UPGRADE PROGRAMME – PHASE I

UPBL CONCEPTUAL DESIGN REPORT

UPBL11: Time resolved and extreme conditions X-ray absorption spectroscopy

Current designated sector:	Facility goes to:
ID24/BM29	ID24/BM23

1.1 SUMMARY

Since the development of Energy Dispersive X-ray Absorption Spectroscopy (EDXAS) at synchrotron sources, no other synchrotron in the world has so heavily invested in high-brilliance EDXAS as the ESRF. Beamline ID24 is presently recognised worldwide as being capable of reaching limits of pressure-temperature space that have been up to recently out of reach for XAS. In parallel, it has become a reference instrument for time-resolved structure-function studies on functional materials. These two classes of experiments are very challenging, and fully exploit the high brilliance and stability of this ESRF beamline.

The proposed Upgrade project will overcome fundamental limitations of ID24 and provide a unique beamline worldwide for EDXAS in terms of spot size, time resolution and energy range, allowing the ESRF to preserve this leading role. The two independent branches of UPBL11 (EDXAS_S "small spot" and EDXAS_L "large spot") combined with the standard EXAFS bending magnet station will provide a unique platform to perform experiments that remain impossible today.

1.2 PROJECT HISTORY

This project merges the EDXAS_S, EDXAS_L and EXAFS CDRs presented in the Purple Book. Modifications to the previous CDRs are:

1. EDXAS_S and EDXAS_L use the full straight section on a time-shared basis (no canting).
2. The ultimate spot size for EDXAS_S now contains the contribution from dynamical theory (missing in the Purple Book version).
3. Constraints from the all-beamlines portfolio floor-plan proposed for the Upgrade mean that the BM29 EXAFS beamline will move to the BM23 port.

The scientific case for UPBL11 has been further refined at the UPBL11 brainstorming meeting (22-23 September 2008).

1.3 SCIENTIFIC CASE

Historical background

Since the first design and evaluation of an EDXAS spectrometer to measure XAFS rapidly using synchrotron radiation, in the early 80s in Stanford (USA) [Matsushita and Phyzackerley (1981)], this technique has spread to many other synchrotron sources worldwide. The main advantages of EDXAS spectrometers with respect to energy scanning spectrometers are: 1 – the speed of acquisition, since all energy points are acquired in parallel using a position sensitive detector, and 2 – the stability of the energy scale and focal spot position, since there are no moving components during acquisition.

In general, EDXAS spectrometers are installed on synchrotron sources having a large horizontal divergence, to allow a large energy bandwidth on the polychromatic beam, sufficient to cover a full EXAFS spectrum in a single shot. This has been the choice of all present or planned EDXAS beamlines worldwide, except the ESRF EDXAS beamline ID24.

An EDXAS beamline that would fully benefit from the high brilliance undulator sources at the ESRF was first proposed by J. Goulon and A. Fontaine in 1987. They proposed an original and non-conventional optical scheme, where the large divergence is artificially created using a strongly focusing mirror [Hagelstein (1997)]. This mirror not only creates a sufficiently large horizontal divergence that the undulator sources do not have, but also performs a first important demagnification of the source. This is why this optical scheme had the potential to produce a micron spot beam.

Motivation for upgrade

In the past ten years, the spot size on ID24 has been drastically reduced, from 50 x 250 μm^2 to 5 x 5 μm^2 (H x V) FWHM. This occurred through implementations and optimisations of the original optical scheme, and through a natural refurbishment programme with better surface quality optics [Pascarelli (2006)]. We are now at a point where no further reduction is possible with the present beamline. Operating with a 5 µm spot using a beamline that was built for a spot 10 to 50 times larger using 20 year old stability standards is already an exploit. However, the ultimate horizontal focal spot size for EDXAS at the ESRF is of the order of 1-2 µm FWHM. The question that we asked ourselves and that was also addressed at the recent UPBL11 brainstorming was: “Is science driving the need for the ultimate spot?”

The answer of course is “yes”. First of all, because the spot-reduction process has gradually given birth to new scientific opportunities, mainly in the fields of hyperspectral mapping [Munoz (2006), Vidal (2006), Munoz (2008) and Aquilanti (2009)] and of “in-situ” studies at very extreme pressures and temperatures (P > 100 GPa, P >3000K) [Andrault (2008), Boehler (2009), Andrault (2009)]. Future opportunities include fast (µs) time-resolved studies of fundamental chemical processes in solution, using micromixers and microchannels.

