects in macromolecular crystallography that are getting increasing attention from the Spanish Community can be classified as:

### **Small crystals.**

Crystals of macromolecules smaller than about 0.1 mm in one direction will present a small diffracting volume and, as a consequence, will diffract weakly. Again the high brilliance of *Synchrotron Radiation* allows to reduce the size of the crystals needed by, approximately, one order of magnitude.

### **Fast data collection and dynamic studies.**

The high brilliance of *Synchrotron Radiation* and the possibility of using simultaneously several wavelengths allows to speed up data collections by (in certain problems) several orders of magnitude. These very fast data collections can be used to follow slow catalytic processes or to trap short lived intermediaries. Fast data collection is always a major advantage, in particular when crystal decay is important (the most frequent situation with unfrozen crystals) and to increase the signal to noise ratio, therefore improving the quality of the diffraction data.

### **Poorly diffracting crystals.**

The resolution of useful diffraction data can often be extended with *Synchrotron Radiation*. The increment in the resolution of the data available has made possible structure determination and refinement in a large number of problems with poor diffracting crystals.

### **High resolution diffracting crystals.**

The possibility of using shorter wavelengths and the higher intensity of the *Synchrotron Radiation* has allowed to obtain atomic resolution (better than 0.8 Å) for a number of protein and nucleic acid crystals.

### **3.3.3. Final remarks**

Synchrotron Radiation is becoming a most valuable support for structural biology and, in particular, for macromolecular crystallography. Spain has now a fast growing Scientific Community in this area with important requirements of Synchrotron Radiation that should sharply increase in the near future. Therefore, it appears most reasonable and sensible to dispose of a national beamline at the ESRF adecuated for macromolecular crystallography. Missing this opportunity would pose again enormous difficulties for the Spanish

Research Community to follow the international pace in structural biology with all its implications, mainly in biology and biotechnology. A collaboration with the protein crystallography Community from Portugal would provide a stronger scientific environment for the development and updating of the beamline facilities in this area.

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### 3.4. SINGLE CRYSTAL DIFFRACTION

### 3.4.1. Introduction

The research projects which are currently in course by the Spanish Scientific Community in the field of Single Crystal cover a wide range of areas in Biology, Mineralogy, Materials Science and Solid State Physics and Chemistry. In particular, transition metal oxides with mixed valence, Transitions-metals-Rare-Earth-Borates, Tectosilicates, organometallic compounds, germanates, porous solids, magnetic materials, superconductors, etc. are some of the systems under investigation. Due to the large number of groups and systems, it would be very difficult to give a detailed list of all the research projects. Because of this, only a relationship of general topics and interested group of users will be presented.

### 3.4.2. Scientific cases

#### **Crystal structure determination of very small single crystals<sup>(1,2)</sup>.**

Almost all groups would like to work with high quality crystal but it is impossible to grow them without defects, twins, etc.. Very often only small crystals are available. These groups work in the fields of Materials Science, Chemistry and Mineralogy. They prepare and study, zeolites, oxides, organic and organometallic compounds where the crystal size is not suitable for standard sources.

Some active groups in this area are:

*Instituto de Ciencias de Materiales de Sevilla (CSIC), Sevilla.  
Facultad de Físicas. Universidad de Sevilla, Sevilla  
Alejandro Conde.*

*Departamento de Química-Física. Facultad de Ciencias Químicas. Universidad de Oviedo.  
Santiago García Granda*

*Instituto de Ciencia de Materiales de Zaragoza (CSIC) Zaragoza.  
Fernando Lahoz.*

*Departamento de Química Inorganica. Facultad de Ciencias. Universidad de Zaragoza,  
Zaragoza.  
Larry Falvello.*

*Centro de Difracción de Rayos X. Facultad de Ciencias Químicas. Universidad Complutense  
de Madrid, Madrid.  
Elena Pinilla*

*Instituto de Química-Física Rocasolano. CSIC. Madrid.*  
Concepción Foces.

*Departamento de Química Inorganica. Facultad de Ciencias. Universidad de Alcala, Madrid.*  
Pilar Gomez Sal.

*Instituto de Ciencia de Materiales de Madrid, (CSIC), Madrid.*  
Enrique Gutiérrez Puebla

Departamento de Química Inorganica. Facultad de Ciencias Universidad de Murcia.  
Jose Vicente

*Instituto de Ciencias de Materiales de Barcelona, (CSIC) Barcelona.*  
Jordi Rius.

*Departamento de Ciencias dos Materiais. Universidad Nova de Lisboa.*  
Maria Ondina Figueiredo

### **Sets of very high resolution data collection<sup>(3)</sup>.**

There are some groups interested in electron density studies, especially in organometallic compounds with  $\pi$ -acceptor ligands with carbon-carbon multiple-bonds. In general, the diffraction data would be collected at low temperature.

*Departamento de Química-Física. Facultad de Ciencias Químicas. Universidad de Oviedo.*  
Santiago García Granda

*Departamento de Química Inorganica. Facultad de Ciencias. Universidad de Zaragoza.*  
Larry Falvello.

*Centro de Difracción de Rayos X. Facultad de Ciencias Químicas. Universidad Complutense de Madrid.*  
Elena Pinilla.

*Universidad Autonoma de Barcelona, Barcelona.*  
Juan F. Piniella

### **Resonant X-ray diffraction**

Several groups are interested in the use of anomalous dispersion to solve the structure of chiral molecules of light elements<sup>(4)</sup>:

*Departamento de Química Inorganica. Facultad de Ciencias. Universidad de Cadiz, Cadiz.*  
Pedro Valerga.

*Instituto de Ciencias de Materiales de Sevilla (CSIC), Sevilla.*  
*Facultad de Físicas. Universidad de Sevilla, Sevilla.*  
Alejandro Conde.

*Instituto de Química-Física Rocasolano. CSIC. Madrid.*  
Concepción Foces.

*Departamento de Cristalografía. Facultad de Geología. Universidad Central de Barcelona.*  
Xavier Solans.

The following groups are interested in collecting single crystal data around the metal absorption edge in 3d-metal-zeolites and aluminophosphates, mixed valence oxides<sup>(5)</sup>, organic-inorganic 1D-systems and minerals. This method also would be applied to the study of the role of some cations and template molecules inside the cages and tunnels in microporous substances<sup>(6)</sup>.

*Instituto de Ciencia de Materiales de Madrid, (CSIC), Madrid.*  
Enrique Gutiérrez Puebla

*Departamento de Química Inorganica y de Materiales. Facultad de Ciencias Experimentales y Técnicas. Universidad San Pablo-CEU. Madrid.*  
Ulises Amador.

*Departamento de Química Inorganica. Facultad de Químicas. Universidad Complutense de Madrid.*  
Loreto Ballester.

*Facultad de Químicas. Universidad del País Vasco.*  
Pascual Roman.

*Departamento de Ciências dos Materiais. Universidad Nova de Lisboa.*  
Maria Ondina Figueiredo

### **Phase transitions<sup>(7,8)</sup>.**

Some groups are interested in this field. For example, the study systems like ammonium-perovskite where the different ammonium-framework interaction possibilities give a rich pressure-temperature phase diagrams.

*Facultad de Ciencias Físicas. Universidad del País Vasco, Bilbao.*  
Javier Zuqiga

*Facultad de Ciencias Físicas Universidad de Barcelona, Barcelona.*  
Antonio Planes.

*Facultad de Químicas. Universidad Complutense de Madrid, Madrid*  
Javier García Jaca.

*Instituto de Ciencia de Materiales de Madrid, (CSIC), Madrid.*  
Enrique Gutiérrez Puebla

### **Other possibilities.**

Besides the lines indicated above, some groups would be interested in doing resonant magnetic scattering experiments<sup>(9,10,11)</sup>, and other groups would like to have the possibility of collecting data under a polarizing electric field<sup>(12,13)</sup>.

*Instituto de Ciencia de Materiales de Madrid, (CSIC), Madrid.*  
Jose Luis Martínez Peña.

*Departamento de Química Inorgánica y de Materiales. Facultad de Ciencias Experimentales y Técnicas. Universidad San Pablo-CEU. Madrid.*  
Ulises Amador.

*Facultad de Químicas. Universidad Complutense de Madrid, Madrid.*  
Javier García Jaca.

*Instituto de Ciencias de Materiales de Barcelona, (CSIC) Barcelona, Barcelona.*  
Elies Molins.

### 3.4.3. Final remarks

This experimental station will be concentrated on diffraction from single crystals, particularly in the area of Materials Science. The extremely high flux, even at high energies (35 keV), makes it suitable for time-resolved diffraction, diffraction from microcrystals, and for diffraction from crystals in absorbing sample chambers such as furnaces, high-pressure cells or cryostats. The wavelength is tunable in the energy range 5-35 keV with an energy resolution close to  $\Delta E/E=10^{-4}$ , making it suitable for the use of anomalous dispersion around X-ray absorption edges. The Spanish single crystal diffraction groups are very interested in doing single crystal data collections, using the "new" Spanish beamline at the ESRF, since it is possible.

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### 3.5. SURFACE SCIENCE

#### 3.5.1. Introduction

The Physics and Chemistry of surfaces and interfaces has been one of the most active fields of research over the past twenty years. One of the reasons that explains this interest is the wide range of applications of these topics, including fields as different as heterogeneous catalysis, wetting phenomena, membranes and liquid-solid systems, interfaces for micro- and optoelectronics, tribology and friction problems, and a large list of issues comprising problems of both fundamental and applied interest. Synchrotron-radiation (SR) based techniques have played a major role during the last years in the advancement of Surface Science, as evidenced for instance by the large number of beamlines devoted to Surface Science related topics in many different facilities around the world. Two reasons explain the critical importance of SR: first, the smaller amount of material to be analyzed in a surface or

interface experiment with respect to a bulk material, second the interest of problems related to properties of buried interfaces. Both topics demand high photon fluxes as the only alternative to achieve good data sets in reasonable periods of time.

