

# FUTURE PERSPECTIVES FOR GILDA, THE ITALIAN CRG BEAMLINE AT ESRF. TECHNICAL AND SCIENTIFIC ASPECTS.

PROCEEDINGS OF THE GILDA MEETING, PALERMO DEC 3-4 2009.

ABSTRACT. This document reports the results of the Meeting hold in Palermo on Dec 3-4 2009 about the future of GILDA, the Italian CRG beamline at the ESRF. The history of the project as well as the limits of the present instrument and the scientific case for the refurbished instrument are presented in the first part of the document. In the second part the conceptual basis for the new design and the technical details are presented. The final section collects the proposals of experimental activities presented by the participants to the meeting.

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SPONSORS AND SUPPORT



## 1. SCIENTIFIC MOTIVATION

## 1.1. GILDA project: history, achievements and actual limits.

GILDA project was proposed in 1989 to provide the Italian community with an easy access to X-ray absorption spectroscopy and X-ray powder diffraction at the that time under construction III generation synchrotron radiation facility ESRF; the main scientific goals were the study of diluted samples, the main technical features were an high monochromatic flux, a small spot size and wide energy range. The proposal was approved and founded by CNR and INFN; after a review of an *ad hoc* nominated International Panel, it was approved also by the ESRF. The design and construction started in 1991, the on-site installation in 1993, the commissioning in spring 1994 and the first user experiments in autumn 1994. Since that time more than 550 experiments have been performed and a total of about 400 publications in International reviewed Journals have been published with an average Impact Factor of about 3.0 [1]. A detailed description of the scientific activity of the beamline during the last ten years can be found in the beamline activity reports elaborated for the last two ESRF Review Panel held in 2004 [2] and 2009 [1] whereas the related panel reports are shown in Sec. 5.1.1 pag. 21 and Sec. 5.1.2 pag. 27. A description of the original design can be found in [3], [4] and in [5]: it consists in a vertically collimating mirror, an horizontally focusing monochromator and a vertically focusing second mirror. Mirrors have a double coating of Pd and Pt in order to achieve cutoff energies of respectively 21 and 27 keV at 3 mrad incidence. This permits harmonics free operation in the energy range between 7 and 27 keV. The original mirrors consisted in 3 segments of 0.5 each in length that were aligned in a clean room off line so with no possibility of on line successive fine alignment. The monochromator focusses the beam horizontally through a bendable second crystal (sagittal focusing) following the idea exposed in [6]. This design permitted to achieve an operating range between 4 and 90 keV, with a spot of about  $1 \times 0.2 \text{ mm}^2$  and an intensity in the range  $10^9 - 10^{11}$  ph/s. This permitted to achieve a record in absorber dilution at  $10^{13} \text{ at/cm}^2$  [7] and a limit noise on transmission spectra of  $10^{-5}$ .

After so many years of continuous operation a refurbishment of several beamline components is needed in order to ameliorate the beamline performance, its reliability and to keep it at the leadin edge among the other similar beamlines at the ESRF and in the world. As a matter of fact during the last two decades relevant technological advances in the field of X-ray optics (mirror and monochromator) have been achieved and a modification of the beamline optics components will allow to improve the beam quality (size, stability and homogeneity) fully exploiting the extreme brilliance of the ESRF X-ray beam. Moreover, the reliability of some components, in particular of the monochromator, is becoming a critical aspect that prevents to fully use the ESRF beam, which is available for more than 5000 hours per year on a 24 hours basis. Such aspects have been also underlined by the last ESRF Review Committee (2009) that in the report Sec. 5.1.2 appreciated the scientific and technical performances and achievements of GILDA and suggested to ESRF to endorse the project, but recommended a substantial refurbishment of the beamline.

In the refurbished version of the beamline some problems encountered during these years that limited the beamline performances (beam inhomogeneity, poor stability) will be overcome and new experimental possibilities will be made available to users

as it will be shown in Sec. 2. This will make GILDA a unique tool for the advanced analysis of materials.

**1.2. Scientific case.** The present proposal is driven by several scientific motivations coming from the Italian community of material scientists, chemists, biologists, physicists, geologists, environmental scientists, archaeometrists. The detailed proposed activities are reported in Appendix 2; in general all of them will heavily exploit one or more of the peculiar experimental aspects described in the introduction. Here we list the main scientific motivations for some fields.

**1.2.1. Environmental science.** In the latest years synchrotron radiation based techniques (XAS, XRD, imaging..) have played a key role in studies of Molecular Environmental Sciences (MES, [8]). One of the most studied topics is the geochemical *cycling* of a number of ecotoxic elements (Pb, Cd, Hg, Zn Cu, Cr, As, Se). These studies are of strategic national interest and at the leading edge of the international research for their relevant implications in predicting, preventing and remedying heavy metal contamination. XAS and XRD studies on soils and minerals containing toxic-element [9] will shed light on a number of issues namely i) the release rate of metals from sulphides, ii) distribution and speciation of toxic elements in soils and particulate, iii) relation between speciation and toxicity in a number of elements.

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**1.2.2. Magnetic materials.** In the field of magnetic materials there are some fundamental issues that still remain unanswered like the origin of ferromagnetism in Diluted Magnetic Semiconductors [10] or a full understanding and explanation of the phenomenon of Exchange Bias [11]. For the first topic, experiments on the local structure of transition metal in p-doped wide-gap semiconductors (GaN) [12] will clarify the interplay between localized spins and free carriers. For the second topic accurate XAS measurements at the interface between the ferromagnet and the anti-ferromagnet layer (for example  $Co_{50}M_{50}$  (M=Co, Pt) and (NiO)) will clarify the relation between the microscopic interface structure and its macroscopic behavior [13].

In the field of applied magnetism, the incorporation of Mn in SiGe nanodots is a topic of relevant technological interest, because it can be a way to produce magnetic semiconductors compatible with the Silicon technology; here the open question is how suppress or control the formation of unwanted  $Mn_xGe_y$  phases.

Also the characterization of more common magnetic materials like interfaces FM-AFM [14] through linear dichroic XAS, new methods for production of magnetic nanoparticles [15] via joint XAS-XRD analysis and the local order in Fe/Co ferrites [16] are topics that will be developed. These experiments need a beamline optimized for XAS using linear dichroism and joint XAS-XRD studies and these requirements will be matched by the new design as shown in Sec. 2.

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1.2.3. *Biophysics.* In the recent years the advent of 3rd generation synchrotron facilities greatly boosted the research on protein crystallography. The 2009 Nobel prize for chemistry has been shared between 3 scientists two of which (Ada Yonath and Venkatraman Ramakrishnan) being former Long Term users of ESRF for their structural studies on structure and function of the Ribosome. However it should be considered that a number of proteins present serious problems of crystallization and/or that a local view around a specific site of the protein can help the resolution of the total structure. For this reason XAS on metalloproteins reveals to be a fundamental tool in the study of these systems. In the present case the study of mitochondrial proteins is foreseen as most of them are involved in metal trafficking inside the cell but the structure is known only for a few [17]. Data will be complemented with NMR results [18] in order to understand the relationship between the protein structure and its function.

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1.2.4. *Earth science.* The study of minor or trace elements in silicate glasses and melts is a fundamental issue in the field of Earth science for its relevance in the petro-genesis modelling of magmatic differentiation that far outweighs their relative abundance. The partial molar thermodynamic properties of these elements as well as their structure is fundamental for a full understanding of the parameters determining the behavior of magmas resulting in different types of rocks from basalt to granites. Optimal use of the information brought by trace element in igneous phases requires an accurate description of their partitioning behavior as a function of phase composition and structure, as well as temperature and pressure. XAS spectroscopy is the ideal tool in this research as it permits to obtain the local structure and the speciation of elements even at levels of tens of ppm [19, 20].

Sec. 5.2.4 pag. 55

1.2.5. *Cultural Heritage.* In the field of cultural heritage, X-ray based techniques (XAS, XRD) with synchrotron radiation offer unique analytical potentials for applications in science of conservation, owing to their non destructiveness and capability of providing analytical information hardly achievable by other techniques. In particular XAS techniques have revealed to be fundamental in the characterization of manufacture [21] and in studies devoted to conservation [22]. Issues that will be addressed are the characterization of metal based chromophores in glasses (ex. mosaic tesserae) and the study of crystalline pigments and of their degradation (copper resinate, smaltino, cinnabar) in order to better target the conservation intervention.

Sec. 5.2.5 pag. 61

1.2.6. *Energy.* Several issues related with the energy production and saving benefit from the use of synchrotron radiation. Improvement of fuel cells namely needs detailed characterization of the various components (proton conductor electrodic materials, interaction electrode-electrolyte) to understand the working mechanism and optimize their performances. For instance, XAS was used to show how In dopants improve the properties of a proton conductor like  $BaCeO_3$  [23]. This approach will be applied to novel proton conductors like  $LaNbO_4$  and  $LaTaO_4$ . Also

Hydrogen storage open questions can be addressed by XAS; indeed it has been recognized that Mg is a potential good material for this purpose and that its poor capacity of incorporating H can be improved by incorporating metal nanoclusters, which increase the interaction with hydrogen [24]. In the future such studies will be extended to Fe and Pd nanoclusters also coupling in-situ experiments of XAS and XRD.

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1.2.7. *Nanoscaled materials and surface physics.* In the field of surface physics many open problems regards interfaces. The possibility of enhancing the sensitivity to atomic bonds parallel or perpendicular to a given surface (as made possible by linear dichroism) will be of fundamental importance for this class of studies.

A first example is represented by solid-solid reactions; while it is well established that after the formation of a thick layer of the reacted phase the kinetics of the process is driven by diffusion [26] a much limited information is available on the initial stages of the process. An example is the reaction  $Ni(Zn)O + Al_2O_3 \rightarrow Ni(Zn)Al_2O_4$ . These studies will benefit from the use of linear dichroism studies in total reflection condition (RefEXAFS).

Another issue is the structure at the interface between ultra-thin film of oxides and metals with particular attention to polar oxides. Indeed due to a macroscopic local polarization these surfaces are unstable but they can be stabilized by epitaxial growth. This means that complex mechanisms come into play to reduce the electrical polarization leading to new structures and macroscopic properties [27]. Surface EXAFS will shed a light on a number of such systems like ultrathin films of MgO on Fe(001), Ag(001), Ni clusters in MgO CeO2 on Pt(111) just to cite a few.

On a more applied point of view, research on nanostructured materials will be focused on novel sensing systems like Zn and ZnO nanotubes [28] with the aim of studying the structural interaction between the tubes and gases like  $NO_2$  gas. Also the structural details of the kinetics of formation of a widely investigated class of materials like metallic nanoparticles coated with polymers will be studied by a combination of XAS and XRD in suitable reaction cells [29].

Finally it is proposed to investigate the details of the energy transfer phenomenon between Rare Earth (RE) luminescent ions and sensitizers like metal nanoparticles. XAS has already demonstrated to be a fundamental tool on this subject [30]. However in this case it is proposed to exploit the X-ray Excited Luminescence (XEOL, [31]) in order to distinguish the optically active RE atoms, to determine their local order and in turn the link between structure and energy transfer effects.

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1.2.8. *Fundamental physics.* Also more fundamental physic open problem can be investigated with this new instruments. An example are the studies under high

pressures; as a matter of fact pressure is a variable of great fundamental importance in basic science as it represents the best way to modify the relative separation and/or the arrangement of constituents atoms and consequently the degree of orbital overlap. This allows an experimental check of the theoretical models used to describe the structure and the properties of matter, i.e. whether a substance is a metal, an insulator, a superconductor or a ferromagnet. In the field of physics of liquids and glasses, high pressure and high-temperature XAS experiments are largely demanded for elucidating the question of the occurrence of polymorphic transitions [32]. For example,  $GeO_2$  is an archetypal *strong* network glass forming system which shares with silica several structural Characteristics; this system shows a pressure-driven structural transition between 6 and 8 GPa from a network of corner sharing tetrahedra (4-fold coordinated Ge) to a dense octahedral material (6-fold coordinated Ge) of the same chemical composition [33]; but the details of the local structure changes occurring at the transition still require clarification in particular the mechanism of the transition i.e. whether it is a continuous process with an intermediate state or a collapse into sixfold Ge-O coordination.

Another issue that will be addressed is the study of dynamical properties of solids. New information on the local lattice dynamics has been made available from recent advances for XAS; for example, the perpendicular mean square relative displacement (MSRD) can now be evaluated, giving original insights on the correlation and on the anisotropy of relative vibrations [34]. Using this potentiality a number of problems will be studied like the origin on Negative Thermal Expansion in solids which results from the opposite effects of positive contributions due to bond stretching and negative contributions due to tension effects which are measured by the perpendicular mean square relative displacement. Also very small effects like change on the bond length due to moderate pressures, isotopic effects [35] or thermal bond changes at very low temperature ( $< Liq.He$ ) will be possible, thanks to the increase sensitivity of the upgraded beamline. The exceptional high quality of data in terms of Signal to Noise ratio (at least in the range of  $10^{-5}$ ), of monochromator stability and reproducibility required by such kind of investigations will represent a challenge in the realization of the beamline.

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## 2. CONCEPTUAL DESIGN

**2.1. Introduction.** After 16 years of continuous operation the GILDA beamline needs a revising of its scientific targets and an upgrade of its instrumentation to continue to perform scientific research at the top level in its specific fields. The upgraded beamline will make profit of the Upgrade Programme of the ESRF. It will allow the advanced analysis of materials using X-ray based techniques namely Absorption Spectroscopy (XAS) and Diffraction (XRD) to carry out research on leading issues in different fields like materials science, fundamental physics, biology, earth and environmental science. We remind that GILDA is a unique instrument for the Italian and international community because it makes available to users an intense photon flux in a high energy range ( $> 20$  keV) that is obtainable only at the ESRF. Peculiar experimental aspects of the refurbished beamline will match

the requirements evidenced by the users in the scientific case; here a brief list is recalled:

- use of grazing incidence/total reflection data collection in linear dichroic mode for surface analysis;
- the combined XAS/XRD in situ data collection under extreme conditions;
- high attainable sensibility for the analysis of diluted samples;
- high quality in term of low noise and linearity for XAS data in transmission mode.

To achieve these targets a particular attention will be devoted to the quality of the beam spot in terms of homogeneity, spatial and energy stability, reduced size and divergence. For the scientific community it will be a fundamental tool to add value to the research carried out in home laboratories opening the perspective of high impact research.

**2.2. Limitations of the previous design.** With the new project we aim in overcoming a series of limitations that were present in the previous design. The first one is the marked spatial inhomogeneity of the beam spot due to the stiffening ribs in the back face of the second monochromator crystal (see [4] for details). The x-ray spot on the sample consists in a sequence of peaks and valleys that, in the case of a sample with a spatially inhomogeneous density, lead to a noticeable noise related to small movements of the beam during the energy scan. Moreover, the horizontal beam size is limited by the dimensions of the ribs to about 1 mm, far above the potential value offered by the high brilliance of the ESRF ring. Because the limit beam size is linked to the rib dimension [36], unfeasible thin ribs are needed to get spots below a few  $10^2 \mu\text{m}$ . Finally, the segmentation of the spot in the horizontal direction (both in terms of intensity and local divergence) prevents the realization of experiments in total reflection conditions with a vertical surface of the sample i.e. perpendicular to the beam polarization (linear dichroic mode).

A second aspect regards the monochromator that operates with two independent axes of rotation, one for each crystal [37]; this design makes the instrument particularly sensitive to floor and ambient vibrations and results in a rather marked instability of the beam intensity and shape only partially compensated by a fast feedback control [38] acting on the first crystal through a piezo actuator. Linked to this peculiar design of the two independent axes of rotation is the complex software needed to run the monochromator, that results in rather slow energy scans.

Finally, the segmentation of the first mirror, which is made of 3 independent sections aligned once in 1994 to focus the beam in the same position, prevents to focus the beam correctly, because the three sections actually focus the beam in three different vertical positions. This technical solution was the only one possible to realize a 1.5 m mirror 20 years ago but nowadays single block mirrors of these dimensions are currently realized.

As already stated above, the last beamline Review Panel nominated by the ESRF to review the beamline activity recognized the quality of the scientific GILDA activity on XAS and XRD but strongly recommended a comprehensive refurbishment of the beamline in order to continue to provide to users a valuable tool for X-ray analysis.

**2.3. Basic design concepts.** To carry out the outlined research programmes, the beamline has to fulfil the following requirements:

- to provide a beam also at high energies ( $E > 20$  KeV). This will permit the structural analysis (using XAS at the K absorption edge) of technologically crucial materials like catalysts (Mo, Pd), hydrogen reservoirs (Nb, Pd), protonic conductors (In, Ba, Ce, Zr), solar cells and transparent conductors (In,Sn), luminescent and advanced magnetic materials (Rare Earths).
- To realize experiments in Grazing Incidence and linear dichroic mode. This will permit the structural analysis of thin films, interfaces or the interaction between adsorbed species and model surfaces, as needed for example in magnetic materials or environmental science.
- To provide an intense and sub-mm beam in the whole energy range. This is needed for the analysis of diluted materials and for the studies under (moderate) extreme conditions of high temperature or pressure.
- To provide a beam with reduced divergence, in order to carry out experiments based on X-ray diffraction and reflectivity.

The refurbishment of the beamline will be realized in three phases. The objective of the first phase is the realization of a suitable optics whereas in the second phase, the basic data collection setups (reflectometer for RefEXAFS[39], 2-dim detector for diffraction, apparatus for low noise transmission EXAFS) will be implemented. Finally, peculiar sample environment apparatus will be realized like a cell for experiments in *operando*- conditions [40], a cell for high pressure/temperature studies. The unique aspects that will have a major impact for the scientific community using this instrument will be:

- the possibility of realizing surface analysis with RefEXAFS coupled to linear dichroism (i.e. with the beam polarization parallel or perpendicular to the surface).
- experiments on diluted samples also in extreme conditions and on the K absorption edges of heavy (namely 4d metals) elements.
- realization of coupled XAS-XRD in situ experiments.

**2.4. The landscape in Synchrotron Radiation Research.** In the early 90s the construction of the ESRF marked a turning point in synchrotron radiation research. A high brilliance, high energy machine was available to the user community with enormous benefits for research possibilities: this has been recently witnessed by the recent attribution of the Noble prize to two ESRF users. After 15 years of successful running, ESRF is going to carry out a major refurbishment program with the aim of boosting research in 5 main topics namely nano-science, time resolved experiments, extreme conditions, imaging and structural biology [41]. The proposed refurbishment of GILDA will meet some of the points of the ESRF upgrade namely for *nanoscience* (study of nanostructured materials and in restricted spatial regions as achieved by RefEXAFS), *extreme conditions* (studies at high pressures and temperatures), and *Structural biology* (structural studies of metallo-proteins in solution) and will open the possibility of a tight collaboration with the other beamlines involved in these topics. Moreover, in the latest years a number of new national facilities (Bessy II, Diamond, SLS, Soleil, ALBA) have been built with the aim of providing high brilliance sources at low energy to the users. In these facilities a number of new beamlines operating from bending magnet and/or undulator sources are dedicated to x-ray absorption and diffraction. In all cases these beamlines cover only one or two of the topics here proposed like surfaces,

TABLE 1. Target day 1 performance of the beamline

Energy range Focused	5-40 keV
Energy range Unfocused	5-80 keV
Flux Focused	$\geq 10^{10}$ ph/s
Flux Unfocused	$\geq 10^8$ ph/s
Beam size	$\leq 200 * 200 \mu m^2$ FWHM
Noise on transmission XAS	$< 10^{-4}$

diluted samples, extreme conditions, high energy and joint XAS-XRD characterizations. And having all these possibilities gathered in a single laboratory will be the strong point of the refurbished GILDA project.

**2.5. Day 1 performance.** In order to satisfy the needs of the user community and to be competitive respect to other projects active in the other synchrotrons we aim in realizing a beamline that will have the following *day 1 performance* (See Tab. 1).

### 3. TECHNICAL DESIGN

**3.1. Layout.** The layout of the beamline is shown in Fig.1: and will consist in 3 hutches, namely an optical hutch (OH) and two experimental hutches (EH1 and EH2) The Optical Hutch will contain the optical elements that will focus the beam in the middle of the second experimental hutch EH2. Here there will be the main experimental apparatus consisting in a multicircle reflectometer supporting all the ancillary equipment for sample environment (vacuum chamber, cryostat, oven) and a bench for the measurement apparatus (ion chambers, fluorescence detector, diffraction 2-dimensional detector). The preceding hutch (Experimental Hutch 1, EH1) will be used for experiments with a non focused beam like EXAFS in transmission mode and low noise conditions.

The optics consists in a collimating first mirror a double crystal monochromator and a focusing second mirror. The beamline will use mirrors in the energy range 5-40 keV. Above 40 keV the monochromator will be the only optical element.

**3.2. X-ray source.** The beamline will take the beam from the high field part (0.85 T) of the BM8 bending magnet of ESRF. In this point the X-ray source has dimensions  $75 \mu m$  hor and  $32 \mu m$  vert. Full Width at Half Maximum. The source is located at 25 m from the first optical element. In the following we will consider the machine running at 6 GeV with a stored current of 200 mA.

**3.3. Mirrors.** The problem of beam focusing is a major issue for the present project. To meet the requirements stated in the scientific case it is necessary to have at the same time high brilliance, flux and beam homogeneity that are difficult to meet at the same time. On other beamlines different optical schemes have been adopted to focus the beam. In some cases sagittal focusing has been chosen ( FAME at ESRF [42], SAMBA [43] and DIFFABS [44] at SOLEIL) . Sagittal focusing, although providing exceptionally intense beams, is not suited for our goals

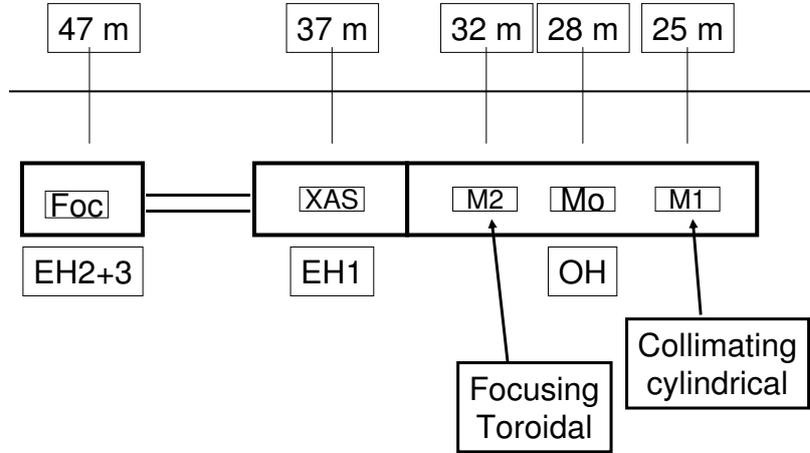


FIGURE 1. Sketch of the proposed beamline. In the upper part of the picture the distance of the various elements from the source is indicated.

as explained above. Good results have been obtained from non-focusing designs (BM29 at ESRF [45], the XAFS beamline at ELETTRA [46]); but this technical solution would restrict the application field of the beamline to concentrated samples that is too limiting for the scientific case presented here. In more recent projects a great interest to toroidal mirrors has emerged driven by the achromaticity of this element and to the strong improvement of the quality of these devices realized in the latest years. This is the case of protein crystallography on bending magnet beamlines at APS [47], B18 at DIAMOND [48] and the refurbished ROBL beamline at ESRF [49]. This choice will be chosen for the present project as it ensures at the same time a high intensity and homogeneous beam with a reduced size.

The first mirror has a cylindrical shape and is used for collimating the beam as it permits to lower the vertical divergence of the beam from  $\approx 40\mu rad$  (determined by the input slits) to a few  $\mu rads$ . As the scattering vector of the monochromator is vertical, this device permits to achieve an instrumental energy resolution well below (less than 25%) the core-hole width of the K edges in the energy range of interest. This will realize an optimized configuration for the collection of XANES data at high energy resolution.

The second mirror will have a toroidal shape and will focalize the beam in a 2:1 condition on the horizontal plane. It will consist in a cylindrical channel cut in a bendable silica substrate. This choice has been shown to minimize the impact of comatic aberrations in the focal spot [47] and will keep at a moderate value the overall length of the beamline. The limited horizontal acceptance of the device (limited to 1mrad in this case) is largely compensated by the high quality of the beam achievable in this way. Considered the space available it will be possible to have up to 3 toroidal channels on the same substrate. The part between the channels section of the second mirror will be left flat to make available to users a non focused beam.

Both mirrors will bear a triple coating Si-Pd-Pt and will work at 2 mrad incidence

TABLE 2. Geometric parameters of the mirrors.

Mirror	Shape	Major Radius	Minor Radius
1	Cylindrical	24.8 Km	-
2	Toroidal	15.8 Km	4.2 cm

angle. Si will cover the region 5-15 keV whereas Pt will cover 15-40 keV so ensuring an harmonic-free operation in this total energy range. Pd will cover the region around 15 keV in order to avoid the cutoff of the Si coating and the absorption lines from the Pt coating. For focusing above 40 keV a solution using graded multilayers is at present under study. Table 2 collects the principal parameters of these optical elements.