Much new science has been made possible [Pascarelli (2003), Mathon (2004), Duman (2005), San Miguel (2005), Pascarelli (2007), San Miguel (2007), Aquilanti

(2007a), Aquilanti (2007b)], and many experiments that remain impossible or very challenging today, will be made possible by a further reduction in spot size. A complete reconstruction of ID24 optimised for the ultimate focal spot would be the natural evolution of high brilliance EDXAS. This is the motivation behind branch EDXAS_S.

However, whilst the spot size was being reduced, a number of other experiments started being more and more penalised. These involve studies on samples which have heterogeneities on the scale of the micron. The typical example is given by applications of EDXAS in the field of heterogeneous catalysis [Newton (2007a)]. The present ID24 has extreme limitations of applicability in this field, since it is practically impossible to measure good quality EXAFS on any of these systems due to the spot being too small. The only work presently possible is being carried out at high energies (E >18 keV), where ID24 is able to produce a reasonably large spot to average out all sample heterogeneities [examples of recent work: Newton (2007b), Newton (2007c), Dent (2007)].

Heterogeneous samples are also common in many other fields where high brilliance EDXAS has unique advantages with respect to energy scanning XAS. Amongst these are applications using differential XAS techniques, for example using X-ray magnetic linear or circular dichroism, where both the speed and the stability of EDXAS are an asset. Examples in this field cover the detection of femtometre atomic displacements using XMLD [Pettifer (2005), Ruffoni (2008)], a field pioneered on ID24, and studies of local structure and magnetism under extreme pulsed magnetic fields using XMCD [Mathon (2007), Sikora (2009)], an emerging application of EDXAS.

The motivation behind branch EDXAS_L is therefore to design a beamline that will deliver a large spot, associated to very high flux in a large energy range, to provide the best conditions for experiments a) that have been pioneered on ID24 or represent emerging applications and b) where the ESRF has largely invested in the past and is presently attracting a very wide user community, including industry (heterogeneous catalysis).

A natural evolution for both branches of UPBL11 in the next ten years will be in the investigation by EDXAS of irreversible processes in the microsecond regime and of ultrafast phenomena in the nanosecond to picosecond timescale. This will be made possible thanks to important investments in detection systems suited for EDXAS. The main advantages with respect to energy scanning XAS are the higher energy and focal spot stability, and that the full EXAFS spectrum is obtained at a single pump-probe cycle.

Science driving the beamline development

A more complete vision was discussed at the UPBL11 brainstorm. Only a few examples are reported here.

a. Static and time-resolved XAS studies at extreme conditions of P , T and H

In situ studies of kinetics: kinetics of phase transitions, reaction kinetics, oxide reactivity at high pressure (HP), pressure induced chemical reactivity in minerals. There are very few examples in literature of in-situ studies of chemical reactions at HP. It is not clear, for example, how a high spin-low spin transition on Fe will modify Fe chemistry at HP.

Melts: Melting of Fe and its alloys: Need to know melting T of Fe at 300 GPa to know the temperature of the core. In transition metals, a systematic dependence of the electronic *d*-band occupancy and the melting slope has been observed at very high pressures. This seems to be attributed to specific local atomic configurations in the liquid. XAS can give direct evidence of preferred local ordering in liquid transition metals and follow its evolution upon compression

Warm Dense Matter (WDM): This state of matter is very little documented. WDM can be produced using an electric discharge through a conducting sample and has an equilibrium lifetime of the order of the µs. Measuring opacities of WDM in the vicinity of core absorption edges by detection of edge shifts and insight on the plasma local order by modifications of XANES features.

Matter under extreme magnetic fields: Phase diagrams (local, electronic and magnetic structure, chemical ordering), polymorphism, pressure induced modifications in local, electronic and magnetic structure.