The Surface Science Community is well represented in Spain, with a significant number of researchers in several different Institutes. Many of them are frequent users of SR facilities, and several others appear as potentially interested. The range of photon energies and fluxes available from the Spanish CRG at ESRF fits well within the needs of this Community in several different fields.

### **3.5.2. Scientific cases**

#### **3.5.2.1. Clean surface and low coverage overlayers ( up 10 Å)**

##### **X-ray Surface diffraction (XSD)**

X-ray diffraction has been in the past the most successful technique for the structural analysis of bulk materials. Over the last ten years, the application of x-ray diffraction to Surface Science problems has been developed to a high degree. Thus, it constitutes nowadays one of the preferred techniques to investigate structural problems of surfaces and interfaces. This is due firstly to the high penetration of x-rays, which facilitates the investigation of surfaces and interfaces in conditions otherwise impossible, and in some cases close to real industrial reactors (e.g. high pressures, presence of liquids, etc.). Second, the well-known theoretical background coming from the experience accumulated in the research of bulk materials makes the data analysis relatively straightforward. Finally, the availability of high fluxes (such as those at ESRF) makes it possible to analyze dynamic processes at surfaces and interfaces in a real-time scale. Conventional surface diffraction methods could be directly implemented by making use of a light baby chamber mounted in one of the beamline diffractometers.

Since the beginning of the ESRF user operation, several groups from Spain have performed experiments in Surface Science at ESRF public beamlines. The submitted and approved proposals are given below :

*“In-situ” structural characterization of the growth of ultrathin Co/Cu(111) and Cu/Co/Cu(111) films*

Camarero, J., de la Figuera J., de Miguel J.J., Ferrer, S., Miranda, R., Ocal, C. Spendeler, L.

*Geometric structure of alkali-metal/Silicon interfaces by surface X-ray diffraction*  
Alvarez, J., Chrost, J., Ferrer, S., Michel, G.E.,

*Characterization of the surfactant activity of Pb during metal epitaxy on Cu(111)*  
Alvarez, J., Camarero, J., de Miguel J.J., Ferrer, S., Miranda, R., Ocal, C. Prieto, J.E.

*Growth of Co and Cu on Co(0001): A study on the influence of the substrate structure on epitaxial growth*  
de Miguel J.J., Miranda, R., Ferrer, S., Alvarez, J., Spendeler, L., de la Figuera J., Camarero, J., Prieto, J.E.

*Reactivity of binary alloys: CO interaction with NiAl(110)*  
Castro, G.R., Isern, H., Alvarez, J. Torrelles, X.

*X-ray surface diffraction of a surface polymerization: Si(110)2x2-Al*  
Asensio, M.C., Avila, J., Davila, M.E., Ferrer, S.

*Structural investigation of the  $\sqrt{3}\times\sqrt{3}R30^\circ \Rightarrow 3\times 3$  transition at the Pb/Ge(111)*  
Michel, E.G., Mascaraque, A., de la Figuera J.

*Structural determination of the Si/Cu(110) Interface*  
Martin-Gago, J.A., Polop, C. Montesinos, A. Ferrer, S., Alvarez, J. Torrelles, X.

However, there are several other groups which are interested in performing in the future experiments in different research areas. Some examples are :

*High resolution surface X-ray diffraction study for the atomic structure determination of the Ge(111)-(2x1) reconstruction<sup>(1,2)</sup>.*  
C. Ocal, E. Artacho Universidad Autónoma de Madrid

*Structural determination of thin binary alloys presenting structural order, chemical order and surface reconstructions (Mn-Pt(111))<sup>(3)</sup>.*  
C. Ocal, F. Soria, Universidad Autónoma de Madrid and Instituto de Ciencia de Materiales de Madrid, CSIC

*Structural determination of ultra thin ordered magnetic films epitaxially grown (or stabilized) on non-magnetic substrates<sup>(3)</sup>.*  
H. Isern and F. Soria, Instituto de Ciencia de Materiales de Madrid, CSIC

*Structural determination of complex reconstructions of semiconductor surfaces, specially from III-V semiconductors: GaAs(311)-(8x1), GaAs(100)-c(8x2)-Ga<sup>(4)</sup>.*  
A. Ruiz, F.J. Palomares, F. Soria, H. Isern, Instituto de Ciencia de Materiales de Madrid, CSIC

*Magnetic properties by resonance magnetic scattering on MBE magnetic superlattices formed by alternating layers of magnetic and non-magnetic materials, the magnetic materials being rare earths (Gd/W, for instance)<sup>(3)</sup>.*

M.Alonso, A. Ruiz, F.J. Palomares, y M.C. Asensio., Instituto de Ciencia de Materiales de Madrid, CSIC

*Resonant surface magnetic X-ray diffraction from Mn-Pt(111) surface alloys<sup>(3)</sup>.*

C. Ocal and F. Soria Instituto de Ciencia de Materiales de Madrid, CSIC

*Investigation of solid/liquid interfaces in electrochemical environment<sup>(5)</sup>.*

H.D. Abruña (also at Cornell University) and C. Limones, Universidad Autónoma de Madrid

*Structure of ordered thin oxide films growth on binary alloys<sup>(11)</sup>.*

H. Isern and X. Torrelles, Instituto de Ciencia de Materiales de Madrid and Instituto de Ciencia de Materiales de Barcelona, CSIC

*Role of surfactants in metal-on-metal epitaxial growth<sup>(7)</sup>.*

J.Camarero, J.J. de Miguel, Universidad Autónoma de Madrid

*Crystallography of epitaxial growth: the role of defects<sup>(8)</sup>.*

J.E. Prieto, A.L. Vázquez de Parga, R. Miranda, Universidad Autónoma de Madrid

*"In situ" analysis of Ag quantum dots grown on GaAs(110): structural characterization<sup>(9)</sup>.*

M. Alonso, Instituto de Ciencia de Materiales de Madrid, CSIC

*Growth mechanisms and atomic structure of surface alloys formed from the deposition of Si and Ge on Cu(110), Cu(100) y Cu(111)<sup>(12)</sup>.*

JA Martin-Gago, J.L. Sacedón, P. de Andrés and C. Polop. Instituto de Ciencia de Materiales de Madrid, CSIC

*Growth and Morphology of epitaxial metals films on rare earth silicide<sup>(13)</sup>.*

JA Martin-Gago, J.L. Sacedón, P. de Andrés and C., Polop Instituto de Ciencia de Materiales de Madrid, CSIC

*Small molecule gas interaction (SO<sub>2</sub>, CO, O<sub>2</sub>) with TiO<sub>2</sub>(110)<sup>(14)</sup>.*

J.A Martin-Gago, E. Román, Instituto de Ciencia de Materiales de Madrid, CSIC

## **X-ray Standing Waves**

X-ray standing waves produced in the total reflection range are useful to investigate the structure of interfaces (membrane-solid, vacuum-solid, liquid-solid, solid-solid), although they are used as well in more bulk-related fields (e.g. localization of impurities). Several different setups are possible: the 90° or backscattering geometry, the conventional Bragg geometry, and the Laue setup. The implementation of the backscattering geometry is planned. This is the less demanding setup from the technical point of view, its requirements being not

far away from those of EXAFS (need of monochromator tunability and a fluorescence detector), and it would be of interest not only for the conventional research in vacuum-solid interfaces, but also in the field of liquid-solid electrochemical interfaces.

The type of studies which could be accomplished in such a facility is summarized in the following :

*Structural properties of metal/semiconductor interfaces using SXRD and XSW<sup>(6)</sup>.*

C. Sánchez, A. Mascaraque, P. Segovia and E.G. Michel, Universidad Autónoma de Madrid

*Localization of gas molecules adsorbed on metallic surfaces*

C. Sanchez-Hanke, E.G. Michel

*Structure of Rare-earth silicides/silicon*

C. Sanchez-Hanke, E.G. Michel

### 3.5.2.2. Thin films (from 10 Å up 10000 Å)

In these systems, in addition to the x-ray diffraction techniques described above, a more specific technique can be used: the x-ray reflectometry. X-ray reflectivity in the range of total reflection is a non-destructive, well-established method since already quite a few years, useful to investigate the thickness and roughness of thin layers. It is extremely sensitive to the actual interface roughness profile of buried interfaces. Since it does not require ultra-high vacuum conditions, it is not a demanding technique in terms of beamtime, as compared to other methods which would provide a comparable information. These properties make it attractive also for conventional quality control of industrial interfaces. As in the previous case, the need of grazing angles (which demand large photon fluxes), and the tunability of SR (which allows to go into the anomalous range), make nowadays of the x-ray reflectivity studies a mainly SR-based technique.

As in the case of ultra thin films, several groups of potential users of Synchrotron X-rays have expressed their interest in performing experiments in the Spanish CRG. Some of the research topics are :

*Structural "in situ" analysis of the epitaxial growth of metallic multilayers. Effects of surfactants.*

M.Alonso, A. Ruiz, F.J. Palomares, y M.C. Asensio., Instituto de Ciencia de Materiales de Madrid, CSIC

*Quantum-well states and structural properties of thin films.*

J.E. Ortega, Universidad del País Vasco

*X-ray diffraction studies of the defects produced in thin films under stress.*

A. Gonzalez-Elipe, A. Fernandez, J. Espinos, J.C. Sanchez Lopez y F. Yubero. Instituto de Ciencias de Materiales de Sevilla.