**3.4. Monochromator.** The monochromator will be a fixed-exit device with a single rotation axis and will use flat crystals. The cooling of the first crystal will be realized with liquid nitrogen in order to stabilize the lattice spacing (and thus, the energy calibration) against thermal drifts connected with the current decay in the ring. Different pairs of crystals will be mounted inside and the crystal change needed to access the whole energy range: Si(311) will cover the interval 5-30 keV, whereas Si(511) will operate in the range 10-80 keV. A further Si(111) crystal will be used to obtain high photon flux in the region 5-15 keV. The crystals will be permanently mounted inside the monochromator and the change will be realized by simple horizontal translation of the instrument. This solution will ensure a high quality beam in terms of temporal stability and beam spatial homogeneity thanks to the use of flat reflectors.

**3.5. Other elements.** Before the first mirror and in analogy with the design of the GILDA beamline a set of 9 attenuators will be mounted. This will permit at all energies the reduction of the thermal load on the subsequent optical elements by absorbing the unnecessary low energy part of the spectrum. In particular with this element we aim in reducing at maximum the thermal bump expected on the first mirror or on the first crystal when operating above 40 keV and that otherwise could severely degrade the energy resolution and the size of the focal spot. A set of cooled primary slits will be mounted after the attenuators and further slits will be placed before and after the monochromator. Before and after each optical element a beam monitor consisting in a fluorescent screen and a linear detector (photodiode or W wire) will be installed for beam characterization.

**3.6. Ray Tracing.** A detailed Ray-Tracing calculation of the parameters of the beamline has been carried out using the SHADOW code [51]. The beamline is shown to provide a high photon flux in a wide energy range and a small beam size in compliance with the experimental requirements cited in the previous sections (See Fig. 2). Table 3 collects all the main parameters derived from the simulation: AN example of the geometry of the focal spot is presented in Fig. 3.

**3.7. Endstation design.** The beamline will have 2 experimental stations: the main one on the focal spot placed in the EH2 (See Fig. 4, top) and a second one in the EH1 (See Fig. 4, bottom). The main apparatus in EH2 will be a 5 circles

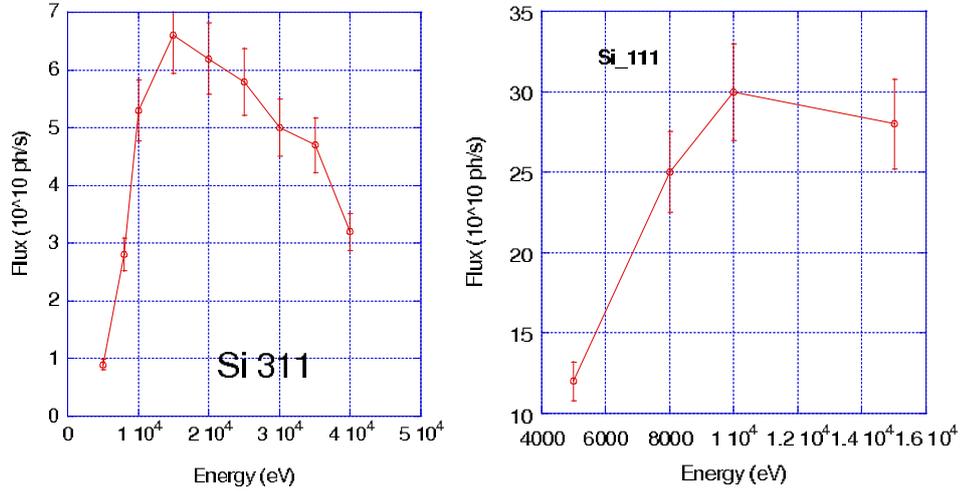


FIGURE 2. Flux foreseen on the focal spot in the case of two possible crystal planes for the monochromator. The simulation conditions are those mentioned in Tab. 3.

TABLE 3. General parameters of the beamline as calculated by ray-tracing. Real values of slope error, about  $2\mu\text{rad}$  of the mirrors have been accounted for in the calculation. Machine parameters were a current of 200mA and a beam acceptance was  $1\text{mrad H} * 0.043\text{ mrad V}$ .

Parameter	Value
Operating Energy range	5.4-70 keV
Flux w Si(311)	$1-7 \cdot 10^{10}$ ph/s
Flux w Si(111)	$1-3 \cdot 10^{11}$ ph/s
Energy resolution w Si(311)	$4 \cdot 10^{-5} - 1 \cdot 10^{-4}$
Energy resolution w Si(111)	$1 \cdot 10^{-4} - 1.5 \cdot 10^{-4}$
Beam size H * V FWHM	$103 * 143 \mu\text{m}$
Beam Divergence H * V	$0.050 * 0.004 \text{ deg}$

reflectometer with a high load ( $\approx 50$  Kg) capability on the sample stage. 3 rotational degrees of freedom (plus two translations) will permit the orientation of the sample in total reflection conditions with both the surface orientations parallel and

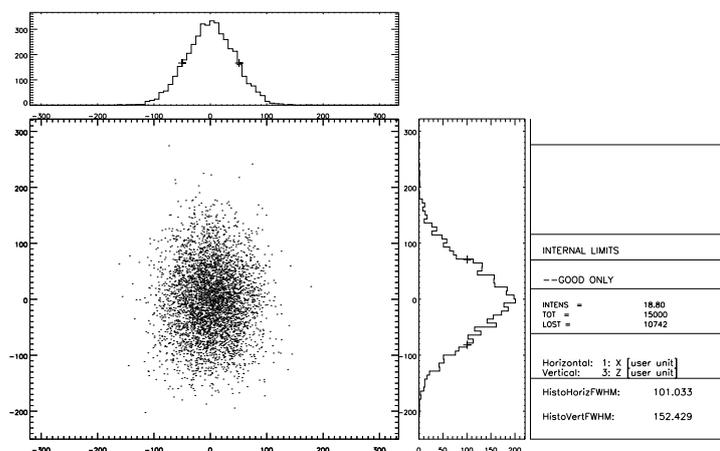


FIGURE 3. Geometry of the focal spot

perpendicular to the beam polarization. The detector arm will move on two rotational degrees of freedom and will bear ion chambers (ICs) and slits for measuring of high quality (at least 5 decades) x-ray reflectivity and RefEXAFS data. Due to the fact of a unique and non-moveable focal point when not used for reflectivity measurements this instrument will support also the further chambers for the samples (high vacuum chamber, high pressure cell, chemical reaction cell, ultra high vacuum chamber, ... ) and this is the reason for the requested high load on the sample stage. The reflectometer will be preceded by an IC for the measurement of the intensity of the incoming beam and a set of slits capable of sizing the beam from 2 cm down to  $20\mu\text{m}$  in both directions. The sample stage will host the experimental chambers that will consist, for a *standard* configuration, in a high vacuum chamber capable to host with a manipulator for standard XAS experiments or a cell for in-situ reactions. In a second phase, the implementation of further sample environment equipments, like a large volume (Paris-Edimbourgh design) high pressure cell or a ultra high vacuum chamber, to be placed in this point should be envisaged in order to extend the data collection capability as required by the user community. Sidewise, an energy resolving detector for fluorescence detection will be installed. Considering the wide energy operation range of this device the best choice will be a multielement High Purity Germanium detector. On the moving arm of the reflectometer we will place two ion chambers in series for the measurement of the transmitted/reflected beam with possibility of measuring an internal energy calibration reference compound. On a bench placed just after the reflectometer a 2-dimensional area detector will be placed for the detection of diffraction spectra from the sample. This will be used for straight XRD experiments coupled to XAS data collection (whenever the XAS energy range is compatible with XRD) or for pressure calibration in High Pressure experiments. In EH1 there will be an apparatus for the collection of conventional XAS spectra in transmission mode. It will consist in a bench hosting two experimental chambers and ion chambers for the detection of the beam before and after the sample. Used in conjunction to a

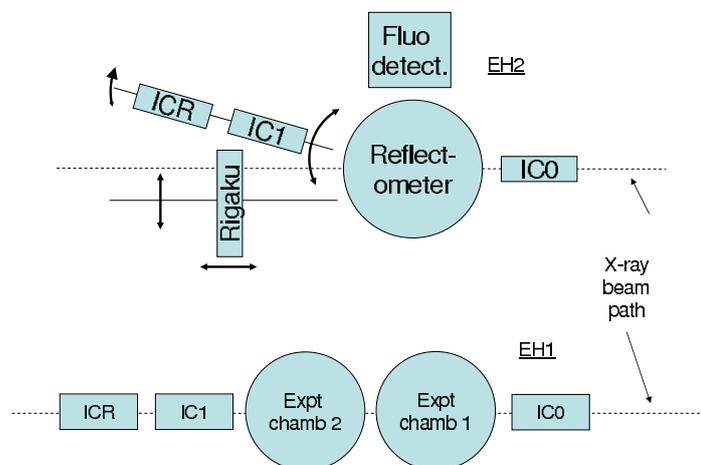


FIGURE 4. Sketch of the experimental endstations in EH2 (Top) and EH1 (bottom).

non-focusing configuration of the beamline it will realize a station for high quality XAS data collection. The ancillary equipment will include *standard* list of tools like a liquid helium/nitrogen cryostat, a cell for chemical reactions gas-solid and a cell for measurements in liquid environment. In the latest phase of the realization an increment of possibilities of sample environment is to be envisaged with the realization of a large volume high pressure cell, a cell for measurement at very high temperature and controlled O activity, a dilution cryostat. For the control of the optical elements and instruments in OH and EHs the standard ESRF hardware and software will be used with a consequent ease of operation for users taking experiments on other ESRF beamlines.

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5. APPEDICES

5.1. **Appendix 1: Beamline Review Panel reports.**

5.1.1. *Report 2004*. Report of the ESRF Beamline Review Panel 2004

chamber for XRD grazing incidence diffraction. Such a wide range offers sample holder for single-crystal XAS data collection and the high temperature conditioning apparatus and technical developments, such as the oscillating applications were achieved also through the implementation of sample quality X-ray absorption spectra of dilute systems. The energy range spans from 4 keV (Ca K edge) to well above 50 keV (Er K edge). Extension of the scientific The science areas should reflect the niche of the beamline for providing high collaboration with academic users groups.

due to the implementation of the translating image plate, performed in diffraction and scattering. Diffraction improved considerably since the last review X-ray absorption spectroscopy (XAS), with the residue devoted to X-ray beamline, in the period 2000-2004 the vast majority of experiments (89%) are for expertise with a new application. Although the beamline is a general purpose experiments on ancient glasses exemplify a synergy of the resident scientific dependent in situ studies as prime examples. In addition the high profile scope, with addition of cluster science, manganese and granular alloys, and time- Since the last review (1997) it is clear that the CRG has widened the scientific communications presented at conferences.

journals for the period 2000-2003, with a comparable number of reports and qualitatively at a very high level. The report lists 165 papers on international towards earth science (42%). The results and publications are numerically and XAS use is more oriented towards solid state physics (74%) and diffraction science (11%) and biological science (7%) the other significant components. The presentation summaries and the publication records make it clear overall the science is predominantly solid state physics (56%) with catalysis (16%), earth magnetic materials, glasses, surfaces and interfaces.

with the following emphasis: catalysis, semiconductor materials, metal clusters, personally presented and commented by staff people and collaborating users document presented to the commission. Accordingly, the research topics were The recent research performed on the beamline is extensively described in the

### **Research – Scientific aspects**

high quality, as was demonstrated in their excellent presentations. The scientific output of the staff and collaborating groups on this beamline is of groups.

chemistry, biology, and earth science problems, serving mainly Italian research established with the goal of investigating the local structures in physics, The General Purpose Italian Line for Diffraction and Absorption (GILDA) was

### **Introduction**

### **Review Panel for BM8 (GILDA)**

The beamline is an excellent facility for XAS studies in the wide energy range from 4 keV to well above 50 keV, particularly in dilute systems, including the capability to undertake experiments under UHV conditions and in the grazing incidence geometry. The performance of the beamline in this type of experiments is comparable to that of similar facilities on 3<sup>rd</sup> generation sources.

### **Instrumentation – Technical aspects**

These were impressive applications exploiting the wide energy range, spectroscopic resolution, stability of the beamline. They include the study of the orientation of Co dimers in a silver matrix with fluorescence detection (PRL 2003), NiO overlayers on Ag(001) (PRL 2003) and sub monolayer sensitivity of Ag on MgO(100) (Surface Science 2003). The catalysis research is characterised by careful measurements on key species under steady state conditions which, when combined with other spectroscopic data derived in home laboratories (e.g. IR spectroscopy), can provide structural insights e.g. Cu/ZSM5 under CO (Angew Chem 2000). The time resolved diffraction experiments have also provided an excellent description of the burning of a template out of a zeolite framework (JACS 2003). Recent studies of Renaissance nanocrystalline glazes highlights the potential of the beamline to archaeometric applications (JAP 2003, Nature 2003).

### **Highlights**

The delivery of beam time (2174 shifts) in the same period indicates that the beamline efficiency complies with the average of ESRF public beamlines. In agreement with the ESRF-CRG contract, 2/3 of the shifts have been allocated to the Italian community by a National Scientific Committee, and 1/3 of the experiments have been allocated by ESRF panels.

The beamline has a substantial oversubscription of 2-3:1 for applications for the CRG's own proportion of the beam time and a significantly higher ratio for the public beam time. The CRG does not utilise the Long Term mechanism. Considering the high involvement of user research groups in developing sampling systems, this is worth considering in the future.

### **Beam time applications**

Opportunity for many potential user communities, including the wider ESRF community. Involvement of industrial partners in the beamline activity remains rather limited.

After 5 to 10 years of operation optical components of the beamline have to be refurbished. The team has presented a short term plan and a medium term perspective. On the short time scale, the second focusing mirror will be replaced, and the alignment of the first one will be checked with the help of the ESRF staff.

In the medium term perspective, the team are discussing the improvements to the monochromator system. The present system suffers from lack of mechanical reliability and long dead time. The team are evaluating possibilities of either improving the present system, or of replacing it with a commercially available one. The Committee agrees with the necessity of improving the mirror system, and strongly supports the need for improving the monochromator system, while preserving the excellent capabilities provided by the dynamical focusing. A limitation to the speed and efficiency of experiments is the necessity for monochromator adjustment at each energy data point; an issue that has to be addressed to keep the beamline competitive.

Over the period since the last review some substantial improvements have been implemented on the beamline in the area of data acquisition systems and sample environment. User feedback suggests that the facility is now user friendly, especially the instrument control and data acquisition systems, which are run on the basis of LabView software (not SPEC).

From the possibilities for implementation of new detection systems presented by the group, the Committee strongly support the suggestion to use Silicon Drift Detector technology, which offers potential improvement over the current system in terms of ease of use and solid angle coverage. The development of Superconducting Transition Edge detector technology presented by the group seems to be at too early a stage to justify the allocation of substantial amounts of CRG manpower and beamtime at present. Nevertheless, the promise of sub-eV resolution is very exciting, and the collaboration with the group in Genova is encouraged.

The UHV facility in the third hutch ("open hutch") has good potential for surface science investigations. However, the demand for the use of this facility seems to be low at present, and characterization and detection systems, e.g. LEED and fluo, are absent. Any further development has to be justified by strong demand from user groups.

The diffraction facility housed in the second hutch accounts for about 11% of beamtime, and mostly involves time-resolved experiments using translating image plate. The group introduced plans for upgrade to the detection system, e.g. *in situ* MAR345 image plate reader system, or a fast CCD. Even with these improvements in place, it is difficult to see how this facility could compete with other world-leading diffraction instruments at the ESRF.

The scientific quality of the staff is of a high standard. The support provided to the user groups is professional and friendly. We were pleased to hear that the staff also have an opportunity to dedicate a good proportion of their time to in-house research. The Committee feel that the appointment of the third beamline scientist should take place as soon as possible, and strongly support the request made by the group for the appointment of another post-doctoral researcher. The beamline has proven to be an excellent training ground for PhD students and young scientists.

### **Staff**

With projected technical developments, this beam line can maintain its high status for the foreseeable future (next 5 years and beyond). In the short term, the beam line can be expected to maintain its strengths but we should also wish to see a further broadening of applications. There is a clear opportunity for combining techniques for *in situ* studies (e.g. XAS with vibrational Raman spectroscopy).

### **Future scientific directions**

### **Future developments**

*Handwritten signatures: P. Lagarde, G. Artoli, J. Evans, JM Barandahan, R. Abela, AM Korsunsky*

ESRF, Grenoble, November 3<sup>rd</sup>, 2004

- The Committee agrees with the necessity of improving the mirror system, and strongly supports the need for improving the monochromator system, while preserving the excellent capabilities provided by the dynamical focusing.
- The Committee strongly support the suggestion to use Silicon Drift Detector technology for upgrading the XAS detection systems.
- The Committee feel that the appointment of the third beamline scientist should take place as soon as possible, and strongly support the request made by the group for the appointment of another post-doctoral researcher.
- The CRG does not utilise the Long Term mechanism in the Italian allocation system. Considering the high involvement of user research groups in developing sampling systems, this is recommended considering in the future.
- The wide ranging XAS capabilities of the GILDA beamline offers opportunity for many potential user communities, including the wider ESRF community.
- The Committee suggests that development of the diffraction activity should be coordinated with other ESRF or CRG beamlines.

**Summary of recommendations**

5.1.2. *Report 2009*. Report of the ESRF Beamline Review Panel 2009

## Review panel for BM8 (GILDA)

**General note:** The panel were impressed with the remarkable quality and quantity of science that the beamline has delivered over the reviewed period of operations.

### Summary of recommendations

- The panel recognises that GILDA plays an essential role for a large user community. It provides valuable and much needed general spectroscopy and diffraction capabilities and the continuation of this provision has to be ensured. The multi-purpose beamline GILDA offers access to high-energy spectroscopy, which is only readily accessible at the ESRF.

- The panel strongly recommends a comprehensive refurbishment of the GILDA beamline to ensure reliable operation and to develop the beamline to a performance level consistent with the planned upgrade of the ESRF. This must be implemented in a systematic and timely fashion to avoid undue difficulties for the user community. Specific points to be refurbished follow in order of priority:

- a) Primary optics: 1<sup>st</sup> priority is the replacement of the current monochromator with a modern high quality spectroscopic grade device, and the installation of a new focusing mirror. This will ensure the provision of a high quality stable and homogeneous beam at the experimental stations of the beamline, and enable improved energy scanning capabilities.

- b) A new multi-element fluorescence detector has high priority. This will reinvestigate the capability of the beamline to study diluted systems which is particularly important, for example in the areas of materials, biological and surface science, chemistry and environmental science.

- c) Given the significant and increasing demand for ReflEXAFS at the beamline, the panel recommends the refurbishment of the reflectivity instrumentation.

- d) The panel recommends that the XRD capabilities of the beamline could be greatly enhanced by the provision of a complementary X-ray fluorescence detector that will give the opportunity of measuring diffraction and absorption at the same time.

- The two scientists that constitute the current staff are not sufficient for running the beamline in the most efficient manner. The permanent staffing level should be increased to include 3 beamline scientists and a technician. The panel then further recommends that the team be completed by the appointment of at least one PhD student and/or post doc.

- The panel encourages the continuation of the transition to the standard ESRF hardware and software.

ESRF, Grenoble, May 27, 2009

W. Paulus, M. Sandström, I. Ascone, D. Bowron, E. Dooryhee, M.L. Fernandez-Gubieda, P. Lagarde



## Introduction

The General Purpose Italian Line for Diffraction and Absorption (GILDA) was established for investigating the local microscopic structure of matter and its relation with macroscopic physical properties, to elucidate problems in physics, chemistry and earth science. The review panel (chair M. Sandstrom) was impressed with the remarkable quality and quantity of the scientific output on this beamline, where the staff closely collaborates with many of the Italian user community, as was demonstrated in the excellent presentations of the staff.

## Research activities

The recent research (2004-2009) performed on the beamline is extensively described in the comprehensive documentation presented to the review panel. The research topics were personally presented at the meeting of the panel and commented on by the staff members with the following emphasis: optoelectronics, nanoparticles, semiconductor and interfaces, archaeology and cultural heritage, followed by an overview of the diffraction activity in earth science and catalysis. The written report also covered studies of materials for energy production and transport, life science, soft condensed matter, catalysis, materials exhibiting special thermal expansion properties, phase transitions, local lattice distortions, instrumentation and data treatment methods.

The main components of the scientific activity are, according to the presentation, 36% solid state physics, 33% earth science, 21% in chemistry or physical chemistry. Materials science is the generally dominating activity, although many other topics are covered on this general purpose beamline with 82% X-ray Absorption Spectroscopy (XAS) and 18% X-Ray Diffraction (XRD) experiments. The results and publications are quantitatively and qualitatively on a very high level. The report lists 215 papers from 2004 to 2008 in international peer-reviewed scientific journals, with the average impact factor close to 3.0. This is a remarkably high output of the 199 experiments carried out in that period.

The high profile archaeometric studies have continued on glasses, lusters and pigments. Reflectance studies have played an important role for the studies of thin films and catalytic reactions. Methods have been developed where e.g. surface and bulk sites for As dopants in Si have been distinguished by changing the penetration depth. New software dedicated to quantitative analysis of EXAFS data collected in total reflectance mode has been developed.

About 70% of the scientific studies are performed on dilute systems reflecting the niche of the beamline for providing high quality XAS spectra by means of fluorescence and total reflectance techniques. The energy range includes the K-edges from Cr to Er, with about 20% of the experiments carried out at energies above 20 keV. That wide energy range, from about 5 to well above 50 keV, offers opportunities for many potential user communities, also including the large ESRF community. Although many of the topics have industrial interest, e.g. the studies on optoelectronic glasses, catalysts and hydrogen production processes, the involvement of industrial partners are mainly via University groups.

### Beam time applications

The delivery of the beam time with 2184 shifts allocated in 10 semesters is in accordance with the average of the ESRF public beamlines. In agreement with the ESRF-CRG contract  $\frac{2}{3}$  of the shifts have been allocated to the Italian community by a National Scientific Committee, and  $\frac{1}{3}$  by the ESRF beam allocation panels. Totally more than 80% of the shifts on this beamline were allocated to Italian user groups.

For the CRG's part of the beam time the factor for the requested to available shifts is about 1.5 to 2. The oversubscription ratio is significantly higher for the public (ESRF) beam time.

### Highlights

There were several impressive highlights covering a wide field of applications and a wide energy range. They include the studies of Er-doped Si nanoclusters, a promising light emitting material in Si-based optoelectronics (Phys. Rev. 2006), and of In-dopants in pure or C-doped Si (Appl. Phys. Lett. 2006). The aggregation of Fe in a GaN-matrix elucidates the ferromagnetic features of magnetically doped semiconductors (PRL 2008). The structure of the Fe/NiO(001) interface with increased spin magnetic moment of the Fe atoms have been characterised (PRL 2006). Depth-selective REBEXAFS measurements, combined with theoretical DFT studies, were used to study the penetration of As atoms into Si surfaces (J. Appl. Phys. 2007). The peculiar phase transitions of Ga in nanodroplets and thin films were studied with XAFS fluorescence (JACS 2007). Sub-nanometric metallic Au particles that sensitise Er photoluminescence (Appl. Phys. Lett., 2006) were investigated, as also the cause of the negative thermal contraction for Au particles (Phys. Rev. B 2008) and in CuCl (Phys. Rev. B 2007). The redox behaviour of Pt nanoparticles on ceria-zirconia support, a three way catalyst, has been studied (J. Phys. Chem B, 3006), as also a catalytic process to split methane and water to produce hydrogen (J. Appl. Cryst. 2005). An archaeometric application revealed the reaction causing blackening of the copper pigment azurite in a XV century painting (Appl. Phys. 2008).

### Technical aspects of instrumentation

The beamline constitutes an excellent facility for XAS studies, particularly for dilute systems, including the capability of grazing angle geometry. A new cell has been developed to allow *in situ* studies of gas-solid chemical reactions. Feasibility studies of a superconducting Transition Edge Sensor, widely used in astronomy with a very high energy resolution, have been performed.

At present some refurbishment is taking place regarding the beamline stepper motors and vacuum control system. Standard ESRF software and instrumentation for vacuum control is being installed.

However, after about 15 years of operation the bulk of the instrumentation has overcome its reasonable operating lifetime. A major refurbishment is necessary to continue reliable operation for the next 5 years and beyond. Especially the optical components, the

The scientific quality of the staff is of a high standard. The support provided to the user groups is professional and friendly, and staff members play important scientific roles in most projects. However, the two scientists that constitute the current staff are not sufficient for running the beamline in the most efficient manner. The permanent staffing level should be increased to include three beamline scientists. A technician is urgently needed. After those additions to the staff, the panel then further recommends an appointment of at least one PhD student and/or post doc. The beamline has a proven record of being an excellent training ground for PhD students and young scientists.

#### **Staff**

With projected technical refurbishments this beamline will not only maintain but also significantly improve its status for the foreseeable future (next 5 years and beyond). The panel recognises that the multi-purpose beamline GILDA plays an essential role for a large user community. It provides valuable and much needed general spectroscopy and diffraction capabilities with access to high-energy spectroscopy. The continuation of this provision, which is only readily accessible at the ESRF, has to be ensured.

#### **Future scientific directions**

A new multi-element fluorescence detector to replace the present 10 year old system still in use will increase the capability of the beamline to study diluted systems. This is particularly important for example in the areas of materials, biological and surface science, chemistry and environmental science. The panel also recommends an enhancement of the XRD capabilities of the beamline by the provision of a complementary X-ray fluorescence detector that will give the opportunity of measuring diffraction and absorption at the same time.