Laser Shocked Matter: dynamical HP – HT experiments to look at chemical kinetics, determination of reaction mechanisms, observe edge shifts and XANES modifications during shock.

b. Time-resolved XAS studies in chemistry and catalysis

Fast time resolved XAS is ideally suited to investigate current catalytic (complex) systems, which are demanding since they are often composed of four to five different chemical species, to obtain an “instantaneous” picture of chemical species and minimise “averaging”, track fast changes in oxidation state and local symmetry, detect short lived intermediate species. Examples of current topics are: dynamic three way catalysts, adsorbate-induced (fast) reconstruction, poisoning, electrocatalysts, hydrogen storage materials, etc.

Processes cover different timescales: In the ms timescale, two kinds of rapid mixing techniques can be used: 1. Sharp and rapid gas pulses coupled to small beds, to probe gas-solid reactions (in-situ operando heterogeneous catalysis, structure-function studies using appropriate combined techniques) and 2. Microfluidic flow type systems with micro-mixers and micro-channels, for fundamental studies of chemical processes (some related to catalytic reaction steps) in solution. On faster timescales (µs and below), XAS can track local and electronic structure modifications and species that are formed during processes such as activation, reaction transients, photochemical excitation.

c. Ultrafast phenomena ns→ps

There is a unique opportunity to perform time-resolved XAS measurements aimed at probing fundamental ultrafast processes in chemistry, biochemistry and condensed matter. To observe the most elementary and fundamental events such as radiative decay, rotational motion, coherence vs randomisation (especially for environment effects), instantaneous field effects, non-equilibrium versus equilibrium dynamics, thermal and non-thermal melting, strain propagation, phase transitions in solids, molecular dynamics, diffusional rotation, and recombination in liquids. Examples are: intramolecular electron transfer in metal complexes, light-induced spin crossover, solvation dynamics, birth of molecules in liquids, binuclear metal-halogen complexes, photoassociation in bimetallic complexes.

d. 2D μXAS mapping of heterogeneous samples in Environmental Science, Earth Science, Heritage Materials, Catalysis, etc.

There is a unique opportunity to perform hyperspectral 2D mapping rapidly, with the micron resolution, providing redox and speciation mapping on heterogeneous samples. EDXAS is particularly powerful for non-invasive studies of precious or sensitive samples or samples under extreme conditions. The fluorescence acquisition [Pascarelli 1999], coupled to elemental 2D mapping using microXRF techniques, pushes further the dilution limit and eliminates the stringent sample thickness requirements needed for transmission measurements.
Major applications can be foreseen for:

- redox and speciation mapping of natural rock samples, automotive catalyst beds, soil contamination, toxic wastes, etc.
- kinetics oriented studies at the μm-scale: time resolved processes and assessment of beam damage.

e. Differential XAS and Time Resolved XAS studies in Materials Science

The differential EXAFS techniques pioneered on ID24 give a unique capability to detect femtometre scale atomic displacements in disordered matter with chemical selectivity. The fundamental processes occurring in technologically relevant energy-driven magnetic materials, such as magnetocoolers (R-R', RCo_2, $LaFeSiH_x$, CoMnSi(Ge), FeRh, etc.), magnetic alloys with shape memory (NiMnGa, Heusler alloys), magnetostrictive materials, strong magnets obtained by hydrogen-based processes, can be investigated at an atomic level and with chemical selectivity. Moreover, the study of the evolution of such tiny effects with pressure opens new capabilities for validating theoretical predictions and can lead to the development of materials with the desired properties.

Differential XAS and time resolved XAS have also great potential in areas where processes occur under extreme environments, such as in the investigation of reversible hydrogen storage processes or materials for nuclear vessels. These include phase transitions of hydrides (borohydrures, alanates, Mg_7MH_x) under high pressure, H-assisted corrosion, Mg-based hydrogen storage (catalytic characterisation of the additive), corrosion of zirc-alloys, etc.

Scientific capabilities that are at present not accessible at the ESRF

Presently, the combination of a small spot size <u>and</u> <u>E</u>XAFS (large k range) is not available at the ESRF. Similarly, the combination of a large k range EXAFS <u>and</u> fast time resolution is not available. UPBL11 will provide full EXAFS in a large k range <u>AND</u> a stable 2 micron FWHM spot <u>AND</u> high time resolution.

- XAS studies of melts at extreme conditions are not accessible now at the ESRF.
- It is not presently possible to carry out EDXAS on heterogeneous samples at energies below ~15 keV.