*Study of the lateral morphology of thin films by grazing incidence X-ray diffraction.*

A. Gonzalez-Elipe, A. Fernandez, J. Espinos, J.C. Sanchez Lopez y F. Yubero. Instituto de Ciencias de Materiales de Sevilla.

*Characterization of binary thin films oxides coatings grown by CVD over technical relevant substrate by reflectometry.*

A. Gonzalez-Elipe, A. Fernandez, J. Espinos, J.C. Sanchez Lopez y F. Yubero. Instituto de Ciencias de Materiales de Sevilla.

*Study of the structure of oxide layers formed at high temperatures on lanthanide-coated stainless-steels.*

J.A. Odriozola, A. Paul, M.J. Capitan, M.A. Centeno, J.J. Benitez. Instituto de Ciencias de Materiales de Sevilla.

*“In situ” and simultaneous study of the defect structure and the electrical response of CdGeON sensors.*

J.A. Odriozola, M.J. Capitan, J.J. Benitez, A. Diaz. Instituto de Ciencias de Materiales de Sevilla.

### **3.5.3. Final remarks**

The operation of a Surface Science station at the Spanish CRG at ESRF would certainly permit the access to this facility to a significant number of groups already working in problems where SR based techniques play a key role. The construction and operation of a Surface Science station does not require extreme modifications of the beamline layout or specifications, and would be extremely beneficial for an already existing, highly motivated Community of users. Small additional investments could make the research developed in this beamline fully competitive at a worldwide scale.

Concerning the potential users of this facility, there already exists a motivated Community which regularly employs SR based techniques. Many of them are also users of the ESRF.

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## **3.6. POLYMERIC MATERIALS AND BIOPHYSICS**

### **3.6.1. Introduction**

The Spanish Scientific Community interested in the use of Small angle diffraction can be directed into polymeric materials and biophysics.

#### **Polymeric Materials**

Part of the Spanish scientific activity in the field of polymer science has been orienttaed in the last time towards the use of synchrotron radiation in different aspects. As an example of this increasing activity it is worth mentioning the importance of the Spanish contribution to the last Europhysics Conference on "Application of Synchrotron Radiation in Polymer Science" held in Hamburg, Germany in 1995<sup>(1)</sup> which joined together some of the most reputed scientists in the field. The use of a powerful radiation source like the synchrotron has been shown to be of importance upon dealing, in general, with phase transitions, structural changes and transient phenomena in materials science. In particular, synchrotron radiation can be used to perform X-ray scattering experiments in both wide and small angle regions<sup>(2)</sup>. By using intense incident X-ray radiation, dynamic experiments including crystallization, phase separation, phase transitions in polymeric systems can be performed on a time resolved basis.

#### **Biophysics: Biological non-crystalline diffraction**

Time-resolved X-ray solution scattering and fibre diffraction methods constitute powerful, unique tools in Biophysics and Structural Biology, which serve to study the structural dynamics of biological systems. Diverse important problems can be investigated with these methods, ranging from the folding of protein chains to the functioning of live muscles, and including the structure and function of supramolecular biological assemblies, such as viruses, protein-nucleic acid regulatory complexes, membranes, and protein fibres.

### **3.6.2. Scientific cases**

#### **3.6.2.1. Polymeric Materials**

The present scientific projects involving synchrotron radiation in the field of polymer science which may eventually be continued in the Spanish beamline at ESRF, are carried out mainly by groups at the Instituto de Estructura de la Materia(IEM), Instituto de Ciencia y Tecnología

de Polímeros(ICTP) both of C.S.I.C., and in the Facultad de Farmacia of the Complutense University of Madrid(FFCM). As a general trend, all of them involve the use of simultaneous **WAXS and SAXS experiments**. Some of them also make use of simultaneous **Differential Scanning Calorimetry** experiments<sup>(3)</sup>. More specifically the scientific cases of interest for the Spanish Scientific Community would include:

### **Phase transformations in liquid crystalline polymers**

Liquid crystals are self-organized systems which may exhibit different states of order affecting directly their physical properties. The study of the phase transition mechanisms is an important topic to be investigated by means of synchrotron radiation.

*Phase transitions in liquid crystalline polybenzoates by simultaneous WAXS / SAXS /DSC<sup>(4,5)</sup>.*

E. Pérez at ICTP.

*Phase behavior of olefin polymers<sup>(6)</sup>.*

E. Pérez at ICTP.

*Phase transitions of liquid crystalline polymer coated-liposomes by simultaneous SAXS / WAXS<sup>(7)</sup>.*

M. Pérez-Méndez at ICTP.

*Crystallization kinetics and fiber formation of blends of polymer liquid crystals and thermoplastic polymers by SAXS and WAXS<sup>(8)</sup>.*

J.M. Gómez-Fatou, M.A. Gómez-Rodríguez at ICTP.

*Crosslinking Polymerization of liquid crystalline monomers in a strong magnetic field<sup>(9)</sup>.*

A. Marcos at ICTP.

### **Crystallization Phenomena**

The crystallization process of a polymeric material is typically accomplished by a primary regime where a rapid increase of crystallinity is observed followed by a secondary regime where the crystallization rate decreases. By combining SAXS and WAXS measurements using synchrotron radiation information can be gained about the crystallization mechanism which may involve increase of crystal thickness, dynamic growth of crystals and formation of lamellar stacks among others.

*Precursors of Crystallization in advanced rigid and semirigid polymers of varying chain flexibility by simultaneous SAXS/WAXS<sup>(10)</sup>.*

T.A. Ezquerro, F.J. Baltá-Calleja at IEM.

*Melting and crystallization behaviour of oligo(aryl ether ketone)s, model compounds of poly(aryl ether ketone)s by simultaneous SAXS/WAXS.*

D.R. Rueda, F.J. Baltá-Calleja at IEM.

*Electric field induced orientation and structure variation of ferroelectric copolymers by simultaneous SAXS/WAXS.*

E. López-Cabarcos at FFUC.

*Influence of thermal treatment in the structure of polyethylene with shish-kebab structure by SAXS<sup>(11)</sup>.*

D.R. Rueda, F. Ania, F.J. Balta-Calleja at IEM.

### **Phase Separation and related phenomena**

Block copolymers are macromolecules composed of blocks of chemically distinct repeat units. Depending on thermal conditions block copolymers undergo an thermodynamic order-disorder transition which may render to a microphase separated systems. The physical properties of block copolymers are strongly dependent on both the phase state and degree of phase separation present in the system.

*Phase separation in block copolymers by simultaneous SAXS/WAXS/ DSC<sup>(12)</sup>.*

Angel Marcos at ICTP

*Phase separation in thermoplastic elastomers based on poly(butylene terephthalate)<sup>(13)</sup>.*

T.A. Ezquerro at IEM.

### **3.6.2.2. Biophysics<sup>(14-22)</sup>**

Researchers from the Spanish Biological Scientific Community started to use synchrotron radiation at European facilities in the late eighties, and by the early nineties they grew to a number of well established groups from public research institutes and universities in Madrid, Barcelona, Badajoz and Murcia, and several individual Spanish scientists working abroad.

The biological materials have particular sample environment and data acquisition requirements, which stem from their own nature: hydrated, radiation sensitive and dynamic. The sample handling equipment should include temperature controlled measuring cells, static and scanning solution measuring cells, fast mixing and/or stopped flow instruments, T-jump, laser photolysis, adapted to the measuring cells. Additionally, on line monitoring instruments like single beam (optical fibre) spectrophotometer and spectrofluorimeter are needed so that

24 hour access to a nearby supporting biological laboratory at EMBL would be highly desirable.

*Modeling solution scattering to deduce protein size and shape; microtubules.*

J.M. Andreu, Centro Inv. Biológicas, CSIC, Madrid.

*Viral structure and assembly; molecular chaperones.*

J.L. Carrascosa, Centro Nacional de Biotecnología, CSIC, Madrid.

*Macromolecular modeling; scattering and hydrodynamics.*

J. Garcia de la Torre, Dep. de Química-Física, Univ. de Murcia

*Chromatin, proteins.*

J.R. Daban, Universidad Autonoma de Barcelona.

*Purple membrane.*

E. Padros, Universidad Autonoma de Barcelona.

*Membrane protein biophysics.*

C. Gutierrez Merino, Universidad de Extremadura, Badajoz.

*Lipid bilayers.*

A. Morros, Universidad Autonoma de Barcelona.

*Phase behavior of mixed aqueous dispersions of dipamitoyl derivatives of phosphatidylcholine and diacylglycerol<sup>(27)</sup>.*

J.C. Gómez-Fernández, Universidad de Murcia.

### 3.6.3. Final remark

The opportunity of having a new facility available to currently perform time resolved SAXS / WAXS in the Spanish beamline at ESRF will doubtless make it very attractive for the engagement of groups which have been users of synchrotron radiation<sup>(24-26)</sup> and also for those who may become potential users of this technique.

