Micro-Soft X-Ray Spectroscopy with the LUCIA Beamline

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Abstract. With the development of new synchrotron radiation machines, which have seen, in the last ten years, the emittance of the beam decreased by several orders of magnitude, new beamlines have been developed which make full use of these improvements. We describe here the LUCIA beamline, which has been implemented at the Swiss Light Source in a collaboration between PSI, SOLEIL and the CNRS.

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INTRODUCTION

In recent years, the race for higher and higher brightness synchrotrons has been made in parallel with the construction of new beamlines exploiting these technical development. As an example of such a trend, the LUCIA beamline has been designed for x-ray absorption experiments over a full EXAFS range, with a spot size on the order of 2 micrometers, from energies as low as 0.8 keV up to 8 keV. The goal of the construction of this beamline was to bring to the scientific community microspectroscopy and cartography techniques, with a lateral definition on the order of one micrometer, for combined studies of low Z elements, like sodium, aluminum, silicon and much heavier ones with the same experimental set-up.

DESCRIPTION OF THE BEAMLINE

Improvement of beamline performance starts necessarily with improvement of the source, which means the synchrotron machine and the photon source itself. New third generation machines like SLS in Switzerland reach in the soft x-ray domain a brightness of the order of 10^{20} around 2 keV, with a source size of 200(h) x 20(v) μm^2 and a position stability of ~1 micrometer. The top-up mode routinely used at this source maintains the emitted photon flux and therefore the thermal load on the optics, constant over days of experiments. The counterpart of this high stability is that the micro-injections of the machine are seen on the flux monitor of the beamline by intensity steps of the order of 0.3%. Therefore measurements of I and I0 during an absorption experiment have to be perfectly linear. The U54 APPLE II undulator installed at the 7M section of the SLS delivers all kinds of linear polarizations up to the 27^{th} harmonic, as well as circularly polarized light of both helicities in the low energy part of the spectrum.

A general sketch of the beamline optics is given in Fig. 1. The beam is first collimated, inside the front end, by a set of cooled horizontal and vertical slits of a maximum aperture of 600 x 600 μm^2, in order to select only the central cone of the undulator emission. Then a vertical spherical mirror at an incidence angle of 0.4° makes an intermediate source whose size is 80 µm (h) and 760 µm (v). A set of two flat mirrors, with an incidence angle variable from 0.4 to 1.2° acts as a low-pass energy filter to remove unwanted harmonics of the undulator. A double crystal monochromator provides a fixed exit beam by utilizing a double cam adjustment of the second crystal. Because of the size of the photon beam at the monochromator position (about 1 x 1 mm^2) and the need for several crystals to cover the full energy range, five crystals (Si(111), InSb(111), KTP(110), beryl(110) and YB_{66}) are set on the same holder and the whole vessel of the monochromator translates perpendicularly to the photon beam to align the correct crystal on the incident beam. All these optical elements, as well as the first crystals, are water cooled.