- Micro-channel mixing is difficult with present beam size.
- Fast redox and speciation 2D mapping with the micron resolution is not available.
- Probing ultra fast processes (ns-ps) by XAS is presently not possible at the ESRF.
- In situ laser heating facility coupled to XAS is not available yet.

Possible future (mid- to long-term) developments after this beamline has become operational

- Picosecond XAS with dispersive detection: requires new detection system → develop 2D streak camera for EDXAS in time regime to get resolution to within single bunch.
- Multitechnique approach for microstructural solid characterisation by coupling EDXAS with vibrational spectroscopies (Raman, IR) and XRD:
  - → capture synchrotron IR radiation from nearby BM23, for enhanced time resolved XAFS/IR experiments;
  - → rapid change of energy for flexibility to choose best energy for simultaneous XRD (now limited by energy of absorbing element).
- Optimise the coupling of EDXAS with optical microscopy and μXRF elemental mapping.
- Expand the available energy range towards lower (E <5 keV) and higher energies (E >28 keV).
- A long-term speculative improvement could be the implementation of a laser shock capability.

1.4 TECHNICAL CONSIDERATIONS

1. UPBL11: EDXAS-S and EDXAS-L

The main difference between EDXAS-L and EDXAS-S resides in the size of the X-ray probe: FWHM spots of the order of 40 x 100 μm^2 and about 2 x 2 μm^2 (H x V) respectively. The technical options to fulfill these conditions are also constrained, for both beamlines, by the requirement of producing a sufficiently large energy bandpass after diffraction by the polychromator. This leads to a required incoming horizontal divergence of about 1 mrad on the respective polychromators.

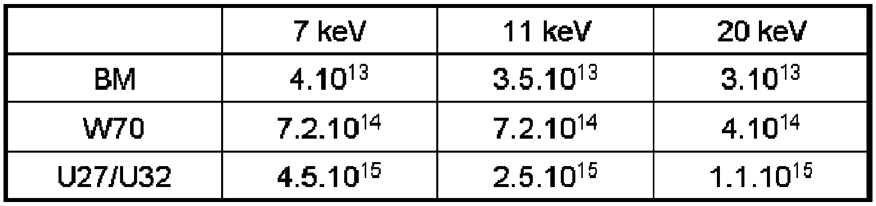
During this initial design process two possible options were considered. The ESRF, as other sources, are now able to provide two independent beams from the same straight section using canted geometry. In this case EDXAS-L and EDXAS-S could be designed as independent beamlines. The principle drawback of this configuration is that it is only possible to install two undulators with a total length of 3.2 metres for each beamline and necessitates the installation of a 7 metre straight section thus limiting the flux available at the sample. The operation of two independent beamlines would also require additional staff that are not available. Alternatively a single beam can be used. This beam can be directed using an appropriate horizontally deflecting mirror either to the polychromator of EDXAS-L or EDXAS-S. In this way the full flux available from a 5, 6 or eventually 7 metre straight section can be exploited. As the beamlines would not run in parallel the staffing requirements are less demanding. This second option has been chosen.

X-ray source

Location:
The document “A Scenario of “All Beamlines” Portfolio at the end of the ESRF Upgrade Programme “Phase I Minimum” Preparatory SAC Meeting, 7 October 2008” positions this facility at the location ID24.

Front end:
The front end should be a “standard” ESRF front end capable of transmitting the photons from the undulators defined below. The front end should allow an unrestricted opening of the primary slits situated at 27 metres of 3.5 mm x 2 mm (H x V). An option to convert the beamline to a UHV beamline up to the polychromators should be left open if an increase in flux at low energies is deemed necessary at a later date.