Plans for beamline monochromator and the mirrors, need replacement in the near future. Plans for beamline refurbishment with design criteria particularly adapted to total reflection/glaning angle mode as well as to conventional high quality EXAFS measurements, were presented by the beamline staff. Those plans take advantage of the Upgrade Plan of the ESRF that will provide an increase in the high brilliance of the source as well as increased stability.



**5.2. Appendix 2: Proposals of experiment at the refurbished beamline.**

5.2.1. *Environmental science.*

## **Environmental geochemistry of "heavy metals": molecular scale mechanisms**

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### **Introduction**

This proposal belongs to the broad context of “environmental sciences”, a wide umbrella covering an extreme variety of topics straddling the borders of life and Earth sciences, physics, and chemistry. Environmental studies are thus by their own nature truly interdisciplinary. The phenomena considered typically depend on a very large number of often vaguely defined parameters, where non linear or even chaotic effects may dominate. For these reasons, especially in the earliest stages, many environmental studies have been of mostly empirical, descriptive nature. However, in the last decades there have been consistent attempts to unravel and understand down to the molecular scale the fundamental mechanisms that control and influence the evolution of specific environmental systems. These efforts led to the development of what is currently known as molecular environmental science (MES; e.g., Brown et al., 1999). Synchrotron-based techniques have played a key role in the development of MES, so that in the last twenty years there was a booming increase of environmental studies making use of synchrotron radiation (e.g., Brown & Sturchio, 2002; Bluhm et al., 2006).

### **Scientific content**

The project addresses a necessarily limited, but quite important, topic of the very wide field of environmental studies, namely the geochemical cycling of “heavy metals”. “Heavy metals” is used here as a descriptive term to encompass ecotoxic elements, most of which are true heavy metals such as Pb, Cd, Hg, Zn, Cu and Cr, whereas others, such as As and Se, are not metals, but share a similar environmental behaviour. These elements are among the most dangerous inorganic pollutants, and are therefore extensively studied. In this sense, the project can be safely considered of national relevance, and in line with cutting edge international studies. While mostly centered on Earth sciences, the topic is nonetheless truly interdisciplinary, involving biologists, chemists, and physicists.

Some fundamental aspects that must be understood in the cycle are the following: in what conditions, to what extent, and by what processes are metals released from the sources; in what form are metals transported, or else what are the processes that reduce their mobility; how are metals transferred to the biosphere, and in what conditions are they most dangerous. Understanding these aspects in a number of specific context is the goal of the project. Examples, by no means exhaustive, of the problems addressed are the following:

1. Distribution and chemical state (“speciation”) of heavy metals in the sources, with special attention to factors affecting a) mobility (e.g., binding to a specific phase), b) toxicity. With respect to synchrotron-based techniques, this task may involve 1) high resolution quantitative determination of mineral assemblages by X-ray diffraction, 2) determination of the valence state from XANES spectra, 3) definition of the local atomic environment by EXAFS. As an example of this kind of studies, we mention the problem of Cr speciation and mobility in soils. Chromium is a typical case of an element for which toxicity is strictly linked to the oxidation state, hexavalent chromium being far more toxic than trivalent chromium. The two valence states can be easily discriminated by XANES (e.g., Howe et al., 2003). Hexavalent chromium is also much more mobile. Trivalent chromium is considered as the thermodynamically stable form in soils; however, it has been suggested that complexing with humic substances might stabilize the hexavalent form, thus enhancing mobility from contaminated soils to water bodies. Therefore, the study of Cr - organic

matter complexes in soils should greatly contribute to elucidate the impact of this element on the soil – water ecosystem, with implications for human health.

2. Mechanisms of release of metals from the sources, e.g. mineral sulphides; this involves performing dynamic *in situ* studies of natural samples and synthetic equivalents, such as time resolved X-ray diffraction and/or absorption spectroscopy on reacting materials; a basic requirement is therefore the availability of a suitable reaction cell, where environmental parameters such as temperature and/or reactant species concentration can be controlled. An important aspect of these phenomena are surface reactions; monitoring of such reactions may be accomplished through techniques such as REFLEXAFS.
3. Controls on the mobility of toxic elements by adsorption/precipitation reactions. Also this task includes both studies on natural materials, and experiments on synthetic phases. Examples of the investigated systems include a) adsorption of heavy metals onto smectites and zeolites, b) incorporation (adsorption vs. precipitation) of heavy metals in mine waste supergene minerals such as iron oxyhydroxides and hydrozincite, c) incorporation of arsenic in the calcite lattice. Here again the main technique is X-ray absorption spectroscopy, possibly with *in situ* dynamic measurements, complemented by X-ray diffraction.
4. Influence of trace elements on the environmental behaviour of some materials (e.g., enhancement of reactivity/toxicity by surface species). Along this line there is an ongoing study on the health effects of crystalline silica. The carcinogenic action of this substance is believed to be mediated through radical species formed and/or modified at the mineral surface. On the other hand, the carcinogenic activity was also related to the presence, crystal chemistry and bioavailability of Fe-species at the surface of quartz. The study is conducted by XAS and REFLEXAFS, complemented by EPR and AFM, on reference materials and industrial samples.

#### **Previous experiences and connections with GILDA**

All proposers have a demonstrable experience of internationally recognized research on environmental mineralogy and geochemistry. Many of them also have an established record of synchrotron-based studies, both a GILDA, at other ESRF beamlines, and other facilities. A very partial list of recent references includes the papers by Di Benedetto et al. (2010), Lattanzi et al. (2010), Malferrari et al. (2008), and Marcelli et al. (2006). With specific reference to GILDA, several successful experiments were carried out, and a very fruitful cooperation with the beamline staff was established (see the GILDA report 2004-2008 to the ESRF review panel). Important aspects that made possible this achievement include: 1) the high quality of the beam; 2) the availability of specific facilities, such as a proficient reaction cell, and the image plate detector, which proved particularly useful for time-resolved studies. With the proposed upgrade of the beamline, this successful record can be even improved. Specific strong points are 1) the expected improvement of beam stability, and therefore of the signal-to-noise ratio, is critical for experiments where the absorber is usually in low concentrations; 2) the expected improvement of the spatial resolution is highly beneficial for typically complex, heterogeneous matrices of environmental samples; 3) the expected overall improvement of REFLEXAFS capabilities should open new possibilities for surface studies of oxidation and/or dissolution and/or adsorption phenomena; 4) many of our studies require the application of both X-ray diffraction and X-ray absorption: with the beamline upgrade, it should be possible to carry out both XRD and XAS in the same experiment, with obvious advantages of time and cost saves. With respect to peculiarities and/or interactions with other ESRF beamlines, we emphasize the following: 1) GILDA will remain one of the few ESRF lines offering the capability of high quality XAS experiments, that are crucial for the project; 2) the results obtained at GILDA could be usefully complemented by microbeam (X-ray microscopy, microdiffraction, micro-XRF) techniques available at other lines.

### **Expected results**

The results expected from the project will represent significant contributions to our understanding of the environmental geochemical cycles of “heavy metals”. Specifically, we expect progresses in 1) rates of oxidation and heavy metal release from mineral sulphides, 2) distribution and speciation of heavy metals in complex environmental matrices such as soils and particulate, 3) ability of specific phases to slow down the mobility of heavy metals, 4) influence of specific species on the toxicity of materials. These results are in line with state of the art international research on heavy metals in the environment, and may have important implications for prediction, prevention and remediation of heavy metal contamination.

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5.2.2. *Magnetic materials.*

### **Atomic structure of SiGe dots Mn-doped grown on Si(001)**

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Diluted magnetic semiconductor (DMS) [1,2] with high carrier spin-polarization can be synthesized by molecular beam epitaxy (MBE) in semiconductor layer structures, exhibiting a very rich magnetic behavior as a function of the chemical composition [3]. Understanding and controlling the spin interactions as well as the roles of defects, dimensionality, and semiconductor host are key elements to develop efficient spin-based electronic devices. Different theoretical models, based on the double exchange model and Zener's p-d exchange interaction, have been proposed to explain ferromagnetic (FM) coupling among 3d-impurities in semiconducting hosts [3-5]. All present theories, however, do not correctly account for the observed magnetization, which is lower than what is expected from the estimate of the local impurity moments. Several evidences suggest that the magnetic properties of DMS are often significantly influenced by the presence of 3d-impurities in non-substitutional sites, as metal clusters, interstitial and antisite defects, which cannot be sufficiently controlled or suppressed in the growth process.

Magnetic Mn-Ge systems have recently attracted much attention due to the possibility to elaborate DMSs with high Curie temperature ( $T_C$ ) [2], and to integrate them on Si devices. However, the question whether the ferromagnetism of Mn-doped systems comes from DMSs or from magnetic precipitates [6,7] is still under intense debate. It is interesting to note that Mn and Ge atoms form several stable precipitates [6-12] as a function of temperature. Those precipitates can contribute to the magnetic properties. The

most stable precipitate is  $Mn_5Ge_3$  alloy with  $T_C > RT$  in the bulk phase [13].  $Mn_5Ge_3$  film grows epitaxially on Ge(111) [14] whereas formation of  $Mn_5Ge_3$  precipitates takes place [11,12] on the Ge(001) if the substrate temperature ( $T_S$ ) is high enough.

Recently, our group discovered ferromagnetism properties on SiGe dots Mn-doped epitaxially grown on S(001). We measured magnetic properties by means of superconducting quantum interface device (SQUID) and x-ray magnetic dichroism (XMCD) at the Mn  $L_{2,3}$  absorption edge measurements. A  $T_C$  of about 230 K was found for this system. It seems that this new ferromagnetic material is free of precipitates as very well attested by energy dispersive X-ray diffraction (EDXD) and rocking curve analysis. These results open the way to the study of Mn-doped SiGe diluted magnetic semiconductor, whose magnetic properties are not influenced by the presence of secondary precipitate phases.

A fundamental step to optimize the magnetic semiconductor properties is the understanding of the interrelationship between the deposition process and the resulting crystalline structure. So, the study of the sample structure is of crucial importance. The use of the extended x-ray absorption fine structure (EXAFS) technique will allow us to correlate the structural properties of the samples to their magnetic characteristics.

In this project we propose a study of structural properties of  $Mn_x$ -doped  $[Si_{0.5}Ge_{0.5}]_{1-x}$  dots with  $x=0.02\pm 0.1$ , grown by MBE on Si(001)2x1 substrate. The samples will be grown *ex-situ* for high Mn x concentration and high sample thickness and *in-situ* for very low Mn x concentration and thin films. The samples prepared *ex-situ* will be capped with amorphous Si, whereas the sample grown *in-situ* will be prepared in an UHV chamber directly connected to GILDA beam line. At this respect, we need a UHV chamber equipped by evaporation sources (supplied by our own), quartz microbalance, LEED system and transfer system (from preparation to measurement chamber). This will

allow investigate for the first time the initial stage of atomic structure formation of DMS free of magnetic precipitates.

The scientist team, which proposes the present project, has gained experience with core levels and ARUPS photoemission spectroscopy, absorption spectroscopy, x-ray absorption magnetic circular dichroism (all using synchrotron radiation), LEED, RHEED, MOKE, AUGER, STM, SEM, EXAFS, SEXAFS applied on several systems (III-V (GaP, InAs, InSb), IV(Si, Ge, Metal/(III-V); Metal/(IV) interface).

As far as the scientific international collaborations on DMS systems are concerned, our group has been working for a long period of time with Laboratoire de Physique des Métaux et des Surfaces, Université de Cergy-Pontoise, Neuville-sur-Oise, 95031 Cergy-Pontoise, France and Laboratoire de Chimie Physique Matière et Rayonnement (UMR 7614), Université Pierre et Marie Curie / CNRS, 11 rue P. et M. Curie, 75005 Paris, France.

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## **Magnetic impurities in semiconductors: linking the local structure to magnetic and optical properties**

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### **Description**

Recently the research in semiconductor spintronics [1] has been focused, on one side, to prove that room temperature ferromagnetism in magnetically doped semiconductors is achievable and, on the other side, in fabricating self-organized ferromagnetic nanocomposites embedded in the semiconductor host matrix with still widely unexplored but remarkable functionalities relevant to nanoelectronics, photonics, and plasmonics. The good candidates for these tasks are two materials classes, respectively, the dilute magnetic semiconductors (DMSs), where a few percent of the cations are randomly substituted by magnetic elements as transition metals (TMs), and the condensed magnetic semiconductors (CMSs), where the presence of robust ferromagnetism correlates with the existence of nanoscale regions containing a large density of magnetic cations. In order to contribute to this emerging research field, we aim in this project to study DMSs and CMSs based on the wide gap semiconductors GaN and ZnO doped with transition metals (TMs), since a strong coupling between magnetic ions and holes is present due to their small lattice constant. In fact, the crystal field models [3] traditionally predict a linear increment of the ferromagnetic transition temperature ( $T_C$ ) with TMs concentration ( $x$ ) and hole density ( $p$ ) but for materials showing strong coupling, where the impurity levels in the gap produces a deep potential that traps holes and shifts the metal-to-insulator transition (MIT) to higher  $p$  values, to obtain higher  $T_C$  a new theoretical approach was proposed [5] as summarized in Fig. 1: by increasing the hole concentration, it may become possible to screen the TMs potential and generate a MIT, restoring in this way the conditions for high  $T_C$  ferromagnetism. This is certainly an appealing perspective that we plan to verify experimentally in Mn-doped GaN grown by metalorganic vapor phase epitaxy (MOVPE).

A parallel branch of this project is dedicated to the MOVPE (Ga,Fe)N material system where we reconstruct the phase diagram of the  $\text{Fe}_x\text{N}$  nanocrystals buried in GaN as a function of the growth temperature. Advanced characterizations as synchrotron radiation x-ray diffraction (SXRD), extended fine structure x-ray absorption (EXAFS) and x-ray absorption near-edge fine structure (XANES), combined with high-resolution transmission electron microscopy (HRTEM) and superconducting quantum interference device (SQUID) magnetometry allow us to detect and to identify particular  $\text{Fe}_x\text{N}$  phases in sam-

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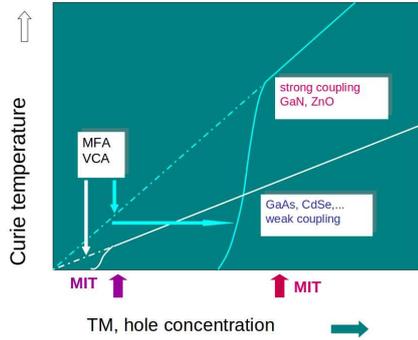


Figure 1: Schematic dependence of the Curie temperature  $T_C$  on the concentration of magnetic impurities and density of hole states at the Fermi level for a weak and a strong coupling. [5]

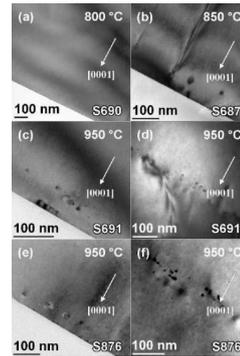


Figure 2: HRTEM images showing the distribution of the Fe-rich nanocrystals with increasing growth temperature. (a) dilute (Ga,Fe)N; (b) Fe-rich nanocrystals concentrated in proximity of the samples interface solely and shifting to the interface between the GaN buffer and the Fe-doped layer (c), (d), (e), (f).

ples fabricated at different growth temperatures (Fig. 2) as well as to establish a correlation between the existence of the specific phases and the magnetic response of the system.

Finally, the TMs-doped ZnO grown by atomic layer deposition (ALD) will be the additional workbench to apply this methodology and getting new insights into the controversial debate of  $p$ -type doping [10] and precipitates-free ZnO [11].

A challenging point will be that of detecting by XAS the details of the electronic structure of Mn:GaN and in particular the occurrence of a hole bound to the magnetic site. Similar descriptions via XAS have been already presented in the case of ligand holes bound to Ni in  $La_{1-x}Nd_xNiO_3$  using *ad-hoc* assumptions [7]. Recent advances in the theoretical calculations of electronic structures based on Density Functional Theory [12, 14] will permit the study also on a total *ab initio* basis as demonstrated on the calculations on bound holes in  $Li_xNi_{1-x}O$  [8]. The theoretical investigations will be performed by using beyond-DFT methods, e.g., LSD+U and Heyd-Scuseria-Ernzerhof hybrid functional, as implemented in the Quantum-Espresso [6] and VASP [9] computational codes. Such investigations will regard the structural and electronic properties of TM-doped GaN and ZnO as well as the magnetic properties of isolated TMs, their interaction with holes and the carrier-mediated magnetic coupling between TM pairs. A recently proposed DFT scheme for calculating X-ray absorption spectra [8] will be also used for a comparison with experimental findings. The attention will be focused on the GaMnN, GaFeN and ZnO-based DMSs.

### Novelty points

**Fermi-level tuning.** Following theoretical suggestions, [4] it has recently been demonstrated experimentally that it is possible to change the charge state of TMs ions in a

semiconducting matrix and, therefore, the aggregation energy by co-doping with shallow donors or acceptors. [2] In particular, it has been proven that in the model case of wurtzite (wz) (Ga,Fe)N fabricated by MOVPE the Fermi-level tuning by co-doping with Mg (acceptor in GaN) or Si (donor in GaN) is instrumental in controlling the magnetic ions aggregation. [2].

**Carrier-mediated ferromagnetism.** We will focus on the optimization of superlattices (SLs) of *p*-AlGa<sub>x</sub>N/GaN structures to be put into contact with (Ga,Mn)N thin layers. Al-GaN/GaN:Mg/(Ga,Mn)N SLs are expected to promote, via modulation-doping and interfacial polarization fields, the local accumulation of holes in (Ga,Mn)N, eventually generating an interfacial 2D hole gas (2DHG) that should trigger the onset of a carrier mediated mechanism. On the side of theory, the relationships between the extent of hole localization and the magnetic coupling between TM atoms will be carefully investigated. As an example, the magnetic properties of Mn in GaAs and the related simulated X-ray absorption spectra will be compared with the corresponding properties and spectra for Mn in GaN. A further comparison will be performed between Mn in GaN and Fe in GaN. Due to the similarity with GaN, these novelty points will be extended to ZnO too.

**Expected results** Our key objective is to demonstrate - by exploiting the most recent discoveries in the field - the presence of hole-mediated ferromagnetism in dilute magnetic nitrides and oxides, particularly (Ga,Mn)N and (Zn,Co)O - and to provide the corresponding phase diagram of the Curie temperature  $T_C(x,p)$ . More specifically, state-of-the-art device design and nanocharacterization tools as the HRTEM routinely conducted to cross-check the structural data, will serve to fabricate and to control the properties of Mn- and Mg-doped heterostructures and superlattices, in which modulation doping and interfacial electrostatic polarization will allow to overcome the hindrances behind the failure of previous experiments, as e.g. magnetic ion aggregation and hole localization by strong *p-d* interaction.

**Experimental aspects and technical challenges** We have already exploited successfully the EXAFS and XANES analysis of (Ga,Fe)N [13]. In that context we have been able to gain insight into the crystal environment of Fe-doped GaN and, through a comparison with *ab initio* density functional theory (DFT) models, to identify the correlation shells related to the Fe ions and thus to reconstruct the surroundings of the TM, also in the case of aggregation. In the frame of this project, we intend to apply the acquired expertise to the investigation of the (Ga,Mn)N structures determining the valence state of Mn and its local structure. These parameters will be compared with DFT calculations to understand the XAS data. For this project we need to use state of the art of the technique in order to obtain good quality data also from single phase (Ga,Mn)N layers. Thus it will be mandatory to have a beam-line providing an intense flux with a high energy resolution and stability in order to exploit at maximum the information from the XANES part. Moreover we will need an experimental setup optimized for analysis on thin films. This will be achieved by having available surface-dedicated data collection techniques like Refl- or Glancing Angle EXAFS. Dealing with non-cubic matrices we need also to exploit the linear dichroism of these samples for a deeper characterization of the local structure around TMs. For this, it is requested that the glancing angle techniques will be applicable also in different orientations of the sample (i.e. surface parallel and perpendicular to the beam polarization

vector). Also the availability of an efficient fluorescence detector will be mandatory due to the noticeable dilution of these samples (about  $14^{14}$ - $10^{15}$  Mn/cm<sup>2</sup>).

**Synergies with other beam-lines** These samples will be also analyzed by SXRD on other beam-lines at ESRF (e.g. ID31, BM20, ID01). In the past this synergy revealed to be of paramount importance for a comprehensive understanding of the experimental results [2]. For EXAFS data collection only the GILDA beam-line at present can fulfill the several requests (intense beam, grazing incidence detection, efficient detector) posed by this class of experiments.

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## Characterization of nanostructured magnetic materials at GILDA beamline

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Presently, magnetic properties of thin films and nanostructures are central to data storage, sensor and device technologies and are increasingly being used in life sciences and medicine. This is because of the novel physical phenomena which appear when a magnetic system is reduced to dimensions comparable to or smaller than specific length scales characterizing the physical properties (size effect). Moreover, the presence of a huge number of surface and interface atoms strongly affects the magnetic behaviour of such materials.

For these systems, the X-ray absorption spectroscopy (XAS) is very important for understanding details of the atomic and electronic structure and thus for correlating these properties to the magnetic behaviour.

In particular, the facilities available at GILDA beamline are very useful for the characterization of three different magnetic systems fabricated in our Institute:

- 1) antiferromagnet/ferromagnet bilayers where interface characterization is needed (Exchange Bias systems)
- 2) Fe-based nanocrystals for studying the thermal induced structural evolution
- 3) ferrite nanocrystals for the investigation of the inversion degree

1) The Exchange Bias (EB) phenomenon [1] observed in systems, where a unidirectional anisotropy appears due to the exchange coupling at the interface between a ferromagnetic (FM) and an antiferromagnetic (AFM) material with a higher anisotropy, is widespread in current technological applications (spin-valve systems, GMR read heads, tunnelling devices, etc). Despite of this, a full comprehension and a universally accepted theoretical description of the phenomenon is still missing, due to the complexity of the interface microstructure responsible for the exchange coupling. Indeed, different factors affect the interface coupling, e.g. the interface roughness, the thickness of both FM and AFM phases, the interface stress, etc. [2, 3]. For these reasons, to control the growth mechanism as well as to carefully characterize the interfacial region are of crucial importance in the study of such a complex phenomenon. We propose to study interface properties in exchange bias (EB) bilayer  $\text{Co}_{50}\text{M}_{50}/\text{NiO}$  ( $\text{M} = \text{Pt, Fe}$ ) systems using X-ray Absorption Spectroscopy (XAS). The study will be carried out with the aim of describing the local environment around the Co, Pt and Fe metals as a function of the  $\text{Co}_{50}\text{M}_{50}$  layer thickness and thus to obtain a detailed description of the interface. The expected results will be used to interpret the interface exchange coupling between a ferromagnetic (FM: fcc-CoPt, CoFe) and antiferromagnetic (AFM: NiO) material, which is the underlying mechanism in the exchange bias phenomenon.

2) Chemically ordered  $\text{L1}_0$  phase alloys such as FePt or CoPt have gained a lot of interest in ultrahigh density magnetic recording media and permanent-magnet nanocomposites because of their large uniaxial magnetocrystalline anisotropy ( $K_u \approx 7 \times 10^6 \text{ J/m}^3$ ) [4]. Generally, FePt nanoparticles are obtained in the chemically disordered face-centered cubic (fcc) phase and a postgrowth annealing treatment at about 600 °C is necessary to induce the transition to the chemically ordered face-centered tetragonal (fct) phase ( $\text{L1}_0$ ). The high annealing

temperature, however, causes coalescence phenomena with the consequent increase of the particle size, size dispersion, and reduction of the magnetic anisotropy.

Recently, we have reported a new chemical strategy for the direct synthesis of FePt alloy nanoparticles starting from a polycrystalline molecular compound, the iron (II) chloroplatinate hexahydrate ( $\text{FePtCl}_6 \cdot 6\text{H}_2\text{O}$ ), in which Fe and Pt atoms are arranged in alternating planes like in the fct FePt structure [5]. The reduction of such compound by 5%  $\text{H}_2$  and 95% Ar at 400 °C leads directly to a highly ordered  $\text{L1}_0$  phase. The low temperature requested to obtain this phase without any evidence of fcc-fct phase transition can be related to the ordered arrangement of the metal ions in the alternating atomic planes present in the  $\text{FePtCl}_6 \cdot 6\text{H}_2\text{O}$  crystals. The heating process of the  $\text{FePtCl}_6 \cdot 6\text{H}_2\text{O}$  powder under reductive atmosphere, was monitored by a thermogravimetric and differential thermal analysis (TGA-DTA) but it was not possible to isolate and characterize each single step, being such processes partially overlapping. For this reason, the simultaneous in-situ acquisition of the XRD and EXAFS spectra during the annealing could be essential to reveal the atomic and structural evolution of the system in the transformation from the  $\text{FePtCl}_6 \cdot 6\text{H}_2\text{O}$  salt to the FePt  $\text{L1}_0$  alloy. This experiment will be possible at GILDA, where an ultra high vacuum chamber fully equipped for sample characterization is available.