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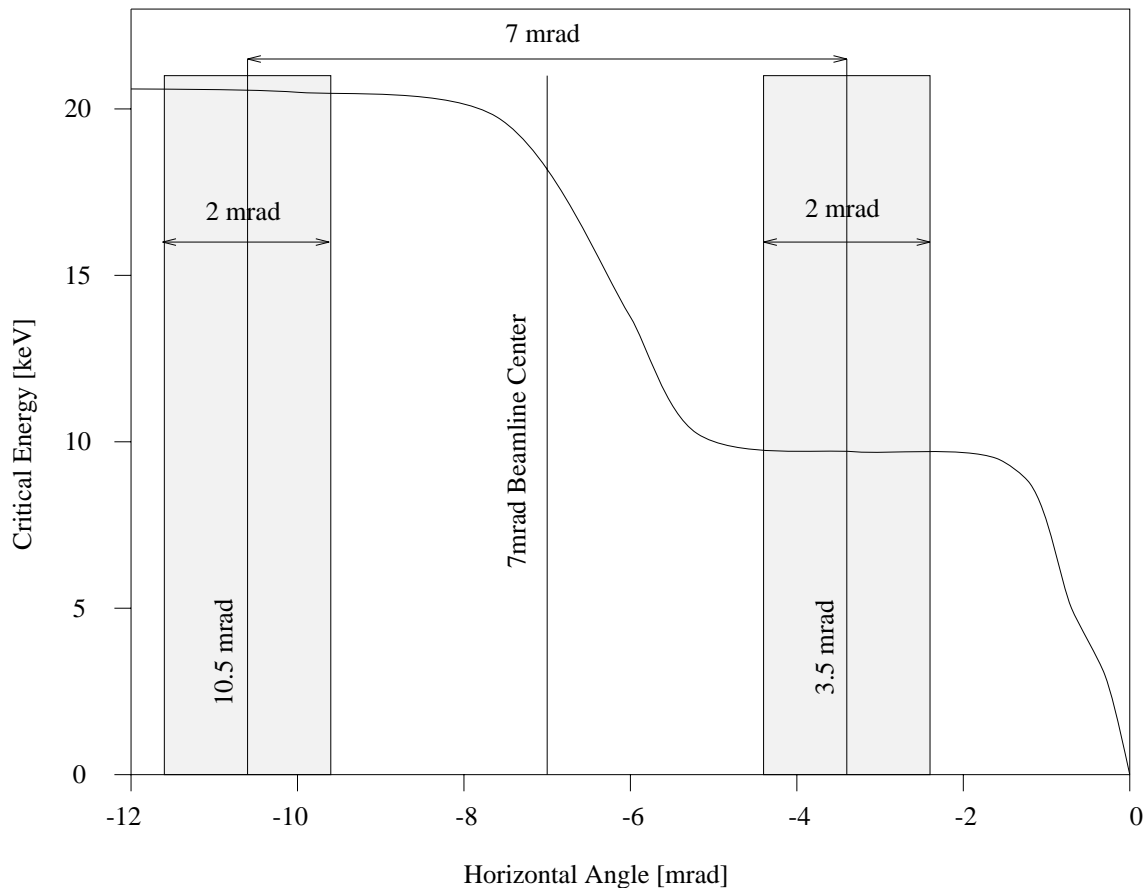
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## 4. THE BEAMLINE DESIGN

In accordance with the general philosophy of the project, the design of the Spanish beamline is not novel, although it is in the state-of-art. Beamlines of similar design have been constructed or are being proposed for other CRG. The majority of the optical elements proposed for the Spanish beamline have been successfully used in a conceptually similar form in other beamlines. There is no doubt that some modifications will be incorporated simply due to the rapid evolution of the instrumentation. In any case, the beamline optics has to be designed to fit the users requirements preserving the exceptional characteristics of the source. Figure 1 shows a general layout of the beamline.



**Figure 2** : Angular profile of the critical energy on the Front End

**Figure 1:** Schematic Layout of the Beamline

See attached A3 page at the end

## 4.1. SPLITTING OF THE BEAM

The beam will be split into two, considering the following characteristics:

- The horizontal radiation fan has 9 mrad of aperture
- The critical energy varies across the horizontal fan
- It is convenient to maximize the separation between beamlines to gain design flexibility.

Figure 2 shows the angular profile of the critical energy over the total angular acceptance on the beamline Front End. Two different plateaus can be distinguished, each one with approximately 4 mrad horizontal opening angle, between -8 to -12 mrad the hard edge and between -1 to -5 mrad the soft edge. It has been decided to split the beam into two fans of 2 mrad each, with a central 5 mrad blocked. Each fan has been centered on a different plateau. The hatched zones in figure 2 correspond to the two regions selected for each beamline. **Branch A** with a critical energy of 9.6 keV is centered on -3.5 mrad and **Branch B** with a critical energy of 20.6 keV is centered on -10.5 mrad. The same beam split solution has been already chosen for the Dutch/Belgium (DOUBLE) and French (FIP) CRG beamlines. The beam separation as well as the beam horizontal dimension, as a function of distance from the source, are shown in table I.

distance from the source (m)	beam width (mm)	beam separation (mm)
25	50	175
30	60	210
35	70	245
40	80	280
45	90	315
50	100	350

**Table I:** beam width and separation of branch **A** and **B** for different distances from the source.

## 4.2. THE SOURCE

The most important characteristics of the electron beam in the storage ring are displayed in table II.

Electron beam energy	$E = 6.04 \text{ GeV}$
current in 2/3 fill mode (multibunch)	$I = 200 \text{ mA}$
current in single bunch mode	$I = 15 \text{ mA}$
horizontal emittance	$\epsilon_x = 3.8 \cdot 10^{-9} \text{ m rad}$
vertical emittance (with 1% coupling)	$\epsilon_z = 3.8 \cdot 10^{-11} \text{ m rad}$
beam lifetime	$\tau \geq 24 \text{ h}$

**Table II:** ESRF machine characteristics

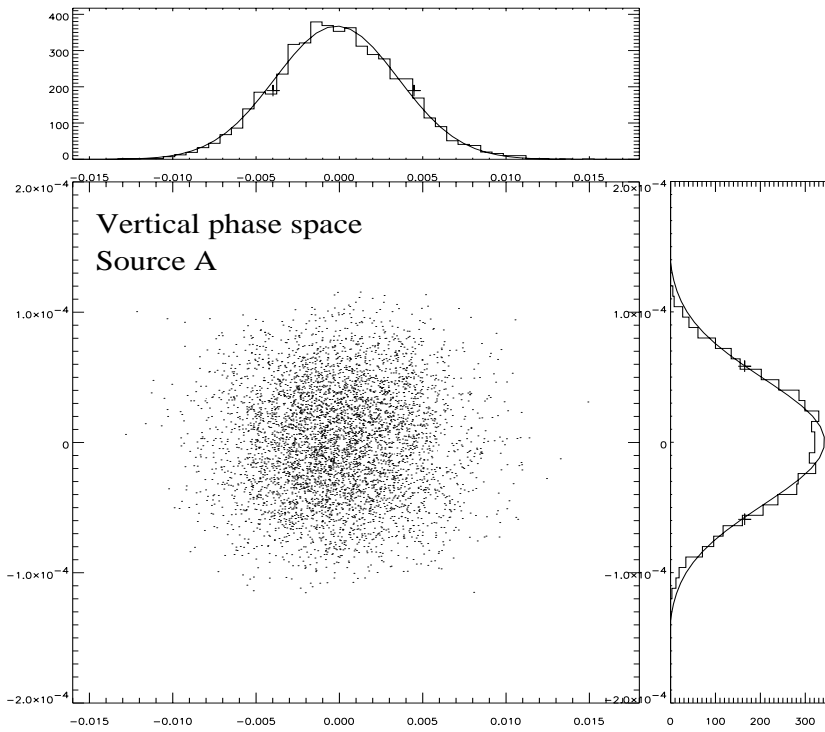
As it has been mentioned the beamline will consist of two branches **A** and **B**. The electron beam characteristics at the source points in the bending magnet corresponding to the middle of those branches are listed in table III.

Branch	magnetic field	critical energy	electron beam parameter			
			$\sigma_x (\mu m)$	$\sigma_z (\mu m)$	$\sigma'_x (\mu rad)$	$\sigma'_z (\mu rad)$
<b>A</b>	0.39987 T	9.6 KeV	91	36	42	1
<b>B</b>	0.8504 T	20.6 KeV	78	36	48	1

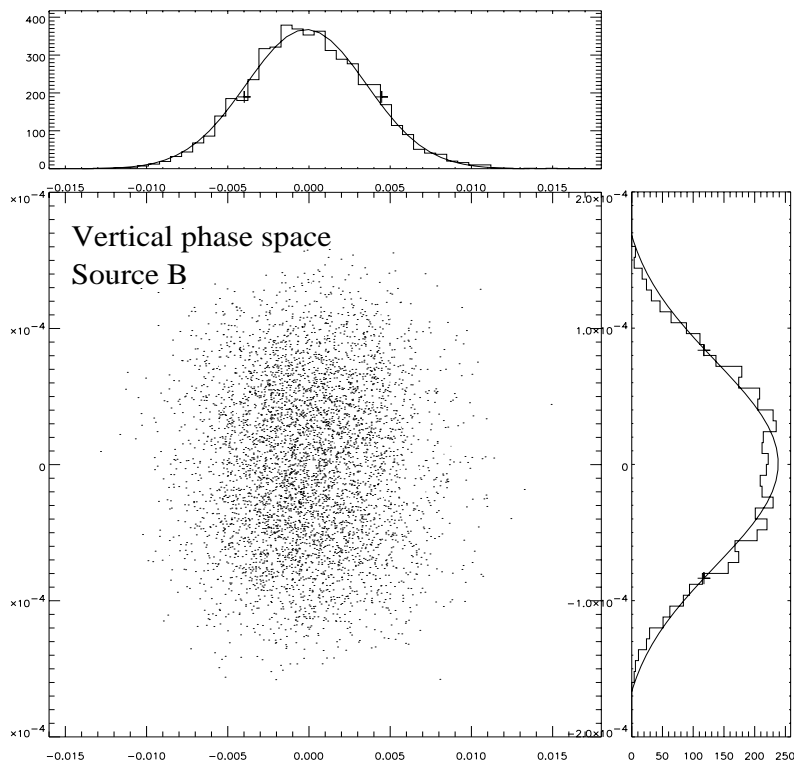
**Table III:** source characteristics

The electron beam in the bending magnet has a very low vertical divergence, fifty times lower than the relativistic divergence limits ( $\approx 56 \mu rad$ ). Therefore to obtain the photon source vertical parameter one can neglect the convolution between the angular extension of the electron source ( $\sigma'_z$ ) with the emission profile of a single electron. Figures 3 and 4 show the density distribution of the source in the vertical phase space ( $z-z'$ ) for branches **A** and **B** respectively. This was obtained from a 5000-ray random simulation, with a gaussian space distribution and a synchrotron source depth.