Undulators:
Calculations have been made for flux at the polychromator for three scenarios at 300 mA using a 5 metre straight section. The table below reports photons/s/0.1%BW for the bending magnet (BM), the 70 mm period wiggler (W70) and the 27 mm or 32 mm undulators (U27/U32):

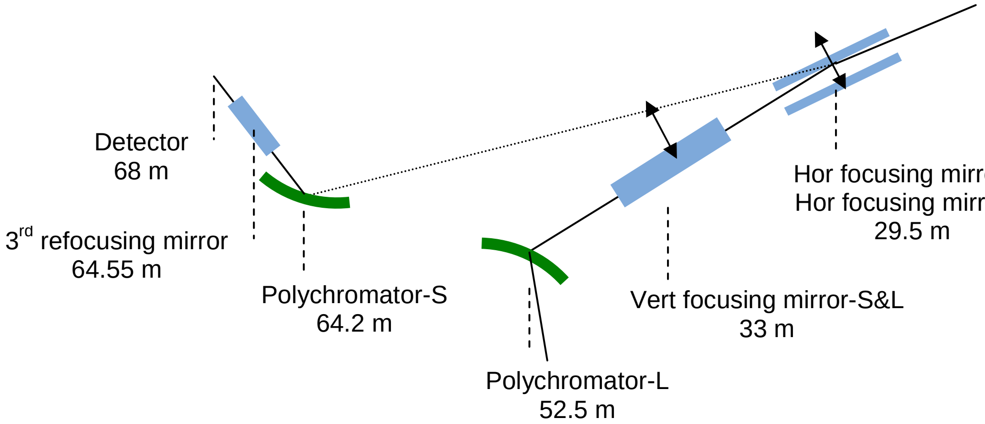


	7 keV	11 keV	20 keV
BM	4.10^{13}	$3.5.10^{13}$	3.10^{13}
W70	$7.2.10^{14}$	$7.2.10^{14}$	4.10^{14}
U27/U32	$4.5.10^{15}$	$2.5.10^{15}$	$1.1.10^{15}$

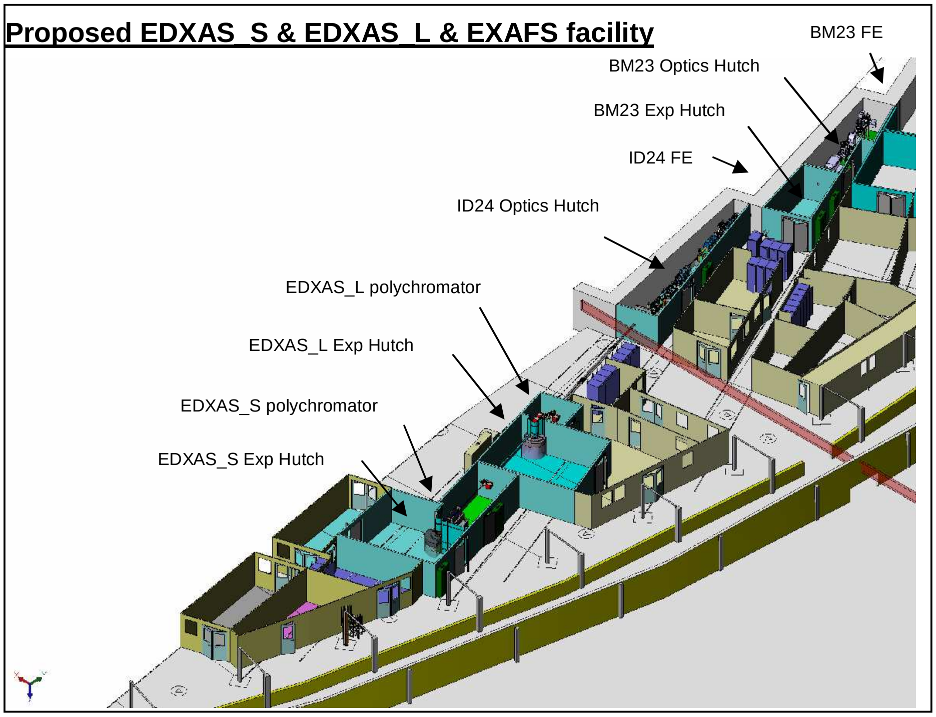
The results show that an undulator source gives the most photons, but also give a lower heat load on the first optics. In order, to achieve the full tuneability over the beamline energy range of 5-30 keV both U32 and U27 undulators are desirable. In the long term, the beamline would request three revolver undulator carriages mounted with U32 and U27 magnetic assemblies. In the commissioning phase a combination of 2 x U27 and 1 x U32 conventional undulators would be sufficient.