3) Among nanoscale magnetic materials, nanoparticles of spinel ferrites are of great interest, not only because of their technological applications but also from the point of view of fundamental science [6]. In fact, they are good model systems for studying the relationship between magnetic behaviour and magnetic structure at atomic level [7]. In addition, the peculiar structural properties and the rich crystal chemistry of spinels offer excellent opportunities for understanding and fine tuning the magnetic properties of the system [8]. Among them, the ferrite spinel structure ( $\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$ ;  $\text{M} = \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$ ) is based on a closed-packed oxygen lattice, in which tetrahedral (called *A* sites) and octahedral (called *B* sites) interstices are occupied by the cations. In general, the cationic distribution in octahedral and tetrahedral sites may be quantified by the inversion degree, which is defined as the fraction of divalent ions in the octahedral sites. It has been observed that, actually, the magnetic properties of  $\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$  are strongly dependent on the distribution of the iron and cobalt ions in the *A* and *B* sites. It can be demonstrated that even small changes in the cationic distribution can result in substantial changes of magnetic moments and of the magnetic anisotropy [9].

As an example, in a recent paper [10], the magnetic properties of cobalt ferrite-silica nanocomposites ( $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ ) with different concentrations and sizes of  $\text{CoFe}_2\text{O}_4$  particles have been studied by static magnetization measurements and Mössbauer spectroscopy. Surprisingly, the results showed that the anisotropy constant (*K*) increases with decreasing particle size: it was found that the *K* value are smaller than the bulk value, and this can be explained by a cationic distribution, which differs considerably from what is usually observed in bulk cobalt ferrite.

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) have been shown to be powerful tools for the structural study of these kind of metal oxides, because of their element-specificity and sensitivity to the local structure. In particular EXAFS gives information about bond distances and coordination numbers of shells surrounding the absorbing atom and it has been recently found to be a useful tool to determine the cation distribution in ferrite spinels. For this reason we propose the systematic study of inversion degree in particles of several spinel ferrites ( $\gamma\text{-Fe}_2\text{O}_3$ ;  $\text{Fe}_3\text{O}_4$ ;  $\text{CoFe}_2\text{O}_4$ ;  $\text{MnFe}_2\text{O}_4$ ) prepared by chemical methods.

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5.2.3. *Biophysics.*

## Mitochondrial metallo-proteomics

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### Introduction

Transition metal ions are required for many aspects of mitochondrial physiology. Copper, iron, manganese and zinc are cofactors in metalloenzymes and metalloproteins within the organelle. Little is known on how cells maintain optimal pools of these metal ions for mitochondrial function. It is however known that metals constitute a large part of mitochondrial content. Mitochondria appears indeed to have at least two pools of iron. One pool is bioavailable and is capable of competing with Mn(II) pool for the metallation of superoxide dismutase Sod2. The second iron pool is less bioavailable, and preliminary evidence suggests that iron is predominantly insoluble Fe(III)<sup>1</sup>. Factors controlling the distribution of iron into these two pools are unknown, but one factor may be the presence of ligands that stabilize Fe(II) levels. The identity of such Fe(II) ligands is not known. Zn(II) pools within the matrix are also uncharacterized, but this pool must be significant as numerous Zn-binding metalloenzymes exist within this organelle. A mitochondrial Zn(II) pool was reported in neurons that can be pharmacologically mobilized during neuronal injury observed in cerebral ischemia <sup>2</sup>.

It is not known how much of the total Cu content of the cell ( $5 \cdot 10^5$  Cu atoms, Cu concentration  $\sim 0.2$  mM)<sup>3</sup> is contained in mitochondria. Mitochondria contain a pool of copper that is distinct from that associated with cytochrome C oxidase (CcO) and Cu,Zn superoxide dismutase (Sod1). A small fraction of mitochondrial copper is associated with these cuproproteins. It appears that the bulk of the remainder is localized within the matrix as a soluble, low molecular weight, ligand complex (CuL)<sup>3</sup>. The CuL complex is conserved in the mitochondria of yeast and mouse cells. In yeast and mouse liver 85 and 70% of the total mitochondrial copper is associated with this matrix CuL complex. Although the identity of the ligand remains unresolved, the matrix CuL pool is accessible to a heterologous cuproenzyme<sup>3</sup>. The CuL pool appears to be used in the metallation of CcO and Sod1 within the IMS. These metal pools are not free in the mitochondria being indeed a large part of the mitochondrial proteome involved in metal trafficking. The pathways of metal ion insertion into mitochondrial metalloproteins during the folding reaction are indeed a topic of intense study. The investigation of the content and alteration of metal pools in mitochondria is therefore an important issue for the understanding of the metalloproteomic data.

The human mitochondrial genome consists of 16,569 base pairs (bp) in length and encodes for only 13 subunits of proteins of the mitochondrial respiratory chain<sup>4</sup>. However, mitochondria contain more than 1000 different proteins, many of them interacting with metal ions<sup>4</sup>. Since the mitochondrial genome encodes a very small subset of the organellar proteome, the majority of mitochondrial proteins are therefore nuclear-encoded and targeted to the organelle. Furthermore, approximately half of mitochondrial proteins are translated on ribosomes associated with the outer membrane (OM) of the mitochondrion through cis-acting signals in the transcripts<sup>5</sup>. Protein import into the mitochondrion occurs in both co-translational and post-translational processes<sup>6,7</sup>.

### **Novelty aspects of the project**

Among the mitochondrial proteins, many are involved in metal trafficking and mobilization from putative metal storage sites to the target metallo-proteins and enzymes. At present, the structure of only a bunch of these is known<sup>4</sup> and even less is known about their function and about the complex pattern of interactions among these proteins that leads to the shuttling of the proper metal ion to the target protein. The pathways of metal ion insertion into mitochondrial metallo-proteins are indeed a topic of paramount relevance due to the essential role played by metallo-enzymes in the mitochondrial respiratory chain. The study of these pathways is also relevant to the understanding, at the molecular level, of diseases related to failures in the proper control of metal-loading of the proteins involved in the respiratory chain<sup>8-13</sup>.

### **Aims of the project, experimental methods and experience of the group**

Under the present proposal we want to address the structural study of mitochondrial proteins able to selectively bind different metal ions like Fe, Mn, Cu and Zn. The study will be undertaken by scientists belonging to the CIRMMP interuniversity consortium that is dedicated to the study of metallo-protein structure-function relationships.

The proteins will be investigated by coupling NMR structure determination and XAS spectroscopy. This approach for the completed structure determination of metallo-protein in solution has been pioneered by our group<sup>14,15</sup> and has been extremely successful<sup>16-20</sup>. However, XAS spectroscopy might also be coupled to X-ray diffraction measurements on protein crystals in order to achieve higher accuracy or by exploring the native metal in solution, in cases when that metal ion cannot be used for crystallization.

The goal of the present investigation is not only to determine the solution structure of the largest possible number of mitochondrial metallo-proteins, but also to identify the metal coordination changes involved in the interaction with partner proteins, in order to establish the pathways of metal transports within mitochondria.

A development of the present proposal can be undertaken in collaboration with other ESRF beamlines, like ID22, where in situ  $\mu$ -XANES can be performed. To this purpose we have isolated whole mitochondria from yeast cells (*S. cerevisiae*) free from endoplasmic reticulum/Golgi and cytosolic metallo-protein contamination and we have established a protocol to obtain the mitochondrial matrix free of the outer membrane and of the intermembrane space obtaining mitoplasts delimited by the only inner membrane. By adjusting the osmotic pressure of the medium it is possible to swell the volume of the mitoplast and the diameter of the organelle can reach about 2  $\mu$ m.

$\mu$ -XANES measurements can be performed on isolated mitochondria and mitoplasts at the Fe, Mn, Cu and Zn K-edges, to be compared to those of purified metallo-proteins, in order to obtain information on the identification and localization of these proteins within the organelle.

### **Technical aspects**

Metallo-protein solutions are intrinsically diluted and contain metal ions at millimolar concentration or, more often, below this level. Furthermore, in order to follow the protein-protein interaction by monitoring the metal ion coordination sphere changes, high accuracy in the determination of the EXAFS parameters is needed. This means to be able to measure over longer k-ranges, extending above 12-13  $\text{\AA}^{-1}$ . To achieve this, large, state-of-the art, energy discriminating detectors are needed, coupled to the possibility to measure data at very low temperature (10-20 K) in order to reduce the radiation damage on the sample.

Ideally, the project will also benefit from the possibility to measure samples containing ultra-low absorber concentration (500-100  $\mu$ M range), to achieve high reliability and easy operation and possibly automation of data collection.

When dealing with diluted samples, contamination from exogenous metals either from construction materials (cryostat, detectors) or by contamination from previously measured samples becomes a relevant problem, especially for ubiquitous metals like Fe, Cu, and Zn.

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5.2.4. *Earth Science.*

**BEHAVIOR OF MINOR TO TRACE ELEMENTS IN SILICATE  
GLASSES/MELTS  
AND RELATIONS WITH MELT CHEMICAL/PHYSICAL PROPERTIES**

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**ABSTRACT**

The aim of this project is

(1) to determine the structural role of dilute to trace elements (i.e., V, Zn, Cr, Cu and lanthanides) in synthetic silicate glasses/melts of granitic and basaltic composition using X-ray Absorption Spectroscopy (XAS) and

(2) to measure the physico-chemical properties (i.e., density, viscosity, heat capacity, partition coefficients of minor elements between crystals and melts) of these glasses/melts. A combination of both studies will allow us to inspect the relationships between the physico-chemical properties of the investigated melts and their structure.

This project involves a close and complementary collaboration between the School of Sciences and Technology of the University of Camerino (I) (synthesis of the glasses, determination of their structure through spectroscopic measurements, data reductions and theoretical modelling) and the Dept. of Earth & Environmental Sciences of the University of Munich (D) (determination of the physico-chemical properties), as well as with the European Synchrotron Radiation Facility at Grenoble (F), (XAS spectroscopy).

**SCIENTIFIC BACKGROUND AND NOVELTY OF THE PROPOSED PROJECT**

Minor and trace elements in igneous petrology have a relevance in the petrogenetic modelling of magmatic differentiation that far outweighs their relative abundance. Optimal use of the information contained in trace element variations within igneous phases requires an accurate description of their partitioning behaviour as a function of phase composition and structure, as well as temperature and pressure. In this manner, the partial molar thermodynamic properties of minor and trace elements in silicate melts as well as the structure of trace elements-bearing silicate melts may contribute to the petrogenetic modelling of such systems. Furthermore, the physico-chemical properties as well as the glass-forming ability depend on how the system responds to the presence of the trace element cations, which in turn reflects in the structure of the resulting melt. With this in mind and since very few data on such silicate melts are available in the literature, a series of investigations into the partial molar properties of trace elements in silicate melts have been carried out in recent years (i.e., Courtial et al., 1999; Romano et al., 2000; Holzappel et al., 2001; Courtial and Dingwell, 2004; Potuzak et al., 2004; Courtial et al., 2004; Giuli et al., 2004) and need to be completed. In addition, the effect of the presence of trace elements in the structure of silicate glasses/melts has also been the subject of preliminary

investigations that need to be enlarged. This research project will lead to a close investigation of the relationships between physical-chemical properties and structure valid for trace elements-containing glasses/melts. These type of information is necessary for a better understanding of the parameters effecting the behavior of magmas and the partitioning of trace elements between melts and crystals in different types of rock compositions, from basalts to granites.

## **MILESTONES**

### **First year of the project**

This phase of the project will allow produce glass samples, with known chemical and physical properties. Standard materials will be chosen and characterized for XAS analysis.

First XAS measurements will be performed. The structural XAS analysis of the samples will be carried out. A high temperature furnace with controlled atmosphere will be designed and tested.

### **Second year of the project**

Modelling of the XANES/EXAFS spectra will be carried out and a structural model built. Additional glass compositions will be produced. XAS measurements will allow to investigate new compositions/elements. The experiments at high T and controlled atmosphere will be carried out.

### **Third year**

Correlation between chemical, physical and structural data on the glasses will be verified and used for extrapolation to natural systems. Natural glass samples will be analyzed. The structural model of the elements in the glasses will be compared with existing data on partition coefficients.

The role of the redox conditions will be investigated and correlated with the other data.

Results will be presented to conferences and published.

## **EXPECTED RESULTS**

The data obtained will be used to understand the relationships between the geochemical behavior of dilute and trace elements in melts and the associated physical and chemical properties. The use of a wide series of samples with different compositions will allow to extrapolate the results from glass analogue to the natural magma compositions. The results obtained on the study of dilute elements will be useful for understanding the behavior of melts and how these elements can affect viscosity. The results obtained on trace elements will be used to verify the behavior of elements in magmatic environments and investigate the partition between crystalline and melt phases. This information will be useful to explain the depletion or enrichment of some elements during magma generation and to give information on the magma origin. Also, all the structural study on transition elements of economic relevance (like V) are of extreme importance in understanding the origin of ore deposits.

## **IMPACT**

The detailed comprehension of the amorphous structure of silicate melts is of fundamental importance for understanding the connection between structural parameters and physical properties. Moreover, it is the prerequisite for quantitatively assessing the structural control on melt properties. Thus, making systematic studies on glass structure as a function of composition

and ambient conditions (P,T, Oxygen fugacity) is extremely important for the possibility to predict melt properties.

Also, it should be noted that the study of structure and properties of glasses is of extreme importance for the technological applications of this class of materials and it is not only confined to the geology-relevant topics.

## **EXPERIENCE OF THE RESEARCH GROUP IN THE FIELD**

Studies involving the synthesis and structural study of silicate glasses and melts representative of natural magmas have been carried out in collaboration with internationally well known research groups (from the University of Munich (D), Bayreuth (D), Toronto (CA), Bristol (UK), Orleans (F), Beijing (China)). The principal objectives of these studies were characterisation of glass structure (with focus on the role of minor to trace elements) as a function of composition, pressure, temperature, and oxygen fugacity. These studies implied synthesis of a large number of silicate glasses with a variety of methods (high-temperature furnaces, gas-mixing furnaces, piston cylinder) and their chemical and physical characterisation.

Accurate analysis by several spectroscopic techniques (mainly XAS) allowed complete characterisation of the structural environment of several transition elements (Ti, V, Cr, Fe, W, Nb) in a variety of synthetic and natural (e.g. Giuli et al., 2002, 2003, 2004, 2005, 2010a, 2010b; Cicconi et al., 2009) silicate glasses with different composition and synthesised at different T, P, fO<sub>2</sub> conditions. Some of the results obtained have already been published on international journals, while few others are still submitted or in press.

## **EXPERIMENTAL DETAILS**

### **1. Technical requirements**

The high energy resolution needed to obtain good XANES data for pre-edge peak analyses and for comparison with theoretical XANES spectra requires the use of a Si (311) monochromator. In view of the low flux obtainable with this monochromator (as compared with the Si (111) ) and of low-concentration of the proposed glass samples (from 0.1 wt% down to 10-100 ppm absorber concentration) it is mandatory to use a high sensitivity detector system like a multielement Ge detector. Moreover, the possibility to collect data at low temperature could further enhance the quality of the data collection for the most diluted samples.

### **2. Further developments**

The use of a high temperature device would allow the investigation of the geochemical role of these elements in the liquid, by melting the glass at the temperatures related to each composition (from 800°C to 1500°C). The investigation will require a furnace equipped with a controlled atmosphere device for studies at reducing as well as oxidizing conditions. The combination of these factors (dilute elements, high temperatures) will highly affect the results which will require the use of high sensitivity detectors and long experimental sessions. The development of a furnace with the control of the redox conditions as well as being used for this project, will be useful for studies in other fields like materials science and chemistry.

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5.2.5. *Cultural Heritage.*

## The Cultural Heritage group of Perugia at GILDA: past experiences and future perspectives

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### Aims of the project and scientific background

The flourishing in the last years of a large number of scientific studies exploiting synchrotron radiation in the field of cultural heritage demonstrates how advanced analytical methodologies are now accessible to scientists working in this field, and how they have become of primary importance to obtain deeper insights into artists' materials and execution techniques in works of art. In particular X-ray absorption spectroscopy (XAS) by synchrotron radiation offers unique analytical potentials for applications in science of conservation, owing to its non-invasiveness and to its capability of providing analytical information hardly achievable by other techniques. XAS is, in fact, a powerful tool to probe the local chemical environment of elements and their valence states, prescindendo of the crystalline or amorphous phase of the investigated materials. This approach is particularly worthy for materials of interest in cultural heritage since glassy and organic amorphous phases are very common matrixes where metal ions are embedded and for which conventional techniques for structural analysis (like X-ray diffraction) can not be applied.

On the base of the experience gained on the use of XAS for investigations in cultural heritage, here we discuss the research perspectives to be developed in this field at the GILDA beam-line of ESRF addressing a variety of issues emerging from our wide research activity spanning from pigments to glass, ceramic and painting materials. In consideration of that, the prospective of a long term experimental activity at GILDA is desirable to carry out XAS measurements aimed at (i) characterizing local structural properties of transition metal ions used as chromophore in crystalline pigments or dispersed in amorphous matrix and (ii) investigating degradation/discolouration processes of pigments.

### Expected results

We, recently, focused on the role of copper as blue and green chromophore agent in ancient glasses and ceramic glazes. The study started within a research project finalized to the investigation of original mosaic *tesserae* from the S. Marco Basilica in Venice. The origin of the different blue/green shades produced by copper ions in glass is determined by the interplay of the two possible tetragonal and square planar limit coordination geometries of copper in an octahedral field according to the Jahn Teller effect. Glass composition and thermal history strongly affect structure modifications and geometrical distortions of the Cu local environment. The structural information provided by XAS measurements are essential to establish the mechanism of formation of different coordination spheres of copper ions leading to changes of the glass chromatic properties in ancient and laboratory standard samples.

Recently, we also started to investigate a new class of pigments deriving from lead antimonate yellow ( $\text{Pb}_2\text{Sb}_2\text{O}_7$ ). Lead antimonate yellow is one of the oldest known synthetic pigments, as its production goes back to at least 3500 years ago. In Western European art, lead antimonate has been used since the 16<sup>th</sup> century as yellow enamel pigment in Italian majolica and later in paintings assuming the name *luteolum Napolitanum* (Naples yellow). Naples yellow is synthesized by roasting mixtures of Pb and Sb oxides; it has a cubic pyrochlore structure that, recently, several scientific studies addressing the characterization of pigments in 16<sup>th</sup>-19<sup>th</sup> century paintings and 16<sup>th</sup> century majolica have demonstrated to exist in a modified form based on a ternary mixture of lead, antimony and tin ( $\text{Pb}_2\text{Sb}_{2-x}\text{Sn}_x\text{O}_{7-x/2}$ ). More recently we have found a further modified form of Naples yellow containing zinc instead of tin that has been observed limitedly to a 16<sup>th</sup> century

Italian majolica conserved at the Victoria and Albert Museum of London. X-ray diffraction and Raman spectroscopy investigations of synthesized yellow pyroantimonates doped by adding Sn or Zn oxides [3] provided the evidence that ternary additional cations induce modifications of the pyrochlore lattice with respect to the  $\text{Pb}_2\text{Sb}_2\text{O}_7$  binary form of the pigment.

Aim of the XAS investigations is to deepen the understanding of the role played by Zn and Sn cations in modified Naples yellow and to demonstrate that doping ions enter the octahedral sites of the pyrochlore lattice replacing  $\text{Sb}^{5+}$  ions.

As far as the investigation of pigment degradation processes we identify few systems for which XAS arises as a particularly suitable analytical tool. Briefly we focused on copper arsenate pigments that, similarly to copper bearing system previously studied, show darkening phenomena that, up to date, have never been investigated. Discolouration of smalt, a potash glass containing  $\text{Co}^{2+}$  ions dispersed in the glassy matrix as chromophore agents, is another quite renowned alteration phenomenon not yet understood. Finally, we also intend to cope with the question of the blackening of cinnabar ( $\text{HgS}$ ) for which, in spite of different analytical studies dedicated to this subject, still definite conclusions on the nature of the alteration products and on the mechanism of their formation are lacking.

### Scientific expertise

Our approach to XAS goes back to its pioneering application to the study of *lustre*, one of the most relevant decorations of middle Age and Renaissance majolica in the Mediterranean basin. *Lustre* imparts to glazes of ceramics surprising metallic reflections and dichroic effects originating by the presence of a thin layer of a colloidal dispersion of silver and copper metal nanoparticles close to the glaze surface. The decoration was produced during a third firing of a previously glazed and decorated ceramic which was covered with a mixture of silver and/or copper salts and oxides. The system was fired at  $600^\circ\text{C}$  in a reductive atmosphere. In these conditions copper and silver ions penetrate into the glaze by ion-exchange with glaze alkali ions and form metal particles.

XAS investigations of original Iranian and Italian renaissance samples at GILDA provided us cluing information to elucidate *lustre* composition and mechanism of formation by a detailed characterization of Cu and Ag valence states and of their local environment [1]. Our results indicated that, case by case, silver and copper can be present both in the form of metal nanoparticles and/or oxidised phases:  $\text{Cu}_0$  and  $\text{Cu}^+$  in red lustre and  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}_0$ ,  $\text{Ag}^+$  in gold lustre. The simultaneous variable presence of metallic and ionized silver and copper in all the examined cases confirmed a lustre formation mechanism where the first step consists of an ion-exchange process between copper/silver ions and the alkali ions of the glaze followed by partial reduction of metal ions.

The natural evolution of this fruitful study was the continuation of XAS investigations of copper chemistry in other systems of interest in cultural heritage and showing similar analytical issues. The interest on copper arises from the large use since antiquity of Cu minerals for production of pigments, coloured glasses and glazes. Among pigments copper resinate needs a special mention since it distinguishes from other crystalline pigments being characterised by an amorphous nature. In fact it was obtained by dissolution of copper acetate in a mixture of resin and siccative oil. The resulting pigment consisted of a complex mixture of copper carboxylate complexes of resin and fatty acids which was used to produce a transparent green layer. Unfortunately the pigment has the tendency of discolouring to brown in a relatively short time. The phenomenon is well known by art-historians, conservators and restores and, although it has been subjected to several scientific investigations, still no definite conclusion has been achieved on the discoloration mechanism. To this end, XAS investigations addressed to the characterization of the local chemical environment and of the oxidation states of copper embedded in the organic matrix of the blackened pigment have been carried out at GILDA on a sample belonging to an original fifteenth-century easel painting [2]. Results have been interpreted in the light of the structural

properties of copper acetate and unaltered copper resinate pigments as determined by XAS combined with UV-vis and mid-FTIR measurements. Experimental data evidenced that copper acetate structure, consisting of bimetal complexes in a bridging bidentate coordination of Cu atoms with four carboxylic groups, is retained in copper resinate through the formation of new binuclear copper carboxylate complexes of Cu(II) ions with the resin and fatty acids. On the other hand the analysis of the blackened original sample clearly showed a modification of the local environment of the Cu complexes characterised by the elongation of Cu–Cu and Cu–C distances. These findings clearly pointed towards a primary involvement of copper complexes in pigment embrowning, although it is still not clear which mechanism triggers the darkening process [4]. Further research work on this subject is in progress.

### **Experimental method and desirable upgrades**

GILDA beam-line offers analytical performances, as for example the wide operational energy range (5-85 keV) maintaining a very good energy resolution, which have been successfully exploited in our XAS experiments. However our studies would benefit of further possible upgrades of the beam-line. In particular the upgrade of both the monochromator and of the focusing optics will allow the improvement of the beam spatial resolution from mm<sup>2</sup> to μm<sup>2</sup>. This is an essential requisite for non-invasive and micro-invasive investigations in cultural heritage in consideration of (i) the intrinsic heterogeneity of the materials at the micro-scale level and of (ii) the restrictions imposed on the number and size of the samples because of the unique and inimitable character of the artworks. As a matter of fact the most common applications of synchrotron radiation in this field exploit the micrometric dimension of the beam achievable in a number of dedicated beam-lines for highly spatially resolved spectroscopic measurements.

The development of a different sample experimental environment, in order to simultaneously carry out XAS and fluorescence measurements and to integrate spectroscopic analysis with diffraction measurements at the same beam-line, represents another valuable upgrade of GILDA that would disclose new analytical perspectives in conservation science. To this aim it would be highly desirable to have, also, a reaction chamber to control sample environmental conditions for time-resolved in-situ measurements. This accessory experimental configuration would be of great interest for (i) the study of degradation processes of ancient materials by artificial aging of laboratory standards and for (ii) the investigation of ancient manufacturing techniques of art objects by laboratory reproduction of the synthesis process.

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5.2.6. *Energy.*

## Local structure in solid oxide fuel cells

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### 1. Scientific background

The high working temperature of Solid Oxide Fuel Cells (SOFC) allows fuel flexibility and the opportunity of exploitation of the excess heat. On the other hand, the high temperature also involves the use of expensive materials and possible device breakdown originated by thermal stress, mostly during startup and switching off. Among SOFC, Proton Conductor-SOFC (PC-SOFC) have the advantage of an easy fuel management, but the development of reliable devices is still waiting for improvements that, with reference to the state-of-the-art proton conductors, mainly concern chemical stability for electrolytes derived from barium cerate and grain boundary resistivity for barium zirconate-based materials. Besides seeking for higher conductivity, the research is involved also in electrodic materials and in the compatibility of the components in the electrolyte-electrode assemblies.