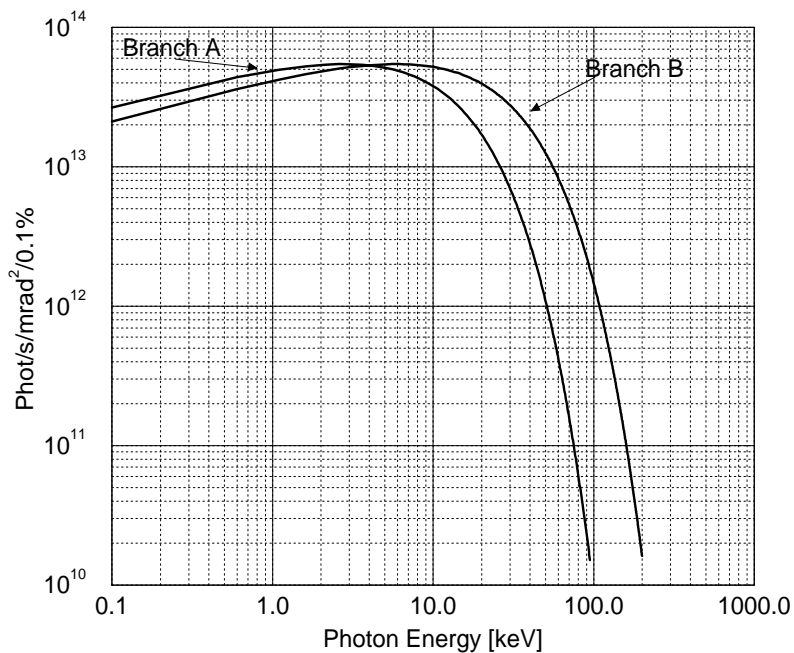
The relevant quantities of interest for characterizing the bending magnet radiation are the spectral flux (brightness) and the brilliance. Figure 5 shows the brightness generated by each source point (soft edge and hard edge) from the bending magnet as a function of energy and figure 6 shows the corresponding brilliance functions.



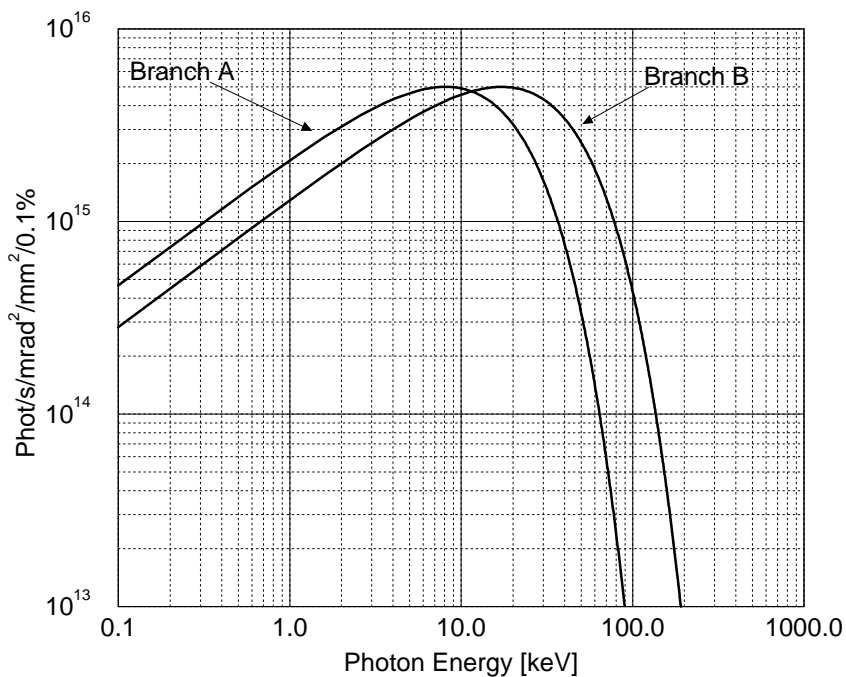
**Figure 3:** Vertical phase space of the source corresponding to Branch A



**Figure 4:** Vertical phase space of the source corresponding to branch B



**Figure 5:** Brightness of the bending magnet sources **A** (soft edge) and **B** (hard edge)

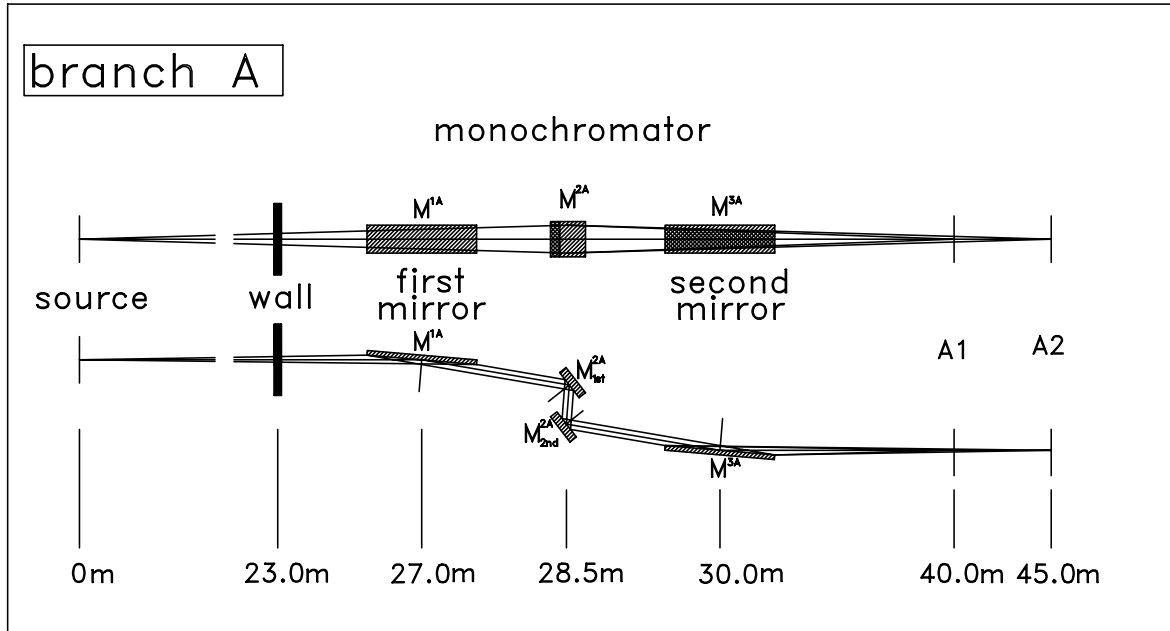


**Figure 6:** Brilliance of the bending magnet sources **A** (soft edge) and **B** (hard edge)

### 4.3. OPTICAL CONFIGURATION

#### 4.3.1. Branch A

The beamline optics should accept the 2 mrad horizontal aperture and produce a small focal spot at different sample positions. It should be also desirable to achieve a high resolution in energy and wave vector. These requirements are fulfilled by the design displayed in figure 7.



**figure 7 :** Schematic representation of beam path for the configuration of Branch A

The beam is first vertically collimated by a one meter long cylindrically bent mirror  $M^{1A}$  of fixed meridional radius. The horizontal focusing is achieved by the second monochromator crystal through a sagittal cylindrical bending. By a second vertically bendable mirror  $M^{2A}$  the beam can be focused to different sample positions 40-45 meters away from the source. At the image plane  $A_1$  (40m), the XAS station will be allocated, while the HRPD station will be at the plane  $A_2$  (45 m). All optical components of the beamline will operate under vacuum. A fixed Be (500 $\mu$ m) window at the front end will be used to separate vacuum between beamline and electron ring. Therefore the effective cut-off energy is around 4 keV. It is important that the main beamline components can be separately vented. In order to reduce the influence in the region of low energy (increasing the real cut-off energy) vacuum gate valves with a berillium disk will be used to separate the different components. In some special cases, if

necessary and if the vacuum conditions are good the Be windows can be opened for maximum flux. For example, at 4 keV operation, it is very important to minimize the thickness of Be between the source and the sample. At this energy a Be foil of 1500  $\mu\text{m}$  reduces the transmission by a factor of 10.

#### 4.3.1.1. First mirror

The first mirror (collimating mirror) with a constant curvature radius ( $R_V^{1A}$ ) will be coated with Rh. The angle of incidence (glancing angle) will be set at 2.5 mrad, which corresponds to a cut-off energy of 26.8 keV. The demagnification  $\mathbf{m}$  is given by the ratio of the distance between the source and optical element ( $\mathbf{p}$ ) and the distance between the image point and the optical element ( $\mathbf{q}$ ). Table IV displays some relevant parameters for the first mirror ( $M^{1A}$ ).