General Layout

Concept for optical design:



This optical layout, when integrated into the available space, would give a hutch/control cabin layout as shown below:



EDXAS-S

The EDXAS-S beamline principle and the technical options are largely inspired from the present EDXAS beamline ID24. An undulator X-ray source on a high beta straight section coupled with a horizontally focusing mirror to enhance the divergence up to the required value is an adequate choice for this project as (i) the demagnification factor resulting from the coupling of the polychromator with the horizontal mirror meets the focal spot requirements, (ii) the high flux delivered by the undulator source is necessary to cope with the scientific goals of the project (two orders of magnitude higher than an option based on a BM), (iii) the heat load on optical elements will be minimised, especially on the polychromator and (iv) the small vertical divergence allows the size of the vertical focusing mirror to be minimised. The optimisation of the positions and the quality of the optical components are the main challenges to fulfill the requirements outlined above for this instrument. With respect to the optical scheme of the present ID24, the principal difference will be in the inversion of the mirrors of the Kirkpatrick Baez (KB) system. Initial calculations have shown that thermal slope errors on the first optical element can be controlled more easily in the horizontal deflecting geometry giving thermal slope errors of less than 0.1 µrad. Additionally the larger separation of the beams at the polychromator of EDXAS L allows easier mechanical designs.

A long beamline is not necessary for this project as first design parameters demonstrate that the source contribution to the final focal spot size becomes rapidly negligible compared to contributions due to slope errors and dynamical diffraction on the polychromator and on the vertical mirrors.

The challenging technical difficulties of this project are:

- The quality of the optical elements (in particular the slope errors requirements of the polychromator and of the mirrors);
- The implementation of the KB mirrors, the polychromator, mirror M3 and the sample environment in a reduced space;
- The implementation of mirror M1 close to the first optical elements of project EDXAS-L and the control of the high heat loads;
- The understanding of the origin of crystal polychromator degradation, occurring (and visible)mainly at low energies and catalysed by interaction with intense photon beams;
- The efficient cooling of all optical elements;
- The automisation of the beamline alignment and focusing procedures;
- The major improvements necessary in beam and component stability;
- The development of a suitable and faster detector for time-resolved EDXAS.

EDXAS-L

An undulator X-ray source both on a high or on a low beta straight section leads inevitably to a high demagnification factor since the source must be coupled to a horizontally focusing mirror to enhance the horizontal divergence up to 1 mrad. Starting from an undulator source, it is therefore not evident how to obtain a “large” focal spot for EDXAS-L. However, observation over the last years has indicated that the focal spot produced by the Laue polychromator can be made sufficiently large (>40 µm) and still contain a good energy homogeneity. This polychromator is rarely being used due to the intrinsic heat load problems associated with Laue optics. However, it has been shown recently that it is possible to use a fixed curvature Laue crystal for various different energies by varying the polychromator to sample distance without significantly degrading its focusing properties. This opens up the possibility of using a liquid nitrogen cooled Laue polychromator which could solve the heat load problems. A prototype concept of this solution will be tested at the existing ID24 facility during 2009.

The EDXAS-L energy dispersive spectrometer with its sample environment has to be installed either before or after the EDXAS-S station. With buildings constraints limiting the length of the beamline in the proposed location to 70 m the polychromator would be situated at 52.5 m.

The challenging technical difficulties of this project are identical to EDXAS-S with additionally:

- The design and the implementation a Laue polychromator of sufficient thermal and mechanical stability;
- The management of the EDXAS-S beam traversing the experimental hutch when EDXAS-L is not operating.

Beamline Properties

	EDXAS-S			EDXAS-L		
Energy	7 keV	11 keV	20 keV	7 keV	11 keV	20 keV
Flux on sample x 10^{14} ph/s	4.5	2.5	1.1	4.5	2.5	1.1
Focal spot size µm (FWHM)	2 x 2	2 x 2	5 x 5	30 x 100	30 x 100	30 x 100
Energy range	5-30 keV			5-30 keV		
Energy resolution	High 10^{-5} to low 10^{-4}			High 10^{-5} to low 10^{-4}		
Energy bandwidth	>15%			>15%		
Time resolution	<1 µs for non-reversible processes					

2. EXAFS - BM23

X-ray source

Location:

The document “A Scenario of “All Beamlines” Portfolio at the end of the ESRF Upgrade Programme “Phase I Minimum” Preparatory SAC Meeting, 7 October 2008” positions this facility at the location BM23.