Then, the investigations in the field of PC-SOFCs concern: i. *novel proton conductors*, with the aim of obtaining at least one of the goals of a better chemical stability, higher proton conductivity, lower working temperature [1]; ii. *electrodic materials*, that should ensure the redox reactions at cathode and anode, easy exchange of reagents and reaction products, mixed ionic-electronic conductivity [2]; iii. *assemblies electrodes-electrolyte*, with thermal and chemical interface stability.

i. *Proton conductors*. The design of new materials needs a deep knowledge of the mechanism of proton conduction, that has been recently investigated by anelastic spectroscopy [3], quasi-elastic neutron scattering [4], Raman and IR spectroscopy [5] and computational analysis [6,7]. The latter deal with the modeling of a section of solid, to determine local properties such as the dopant-host oxide interaction, the vibrational frequencies of oxygens interacting with protons and the activation energy of proton transfer between adjacent oxygens. Computational studies validated by experimental data and, reciprocally, integrated approaches in which the theoretical model contribute to the interpretation of experimental data are not very frequent [8]. The analysis of the electrolyte local structure by x-ray absorption spectroscopy (XAS), a technique that can yield information selective for atomic species on local structure, static and thermal disorder, harmonicity of vibrations, has been suitably pursued only recently [9-12]. Among the novel non perovskite-like conductors, materials whose structure is characterized by tetrahedral MO<sub>4</sub> moieties such as the derivatives of LaNbO<sub>4</sub>, involve the possibility of suitable device development [13,14] and of deeper knowledge of the mechanism of proton conduction.

ii. *Electrodic materials*. The core of a fuel cell is the electrolyte; however, the efficiency of the electrodes and their compatibility with the electrolyte are fundamental issues to determine the overall electrodes-electrolyte assembly performance. The studies on PC-SOFCs often concern composite materials for cathodes and anodes; for instance, in ref. [15] the electrolyte is a BCZY mixed oxide, the anode is a Ni-BCZY composite and the cathode a (BSCF-BCZY) composite. An integrated experimental-computational approach, where the theoretical analysis is carried out by ab initio MD and MC simulations at the DFT level, is getting increasing relevance in the research on electrodic materials [16]. Experimental evidences on chemical environment and oxidation state [17] of electrocatalysts can be obtained by XAS spectroscopy, that could also be applied in operative conditions [18] providing support to the computational approach [19,20].

iii. *Electrodes-electrolyte assembly*. Among the perspectives relative to this topic, the possibility of reducing the working temperature by fabrication of thin-film devices, such as micro fuel-cells for portable systems (e.g. computers) should be mentioned [21]. The electrode-electrolyte assembly

brings about further problems concerning the interface chemical [22] and thermal [23] stability. The XAS technique can have important applications in the study of the electrolyte-electrode interface and in the interface substrate-electrolyte in the thin-film assemblies [21]. In this field, some investigations on PC-SOFC materials have been carried out by electronic microscopy and elemental EDS analysis. An alternative approach, selective for atomic species and allowing to get informations on the interface at different depths, can exploit the x-ray absorption spectroscopy in grazing incidence, or also in total reflection geometry, as it was demonstrated with other heterojunctions [24].

## 2. Skills and previous experience

The proposers have been involved in PC-SOFCs (Proton Conductor-Solid Oxide Fuel Cells) starting from a research activity in heterogeneous catalysts, that brought about an extension of the thematics of the group to solid state ionic conduction [9-12, 25-26]. The skills acquired in the study of heterogeneous catalysts concerned the synthesis and the structural characterization of nanostructured materials [27], and the structure-property correlation [28]. The structural investigations on materials have been carried out by in-house instrumentation and in several XAS and XRD experiments that were awarded with beamtime in some of the most important european synchrotron radiation facilities (ESRF Grenoble, DESY Hamburg, Elettra Trieste). In the course of several years of activity with synchrotron light, devices for in situ XRD and in-situ XAS were also projected and constructed in collaboration with the scientific and technical staff of GILDA [29-30].

## 3. Project and impact

Previously to our activity, only a few and partial studies on the local structure of SOFC and PC-SOFC materials by X-ray Absorption Spectroscopy (XAS) have been carried out. To this respect, it is worth to notice that in a recent paper, suggestively entitled: "Think locally-Linking structure, thermodynamics and transport in grossly non-stoichiometric compounds and solid solutions" (N.L. Allan et al., J. Mat. Chem. 18, 2008, 4124), it is highlighted that the local structure strongly influences the ionic transport properties of a defective solid oxide. Our approach involves a central role of XAS spectroscopy in obtaining local structure information, the use of various complementary experimental techniques (XRD, IR, QENS), and the close collaboration with computational groups to obtain a deeper insight in the solid state mobility of ionic species. The integrated computational-experimental approach to the problem of solid state proton conduction is already operative [31] and constitutes one of the most relevant features of this project.

*New proton conductors.* One of the goals of our research in the field of solid oxide fuel cells is the design of new proton conductors working in the range of 400-600 °C. The study of local structure by XAS represents a crucial issue of this project, which will involve the skills of other teams for functional characterization, and complementary experimental techniques such as quasi-elastic neutron scattering (at ILL) to investigate proton dynamics and high resolution XRD (at ID31-ESRF) to obtain information about long-range structure of the investigated materials. The analysis of the local structure of perovskite-type proton conductors [9-12, 25-26], correlated to ionic conductivity and thermogravimetry data, allowed to conclude that for this class of compounds the dopant ionic radius has a minor effect, if not relevant at all, on the mechanism of proton conduction; on the other hand, it is crucial that the insertion of the dopant into the structure of the matrix oxide does not significantly alter the electronic structure of the host oxide [12, 25, 31]. Then, it could be argued that proton diffusivity in perovskites is a property intrinsic to the host oxide, that can be altered, and possibly deteriorated, by the insertion of dopants. In order to check this conclusion with different proton conductors, and eventually design new materials, an integrated experimental-computational approach will be applied to non-perovskitic proton-conducting oxides. In this class of compounds, much interest is raised by materials derived from LaNbO<sub>4</sub>, (LN) LaTaO<sub>4</sub> (LT) [14] and LaBaGaO<sub>4</sub> (LBG) [7], characterized by the presence of not-interconnected tetrahedral moieties MO<sub>4</sub> (M= Nb, Ta, Ga) alternated by the other structural cations (Ba<sup>2+</sup> and La<sup>3+</sup> for LBG, La<sup>3+</sup> for

LN and LT). In order to achieve proton insertion, niobates and tantalates are doped in the lanthanum site with bivalent cations, while in LBG the stoichiometric ratio La:Ba is modified to get barium excess; for all these oxides, the lack of positive charge induce the formation of O<sup>2-</sup> vacancies. Then, oxydryl defects can be introduced into the structure by dissociative water adsorption. The analysis of inter- and intra-tetrahedral proton diffusion as a function of the lattice modifications induced by doping and proton insertion is the fundamental issue of these studies.

***Compatible electrodic materials.***

*Anodes.* The anodes for PC-SOFCs usually consist of a cermet constituted by a metal-based oxidation catalyst and a protonic conductor, that is very often the same oxide used for the electrolyte. In this way, catalytic activity, electronic conductivity, proton diffusion towards the anode/electrolyte interface and chemical/thermal compatibility between materials are ensured. The anodic materials that will be investigated belong to this class of composites. The metals will be Ni, Cu and Pd. As concerns the structural characterization, XRD experiments will be integrated by XAS experiments, carried out also at working temperature and in reducing environment, to determine oxidation state and chemical environment of the catalytic component.

*Cathodes.* The research of novel materials for PC-SOFC addresses questions even more complex than those concerning anodic materials. A suitable cathode, besides being an oxygen reduction catalyst, should be a good anionic and electronic conductor and possibly, in order to extend the H<sub>2</sub>O production to the whole cathode volume, also a protonic conductor. To date, the proposed solutions are rather empirical, putting forward composite materials constituted by a intimate mixture of reduction catalysts, anionic and protonic conductors [15]; as it was pointed out [22], the composite should present the further advantage of an improved thermal compatibility with the electrolyte. The local and long-range structure of various mixed oxides will be investigated, also from the view point of compatibility with the electrolyte and of the catalytic mechanism, with the final aim of designing homogeneous and efficient cathodic materials. Studies of thermal-chemical compatibility of electrode and cathode are essential to the development of suitable technological devices. As a first approach to this topic, thin cathodic films will be deposited on the electrolyte pellet and subjected to thermal treatments in oxidising and reducing environment. XAS and XRD experiments carried out in grazing incidence geometry will allow to detect the possible formation of new phases produced by interdiffusion. XRD and XAS experiments will also be carried out in different conditions of temperature and O<sub>2</sub> partial pressure, to detect phase demixing and the oxidation state of the constituent cations.

### **3. Experimental details**

Most of the previous XAS studies on SOFC were carried out at GILDA, at the K-edge of heavy elements. For these investigations, the high fluxes of high energy photons suitable at GILDA were necessary. This beamline feature will also be required in the envisaged investigations, as the high working temperatures and requested characteristics of the materials will still involve the use of oxides constituted by heavy elements and the opportunity of exploiting the K-edges will allow high resolution local structure analysis.

Moreover, the envisaged extension of the research activity to electrodes and to electrode-electrolyte assemblies will also involve, as above described, the investigation of heterojunctions by grazing incidence techniques. To carry out these part of the project, it is required a highly collimated beam and the REFLEXAFS geometry apparatus already available at GILDA. Catalytic activity at the electrodes will require in-situ experiments to study the structure and oxidation state of the active species in operative environment.

### **4. Results expected**

- Structural characterization of materials for fuel cells working in the range 400-600 °C
- Investigation of the mechanism of solid state proton conduction, through an integrated experimental-computational approach

- Design and synthesis of new electrolytic materials
- Design and synthesis of thermally and chemically compatible electrodic materials
- In situ structural characterization of the electrolyte-electrode assemblies and correlation with the functional properties of the devices.

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## Study of nanocatalyst structure and activity in hydrogen storage materials by in-situ X-ray Absorption Spectroscopy

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### *Background and proposed activity*

In the search for energy-storage materials suitable for the hydrogen (H) economy,<sup>1</sup> one of the current research strategies is focused on the improvement of materials function by modification of the microstructure and/or surface properties. Nanostructured materials with a high surface-to-volume ratio are often employed, thereby reducing the atomic H diffusion path necessary for the metal-hydride reversible phase transformation. Since some elements which form chemical or interstitial hydrides do not possess the catalytic properties necessary to dissociate the H<sub>2</sub> molecule at the surface, catalysts (e.g. transition metals, TM) are usually dispersed at the surface or in the matrix. One such example is provided by magnesium, a highly attractive H-storage material thanks to its high gravimetric H-capacity, abundance and low cost. Unfortunately, it is well known that its catalytic properties are poor and that its metal-to-hydride transformation kinetics are sluggish. Both nanostructuring and catalysts dispersed at the nanoscale (*nanocatalysts*) are interesting approaches to improve the material's properties, leading to practical applications. Another interesting case is that of carbon nanostructures, like single-walled carbon nanotubes and nanohorns. These graphene-like materials display a weak binding energy (physisorption) to hydrogen, so that cryogenic temperatures and very high pressures are required to obtain appreciable (but still rather low) H-capacities. It has recently been suggested that this situation can be improved adding TMs or alkali-earth elements, either by incorporation into the structure or by decoration with very small clusters.<sup>2</sup> The effect of these additives can be of two kinds: i) to polarize the hydrogen molecule and increase its binding energy to the carbon nanostructure, and ii) dissociate the molecule and activate a spillover mechanism of atomic hydrogen from the catalyst to the host.

Besides the technological challenges that require breakthrough achievements, fundamental questions remain to be answered on the microscopic role played by the nanocatalysts. For instance, it has been suggested recently that during H desorption the catalyst migrates in the search of H atoms, diffusing inward from the surface to bulk.<sup>3</sup>

Our project aims at the study of nanocatalysts in H-storage materials by means of X-ray Absorption Spectroscopy (XAS). In particular, the ambitious goal of the proposal is to investigate both the structural and the functional properties, the latter by *in-situ* experiments during H uptake and release using a suitable sample environment to control the temperature and H<sub>2</sub> pressure. The feasibility to collect at the same time rapid XRD patterns will be investigated.

### *Novelty and expected results*

Our approach has significant elements of novelty which are expected to advance significantly the knowledge on H-reaction mechanisms in nanostructured H-storage materials. First of all, the study in different materials classes of the local structure of the catalysts, which might be dispersed at different scales (from atoms to clusters) and could form chemical bonding with the host material. We plan to study nanoparticles (NPs) and thin films of light-weight metal hydrides, and also graphene-like carbon nanostructures. The characterization of nanocatalyst structure and chemical state is of paramount relevance, both in the as-prepared form and upon H-sorption cycles at different temperatures. In this respect XAS, with its local structure sensitivity and elemental/chemical state specificity, offers features superior to X-ray diffraction (XRD). Furthermore, the study of the nanocatalyst action, brought about by the determination of the local structure and chemical state *in situ* during H-sorption experiments, would

open the door to a number of possible investigations in the cutting-edge research field known as nanocatalysis.<sup>4</sup>

*Investigators' capabilities, experience and previous results*

The research group at the Department of Physics-University of Trento has a long standing experience on the synthesis and characterization of hydride forming materials. This research activity has experimental character and is carried out by using different apparatus: r.f. magnetron sputtering, pulsed laser deposition and e-gun deposition for the synthesis of innovative materials, high resolution scanning electron microscope equipped with EDS system for their morphological and compositional analysis, XRD for their structural characterization. The evolution of void-like defects in the material upon repeated hydrogen absorption and desorption cycles is studied by positron annihilation spectroscopies<sup>5</sup> such as Doppler broadening spectroscopy, coincidence Doppler broadening spectroscopy and positron annihilation lifetime spectroscopy. Thanks to long term collaboration with other national research groups, the samples are also analyzed by techniques such as XRD analysis in grazing incidence (GI-XRD) and TEM. The functional characterization of the materials is carried out by using a home-made Sievert's kind apparatus that allows the study of the thermodynamic of the metal-hydrogen system and the kinetics of the metal-to hydride (and reverse) phase transition.<sup>6</sup>

Previous work in this field was focused on the preparation and characterization of innovative Mg-based materials: model systems were prepared to study of the role of transition metal nanoclusters in the catalysis of the kinetics of the metal-to-hydride phase transition. This activity was supported by the participation in a MIUR national project and in a FISR national project and by two accepted projects at the GILDA beamline. The studies have proved that transition metal nanoclusters dispersed in the Mg matrix act as nucleation site for the metal to hydride (and reverse) phase transition and promote the formation of fast diffusion paths for hydrogen formed by interconnected Mg domains<sup>7,8,9,10,11,12,13</sup>. The first XAS experiment also showed that the hydrogenation process in Nb-doped Mg thin films is connected to the formation of Nb-hydride clusters, that break in smaller fragments upon dehydrogenation. The most recent XAS experiment at the Nb K-edge of Nb catalyzed magnesium, in connection with experimental data on the evolution of the hydrogen desorption kinetics upon repeated H<sub>2</sub> sorption cycles, indicates that the progressive aggregation of Nb to form larger clusters partially reduces the catalytic activity of the TM additive<sup>8</sup>.

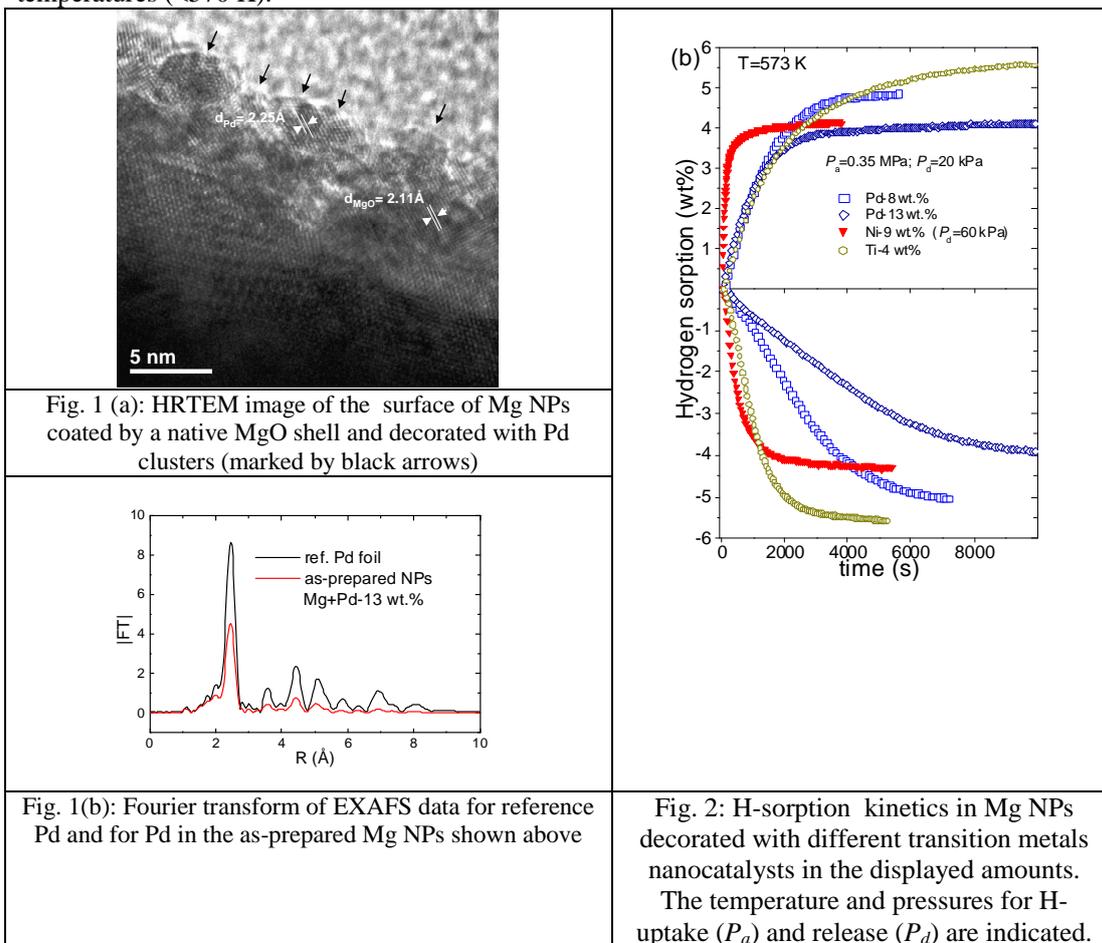
The research group at the Department of Physics-University of Bologna carries out research on nanostructured and metastable material since several years. The know-how of the Bologna group includes: preparation of nanophase materials by physical methods based on mechanosynthesis and inert gas condensation; magnetism, magnetotransport phenomena and magnetoelastic coupling in mesomagnetic materials; structural analysis of nanophase and disordered materials; thermal stability, kinetics processes and diffusion, thermodynamics and lattice dynamics in low-dimensional systems. Especially relevant for the present project is the research on nanostructured metal hydrides, which has been supported by the participation in two national FISR projects. The first approach in this research line concerned the preparation of nanocrystalline magnesium hydride with transition metal additives by mechanosynthesis to accelerate hydrogen sorption kinetics,<sup>14</sup> the mixing of magnesium and carbon with surfactant agents (benzene)<sup>15</sup> and the realization of Mg/Mg<sub>2</sub>Ni nanocomposites.<sup>16</sup> Currently the group is conducting an innovative study on the metal-hydride transformation kinetics in Mg NPs prepared by inert-gas condensation and decorated with transition metal cluster at the surface.<sup>17,18</sup>

The NPs synthesis apparatus based on the principle of inert-gas condensation of metallic vapours operating in the group's laboratories displays unique features in Italy since it allows the production of amounts of material suitable for most analysis techniques and in-situ compaction to yield nanocrystalline solids. Instruments for the analysis of metal-hydrogen interaction based on volumetric and calorimetric principles are available together with X-ray diffraction and electron microscopy equipment. A gas-volumetric apparatus (Sieverts) has been designed and realized within the research unit specifically for the analysis of hydrogen sorption in nanostructured materials.

The Bologna group has a consolidated experience in the field of X-ray absorption spectroscopy (XAS) with synchrotron radiation, in particular for the study of metal and semiconductor nanostructures.

Several XAS experiments on NPs have been carried out at GILDA and at other beamlines at ESRF and ELETTRA. In particular, during the last years we have investigated iron/iron oxide core-shell NPs, by EXAFS and XANES measurements both at the Fe and O K-edge,<sup>19</sup> XMCD,<sup>20</sup> and DAFS.<sup>21</sup>

XAS measurements at the Pd K-edge on Mg nanoparticles decorated with Pd clusters have been carried out recently at the GILDA beamline in the framework of project CH-2942. The morphology of these NPs is shown by the high-resolution transmission electron microscopy (HRTEM) picture of Figure 1a. Pd appears as a non-continuous layer on top of the cubic MgO shell which surrounds the hexagonal magnesium core. The presence of Pd is vital in obtaining good and stable H-sorption properties. Indeed, NPs that were previously almost inert can now uptake and release H very fast even at relatively low temperatures (<570 K).<sup>18</sup>



EXAFS measurements have been carried out on these NPs both in the as-prepared condition and at different steps of H-sorption cycles. In the as-prepared condition (see Fig. 1b) the local structure of Pd experiences a reduced coordination number and a small contraction of the interatomic distance if compared to reference Pd, a picture compatible with the formation of small (few nm) Pd clusters on top of the MgO shell. No indication of Mg-Pd alloying is observable in as-prepared NPs: this will occur upon heating to the H-sorption cycling temperature. The analysis of this experiment is still in progress.

The effect of other transition metals, namely Ni and Ti, on the H-sorption properties of Mg NPs has been investigated by a volumetric Sieverts apparatus as shown in Figure 2.

The research unit at the CNR-IOM working on the GILDA beamline (Grenoble-F) has considerable and thorough experience in the field of synchrotron radiation techniques and all the expertise necessary to successfully plan and perform experiments. Its skills covers not only the experimental part but also the

data processing for x-ray absorption spectroscopy and x-ray scattering experiments; most part of the research performed up to now is about the clustering process of dopant species in dielectrics and on the effect of the local structure at sub-nanometer level on the macroscopic properties of materials (see Refs. 22,23,24,25,26 as an example of recent literature). It has a daily access to the GILDA instrumentation, that is very attractive to realize a new cell for in-situ measurement that has to fit with the existing apparatuses; moreover, it has access to the in-house research beamtime of the proposer that can be partially employed to test the performance of the new cell.

### *Specific experimental aspects*

An ideal continuation of the above mentioned experiments and a good starting point for the present proposal would then be the in situ investigation of H-uptake and release in Mg NPs and thin films doped with TMs. Subsequently, the study will be extended to other light-weight metal hydrides and carbon nanostructures with nanocatalysts. To this purpose, it will be necessary to build a dedicated sample environment cell that allows control of the temperature and pressure of hydrogen. First attempts to study the H-release *in situ* have been made during experiment CH-2942 using a furnace under vacuum, and have permitted to follow the transformation that takes place in the Pd local structure reflecting a different coordination with Mg. However, the reverse transformation (on H-uptake) could not be studied because the sample environment was not conceived for elevated pressures. Moreover, only heating ramps could be performed to stimulate H-release, while it would be more efficient to carry out isothermal measurements and stimulate H-uptake and release by changing the hydrogen pressure. This would also allow for time-resolved studies if the kinetics of the transformation is sufficiently slow. Typical values of the environment parameters would be:  $80\text{ K} < T < 620\text{ K}$  and pressure ranging from vacuum to the maximum possible value (at least  $\approx 5\text{ bar}$ ).

### *Outlook*

We believe that the possibility to perform XAS at the nanocatalyst edge during H-sorption experiments would be of extreme interest for many groups working on nanostructured H-storage materials. In-situ probes are highly appealing both for a basic understanding of reaction mechanisms and for materials optimization. To our knowledge, XAS would represent a novelty in this field; some efforts have been made using TEM, while most experiments have employed XRD. The Bologna group has already started a collaboration with a group at Aarhus University, Department iNANO, specialized in real-time diffraction studies of H-sorption. First measurements have been performed at Max-Lab synchrotron in Lund, on Pd-decorated Mg NPs inserted in a sapphire capillary that was radiation heated and connected to a pressure control manifold. In general, in all cases where the catalyst is found in very small clusters or is atomically dispersed in the host, diffraction cannot provide useful information on its state and activity, so that a synergy between diffraction and XAS measurements could represent a significant step forward.

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5.2.7. *Nanoscaled materials and surface physics.*

## Foundations of reactivity in the solid state

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### 1) Scientific background and description of the project

The assessed theory of the kinetics of solid state reactions essentially describes the growth of a product phase enclosed between two grains of the reagent phases. In this treatment, various kinetic processes are considered, depending on the nature of reagents and product, the process variables, and the extent of the reaction. In particular, as the reaction proceeds and the product layer becomes thicker, local chemical equilibrium is possibly attained at each interface so that the growth becomes kinetically controlled by diffusion in the product layer [1].

Useful additions to this general treatment take into account kinetic control by other processes, such as heat transport or interface mobility. The latter case is particularly interesting as it extends the theoretical approach towards the initial stages of the reaction, when the product layer is thinner and the growth rate is constant (linear growth).