First mirror	angle of incidence (mrad)	p (m)	q (m)	$m_V$	cylinder radius $R_V^{1A}$ (km)
$M^{1A}$	2.5	27	$\infty$	$\infty$	21.6

**Table IV:** focusing parameters for the first mirror from branch A.

This mirror has two functions, primarily to suppress the higher order harmonics of the energy selected while totally reflecting the useful energy and also to reduce heating of the subsequent optical element. Due to the high power loads of the ESRF beams ( $\sim 150$  Watts) cooling of the mirror will be mandatory. Secondly, to collimate the vertical divergence of the beam in order to optimize its energy resolution which would be determined only by the Darwin width of the first crystal of the monochromator. These results in a resolution increase between 5 and 10 times, depending on the crystal type used.

#### 4.3.1.2. Monochromator

The monochromator will be of the pseudo channel-cut type with two fixed Si(111) crystals moved together by a simple goniometer circle, in the (-n,+n) configuration. The possibility to change both crystals on the monochromator according to resolution requirements (i.e. Si(311)) will also be considered. The first monochromator crystal will be water cooled while the second will be kept at room temperature. The second crystal will be equipped with a

piezoelectric driver that will allow to change very slightly its Bragg angle (pitch adjustment) in order to reduce the harmonic content of the beam, if necessary, and to keep the transmission of the monochromator constant during long time intervals. Also, a bender will curve sagittally<sup>(1,2)</sup> that crystal in order to dynamically focus the beam at the sample positions  $\mathbf{A}_1$  and  $\mathbf{A}_2$  (see fig. 6). The position and dimension of the focused beam should be kept constant during a  $\sim 1$  keV energy scan, standard in a EXAFS measurement. This will require very accurate mechanics as, for example, it has been previously achieved at the Italian CRG<sup>(2)</sup> beamline (Gilda). This monochromator is possibly the most technically demanding component of this CRG project. The monochromator will be located at a distance of 28.5 m from the source. Table V shows the focusing parameter for the second monochromator crystal ( $M_{2nd}^{2A}$ ) for an energy of 12.4 keV ( $1\text{\AA}$ ).

Monochromator 2nd crystal	angle of Bragg @ $1\text{\AA}$ (degrees)	p (m)	q (m)	$m_s$	cylinder radius $R_s^A$ (m)
$M_{2nd}^{2A}$	14.24	28.5	11.5	0.40	2.61
$M_{2nd}^{2A}$	14.24	28.5	16.5	0.58	3.33

**Table V:** focusing parameters for the second monochromator crystal from branch A.

#### 4.3.1.3. Second mirror

This cylindrical bent mirror is the last element of the optics and will be used for meridional focusing of the beam at the different sample positions. The mirror serves to increase the flux on the sample and to stare vertically the beam if needed. In addition, the non dispersive mirror setting achieved by having two mirrors in (n,-n) configuration, eliminates the vertical excursion of the beam when the mirror incidence angle is changed. The mirror focusing parameters are shown on table VI.

Second mirror	angle of incidence (mrad)	p (m)	q (m)	$m_v$	cylinder radius $R_v^{3A}$ (km)
$M^{3A}$	2.5	$\infty$	10	0	8.0
$M^{3A}$	2.5	$\infty$	15	0	12.0

**Table VI:** focusing parameters for the second mirror from branch A

### 4.3.2. Branch B

As in the case of branch **A**, the optics should accept the 2 mrad horizontal radiation and produce a small focal spot at different positions (**B**<sub>1</sub>, **B**<sub>2</sub>, and **B**<sub>3</sub>) in the experimental hutch **B**. The design chosen is in this case similar to one selected for branch **A** (see figure 8), with the only difference that the first mirror ( $M^{1B}$ ) is flat. The horizontal focusing is achieved by the second monochromator crystal ( $M_{2nd}^{2B}$ ) through a sagittal cylindrical bending<sup>(3)</sup>. For focusing in the meridional plane a cylindrical bent mirror ( $M^{2B}$ ) will be used. The vacuum of the main components will be separated by fixed Be Windows.

#### 4.3.2.1. First mirror

The main function of this mirror is to reduce the heat load of the first monochromator crystal, additionally to reject the higher order harmonics. Since a coating with Rh is planned, in normal operation, the glancing angle will be ~ 2.5 mrad, which corresponds to a cut-off energy of 26.8 keV. This incidence angle can, if necessary, be changed. Again cooling will be required.

#### 4.3.2.2. Monochromator

The technical requirements of this monochromator are relatively simple compared to those of branch **A**, since the measurements will be performed at a constant energy. Therefore, dynamically focusing will **not** be necessary. Energy scans around an adsorption edge with a moderate stability will be only necessary in the case of anomalous scattering. In this case, again a pseudo channel-cut type monochromator will be used. Two Si(111) crystals are foreseen and they will rotate by a single table, in the (+n,-n) configuration. The Si(111) Darwin width meets the bandwidth necessities for resonant anomalous scattering measurements. Additional harmonics rejection will be obtained by angular detuning. The first crystal will be flat, while the second one will be bent in the horizontal plane focusing the beam at different positions **B**<sub>1</sub>, **B**<sub>2</sub> and **B**<sub>3</sub> (see figure 8). Since part of power (~ 50% @ 2.5 mrad) will be lost in the first mirror, water-cooling system for the first monochromator crystal will be sufficient. The monochromator will be located at a distance of 32 m from the source. Table VII collects the focusing parameters for an energy of 12.4 keV (1Å).

Monochromator 2nd crystal	angle of Bragg @ 1Å (degrees)	p (m)	q (m)	$m_s$	cylinder radius $R_s^{2B}$ (m)
$M_{2nd}^{2B}$	9.18	32.0	16.0	0.50	3.40
$M_{2nd}^{2B}$	9.18	32.0	18.5	0.58	3.74
$M_{2nd}^{2B}$	9.18	32.0	25.0	0.78	4.48

**Table VII:** focusing parameters for the second monochromator crystal on Branch **B**

#### 4.3.2.3. Second mirror

The meridional focusing at different positions downstream will be obtained with a variable cylindrical bent mirror coated with Rh. As in the first mirror, a variable glancing angle is foreseen. Table VIII shows the most relevant characteristics of this geometry.

Second mirror	angle of incidence (mrad)	p (m)	q (m)	$m_v$	cylinder radius $R_v^{3B}$ (km)
$M^{3B}$	2.5	33.5	14.5	0.43	8.1
$M^{3B}$	2.5	33.5	17.5	0.52	8.2
$M^{3B}$	2.5	33.5	23.5	0.70	11.1

**Table VIII:** focusing parameter of the second mirror on branch **B**

#### 4.4. PERFORMANCE OF THE OPTICAL CONFIGURATIONS

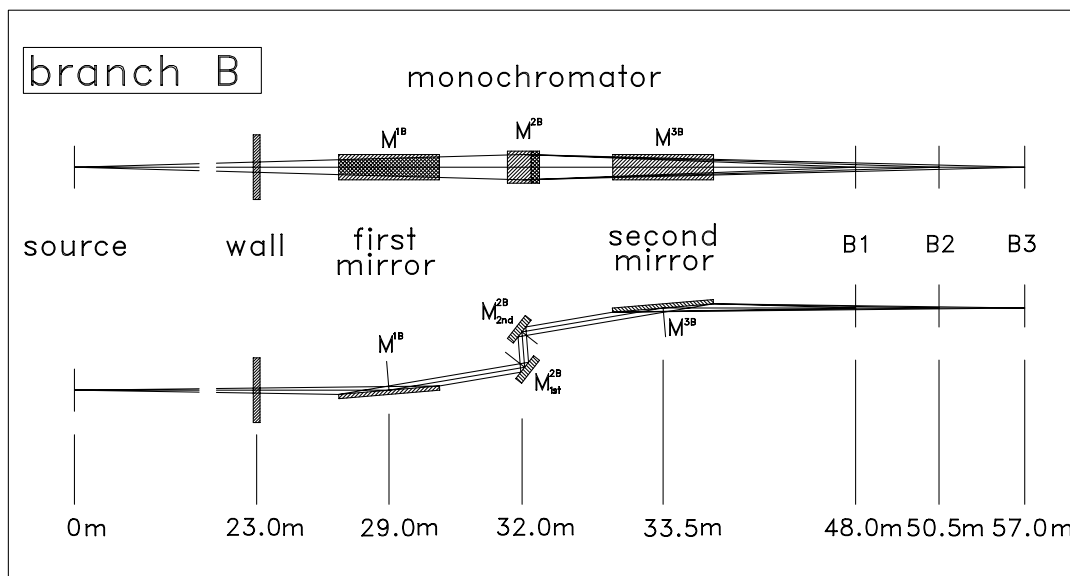
The optical design for both branches has been checked by ray tracing. As an example Figures 9 and 10 show, for branch **A**, the intensity distribution in real space of the beam at 12.4 keV (1Å) focused at 40.0 (**A**<sub>1</sub>) and at 45 (**A**<sub>2</sub>) meters from the source, respectively. The vertical and horizontal units are centimeters. The sagittal spherical aberration is bigger at the focus plane **A**<sub>1</sub> than at the plane **A**<sub>2</sub> and it affects the vertical divergence of the beam. For this reason, the high resolution powder diffraction station has been allocated in position **A**<sub>2</sub>, while the X-ray absorption spectroscopy station in position **A**<sub>1</sub>. Table IX summarizes the results

obtained by ray tracing (SHADOW)<sup>(4)</sup> simulations at 12.4 keV and 200 mA electron current in the different focal planes on branch **A** and **B**, respectively.