Front End:

The front end should be a “standard” ESRF front end capable of transmitting the photons from the bending magnet source. The front end should allow an unrestricted opening of the primary slits situated at 26.5 metres of 20 mm x 1 mm (H x V). The beamline will be aligned on the -9 mrad axis on the hard radiation end of the dipole magnet. An option to convert the beamline to a UHV beamline up to the sample should be left open if an increase in flux at low energies is deemed necessary at a later date.

General layout

The hutch/control cabin layout for BM23 is illustrated as part of the “Proposed EDXAS_S & EDXAS_L & EXAFS facility” figure above.

Concept for optical design

This beamline would be designed to perform XAS with an excellent signal-to-noise ratio, stability, versatility, reliability and high automation level. To preserve these standards, the optical scheme will remain relatively simple and similar to the present BM29.

The first optical element is a double crystal, fixed exit, double cam type monochromator manufactured by Kohzu (Japan). The two crystals are in (+,-) geometry and diffract in the vertical plane. An angular range between 4.5 and 45 degrees is accessible. Crystals typically used on BM29 include Si(111), Si(311), and Si(511). We propose to permanently install these three pairs of crystals within the monochromator vacuum vessel and couple them with a precise horizontal transverse translation. Furthermore, we propose an upgrade to the present monochromator cooling scheme from a closed loop, cryogenic helium gas circuit to a liquid nitrogen circulator in order to avoid mechanical vibration and improve the beam stability.

Downstream of the monochromator a pair of flat mirrors rejects harmonics. The angle of incidence will be variable between 2 and 5 mrad, and three reflecting stripes (Si, Pt, Rh) can be selected to cover the large operational energy range from 4 to 40 keV. The height of the beam reflected by the double mirror system is independent of incidence angle. Vertical focusing is achieved by meridionally cylindrically bending the second mirror with radius of curvature continuously variable between 2 km and infinity. A vertical focal spot size between 40 and 60 µm FWHM is obtained. The mirror could be bypassed for high energy operation above 40 keV.

For the upgraded beamline we propose to add to the present BM29 capabilities the three following possibilities by order of priority:

1. The possibility to perform Quick EXAFS operation with a rate of 1s per EXAFS spectra with good signal to noise ratio up to $k = 20$ Å^{-1}.
2. A micro-XAS station with moderate spatial resolution of 3 x 3 µm^2 up to k=18Å^{-1}. The micro-XAS station would consist of a KB mirror arrangement based on achromatic graded multilayer, collecting 0.2 mrad in horizontal and the whole beam in vertical. The proposed solution has already been tested successfully on BM29 [Ziegler (2008)].

Besides the standard transmission mode, options for detection modes include: energy resolved fluorescence, total fluorescence or total electron yield. An upgrade of the fluorescence detector should be envisaged. The addition of an analyser could be also envisaged. The BM29 experimental setup is completed by the option to collect complementary X-ray diffraction patterns through a MAR image plate detector mounted off the beam axis.

1.5 REFERENCES

Andrault D., Muñoz M., Bolfan-Casanova N., Guignot N., Perrillat J. P., Aquilanti G. & Pascarelli S. (2008). "The Perovskite to Post-Perovskite phase transition in Al-bearing (Mg,Fe)SiO_3: A XANES in-situ analysis at the Fe K-edge " (invited presentation at AGU 2008)

Andrault D, Muñoz M., Bolfan-Casanova N., Guignot N., Perrillat J.P. Aquilanti G. and Pascarelli S.

submitted (2009)

Andreani M., Grauby O., Baronnet A. & Muñoz M. (2008). European Journal of Mineralogy, 20, 159-171.