In both cases, i.e. diffusion control or interface mobility control, a basic assumption is that a product layer already exists. As matter of fact, practically nothing is presently known about the very early stages of the process, when the product layer is not yet formed and the chemical reactivity is entirely controlled by interfacial aspects. This quite surprising lack of basic understanding is related to the fact that the subject is largely unexplored mainly because of the lack of an established probe.

Quite impressively, the scientific community still needs an assessed agreement concerning the procedures and the aforementioned experimental probes required to investigate this topic, as well as a sound common background connecting the different areas that can seemingly provide important contributions to the advancement of knowledge, and that conversely can profit from that advancement.

Aim of the project is therefore to reach a basic understanding of the very initial stages of solid state reactions. We want to make clear that the main objective is to contribute to the advancement of knowledge in a very basic but somehow unexplored area of science which is at the crossroad of many disciplines.

Only one reaction scheme is considered in the project. This is the formation of a spinel phase ( $AB_2O_4$ ) from the parent oxides ( $AO$  and  $B_2O_3$ ). Besides being very probably the best known solid state reaction, this choice appears the most appropriate both in term of flexibility and simplicity, two features that have been considered a true need in facing a topic of such a fundamental kind. To list just the most significant aspects, we remind, for what concerns flexibility, that a large number of spinels with many different A-type or B-type cations are known in the literature, and that parent oxides with different structures are available for experiments.

Two spinel forming reactions will be studied:

$NiO$  and  $Al_2O_3$  to yield  $NiAl_2O_4$  and  $ZnO$  and  $Al_2O_3$  to yield  $ZnAl_2O_4$

This choice has been done essentially because these reactions have been intensively studied in the past for what concerns the parabolic growth regime [see 1 and references therein]. In addition, in both the  $Zn/Al/O$  and  $Ni/Al/O$  phase diagrams, the spinel is the only stable compound. An additional advantage is that  $Al_2O_3$  can be easily found in form of large single crystals cut along different orientations, and therefore the possibility of exploring different topotactical relationships is made easier.

By holding fixed one reactant ( $\text{Al}_2\text{O}_3$ , corundum structure) it is possible to classify the two model cases based on the structural rearrangements that take place at each interface.

1)  $\text{NiO}/\text{Al}_2\text{O}_3$  (halite/corundum structures) system: the arrangement of oxygen atoms is face-centered-cubic (fcc) in NiO and hexagonal-close-packed (hcp) in corundum. Taking into account that in the spinel the oxygen substructure is fcc, the rearrangement has to occur only at a single interface (spinel/corundum).

2)  $\text{ZnO}/\text{Al}_2\text{O}_3$  (wurtzite/corundum structures) system: the arrangement of oxygen atoms is hcp both in wurtzite and in corundum. Therefore, the oxygen substructure has to rearrange from hcp to fcc at both reaction fronts.

With the ambitious goal to study the very early reaction stages of solid state reactions, it is proposed a novel approach which is based on the reduction of the dimensionality of (at least one) reactant by using thin films. We expect that the transition, in particular, between the early regime and the intermediate regime might be directed towards different products and investigated by changing the dimensionality of the reactive couple.

The following experimental approach will be followed.

Thin layers of NiO and ZnO will be deposited by RF-magnetron sputtering on properly oriented  $\text{Al}_2\text{O}_3$  single crystals kept at room temperature. In order to investigate the role of topotactical relationships on the reactions, three different orientations of  $\text{Al}_2\text{O}_3$  crystals will be used: (0001), (11-20), (10-12).

Films of different thicknesses, from 10 nm up to 1  $\mu\text{m}$ , will be deposited. The film formation will be monitored with a thickness-meter based on a quartz microbalance. Different film thicknesses will allow investigation of the expected transitions between the aforementioned different regimes. In order to give further insight into the regime governed by interfacial movement, another experimental approach will be also used: a film of the stable spinel phase will be deposited in between the two reactants.

It may be worth noting that a reaction in the solid state usually takes place at very high temperatures (say  $T > 800$  °C). In this case, the thermal broadening of (for example) the diffraction effects makes an *in situ* investigation extremely difficult. However, this limitation can be overcome by quenching samples at different advancement degrees, and by studying them in the most appropriate conditions. Heat treatments in appropriate atmosphere will be performed in the range 700 – 1000 °C until the solid state reaction(s) under investigation is fired up. Different advancement degrees will be obtained by quenching the reacting couples after different firing times.

The various samples (i.e., before and after the heat treatments, in the different regimes, with different advancement degrees and different crystallographic orientations of the  $\text{Al}_2\text{O}_3$  crystal) will be investigated using several different probes. The complexity and novelty of the problem impose to face the study by using several techniques that are expected to give complementary results. For example it is required to use both X-ray and electron diffraction in order to identify and solve the structure of reaction products and intermediates as well as to characterise the relation at interfaces. The difficulties due to the novelty of the approach, dimensionality of the examined systems, stabilisation of non stable phases by topotaxy require indeed to bring together results from independent probes:

- Morphology of the films and its variations with the advancement of the reactions will be studied by means of atomic force microscopy (AFM) inspections. Different values of interfacial free energy, due to different topotactical relationships, can direct the interfacial reaction towards different products. New interfaces, produced during the reactions, might be characterised by different topotactical relations and energies, and therefore might cause the

film morphology to change. The AFM equipment is already available at the GILDA laboratory at ESRF.

- Structure of the reactants/products interface and of the reaction products will be investigated by employing transmission electron microscopy (TEM). Nowadays, standard TEMs attain a point-to-point resolution lower than 2 Å, which is of the same order of the interatomic distances. Under suitable experimental conditions, when operating the microscope in High Resolution (HRTEM) mode, atoms can be resolved and observed along major crystallographic directions [2]. HRTEM will thus allow us to unravel the projected structure at the interface as well as any topotaxy among reactants and products.
- Details of the local structure (nearest neighbours nature, number and distance) as a function of thickness of the reaction products will be obtained by means of Reflection Extended X-ray Absorption Fine Structure (RefEXAFS). The experiments will be performed at GILDA (BM08 @ ESRF). Extended X-ray Absorption Fine Structure (EXAFS) permits the analysis of the local structure around a chosen chemical species. Due to the low cross section of the interaction between matter and X-rays, this technique is mostly used for the analysis of bulk systems. However it is also possible to confine the probe beam in the first few nm below the surface by shining the sample at a sufficiently low incidence angle. When the conditions for total reflection are met, the probe beam is completely reflected and only an evanescent wave enters into the sample with an extinction length  $\lambda$  of the order of a few nm. This technique (RefEXAFS) presents several advantages with respect to other surface analysis methods: i) it can be carried out in air or in gas (so there is no need of Ultra High Vacuum); ii) it can be applied regardless to the electrical transport properties of the substrates (conducting or insulating); iii) it probes a sufficient sample depth to avoid the problems of an extreme surface information found in other methods like X-ray Photoemission Spectroscopy.

### 2) Novelty of the project

Solid state reactivity in its various aspects plays a significant role in many different areas of science, such as Crystallography, Mineral Physics and Earth Sciences, Physical Metallurgy, Ceramic Science, Semiconductor Physics, Solid State Chemistry, but the basic knowledge and the main results (not to speak of the language itself) are not always well shared among the disciplines. Surface Science and Catalysis provide an ample background of knowledge on the transformations and reactions occurring at a free interface, while the processes occurring at the boundary between two condensed phases are an important topic in many of the scientific areas above quoted, for instance in the investigation of phase transformations or growth of thin films. All this knowledge provides important starting points but does not directly face the processes occurring when a *single* interface between two grains of the reagent phases is progressively turned into *two* different interfaces between each reagent and the newly formed product. So, for an extremely ample set of heterogeneous reactions, *i.e.* the reactions involving two condensed phases as reagents and producing a different crystalline phase, the present state of art is that thermodynamics gives tools to predict whether or not the formation of a particular product can occur, and the assessed kinetic theory gives tools to predict the growth rate of this product when diffusion is the rate determining step. However, we do not really understand the mechanism through which this product is formed. This means that we have no general knowledge of the very basic aspects of the chemical reactivity in the solid state; for instance we ignore how and why a reaction actually goes towards one or another polymorph, a compound or a broad range solid solution, a stable or metastable product.

### 3) Expected results

To sum up, the interest for a better understanding of the very early stages of solid state reactions is a current issue in the mineralogical community and is expected to propagate rapidly to materials science and solid state synthesis, where the interest is seemingly confined at present to specialized areas. We finally note that understanding how the interfaces between condensed phases and their time evolution affect chemical reactivity is nanoscience by itself, so that it is almost impossible to quote all the expected connections of this research project with nanosciences and nanotechnology. In particular, a better understanding of these aspects is expected to provide strong impact on the knowledge of the chemical mechanisms underlying the deposition of thin films on various substrates, a preparative technique that spans a broad range of applications such as catalysis, photoluminescence, spintronics, information storage (magneto-resistance and related properties).

#### **4) Experience of the proposing team**

The research activity of Paolo Ghigna has been mainly devoted to the study of the defect properties of oxides (cuprate superconductors, perovskite oxides, spinels, garnets and fluorite structure oxides). More recently, new research activities have been started on the study of the short range structure on superionic glass conductors and on the application of synchrotron radiation techniques (XMCD and x-ray resonant scattering) for studying the magnetic properties of superparamagnets (Mn<sub>12</sub>Ac and Fe<sub>8</sub>) and the orbital order in perovskites. Another research subject recently started involves the application of ReflEXAFS to the study of the very initial stages of solid state reactions. For this project, Paolo Ghigna has designed and developed an high temperature furnace for in situ studies which is currently installed at the BM08 beamline at ESRF (Grenoble). The application of synchrotron radiation techniques to the study of nanostructure materials is another field of research to which Paolo Ghigna is dedicating increasing interest. Paolo Ghigna is author, besides of many communications to international conferences, of more than 110 scientific articles on international journals, and book chapters on oxide superconductors and colossally magnetoresistive manganites. He recently has operated as the editor of a book on the Solid State Chemistry of *4f* elements. Moreover, he has acted as a reviewer for journals such as Dalton Transactions, J. Solid State Chem., PCCP, Chem. Mat., J. Phys. Chem. B, J. Mater. Chem., Phys. Rev. B, Phys Rev Lett.

#### **5) Peculiar needs and aspects of GILDA in the framework of this project**

GILDA is most probably the only laboratory in the world capable of performing ReflEXAFS experiments rewardingly. When measuring the reflectivity of the sample as a function of the energy, the probed region is only a few nm thick and no contribution to the spectrum comes from the lower parts of the sample. One of the objective of the project is to couple the ReflEXAFS spectrometer to suitable system for *in situ* sample erosion (Focused Ion Beam, Ar sputtering, etc.). In this way it will be possible to obtain information also along the direction perpendicular to the film surface, and hence realize an apparatus with strong depth profiling capabilities and with a spatial resolution of the order of  $\lambda$ , i.e., a few nm.

#### **6) Collaborations with other beamlines**

Combined to the above described experiments, in the framework of this project, it is also planned to continue the implementation of the  $\mu$ -XANES mapping technique of buried interfaces, which has been recently developed in collaboration with scientists at beamline ID24 at ESRF [3].

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## **Interface structure of metal/oxide ultrathin films and nanoparticles**

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### **Description of the proposed activity and scientific background**

Metal/oxide nanostructures are the subject of considerable current interest in view of their applications in the field of catalysis, sustainable energy systems, microelectronics and mechanics. There is ample consensus that in order to understand the physical behaviour and possibly optimize the performance of the devices based on such structures it is very important to characterize the systems at the atomic scale in terms of their atomic structure, morphology and electronic properties. For this reason a number of studies have focussed on model systems, i.e. crystalline metal/oxide ultrathin films or nanostructures prepared in very well controlled conditions on single crystal substrates [1]. It soon became clear that these systems are interesting also in their own right as new materials with properties significantly different from those of the corresponding bulk phases [2].

An important class of systems in this context are polar oxide ultrathin films or nanostructures, i.e. low dimensional systems which expose surfaces with a macroscopic polarization along their perpendicular axis and a consequent instability of electrostatic origin [3]. Such systems, though unstable in the bulk phase, can be stabilized in the form of thin films and nanostructures by epitaxy [4]. Complex mechanisms may come into play to reduce – at least partially – the electrical polarization, leading to new structural, electronic, catalytic and magnetic properties [5]. Polar orientations have been so far mainly studied in simple materials, the most representative example being rock-salt ionic oxides with the (111) surface orientation.

In the same context, another system of great applicative interest is cerium oxide and related nanostructures. Due its ability to quickly store and release oxygen, depending on the ambient conditions, cerium oxide and related compounds are used in automotive exhaust emission control, to oxidize CO and hydrocarbons and simultaneously reduce NO, in solid-oxide fuel cells, as electrolytes, in the field of hydrogen production, through the water-gas shift reaction, and they even have potential application in solar cells [6].

In this framework, we plan to perform a series of structural studies of metal/oxide ultrathin films and nanostructures by means of X-ray Absorption Fine Structure (XAFS), building on our previous experience in the field. Our studies will mainly focus on three classes of systems: 1) interfaces between metallic nanoparticles and oxides; 2) rock-salt oxide films and nanostructures exposing polar surfaces; 3) cerium oxide ultrathin films and nanostructures. In the following, the goals of our activity are shortly described.

#### **1) Interfaces between metallic nanoparticles and oxides**

We intend to study the structure of noble and transition metal clusters either self-assembled on rock-salt oxide surfaces from the gas phase, or pre-formed and embedded in an oxide matrix. We are interested in the structural rearrangements of the metal clusters due to the reduction of dimensionality and to the presence of the oxide. Our study will also focus on the formation of possible non-stoichiometric phases at the interface. The materials to be studied are:

- i) Au nanoparticles on MgO ultrathin films on Fe(001) or Ag(001): effect of the MgO film thickness on the charge transfer and on the structure of the metal clusters.
- ii) Ni preformed clusters in an MgO matrix: structure of the particles as function of size and chemical structure of the Ni/MgO interface.

#### **2) Rock-salt oxide films and nanostructures exposing polar surfaces**

We intend to study the structure of NiO and FeO films grown on Au(111) and Pt(111). The main subject of our study will be a determination of the structure, orientation and strain of the films grown with different kinds of oxidizing gas, which may stabilize the different metastable phases theoretically calculated [5]. The presence of the metallic substrate may partially compensate the polarity of the oxide, either by charge screening or by charge transfer. Both mechanisms are strongly determined by the interface distance, a very important parameter, which we expect to be able to determine by the analysis of XAFS measurements.

### 3) Cerium oxide ultrathin films and nanostructures

The structure and strain of cerium oxide films of different thickness and with different preparation procedures (oxidizing gas, growth temperature, etc.) on Pt(111) and possibly on other (111) substrates will be compared. The interfacial phase which stabilizes epitaxial films, in spite of the very large lattice mismatch of ceria and most transition and noble metals (30-40%), will be investigated.

#### **Novel aspects**

Although metal/oxide nanostructures are widely studied as model systems for catalysis, the determination of the structure-properties relationship is a very difficult task to be achieved. In particular the structure of small metal particles on ultrathin oxide films stabilized by charge transfer, the stabilization of oxide films with polar orientation and the atomic scale characterization of cerium oxide structures are still largely unexplored fields. We believe that by XAS measurements on GILDA we may contribute to a progress of knowledge in this field.

#### **Expected results**

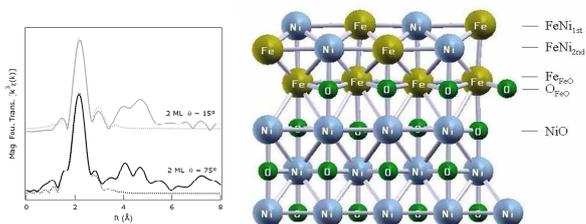
We expect to be able to obtain a complete characterization of the investigated systems in terms of their structure and of the interfacial phases which stabilize them. We expect this characterization to be very relevant to understand the properties of the nanostructures and to help obtain a complete model for their behaviour.

In particular we expect to determine the structure of metal nanoparticles on/in oxides and to correlate it with the observed electronic/magnetic properties. We also expect to determine the different phases stabilized in polar oxide films by the different preparation conditions and to determine the oxide-substrate distance, which is very relevant in understanding the stabilization mechanisms and the properties of the films. Concerning cerium oxide films and nanostructures we expect to be able to determine the structure and the strain and to have information on the interfacial phases which play a role in the epitaxial growth of such films. These results are expected to be of great help in understanding the electronic properties and the reactivity of cerium oxide nanostructures.

#### **Previous experience**

The proposers have a longstanding experience in the growth and characterization of metal/oxide nanostructures. In our laboratories we have two UHV systems for the growth of self assembled metal/oxide nanostructures and preformed mass-selected metal clusters. The apparatus are equipped with tools for chemical, structural, electronic, morphologic and magnetic characterization. In recent years we have often used XAFS to obtain a more detailed structural and chemical characterization of several metal/oxide systems under study. The results of the analysis of XAFS measurements have helped to obtain a deeper understanding of the systems under study. For example, we studied the Fe/NiO/Ag(001) system, which represents a model epitaxial ferromagnetic / antiferromagnetic bilayer system grown on a non magnetic substrate. This system is interesting for the applications in spin valves or in magnetic memories, due to the exchange bias effect [7]. By means of polarization-dependent Ni K-edge XAFS measurements performed at the GILDA beamline [8,9,10] and O K-edge measurements at the ALOISA beamline, ELETTRA [11], we have fully characterized the

NiO/Ag(001) interface in terms of the structure, strain and interface distance between NiO and Ag. The results obtained were in full agreement with the ones of ab-initio calculations [9].



**Fig.1:**Left:  $k^3$ -weighted magnitude of the Fourier transforms (solid line) and fit (dashed line) of Fe K-edge near EXAFS spectra in two scattering geometries on a 2 ML Fe film on NiO/Ag(001). Right: sketch of interface structure of Fe on NiO, with an FeO interface layer, as resulting from the fitting of EXAFS spectra and DFT calculations [13].

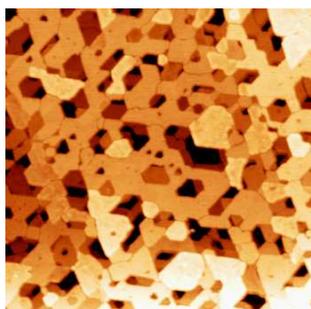
Concerning the Fe/NiO interface, the structure which resulted from the analysis of the XAFS data acquired at GILDA on the Fe K-edge is summarized in Fig. 1 [12,13]. Also in this case the obtained results are in good agreement with theoretical calculations [13] and raise interesting questions on the influence of interface structure on exchange bias. This subject is under study by MOKE and nuclear

resonant scattering technique and has been the object of three runs at ID18, ESRF [14]. For comparison we also studied the Fe/MgO/Ag(001) interface by means of EXAFS measurements on the Mg K-edge (SA32 beamline, LURE) [10,15] and on the O-K edge (1.1 beamline, SRS) [10,15] and by Fe K-edge measurements at the GILDA beamline [16].

Concerning the systems under study in the present project, we have shown by XPS that the electronic properties of Au nanoclusters on ultrathin MgO films on Fe(001) are strongly dependent on the thickness of the MgO film [17] (Fig.2). The measurements have been performed at the APE beamline, ELETTRA. The results are in agreement with theoretical ab-initio calculations, which predict a charge transfer from the Fe substrate to the Au clusters [17].

In a different experiment we have grown mass-selected Ni clusters embedded in MgO and characterized their inner structure by TEM, however the composition of the interfacial phase is still unknown.

Concerning polar films, so far we have studied the growth of MgO films on Au(111) for different preparation

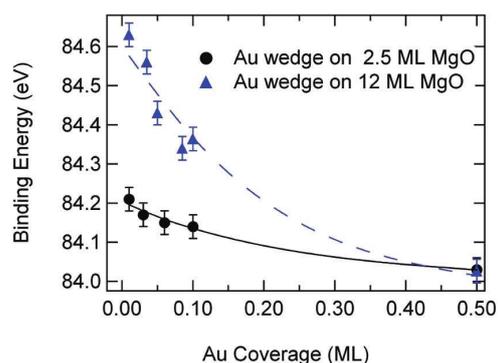


**Fig.3:** 200 nm  $\times$  200 nm STM image of a 2.5 ML CeO<sub>2</sub> film on Pt(111) grown using atomic oxygen as the oxidizing gas.

## Methodology

conditions. The study was performed by XPS, STM/STS and by GIXRD measurements at beamline BM32, ESRF. We stabilized the MgO(111) orientation, but a complete description of the polarity compensation mechanism would be significantly helped by a determination of the MgO/Ag distance.

Recently we have also started the study of cerium oxide ultrathin films and nanostructures on Pt(111) using either atomic or molecular oxygen as the oxidizing gas. The two procedures result in a different LEED pattern at the first stages of growth, probably due to a different structure at the interface. We have also measured the stoichiometry of the films in the different preparation conditions and characterized the surface morphology by STM (Fig.3).



**Fig.2:** Au 4f<sub>7/2</sub> binding energies as a function of Au coverage for two different MgO films of 2.5 ML (black circles) and 12 ML (blue triangles) thickness on Fe(001) [17].

All the measurements foreseen require a high photon flux in the total reflection geometry in order to maximize the signal from low-dimensional structures. The samples will be grown ex-situ and capped with suitable materials, as in our previous experiments, to avoid sample contamination due to atmospheric pressure exposure.

The measurements will be performed at the Au L<sub>3</sub> edge and Ni K-edge for the metallic nanoparticles. Ni and Fe K-edge measurements will be measured for polar oxide films, while Ce L<sub>3</sub> edge measurements will allow the structural characterization of cerium oxide films and nanostructures. The data will be acquired in the fluorescence mode and in at least two different orientations between the X-ray polarization direction and the sample normal, to have information on the in- and out-of-plane structure.

### **Collaborations**

This research activity is performed in collaboration with Italian and foreign institutions. In particular the studies will be carried out in collaboration with the group of Prof. G. Pacchioni at the University of Milano-Bicocca, where DFT calculations on these systems will be performed. Furthermore, the activity of polar oxide films is presently performed also in close collaboration with the group of Prof. H.-J. Freund, at Fritz-Haber Institute in Berlin and with J. Goniakowski, at the Institut des NanoSciences de Paris for the theory. The activity on cerium oxide instead is performed also in collaboration with the group of Prof. M. Reichling at the University of Osnabrück, Germany.

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**Titolo**

Surface Chemistry of NO<sub>2</sub> adsorption on Zinc Oxide Quasi 1-D Nanostructures

**Proponenti (nome, affiliazione)**

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**Application of experiments at GILDA**

ZnO is a wide-bandgap n-type semiconductor  $E_g=3.37$  eV at 300 K with a large exciton binding energy, transparent in VIS and biocompatible. Applications of ZnO cope UV lasers, piezoelectric devices, field emission, gas sensors, dye-sensitized solar cells and photocatalysts. A wide variety of shape are possible for Zn/ZnO nanostructures: tetrapods, flower-like, nano-saw, nano-combs, nano-pins, Y-shape, crossed ribbons. ZnO nanomaterials can be used as UV detector, PL devices and nano electromechanical oscillators.

Quasi 1-D morphologies are characterized to have all but one dimension below 100 nm: nanowires, nanobelts, taper-like and flat-roofed tubes, trumpets. One peculiarity of ZnO 1-D structures is to be a very good gas sensors at low concentration (ppm) and ambient temperature (300 K): nanorods vs. ethanol (Xu et al., 2007); nanowires vs. humidity (Zhang et al, 2005); Zn/ZnO nanotubes (di Stasio, 2004; Baratto, di Stasio et al, 2004); nanotubes, nanowires vs. H<sub>2</sub> and ethanol (Lin et al, SAB 1995; Rout et al, 2006); nanocrystals vs. CH<sub>4</sub> (Bhattacharyya et al, 2008).

Our group synthesized some year ago Zn nanotubes and hollow nanofibers via a evaporation of metal zinc and vapour condensation in flow reactors (di Stasio, 2004). Such objects were characterized via SEM, TEM, XRD (di Stasio, 2004; di Stasio, Dal Santo, 2006). The use of such Zn nanotubes for gas sensing application was proposed by our group to the Gas Sensor Lab of University of Brescia. The experiments were performed in the climatic chamber available at the partners site. Three types of Zn powders were testes, i.e. hollow fibers, aggregates of Zn nanoparticles and commercial dust of Zn. The materials were preliminary oxidized at low temperature for 24 h (200 °C, 50% RH), thereafter the resistivity changes of Zn powders were monitored. Pre-oxidation was aimed to create a film of some nanometer of ZnO at surface of Zn powders. Different gas species were introduced in the test chamber at controlled concentrations, such as ammonia, carbon monoxide, ethanol. A volt-amperometric technique was used with constant bias (10 V) and constant humidity (50% RH) with temperature in the range 20 to 150 °C. The main results were the following. The sensor response of Zn powders was selective with respect to NO<sub>2</sub> and completely reversible. It was strongly depending on of powders microstructure (morphology and size). In particular, at 20 °C (50 % RH, 0.4 ppm NO<sub>2</sub>) the relative resistivity change of hollow nanofibers was found to be four order of magnitude larger with respect to commercial Zn and two orders of magnitude larger with respect to aggregates of nanoparticles.