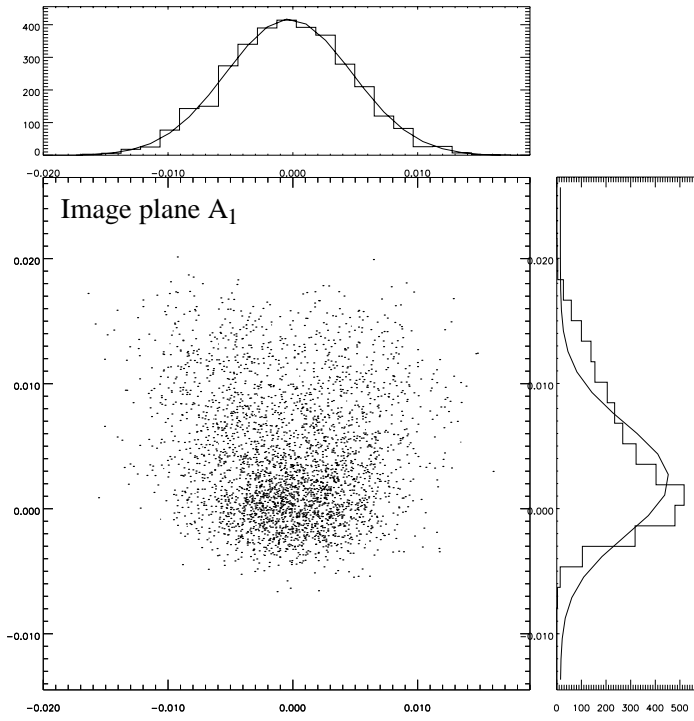
Image plane	Flux Photons/s	$\Delta E/E$	dimensions	
			real space (h x v) mm x mm	vertical phase space $\mu$ rad x mm
<b>A<sub>1</sub></b>	$2.7 \times 10^{12}$	$1.5 \times 10^{-4}$	0.07 x 0.09	224 x 0.10
<b>A<sub>2</sub></b>	$2.7 \times 10^{12}$	$1.5 \times 10^{-4}$	0.14 x 0.08	154 x 0.08
<b>B<sub>1</sub></b>	$2.4 \times 10^{12}$	$4.0 \times 10^{-4}$	0.10 x 0.09	167 x 0.09
<b>B<sub>2</sub></b>	$2.4 \times 10^{12}$	$4.0 \times 10^{-4}$	0.09 x 0.10	143 x 0.10
<b>B<sub>3</sub></b>	$2.4 \times 10^{12}$	$4.0 \times 10^{-4}$	0.13 x 0.12	103 x 0.12

**Table IX:** results of ray-tracing calculations for both branches.

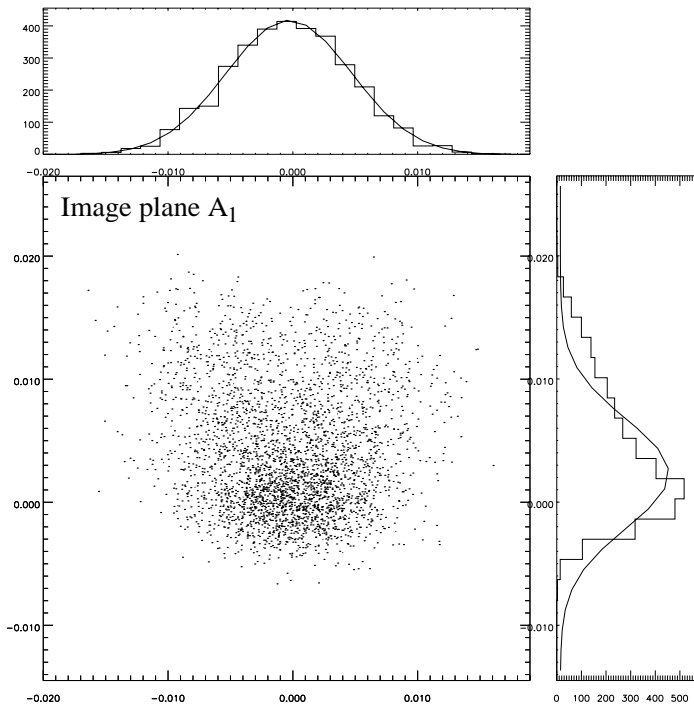
The beam dimensions, given in table IX, are ideal and, as experience shows, the real dimensions will be around a factor 10 larger in reality due to optical aberrations and mechanical inaccuracies. A more detailed ray-tracing calculation including slops errors and rugosity is been made and will be finished within the next months.



**Figure 8:** Schematic representation of beam path for the configuration of Branch **B**



**Figure 9:** Intensity distribution in real space at focal plane  $A_1$  @ 12.4 KeV



**Figure 10 :** Intensity distribution in real space at focal plane  $A_2$  @ 12.4 keV

## 4.5. EXPERIMENTAL HUTCHES

### 4.5.1. Hutch A

This hutch will contain two or possibly three experimental stations:

I) X-ray absorption spectroscopy.

A transmission EXAFS spectrometer is foreseen before the powder diffractometer at the focus plane  $A_1$  (see fig. 6). Space will be left free to accommodate sample environmental facilities such as gas reactors, etc.. For fluorescence measurements a Multi-element solid state detector is foreseen, for transmission experiments photo-diodes, total electron yield, ionization chambers and gas filled proportional detectors, etc. Facilities for sample heating and cooling are, also, planned.

II) X-ray standing waves

A relatively simple set-up for performing X-ray standing waves experiments under normal incidence conditions will be foreseen at the same place of the EXAFS station. It will consist of a removable baby chamber that will house the samples in a UHV environment. The fluorescence detector will be the same which will be used for EXAFS experiments.

III) High resolution powder diffraction

A high resolution powder diffraction set-up will be installed at the focal plane  $A_2$  (45 meter from the source). A heavy-duty  $\theta$ - $2\theta$  diffractometer with a distance from the center to the detector of at least 50 cm is foreseen in order to study samples in different environments such as ovens and cryostats. The detector arm will be rigid enough to accept heavy detectors (~ 7 kg). Capillary or flat-plate samples will be accommodated. Various sample chambers should be mounted on the  $\theta$ -axis of the diffractometer.

### 4.5.2. Hutch B

It will be equipped with three stations:

I) Macromolecular crystallography.

The instrument for biological macromolecular crystallography will be a 4 circle diffractometer with a two dimensional area detector, a single counter for fluorescence measurements at absorption edges, and cryogenic crystal cooling by gas stream. The atomic resolution, for data collection will be between 1.4 Å and 2.1 Å with a maximum lattice cell between 100 Å and 600 Å, respectively. This system will be supported on a high precision motorized bench available to move the setup quickly and precisely from and to the beam axis.

## II) Single crystal diffraction.

Single crystal diffraction including surfaces, interfaces, superlattices and thin films will be performed with an eight-circle diffractometer usually operating in the z-axis geometry. The diffractometer will have its main axis in the vertical and should be able to house loads up to 50 kg. In this way UHV baby chambers, magnets, cryostats and reactor cells should be easily accommodated. In addition to the standard circles for orienting the sample and the detector, additional motions to align the surface normal along predefined directions (vertical or horizontal) will be required for interface scattering experiments, as it is customary in surface diffraction. For high resolution experiments, a  $\theta$ - $2\theta$  set-up together with a goniometer head will be installed in the detector arm in order to use a crystal analyzer. The detector arm has to be rigid enough to allow the installation of heavy detectors if necessary. This should be an accurate instrument with a confusion sphere diameter of  $\sim 50 \mu\text{m}$ .

## III) Small angle scattering.

Non-crystalline diffraction experiments will be possible by reducing the parasitic scatter with the aid of three slits: two collimating slits and a guard slit. The first collimating slit will be placed immediately after the last optical element, i.e the second mirror, and will cut off any parasitic scatter due to any imperfections in optics. The second collimating slit will be placed downstream as close as possible to the sample position so that the converging beam can be appropriately defined and, once again, the parasitic scatter removed. Finally, the guard slit will be placed immediately before the sample so that any scatter coming from the edges of the second slit can be removed. This assembly defines the size of the beam spot and, therefore, the minimum observable diffraction/scattering angle. As regards the camera itself: as

it is common practice we will place the detector<sup>(5)</sup> at the changeable focal position to achieve maximal angular resolution in the patterns, whilst the specimen is placed at a fixed position immediately after the guard slit. The distance between sample and detector will be varied between a few centimetres for high angle measurements up to 7 meters for low angle experiments. The space between the sample and the detector will be evacuated using a vacuum pipe consisting of different sections so that its length can be adjusted to the required dimensions. The entrance into the pipe will be made vacuum tight using a thin mica window (no scatter!) whilst the back end will consist of a 90% transmitting metal grid supporting a very thin plastic film. This approach will deliver flexibility and obviate the need for a complex and expensive vacuum system inside which the detector (which generally operates at high pressures, e.g. a proportional gas chamber) and other components must be placed. Finally, the whole assembly will be mounted on to an optical bench incorporating fine adjustments for alignment (e.g. beam stop, detector, sample, etc..). Standard equipment such as a furnace, cryostat, reaction cells and sample changes will be available.

It has been estimated that with the nominal slits setting allowing the full beam to impinge the crystal, the horizontal and vertical resolutions will be at least 600 Å and 2500 Å respectively<sup>(6,7,8)</sup>. These values can be increased in practice by a factor of 5 or more, thanks to the high flux of the ESRF by slitting down the beam.