Aquilanti G., Trapananti A., Minicucci M., Liscio F., Twaróg A., Principi E., & Pascarelli S. (2007). Physical Review B 76, 144102

Aquilanti G., Libotte H., Crichton W. A., Pascarelli S., Trapananti A. & Itié J.P. (2007). Physical Review B 76, 064103

Aquilanti G., Pascarelli S. Mathon O. Muñoz M. , Narygina O and Dubrovinsky L., J. Synchrotron Rad. (2009) in press

Boehler R., Musshoff H.G., Ditz R., Aquilanti G., and Trapananti A.

submitted (2009)

Dent A. J., Evans J., Fiddy S. G., Jyoti B., Newton M. A. & Tromp M. (2007). Angewandte Chemie, 46, 5356 –535

Duman E., Acet M., Wassermann E. F., Itié J.P., Baudelet F., Mathon O. & Pascarelli S. (2005). Physical Review Letters 94, 075502

Hagelstein M., San Miguel A., Fontaine A. & Goulon J. (1997). J. Phys. IV France 7, C2 303-308

Mathon O., Baudelet F., Itié J.P., Polian A., D'Astuto M., Chervin J.C. & Pascarelli S. (2004).

Physical Review Letters 93, 255503

Mathon O., van der Linden P., Neisius T., Sikora M., Michalik J. M., Ponchut C., De Teresa J.M. & Pascarelli S. (2007). J. Synchrotron Rad. 14, 409-415

Matsushita T. & Phyzackerley R.P. (1981). Japanese Journal of Applied Physics 20, 2223-2228

Muñoz M., De Andrade V., Vidal O., Lewin E., Pascarelli S. & Susini J. (2006). Geochemistry Geophysics Geosystems, 7, Q11020

Muñoz M., Pascarelli S., Aquilanti G., Narygina O., Kurnosov A. & Dubrovinsky L. (2008).

"Hyperspectral micro-XANES mapping in the diamond-anvil cell: Analytical procedure applied to the decomposition of (Mg,Fe)-ringwoodite at the upper/lower mantle boundary" High Pressure Research 28, 665-673 **(**2008)

Nagai Y., Dohmae K., Ikeda Y., Takagi N., Tanabe T., Hara N., Guilera G., Pascarelli S., Newton M. A., Kuno O., Jiang H., Shinjoh H. & Matsumoto S. (2008). Angewandte Chemie Int. Ed. 47, 9303 – 9306 (2008)

Newton M. A. (2007). J. Synchrotron Rad. 14, 372-381.

Newton M. A., Belver C., Martínez-Arias A., Fernández-García M. (2007). Nature Materials, 6, 528-532

Newton M. A., Belver C., Martínez-Arias A., Fernández-García M. (2007). Angewandte Chemie, 46, 8629

Pascarelli S., Neisius T., De Panfilis S. (1999). J. Synchrotron Radiation 6, 1044.

Pascarelli S., Aquilanti G., Crichton W. A., Le Bihan T., Mezouar M., De Panfilis S.,. Itié J. P, & A. Polian (2003). Europhysics Letters 61, 554

Pascarelli S., Mathon O., Muñoz M., Mairs T. & Susini J. (2006). J. Synchrotron Rad. 13, 351-358

Pascarelli S., Ruffoni M., Trapananti A.**,** Mathon O., Aquilanti G., Ostanin S., Staunton J. B., & Pettifer R. F. (2007). Physical Review Letters 99, 237204

Pettifer R., Mathon O., Pascarelli S., Cooke M. & Gibbs M. (2005). Nature 435, 78

Ruffoni M. P., Pascarelli S., Grossinger R., Sato Turtelli R., Bormio-Nunes C., & Pettifer R. F. (2008). Phys. Rev. Lett. 101, 147202

San Miguel A., Merlen A., Toulemonde P., Kume T., Le Floch S., Aouizerat A., Pascarelli S., Aquilanti G., Mathon O., Le Bihan T., Itié J.P. & Yamanaka S. (2005). Europhysics Letters 69, 556

San Miguel A., Libotte H., Gauthier M., Aquilanti G., Pascarelli S. & Gaspard J.P. (2007). Physical Review Letters 99, 015501

Sikora M., Mathon O. van der Linden P. , Michalik J., de Teresa J.M., Kapusta Cz., and Pascarelli S (2009) Physical Review B 79, 220402(R)

Vidal O., De Andrade V., Lewin E., Muñoz M., Parra T. & Pascarelli (2006) S. J. Metamorphic Geol., 24, 669

Ziegler E., Aquilanti G., Mathon O., De Panfilis S. & van Vaerenbergh P. (2009). X-ray Spectrometry 38, 250