Our group tried to explain such amazing results and a cooperation was made with the ISTM-CNR to perform DRIFTS experiments (di Stasio, Dal Santo 2006). Samples of Zn identical to the ones used in NO<sub>2</sub> sensing experiments were pre-oxidized following the identical procedure of the gas sensing experiments. Thereafter each sample was positioned in a cell flowing NO<sub>2</sub> mixed with Helium at a concentration of 1000 ppm. The cell was heated up from 20 to 300 °C. Temperature was hold constant for 6 minutes before each spectra data acquisition. The temperatures for recording spectra were 50, 100, 150, 200, 250, 300 °C. After cooling down in the NO<sub>2</sub>/He flow comparative spectra were recorded for each sample to compare and check invariance of species with the spectra at the start of heating.

The infrared spectra of Zn aggregates (Fig. 3) were markedly different from Zn hollow nanofibers (Fig. 4). The doublet at 1600-1628  $\text{cm}^{-1}$ , which was present in both the spectra at low temperature, was an indicator of  $\text{NO}_2$  adsorption on the sample surface. Nevertheless at increasing of temperature, while for both fibers and aggregates a progressive vanishing of the doublet was observed, to indicated progressive desorption of  $\text{NO}_2$  at higher temperature, only in the case of hollow nanofibers a peak appeared at 2500  $\text{cm}^{-1}$ . The increase of peak intensity (height) of this last was tightly correlated to the decrease of peak at 1628  $\text{cm}^{-1}$ . This fingerprint of hollow nanofibers was interpreted on the basis of a possible mechanism of  $\text{NO}_2$  polymerization at the surface of fibers. The issue is still an open challenge.

The aim of our proposal is to follow at GILDA the dynamics of adsorption of  $\text{NO}_2$  at surface of Zn nanotubes. We propose to perform experiments by REFLEXAFS in the stagnation chamber available at GILDA. The chamber should be filled of a mixture of  $\text{NO}_2$  and Helium at concentrations between 1 and 1000 ppm (for instance 1, 200, 400, 800 ppm). Our objective is to obtain information about the chemical bounds which are formed at the sample surface during exposure to  $\text{NO}_2$ /Helium mixture.

#### **Originality of proposal**

The Zn nanotubes are not available in commerce. Our group has the skill to synthesize them with certain properties (diameter, external surface) according to certain experimental parameters used in the synthesis. Apart from the sample material it seems that REFLEXAFS is the only way to observe on line the surface chemistry of  $\text{NO}_2$  absorption on the nanotube surface. From some geometrical consideration we argued that the macroscopic difference between nanotubes and other powder morphology is the external surface. We estimated the specific surface increase for nanofibers to be between 40 and 160 with respect to nanoparticle aggregates and 300 with respect to commercial Zn powders. Thus, the coordinating centers for  $\text{NO}_2$  are expected to increase in the case of nanotubes. Another interesting point is that both in the gas sensing and in the DRIFTS experiments the properties observed during exposure di ppm  $\text{NO}_2$  (electrical resistivity and absorption spectra in the two cases, respectively) turned back to the original at starting of the experiments when refluxed in pure inert gas. Therefore the surface chemistry involved seems to be reversible and strongly depending on temperature. The dynamics (time behaviour) of the REFLEXAFS measurements at increasing/decreasing of temperature could be compared to DRIFT spectra and used to explain the amazing variation of electron/hole carriers when temperature is varied from 20  $^{\circ}\text{C}$  to 150  $^{\circ}\text{C}$  (factor 100 for nanotubes, factor 10 for aggregates).

#### **Expected results from the proposed experiments**

We expect to explain the mechanism of  $\text{NO}_2$  adsorption at the surface of Zinc nanotubes vs. variation of temperature and  $\text{NO}_2$  concentration, which was not understood after DRIFTS and gas sensing experiments. These last demonstrated a huge concentration of electric carriers in excess during the  $\text{NO}_2$  ppm exposure. Another useful information that is expected after experiment at GILDA is the knowledge of location of gas adsorption sites with respect to the solid surface. Eventually the analysis at XRD of the samples may be compared to get information about the crystallite size.

#### **Experience with Synchrotron Radiation of the proponents**

In the previous experiments performed at ELETTRA at Austrian Beamline we studied the process of oxidation of zinc particles. Both particle synthesis and oxidation were obtained in the gas-flow. The study allowed to follow the competition between the effect of re-evaporation and surface oxidation which undergo the zinc nanoparticles. Also an effect of shrinking of particles during oxidation was observed.

Our group has experience at ESRF since 2004. The proponent is co-proposer of about seven proposals and about five experiments performed at ESRF on ID09b and ID02 beamlines in cooperation with a French group (PALMS-University of Rennes). One work in cooperation has been performed on carbon samples using NEXAFS at Berkeley (di Stasio, Braun, 2006). These experiments allowed to gain fundamental comprehension on the mechanism of carbon creation and clustering in flame of hydrocarbons (di Stasio et al, 2006; di Stasio, Braun, 2006; Mitchell et al, 2009; 2010).

### Peculiarity of GILDA BL useful for the proposals with respect to other BLs

The skills at GILDA beamlines are first-class. It is possible to perform REFLEXAFS in-situ in a creation chamber available at that beamline inside which the operating temperature can be adjusted during the exposure of Zinc nanotubes to  $\text{NO}_2$ .

### Other possible cooperations in the framework of the proposal

The proponent group is the Italian responsible of CNR cooperational agreement with Russian Academy of Science 2008-2010, Institute of Chemical Kinetics and Combustion. Also is the Italian partner of the project Galileo-Egide 2009-2010 for cooperation with PALMS-University of Rennes. The activities with both partners are ongoing since several years. Every possible development/project can include such partners. Also we never apply for proposal at GILDA and we feel that the cooperation with this group at ESRF should be started.

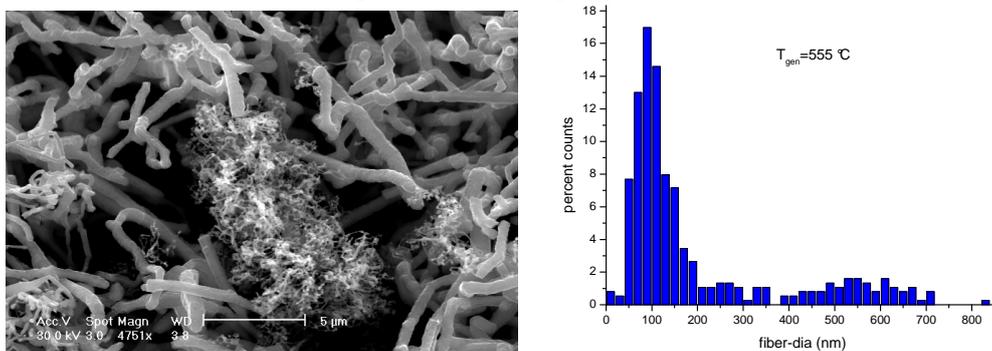


Fig. 1. Experimental fabrication of hollow Zn nanofibers (di Stasio, 2004).

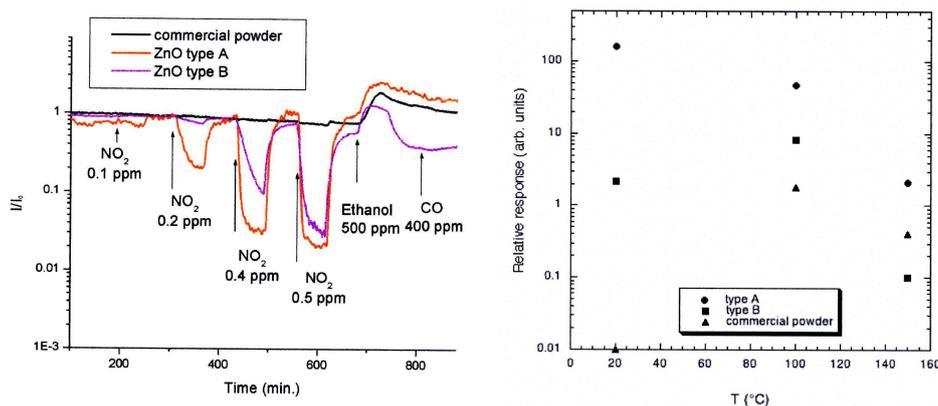


Fig. 2. Relative electric current response of differently shapes Zn powders. Circles are hollow nanofibers), square are nanoparticle aggregates and triangles is commercial dust powders (Baratto, di Stasio, et al. 2004).

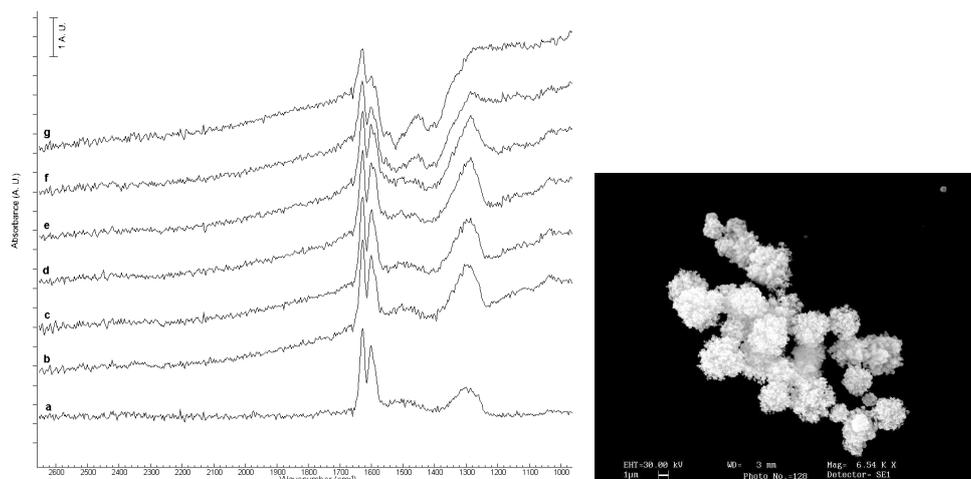


Fig. 3. DRIFTS spectra recorded for Zn nanoparticle aggregates. Details are reported in (di Stasio, Dal Santo, 2006)

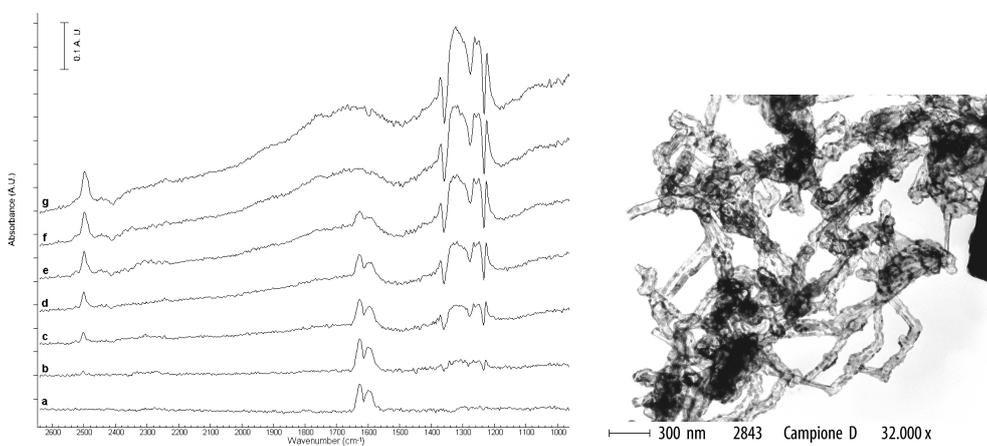


Fig. 4. DRIFTS spectra recorded for Zn hollow nanofibers. Details and SEM, XRD characterization are reported elsewhere (di Stasio, Dal Santo, 2006).

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## **In situ time-resolved XAFS analysis of silver nanoparticle formation by chemical reduction in polymer solution**

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### *1. Background and general project description*

Nanostructured materials are today intensively investigated because of novel properties that matter exhibits when a dimension is in the nanometric scale. In this context, metal nanoparticles, mainly because of their outstanding optical and magnetic properties, are high-ranked and the capacity to produce and manipulate them in a controlled way is of relevance in the field of functional advanced materials.

In order to avoid particle aggregation and oxidation, organic polymers are often used to protect/cover the particle surface. Moreover, their optical properties, due to the proximity with the metal surface, may be enhanced (due to the so-called Surface Enhanced Raman Scattering-, Surface Enhanced Fluorescent Scattering- Effect, etc...) Hybrid organic-inorganic nanocomposites, find application in magneto-optical and electro-optical devices, solar cells, bio-labels, etc. For these reasons, an understanding of the mechanism of formation and growth of metal nanoparticles covered with organic polymers is an important challenge both in fundamental and applied research [1-7].

Recently, we have studied a preparation method for polymer covered silver particles, based on the reduction in water of  $\text{Ag}^+$  ions with ascorbic acid in the presence of a low concentration of a commercial naphthalene sulfonate polymer (Daxad 19). We were able to control the particle morphology by simply varying the reaction temperature in the range 5°-60°C. With a 0.54% w/w polymer concentration, we have obtained polycrystalline silver rods, platelets and single crystal particles at 5°, 10° and 40°C respectively [8].

With the aim to explore the role of the polymer in the formation of the different structures, Dynamic Light Scattering (DLS) and Small Angle X-ray Scattering (SAXS) investigations have been performed [9]. In particular, using time resolved SAXS technique, we have monitored the first stage of the formation of crystalline colloidal  $\text{Ag}^0$  particles obtained by  $\text{AgNO}_3$  reduction with ascorbic acid in an aqueous acidic solution of a Daxad 19. The reduction was induced and controlled by the slow addition of ascorbic acid at a fixed rate, thanks to the experimental setup illustrated in Fig.1; in this way, we were able to monitor the first stage of formation of colloidal silver crystals occurring with a characteristic time of about 200 seconds [10].

We have observed the nucleation and growth of primary nanoparticles, assisted, when the reaction temperature is 40°C, by the development of long range spatial correlations as the reduction process goes on. This correlation can be associated with coherent fluctuations of the electron density around a critical point. They are attributed to the aggregation of the primary nanoparticles driven by the Ag-polymer interactions. These interactions provide a “dynamic template”, characterized by the transformation from mass fractals to surface fractals, on which the silver-polymer nano-composites form, following, thus, a two step aggregation process [10]. Further on, *in situ* time resolved studies are in progress to investigate if the correlation lengths and primary particle size are dependent on the polymer concentration in the solution and on the temperature reaction.

In Fig 1 is shown a typical experimental setup for X-ray dynamic scattering. The reduction process takes place in the beaker where a solution of the reducer (ascorbic acid), at a controlled rate, is added with a motorized syringe to the precursors (aqueous solution of  $\text{AgNO}_3$  + Daxad). The

solution, with the aid of a peristaltic pump, is then transferred under the beam focus. After the reduction, the nucleation and growth of silver particles covered with the polymer occurs. The experimental study of these processes on the atomic scale would lead to a deeper knowledge of the particle formation mechanism.

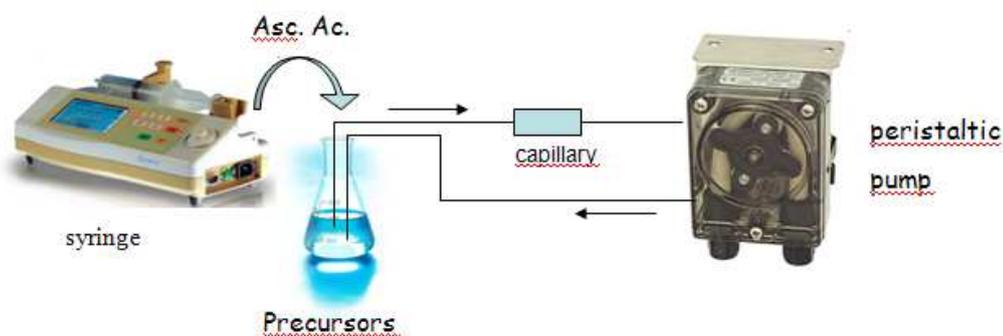


Figure 1: Experimental set up for time resolved in situ measurements

The absorption X spectroscopy (XAS), is the structural investigation technique best suited to characterize the reduction process through the study of the valence state of silver and its local structure; on the other hand, the diffraction gives the opportunity to correlate the processes on the atomic scale to their evolution in the nanometric scale, studied with SAXS.

Thanks to the instrumentation present by the GILDA beamline at ESRF, it would be possible, by using the XAS and XRD techniques, to monitor the steps before the particle nucleation and growth ( i.e. the  $\text{Ag}^+$  ions reduction and  $\text{Ag}^0$  aggregation to form Ag clusters). The simultaneous XAS and XRD analyses represent an approach with great potentialities in the study of the chemical physics principles governing the transition from the solution to the solid state.

## 2. Novelty Points

Long range spatial correlations characterize a wide variety of physical systems [11]; the understanding of these correlations represents a challenge in theoretical physics in last decades and although simple models as for example diffusion limited aggregation [12], self-organizing criticality [13], work well in the description of several phenomena, new and more complex insights enrich this field of research. In our case study, the correlations arise from local polymer- $\text{Ag}^+$  interactions that originate the nodes of a dynamic matrix. This can be considered an unusual feature in the *templating* synthesis method, and time resolved XAS, could be a powerful tool to understand how local events, such as polymer- $\text{Ag}^+$  interactions, can drive and determine events on larger scale length.

## 3. Results expected

The hybrid organic-inorganic system that we want investigate with in situ and time resolved XAS and XRD techniques at GILDA would constitute a model system well suited to get important new insights as regards the organization of matter from solution to the solid state. In particular we expect to investigate the following points:

- i) the reduction of  $\text{M}^+$  ions ( $\text{M} = \text{metal}$ ),
- ii) the aggregation of  $\text{M}$  atoms

- iii) the nucleation of M clusters
- iv) the growth to crystalline metal/polymer well defined structures and last but not least the role that the polymer plays in each process.

In a previous SAXS study we have observed, during the reduction process at 40°C, a relevant development of long range fractal correlations that drive the ordered aggregation of primary particles (clusters) to form the final particles [10]. In this aggregation process the polymer, coordinated through its sulphonic groups to Ag, is other than a dispersant agent to avoid particle aggregation, an ordinating agent. In order to clarify this point, we plan to follow the Ag<sup>+</sup> reduction process by in situ, time resolved EXAFS measurements at different polymer concentrations at 40°C. We expect to monitor the aggregation process through the polymer concentration. At the same time we can follow, through in situ time resolved XRD measurements the nucleation and growth of 200nm crystalline Ag particles.

Analogously, we plan to study the systems at 5° and 10°C where other hybrid Ag/polymer micrometer sized structures (i.e. rods and platelets) have been observed [8].

To conclude, by studying this model system, we should gain information on the interplay between inorganic and organic matter in the formation of well defined crystalline structures and be able then to design and tailor the size and shape of the hybrid nanomaterials to optimize their properties for application.

#### 4. Description of the group expertise

The group has experience in the chemical preparation of nanocomposites and in their chemico-physical characterization.

**Gaetano Campi** is a PhD physicist with experience in the X-ray and neutron diffraction techniques. He is the author of 3 proposals, all approved, at Elettra by the Austrian SAXS beamline, dealing with the study of nucleation and growth of polymer-assisted silver structures. Since 2004, Dr. Campi and Dr. Suber collaborate on the study of the formation mechanism of silver nanoparticles.

**Patrizia Imperatori** is a chemist with experience in single crystal, powder and thin film x ray diffraction using conventional and grazing incidence techniques. Surface diffraction on clean reconstructed surfaces and metal overlayers deposited on semiconductors, using synchrotron radiation. Structure determination from single crystal, powder and surface data by *ab-initio* methods and structural refinements by Rietveld method.

**Alessandra Mari** is a chemist, PhD student, with experience in organic synthesis and metal particle synthesis.

**Lorenza Suber** is a PhD chemist with almost 20 years experience in the chemical synthesis and characterization of metal and metal oxide nanoparticles and nanocomposites. She has received in 2002 a one year NSF grant (DMR 010244) as Research Scholar by Clarkson University, Potsdam (USA) on the synthesis of functionalized Ag particles as bio-labels. During her stage, she has met Prof. Privman working on numerical investigations of nucleation and diffusive growth of metal nanoparticles. She is author of 50 JCR articles and recently she has co-authored the book chapter: Approaches to Synthesis and Characterization of Spherical and Anisometric Metal Oxide Magnetic Nanomaterials in Magnetic Nanomaterials, Ed. Challa Kumar, Wiley-VCH 2009.

#### 5. Instrumentation necessary at GILDA to realize the project

The low-cost, portable instrumentation necessary at GILDA to perform the in situ, time resolved experiments is reproduced in Figure 1.

## 6. Collaborations

We have a long standing collaboration with Dr Heinz Amenitsch by the Elettra Austrian Synchrotron Beamline on the SAXS study of polymer-assisted silver structure formation mechanism. The XAS spectroscopy at GILDA is essential in order to study the first stages of the silver structure formation. It allows to investigate the  $\text{Ag}^+$  ions reduction process ( $\text{Ag}^+ + 1 e \leftrightarrow \text{Ag}^0$ ) and then the aggregation of Ag atoms to form Ag clusters.

Finally, in order to complete our investigation on the particle formation mechanism, we plan to ask the collaboration of the Privman's group, well-known expert in this field [14], for a theoretical modeling based on the experimental results obtained.

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Study of the photoluminescence emitting centers and energy transfer effects  
in metal and rare-earth co-doped dielectrics for nanophotonics

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CNR-IFN and Dept. of Physics Università di Trento (Francesco Rocca)  
Università di Padova (Giovanni Mattei)  
Università Ca' Foscari di Venezia (Enrico Trave)

*Background and proposed activity*

The scientific focus of the present project is on the investigation of the fundamental physical processes controlling the emission of rare earth (RE) ions,  $\text{Er}^{3+}$  in particular, embedded in dielectrics. Er-doped glasses played a role of paramount importance in the development of optical telecommunication technology during the last two decades, since the characteristic 1.54  $\mu\text{m}$  emission matches the window of minimum loss in silica-based optical fibers [1,2]. However, one of the main drawbacks of Er-doped dielectric matrices is represented by the typical low gain per unit length: the small cross section values, around  $10^{21}\div 10^{20}$   $\text{cm}^2$  [3], require Er concentrations up to  $10^{20}\div 10^{21}$   $\text{cm}^{-3}$ , well beyond its solubility limit in most of the silicate host matrices. For Er-doped silica, a recently suggested way to overcome the modest Er excitation cross section is the metal co-doping with species like Ag or Au as nanoparticles (NPs), which promote a "sensitization" or energy transfer process with a consequent increase of the Er photoemission. In particular, sub-nanometric metal NP (Ag or Au) can act as nanoantennas producing a non-resonant energy transfer process to the RE [4,5,6,7], and this process is particularly interesting since it involves a broad-band excitation of the RE. Among the factors controlling the RE emission in this composite system, both the RE site in the matrix and the cluster size (if in the sub-nanometer range) are expected to play a major role. In this framework, the XAS spectroscopy is of primary interest and has already demonstrated to be the elective tool to relate the structure at the atomic scale with the RE emission in different materials [8, 9,10,11 and Refs. therein].

In this general framework we propose to experimentally investigate the energy transfer phenomenon and the Er PL emission, with the final aim to find out new strategies to optimize the RE emission efficiency, by a series of experiments based on the x-ray absorption spectroscopy; we will focus our analysis on glasses (mainly silica-based) and crystalline alumina, doped with Er and with transition metal ions by different techniques (ion implantation, sol-gel, sputtering, ion exchange).

This project will be developed in the following steps.

i) First, to relate the Er photoluminescence to the system structure and in particular to the Er site a series of XAS experiments of Er in different glasses will be performed. In this case, the use of ion irradiation and subsequent annealing, being capable to modify the Er site [12] is expected to shed light on the relation between the Er site and its photoluminescence emission. The experiments performed in the past showed that this relation exists; nevertheless, the role of the optical inactive Er centers has now to be considered; the experimental technique that could solve this point, if any, is the x-ray absorption optical luminescence (XEOL) [13,14,15]. For this reason, an important aspect will be to study of the feasibility of XEOL experiments on rare-earth doped materials. The experimental apparatus that we will realize for this purpose will be functional in a standard synchrotron radiation beamline equipped for x-ray absorption experiments. It will allow measuring the photoluminescence response in the infrared and visible region upon excitation in the x-ray range. These results will contribute to assess the potential and limits of the XEOL technique, that are still far from being understood, and in particular for this class of materials [13]. In the best case, the XEOL signal will carry all the information on the local site of just the active Er ions: if so, the XEOL analysis will give directly the information on the Er luminescent centers, so providing a major achievement to relate the details of the Er site with the Er photoluminescence efficiency.

ii) As a second step, the role of the metal aggregate as sensitizers for the Er ions will be addressed. We will focus on the investigation of the very early stage of the metal nucleation, i.e. few-atoms clusters. The XAS is an elective tool to investigate the structure of few-atoms aggregates. To this respect, we also plan to investigate how the white beam x-ray irradiation can be used to control the nucleation

process. Despite the potential multiple interests in this field (because few atoms clusters are efficient sensitizers for Er [16] and because the heterogeneous nucleation phenomenon is at present still quite unclear), few papers exist on the subject [17 and Refs. therein]. We will place a suitable chamber hosting a sample holder in the white beam section of the beamline, to irradiate metal-doped glasses in order to induce the precipitation via a non-thermal process driven by the defects produced into the matrix. Finally, the optical properties (infra-red and visible emission) of the few-atoms aggregates are still a matter of debate: we intend to use the XEOL technique in this range of emission wavelengths to understand the structure responsible of these bands.