#### **4.6. CONTROL ELECTRONIC AND DATA ACQUISITION**

The philosophy adopted for the control system and data acquisition has to be as compatible as possible to the ESRF standard. The beamline will have its own control system and its own network in order to run autonomously. A router will allow communication with the rest of the ESRF and the outside world, and also will allow access to the Machine Control System through a gateway to get parameters like machine current intensity, etc. A dedicated X terminal will be connected to the private machine network to control the shutter mode (automatic or not). Each branch will have a main UNIX workstation (HP, Sun) running X11/Motif GUI or CLUI (Command Line User Interface) client like SPEC. The workstation will be used for beamline control system and often for data acquisition. Other UNIX workstations or X terminals will be also added for preliminary data analysis. On the lower level are the VMEs using Motorola MVME167 68040 CPU running OS-9, used for instruments control. At least one VME crate per branch will be used for the control of the

optics components, vacuum, slits, attenuators, etc. and at least one more crate will be used for data acquisition. For beamline control these crates drive a large number of serial lines, digital or analog inputs/outputs and axis control. It is also foreseen to use GPIB devices by means of LAN/GPIB converters directly connected to Ethernet. The security aspects will be left to the PLCs, which are in charge of the vacuum and Personal Safety System interlocks. The PLCs will be accessed via serial lines by the VME. PCs can be also used as standalone systems mainly to run commercial acquisition systems: Multi-Channel Analyzer, CCD camera, Image plate scanner, etc.

#### **4.7. SUPPORT LABORATORY**

It is foreseen to have a 120 m<sup>2</sup> extra building or local. This PLUO (Preparation Laboratories and User's Offices) will be used for the beamline personal and user's offices. Additionally, in this building two small laboratories and a small workshop (mechanical/electrical) are planned. One laboratory will have facilities for protein crystal preparation and the other one for non biological sample preparation. Users will also find extensive computing facilities for on-line data evaluation.

#### **4.8. REFERENCES**

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## Optical Hutch

splitter vessel	400
water cooled mask	
vacuum vessel	
ion pump 230 l/s	
subtotal	400
+ 20% contingency margin	80
<b>Subtotal</b>	<b>480</b>

### Branch A

Horizontal primary slits (HPS)	110
Vertical primary slits (HPS)	110
Attenuator type 2-3 axes	75
Beamline shutter (X-ray absorber)	60
Be window/valve	45
Collimating mirror + vessel + mechanics (water cooled, housed in UHV)	1100
Be window/valve	45
Beam position monitor (BPM)	220
Double crystal monochromator (housed in UHV):	1300
1st crystal flat and water cooled	
2 <sup>nd</sup> crystal sagittal focusing	
Be window/valve	45
Vertical focusing mirror of variable curvature (housed in UHV)	1000
Be window/valve	45
Beam position monitor (BPM)	220
Horizontal secondary slits (HSS)	75
Vertical secondary slits (VSS)	75

Safety shutter	70
Vacuum pumps and vacuum gauges	360
Support frames	550
Vacuum tubes, bellows, etc	150
subtotal	5655
+ 20% contingency margin	1131
<b>Subtotal</b>	<b>6786</b>

### Branch B

Horizontal primary slits (HPS)	110
Vertical primary slits (HPS)	110
Attenuator type 2-3 axes	75
Beamline shutter (X-ray absorber)	60
Be window	30
Flat mirror + vessel + mechanics (water cooled, housed in UHV)	900
Be window	30
Beam position monitor (BPM)	220
Double crystal monochromator (housed in UHV):	1300
1st crystal flat and water cooled	
2nd crystal sagital focusing	
Be window	30
Vertical focusing mirror of variable curvature (housed in UHV)	1000
Be window	30
Beam position monitor (BPM)	220
Horizontal secondary slits (HSS)	75
Vertical secondary slits (VSS)	75
Safety shutter	70
Vacuum pumps and vacuum gauges	360
Support frames	550
Vacuum tubes, bellows, etc	150

subtotal	5395
+ 20% contingency margin	1079
<b>Subtotal</b>	<b>6474</b>

**Experimental hutch A \***

2-circle diffractometer + ancillary	550
XAS equipment	350
Extra secondary slits for SAXS	75

subtotal	975
+ 20% contingency margin	195
<b>Subtotal</b>	<b>1170</b>

**Experimental hutch B \***

Macromolecular crystallography station	1600
8-circle diffractometer	950
Extra secondary slits for SAXS	55
SAXS camera + translation stage + bench + mounting system	2070

subtotal	4675
+ 20% contingency margin	935
<b>Subtotal</b>	<b>5610</b>

**Total (capital) 26124**

\* The budget indicated for the equipment of both experimental hutches are orientative. The important figure is the global one (6780kFF).

## 5.2. SALARY AND TRAVEL COSTS

It is planned to have two full time scientists, two engineers and one technician staff during the construction period, in order to achieve the task of the beamline construction. This cost is estimated at:

**Subtotal**                    **1150 kFF/year**  
(salary construction time)

For the operational use of the beamline, three scientists, two engineers and one technician are considered necessary on a full time basis for both stations with an estimated cost of :

**Subtotal**                    **1450 kFF/year**  
(salary operation time)

The salaries are calculated on the basis of the ESRF standard, and assuming a partial support for the people on leave from Institutions without teaching duties (i.e. CSIC). The assistance of *pre-doctoral* and *post-doctoral* students with the corresponding scholarships is also *expected with no cost for the CRG*.

Because of the different geographical origins of the CRG people, a small budget is necessary to speed up travel. This cost is estimated at:

**Subtotal**                    **40 kFF/year**  
(travels)

## 5.3. OPERATION COSTS

The operation costs per year for running the beamline efficiently are estimated as follows:

### Recurrent costs

PLUO rent (120 m <sup>2</sup> )	180
secretarial services	50
technical services	28
administrative services	25
use of cranes and handling facilities	15

network connection	30
electricity	15
liquid nitrogen	5
Fluids	15

deionised water  
industrial water  
gases

**subtotal 363**

**Maintenance costs**

repairs of electronics	280
repairs of vacuum system	280
gaskets, pipes, gauge heads	150
computer components, software	150

subtotal 860

+ 20% safety margin 172

**Subtotal 1032**

**Contingencies 200**

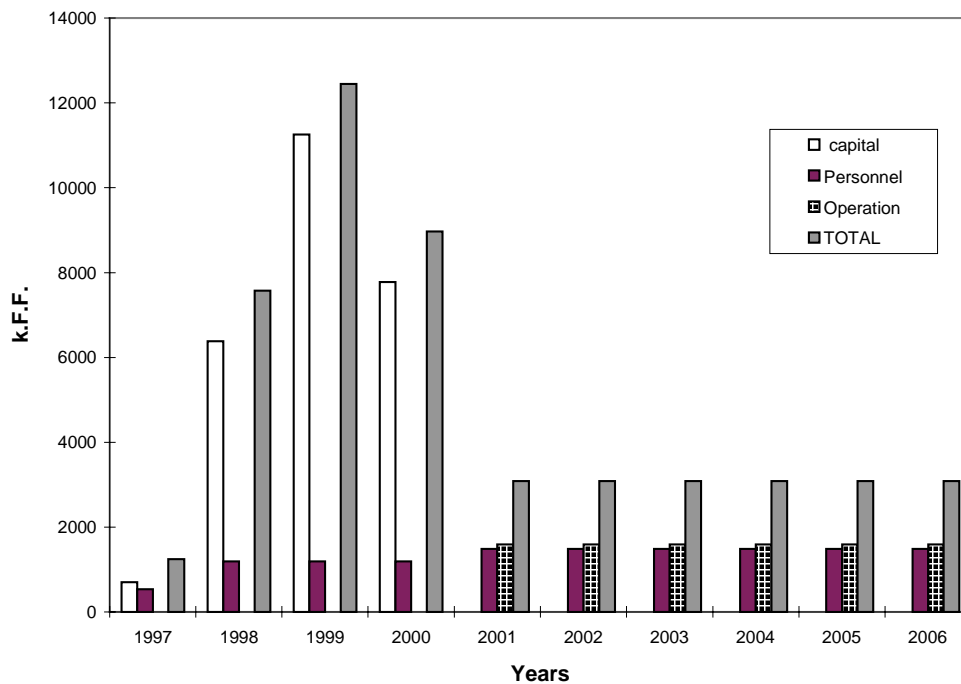
**Total (operation cost) 1595 kFF/Year**

## 6. TIME SCHEDULE AND SPENDING PROFILE

DESCRIPTION	1996			1997												1998												1999												2000												2001												
	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11
General design and presentation final proposal to SAC	██████████																																																															
Approval from SAC & Contract with ESFR				██████████																																																												
Final design & Technical specifications of Optical and experimental Hutches				██████████																																																												
Construction (including electrical power & fluids) of hutches and control cabins and radiation tests																██████████																																																
Final design & Technical specifications of Optical components (slits, monochromators, mirros, etc)				██████████												██████████																																																
Call of tender & construction of Optical components (splitter vessel, slits monochromators, mirros, etc)																												██████████																																				
Reception, installation and commissioning of Optical components																												██████████												██████████																								
Final design & Technical specifications of components for experimental stations																												██████████												██████████																								
Call of tender and construction of components for experimental stations																																								██████████												██████████												
Reception, installation and commissioning of components for experimental stations																																								██████████												██████████												
Beamline commissioning																																																				██████████												
User beam																																																				██████████												

The expending profile has been calculated for the 4 years construction time and 6 years of operation, again the figures given fellow are in kilo French Francs (kFF).

<b>Years</b>	<b>Capital</b>	<b>Personnel and Travels</b>	<b>Operation</b>	<b>TOTAL</b>
1997	700	540	-	1240
1998	6384	1190	-	7574
1999	11260	1190	-	12450
2000	7780	1190	-	8970
2001	-	1490	1595	3085
2002	-	1490	1595	3085
2003	-	1490	1595	3085
2004	-	1490	1595	3085
2005	-	1490	1595	3085
2006	-	1450	1595	3085
<b>TOTAL</b>	<b>26124</b>	<b>13050</b>	<b>9570</b>	<b>48744</b>



Graphical representation of the spending profile.

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