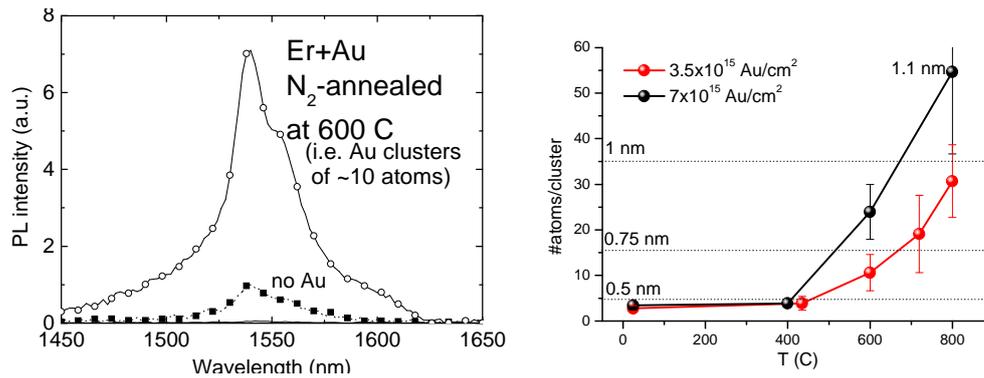
#### *Novelty and expected results*

This project has different aspects of novelty; the most ambitious is the implementation of a XEOL apparatus for the rare-earth emission in the infrared, that will allow assessing the potential and limits of this technique for this class of materials, that is far from being understood. Moreover, while the nanoclusters investigation by the XAS spectroscopy has been deeply explored, not so much has been done on the very early stages of the heterogeneous nucleation process of a metal in a matrix. This point is relevant for the project because it will allow understanding how to optimize the energy transfer process between the sub-nanometric aggregate and the rare-earth ions. On the other hand, it will allow quantifying the heterogeneous nucleation process, that is not easy to predict theoretically. Moreover, the infrared-visible emission of sub-nanometric aggregates is far from being understood and the XEOL could be the elective tool to relate them to the specific cluster structure. The implementation of a chamber to host the samples in the white-beam section of the beamline will allow to investigate how the white x-ray radiation damage can be used to control the cluster nucleation. At present few papers on metal-doped glasses have shown that large clusters can be obtained by a combined employ of x-ray irradiation and annealing, but the nucleation phenomena that are at the basis of this result are far from being understood.

The realization of a XEOL apparatus working in the infrared-visible region would be very interesting also for a wide class of different luminescent systems, as for example the ZnO-based ones, where preliminary tests showed promising results [18].

#### *Investigators' capabilities, experience and previous results*

The research unit at the CNR-TASC working on the GILDA beamline (Grenoble-F) has considerable and thorough experience in the field of synchrotron radiation techniques and all the expertise necessary to successfully plan and perform x-ray based experiments. Its skills covers not only the experimental part but also the data processing for x-ray absorption spectroscopy and x-ray scattering experiments; most part of the research performed up to now is about the clustering process of dopant species in dielectrics and on the effect of the local structure at sub-nanometer level on the macroscopic properties of materials (see Refs. [12,16,19,20,21,22] as an example of recent literature). As an example, in the figure it is reported an example of the PL results on Er+Au doped silica and the corresponding structural results from a first EXAFS experiment. The research unit has a daily access to the GILDA facility that is mandatory to implement new apparatuses onto the existing instrumentation; moreover, it has access to the in-house research beamtime of the proposer that can be partially employed to test the operation of new equipments.



Left panel: the presence of 10-atoms Au clusters in a Er-doped silica greatly enhances the Er 1.5  $\mu\text{m}$  PL emission. Right panel: Au cluster size as a function of the annealing temperature in a Er+Au implanted silica, as from EXAFS spectroscopy.

The research unit at Trento has been working on XEOL in the visible range since many years, especially on quantum-confined luminescent silicon nanostructures (porous Silicon, nc-Si in silica) and semiconductors. They have developed special equipment and electronics for XEOL experiments at synchrotron radiation facilities, mainly in the visible range. The most recent example of application of XEOL to XAFS is on luminescent nanostructures based on ZnO, that were measured either by collecting the light with a lens in standard configuration either through a SNOM apparatus, thus allowing to detect the XEOL with sub-micrometric spatial resolution [23]. The group of Trento is also participating to the GILDA Beamline, and is currently active in studying the optimization of photonic properties in glasses and glass-ceramics, thus joining specific competences with the other units.

The research unit at the Università di Padova has a consolidated experience in the field of composite glasses in particular for optoelectronic applications: it covers both advanced synthesis processes (ion implantation/irradiation, annealing in selected atmosphere) and state-of-the art characterization techniques (Rutherford backscattering spectrometry, x-ray diffraction, transmission electron microscopy, optical absorption and photoluminescence). The consolidated collaboration with people of the research unit of CNR-TASC of the GILDA beamline has widely demonstrated the success of synchrotron radiation-based techniques on composite glasses for optoelectronics [19,24,25 and Refs. therein].

The research unit at the Università Ca' Foscari di Venezia has a strong experience on doped glasses [26, 27, 28, 29]; its expertise include both the synthesis of doped-glass dielectrics by deposition via magnetron co-sputtering and by metal-for-alkali ion exchange (possibly drive by an electric field) and the optical characterization.

#### *Specific experimental aspects*

Besides the needed XAS experiments for the investigated diluted systems that will be performed in conditions that are standards for the GILDA beamline (but generally not found elsewhere), we plan to test and use a XEOL apparatus in the visible-infra-red range. The existing apparatus of the Trento Unit transfers the collected light to a dispersive spectrometer through an optical fiber. A CCD detector allows to monitor continuously the changes of the XEOL bands as a function of the energy of the exciting X-ray beam. Different geometries can be selected for the collection of the light inside the vacuum chamber. Imaging is also possible, using a PMT as detector. For the IR range, only a single detector is available, thus this part will need a dedicated financement. Also possible developments of time-resolved experiments will require new detectors and electronics. The apparatus will allow measuring the XEOL signal together with the x-ray fluorescence one and will be specifically designed to be used on thin films. Due to sample dilution, a special care will be devoted to identify the best geometry to maximize the signal collection; the use of cylindrical lenses and specific sample orientation (by means of a suitable goniometer) are expected to be crucial to optimize the signal to noise ratio. The use of a suitable sample cooling systems will be also considered.

Moreover, a chamber for the white beam x-ray irradiation, equipped with a 1-axis sample holder, working at room temperature, will be placed in the white-beam section of the beamline.

#### *Possible collaborations*

The experiments proposed in this project could be complemented with others on different ESRF synchrotron radiation beamlines. In particular, XANES experiments in a beamline equipped with a high resolution x-ray fluorescence spectrometer could help to identify the oxidation state of the metal atoms in the dielectric matrices.

#### *Outlook*

The investigation of the potential and limits of the x-ray excited optical luminescence in the infrared and visible region is likely of great potential interest for different research groups working on light emitters. The possibility of white-beam irradiation is also of interest not only for this project, where it will be used as tool to control the metal nucleation, but also for the investigation of the radiation damage effects on different materials, from soft to hard matter.

The scientific purpose of the project, i.e. to understand the fundamental physical processes controlling the emission of rare earth ions embedded in dielectrics, will allow to find new strategies to increase the Er PL emission efficiency.

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5.2.8. *Fundamental Physics.*

*Installation of a Paris-Edinburgh press at GILDA beamline:  
new opportunities for XAS studies under extreme pressure and temperature*

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The aim of the present proposal is to enlarge the experimental capabilities of the Italian CRG beamline GILDA at the ESRF through the installation of a large volume apparatus such as the Paris-Edinburgh press for x-ray absorption spectroscopy (XAS) experiments at high pressure and high temperature.

Of the three thermodynamic variables temperature, pressure and magnetic field, pressure has been by far the less utilized. Recent advances in the notably difficult technology of high pressure devices (diamond anvil cells and large volume presses) now permit quantitative studies of matter up to Megabar pressures over a wide range of temperature using a large variety of different experimental techniques.

Pressure is a variable of great fundamental importance in basic science. Applying high pressure to condensed matter is the best way to modify the relative separation and/or the arrangement of constituents atoms and consequently the degree of orbital overlap. This allows experimental verification of the theoretical models used to describe the structure and the bulk properties of matter, i.e. whether the substance is a metal, an insulator, a superconductor or a ferromagnet.

In the field of geosciences, high pressure has necessarily to be coupled with high temperature to identify the materials constituting the Earth interiors not directly available for sampling and to determine their properties, i.e. structure, abundance of chemical elements, melting temperature or sound speed governing global planetary processes such as heat flow, mantle convection regime and plate tectonics [1]. High pressure experiments are also increasingly employed in material science. Under pressure the reactivity is altered with changes of the electronic structure and bonding character for the synthesis and design of novel materials not available by other means, including pure superhard materials, liquid and glassy polymorphs [2, 3].

If diffraction methods are still the predominant HP techniques for structural studies involving synchrotron radiation, X-ray absorption spectroscopy (XAS, including EXAFS, XANES and XMCD) offers a complementary description of matter under pressure: on one side it gives a local picture since it probes, with chemical selectivity, the local environment around the photoabsorber atom; on the other side it is sensitive to pressure-induced electronic transitions since it probes the electronic density of states above the Fermi level.

For example, in the field of physics of liquids and glasses, high pressure and high-temperature XAS experiments are largely demanded for elucidating the question of the occurrence of polyamorphic transitions [4]. While solids are known to transform between polymorphs having different structure and physical properties in response to pressure and temperature, the occurrence of analogous density-driven phase transitions between amorphous or liquid structures of the same chemical composition is still the subject of intense debate. Theoretical models and simulations have shown that liquid-liquid phase transitions are possible and most likely to occur in the undercooled liquid regime for some elements or compounds observed to have *unusual* negative slopes (Ge, Si, Ga, Bi, H<sub>2</sub>O) or one or several maxima (Cs, Rb, Se, Te) of their melting curve at high pressure.

From the experimental side, however, support for the existence of these transformations is still rare. In order to investigate experimentally the occurrence and the nature of pressure induced structural changes in liquids and glasses, and hence provide insights into the accompanying changes in the physical properties such as resistivity or specific heat, it is necessary to conduct *in-situ* high pressure experiments. XAS spectroscopy provides an important element-specific determination of

the short-range features of the partial radial distribution functions complementary to the information provided by neutron and x-ray scattering experiments.

The aim of the present proposal is to kick off high pressure studies using x-ray absorption spectroscopy at beamline GILDA. Due to spot size limitations, diamond anvil cells cannot be used at energy scanning XAS beamlines. Nonetheless, large volume pressure cells where the sample size is of the order of mm can be successfully implemented.

Here we propose to install a large volume Paris Edinburgh press based on a previous design adapted to XRD and XAS experiments, featuring special anvils with a tungsten carbide (WC) inset [5] to reach pressures up to 12 GPa. In order to reach higher pressure up to 18 GPa, polycrystalline diamond inset anvils have also been developed. A sintered boron gasket hosting the sample cylinder is placed in the middle of the two anvils. The sample cylinder is surrounded by a graphite tube which acts as a heater when high current is passed through the anvils. Using this technique it is possible to reach pressures of 18 GPa and temperatures of 2000 K using currents of 200 A.

For pressure measurements, the diffraction pattern of the sample and/or one or several pressure marker has to be measured and the P-T conditions inferred from the corresponding equation of states. The temperature readout is performed by an insulated thermocouple placed in the sample gasket.

Although the attainable pressures are typically of one order of magnitude lower than those achievable with diamond anvil cells, XAS spectroscopy using large volume devices may offer actual advantages respect to high pressure XAS using diamond anvil cells at energy dispersive beamlines [6]. The sample is bigger and the collected data are not limited in the energy range by the occurrence of diffraction peaks from the sample environment (diamond anvils). Therefore, data are of generally higher quality respect to those collected using diamond anvil cells, and quantitative information on the structure around the photoabsorber above the first shell of neighbours, such as the local geometry of the materials under investigation can be obtained with higher accuracy through advanced data analysis methods including multiple scattering effects.

This proposal has a clear instrumental character in order enlarge the experimental capabilities of GILDA beamline in the area of science at extreme conditions (one the main highlight areas of the ESRF upgrade program). The success of such a project will be beneficial for a large user community using X-ray absorption spectroscopy for science at extreme conditions.

Following the research interests of the proposers in the field of liquids and glasses, as a case study, we propose to investigate vitreous Germania, or  $\text{GeO}_2$ , an archetypal 'strong' network glass forming system which shares with silica several structural characteristics. The discovery of a pressure-driven structural transition between 6 and 8 GPa from a network of corner sharing tetrahedra (4-fold coordinated Ge) to a dense octahedral material (6-fold coordinated Ge) of the same chemical composition ("polyamorphism") [7] has enhanced interest on the high pressure behaviour of this amorphous compound. The details of the local structure changes still require clarification, and the mechanism of the transition - whether it is a continuous process with an intermediate state or a collapse into sixfold Ge-O coordination - is still a matter of intense debate [8,9,10]. In one of these recent studies [8], the local structural changes in amorphous and crystalline  $\text{GeO}_2$  up to 13 GPa have been investigated using XAS and a Paris-Edinburgh press and the evolution of the first shell Ge-O distance with pressure has been obtained from the analysis of new high quality and accurate EXAFS data collected at the ESRF energy scanning beamline BM29. Thanks to this work, we will have the opportunity to compare our data with the state-of-the art high pressure EXAFS using a Paris Edinburgh press and hopefully go beyond the results reported on previous studies. Indeed, the question of the pressure-driven changes of the intermediate range order linked with the evolution of the intertetrahedral Ge-O-Ge bond angle and of the Ge-Ge second shell distance has not been addressed on [8].

The lower energy operation limit of XAS experiment with Paris-Edinburgh presses is given by the boron gasket absorption. The availability of both horizontal (h-FWHM 1 mm) and vertical (v-FWHM 100  $\mu\text{m}$ ) focusing at GILDA beamline is expected to extend the energy range down to the Fe K-edge, with promising perspectives to cover all the K-edges of 3d transition metals (Fe, Co, Ni). This achievement will open novel possibilities for experiments, relevant to geophysics and magnetism not possible at the moment at other beamlines equipped with large volume devices.

Above 15 keV, the spectral quality is no longer limited by gasket absorption and this is the most promising energy range for operation. Such a energy range is largely uncovered by XAS experiments with diamond anvil cells because the density in energy space of Bragg diffraction peaks from the diamonds becomes too high, and the use of the DAC becomes prohibitive.

Although XAS experiments with PE presses are normally performed in transmission mode, the high flux ( $10^{10}$ - $10^{11}$  photons/s) achievable at GILDA with both horizontal and vertical focusing and the availability of a 13-elements high purity Ge detector should allow also for fluorescence detection through the gasket for the study of diluted systems at high pressures and temperatures.

The possibility of studying diluted compounds under pressure would open a broad field of scientific domains. Between the most relevant are the study of diluted elements in geophysical compounds, ions in aqueous solutions or metal sites, changes in the environment of metal sites in proteins.

The installation of the press and the first experiments on vitreous  $\text{GeO}_2$  will be done by the beamline staff in collaboration with researchers based at the University of Camerino (A. Di Cicco, M. Minicucci and E. Principi) and at the University of Trento (A. Fontana, L. Orsingher).

The main proposer and the XAS group at the University of Camerino have been carrying out a longstanding research program at synchrotron radiation facilities (ESRF, SOLEIL) focused on the investigation of the structure of liquids and glasses under a variety of thermodynamic conditions ranging from low to very high temperatures and pressures. In particular the local structure of the stable and deeply undercooled liquid phase, nucleation processes and occurrence of liquid-liquid phase transitions of several metals and semiconductors (Ga, Bi, Sn, Ge) have been investigated using XAS at high pressure [11]. A research program aimed at the structural investigation of amorphous semiconductors (a-Ge, a- $\text{Si}_x\text{Ge}_{1-x}$  alloys) and archetypal strong glasses under extreme pressure has been recently funded within the framework of an Italian PRIN project. The past research activity of the main proposer and of the Camerino group has also included the development of instrumentation for combined XAS and XRD experiments under extreme thermodynamic conditions at the BM29 experimental station of the ESRF [12].

The research activity of the group based at the University of Trento is focused on the investigation of the vibrational dynamics of disordered systems. Recently, particular attention has been devoted to the investigation of the vibrational density of states and the elastic properties of permanently densified glasses (including archetypal strong glasses such as vitreous  $\text{SiO}_2$  and  $\text{GeO}_2$ ) by using optical (Raman and Brillouin), x-rays and neutron spectroscopies [13]. The structural characterization of permanently densified glasses by EXAFS at GILDA beamline to elucidate the correlations between local structural changes and dynamical properties is also part of the recent research program of this unit.

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## EXAFS studies of the local dynamical properties of solids

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In the last years, a significant progress has been made in understanding the effects of thermal disorder on EXAFS spectra. The interest is twofold. On the one hand, the very meaning of the quantities measured by EXAFS is now better understood and their accuracy is increased; in particular, the difference between inter-atomic distances and corresponding thermal expansions measured by EXAFS and by Bragg diffraction has been recognized and experimentally detected [1], and the non-negligible effects of the distribution asymmetry are routinely taken into account by the cumulant approach [2]. On the other hand, new information on the local lattice dynamics has been made available; for example, the perpendicular mean square relative displacement (MSRD) can now be evaluated, giving original insights on the correlation and on the anisotropy of relative vibrations [3]. The most relevant applications have been the detection of the isotopic effect on the parallel MSRD and on the bond thermal expansion of germanium [4], as well as the systematic study of the local mechanisms of negative thermal expansion (NTE) in crystals [5].

These recent achievements open new perspectives for a wealth of investigations on physical properties of materials connected to local lattice dynamical effects.

1) *Coefficient of bond thermal expansion.* The recent investigations performed on model compounds such as copper [3] and germanium [1,4] have demonstrated the ability of EXAFS to measure the thermal expansion of the nearest-neighbors (NN) bond, which is intrinsically different from the lattice expansion measured by Bragg diffraction. The NN bond expansion has been found always positive in all the systems explored up to now, including crystals affected by strong negative thermal expansion (Fig. 1) [5]. As a consequence, it has been suggested that EXAFS experiments allows us to directly monitor and disentangle the two conflicting contributions to the overall lattice thermal expansion (such as measured by Bragg diffraction): the positive bond-stretching contribution, measured by the first EXAFS cumulant, and the negative contribution due to tension effects, measured by the perpendicular MSRD.

As a natural development of these recent achievements, it is now reasonable to seek a quantitative evaluation of the *bond* thermal expansion coefficient, comparable in accuracy to the *lattice* thermal expansion coefficient that is currently obtained from dilatometry or diffraction patterns. To this purpose, it is necessary to perform a very high number of short-spaced temperature dependent EXAFS measurements, extending down to the lowest possible temperature, in order to allow an accurate polynomial fit to the temperature dependence of inter-atomic distance, giving rise to a meaningful first-order derivative. From the experimental point of view, this research program requires to exploit the ultimate limits of resolution and accuracy in distance determination achievable by EXAFS, and possibly to obtain sample temperatures lower than those available from liquid Helium cryostats.

The coefficient of bond thermal expansion, once evaluated with sufficient accuracy, could be interpreted within the framework of the Grueneisen theory, giving new insights on the origin of negative thermal expansion, and more generally on the relations between local and average thermal properties.

2) *Very low temperatures.* The possibility of achieving lower sample temperatures than the liquid He temperature is relevant not only for the investigations on bond thermal expansion and negative thermal expansion. The availability of a He<sub>3</sub> cryostat could open new perspectives for the study of relevant low-temperature phenomena, such as structural and/or magnetic phase transitions, whose understanding could benefit from the information available from a local probe such as EXAFS.

3) *Moderate pressures.* A strong interest has been developed in the last years for high pressure studies; the use of anvil cells and energy dispersive detection modes is necessary to achieve very high pressures; the accuracy of EXAFS spectra measured in such conditions cannot however compete with the accuracy of experiments performed by using standard step-by-step monochromatized beams. On the other hand, high accuracy pressure-dependent EXAFS investigations on model compounds are necessary to calibrate the technique and to test theoretical predictions, similarly to the work done in recent years as a function of temperature. To stress the relevance of the problem, one can notice that no direct evaluation of the pressure dependence of the NN bond distance is still available for a model system such as copper. This kind of calibration work could be performed by means of a standard transmission apparatus and of a Paris-Edinburgh cell in a range of moderate pressures (below say 6 GPa).

4) *Isotopic effects.* The recent measurements performed on the two isotopes 70 and 76 of germanium have stressed the peculiar ability of EXAFS to measure directly and quite easily the primary isotopic effect, say the different amplitude of atomic vibrations at low temperatures, in the quantum regime. It has to be stressed that the direct measurement of the isotopic effect on atomic vibrations has never been attempted by X-ray diffraction (the accurate measurement of the X-ray diffraction Debye-Waller factor is still more difficult than the measurement of the EXAFS Debye-Waller factor). Besides, the isotopic differences in the MSD measured by EXAFS are directly connected to the isotopic effect in the bond thermal expansion, which have been detected too. These findings open new possibilities for the further studies of the isotopic effects in different systems. This research is proposed in cooperation with researchers from Latvia (J. Purans et al.) and from the Russian Federation (S. I. Tiutiunnikov et al.)

The achievements of the goals depicted in the previous list of topics is expected to lead also to a progress in the understanding of fundamental EXAFS and in exploring the ultimate limits of accuracy of experiments and data analyses, with the non secondary effect of contributing to enhance the overall reliability and credibility of EXAFS results. Here is a list of open problems.

a) First-shell contributions: the increase of the signal to noise ratio, and the corresponding extension of the useful k range, is particularly important in the case of light scatterers, such as oxygen, and would contribute to a better characterization of the local structure and dynamics in various systems, such as NTE oxides (e.g. Cu<sub>2</sub>O) or superconductor materials.

b) Beyond the first shell: the superposition of the contributions of several single and multiple scattering paths has prevented, up to now, the accurate characterization of the single-shell distance distributions, in terms of thermal expansion and third cumulants; an increased experimental accuracy could help in obtaining more refined results and/or in a more effective test of theoretical simulations of EXAFS signals.

c) Some controversial issues still exist concerning the interpretation of EXAFS results, such as the relations between thermal expansion and third cumulant for the different coordination shells or the meaning and usefulness of the effective pair potential and its connection to the bare pair potential on the one hand and to the crystal potential on the other. Different theoretical approaches are giving interesting hints, which demand accurate experimental verifications.

d) Structural analyses based on the PDF from neutron or X-ray total scattering are becoming more and more frequent, and total scattering is sometimes considered to represent a challenging alternative to EXAFS. A thorough assessment of the relative merits of the two techniques and of their degree of complementarity would greatly benefit from very accurate measurements on selected model compounds and on systems of scientific interest.

The quality of the results achieved up to now is strictly related to the overall performance of the synchrotron radiation beam-line, in terms of mechanical and electronic stability, repeatability and reliability. As a matter of fact, while distance variations of the order of  $10^{-3}$  Å can be routinely measured, in some positive cases the resolution has been reduced to  $10^{-4}$  Å, while in some other cases the error bars were larger than the distance variations to be measured.

The realization of the different parts of the proposed research program requires the availability of a beam-line specifically designed to achieve the highest levels of mechanical and electronic performance for XAFS spectroscopy in transmission.

The group of proposers is working on XAFS with synchrotron radiation since the first Eighties, and participated to the design and realization of experimental apparatuses in Frascati (PWA) and Grenoble (BM08-Gilda). It has enough experience and know-how to effectively participate to the design and realization of specifically tailored instrumentation, such as control and detection systems and very-low temperature cryostats.

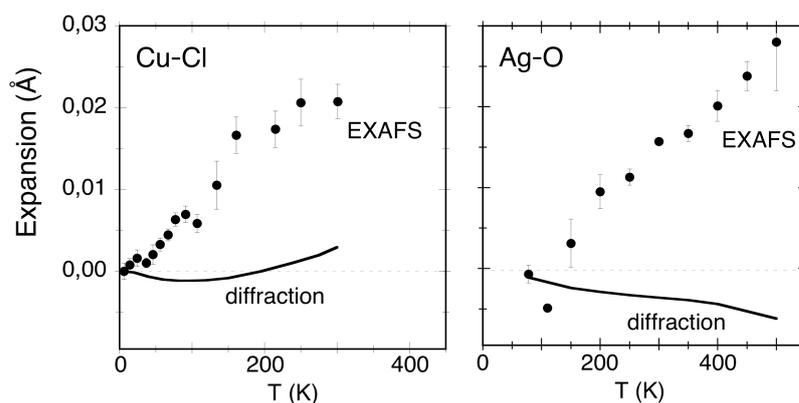


Fig. 1 - Temperature dependence of the nearest-neighbours interatomic distance measured by EXAFS (bond thermal expansion) and by Bragg diffraction (proportional to the lattice thermal expansion) in two NTE crystals, CuCl and Ag<sub>2</sub>O [5].

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