LUCIA (X07M) Beamline Layout

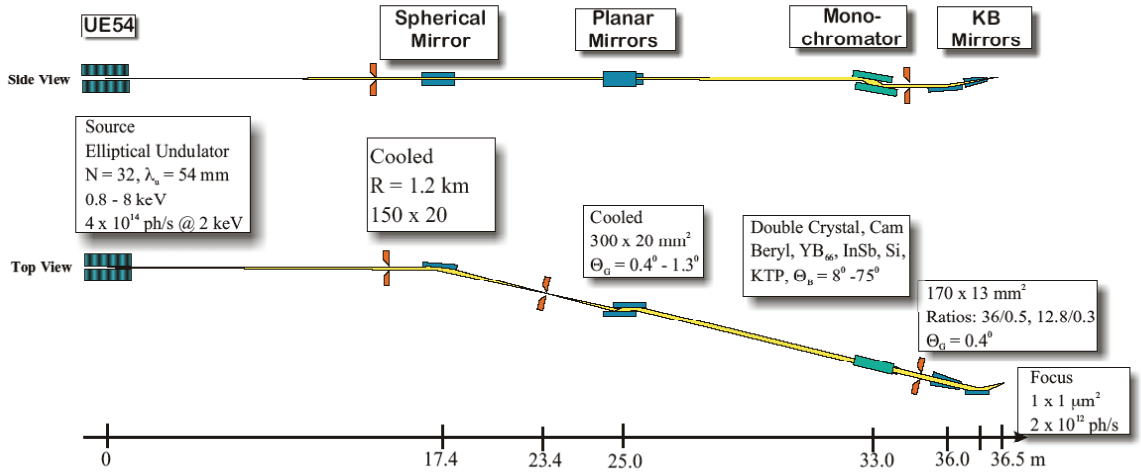

FIGURE 1. Design of the LUCIA beamline.

The focusing system is located about 3 m downstream of the monochromator; it uses two mirrors in a Kirkpatrick-Baez (K-B) configuration with an incidence angle of 0.4°. Each mirror is bent elliptically by a mechanical system with two motorized actuators first developed at ESRF and adapted here for a high-vacuum use. The first mirror focuses the beam vertically; it images the photon source, while the second one, located 30 cm downstream, images the horizontal dimension of the intermediate source. More details on the design of the beamline can be found in [1]. Between the K-B chamber and the experimental chamber are two successive beryllium windows (the first 7 µm thick and fixed, and the second 100 µm thick and mounted on a gate valve) allow for operation from atmospheric pressure at high energy to very high vacuum, with a transfer line for sensitive samples. Transmission, total electron yield and fluorescence detection can be made simultaneously by means of a silicon pin diode (T), a silicon drift diode (FY) and a measure of the drain current (TEY). The I0 signal is monitored by the total electron yield from a 700 Å thick nickel deposit on a 2 microns polymer foil, measured just after the last K-B mirror. The size of the beam at the titanium K-edge has been measured using a knife edge scan and monitoring the fluorescence of a square titanium dot (courtesy of CXSRO –Berkeley) as the dot is swept across the beam. The measured FWHM is on the order of 2 micrometers (Fig. 2) and confirms results from ray tracing calculations taking into account the measured roughness of the optics.

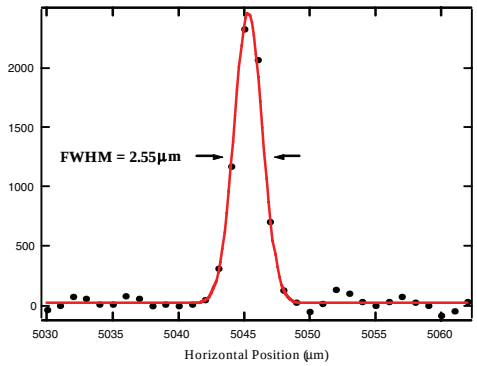

FIGURE 2. Horizontal shape of the spot at 5 keV.

While for imaging experiments the size of the beam is the most relevant parameter, its spatial stability when the energy is scanned is also of great importance for microspectroscopy. By a careful alignment of the monochromator and then a continuous tuning of the positions of the crystals, the focused beam can be kept at a fixed position (within 1 µm) over a full EXAFS scan. This is illustrated in Fig. 3 in the case of a 5 µm mesh powder at the phosphorus K-edge, where, by switching off the corrections, the movement of the beam on the sample grains increases the signal to noise ratio, with some spurious kinks, and disturbs the shape of the baseline. Note that, in this case, the Bragg angle varies from about 70 to 42 °.

The APPLE II device allows for changes in polarization without affecting beam position on the sample. This is of fundamental importance for microspectroscopy experiments since it would be difficult to keep the position of the sample within a few micrometers while it is rotated for polarized studies, and has been checked by measuring the linear dichroism signal at the Cr K-edgein a synthetic ruby crystal.

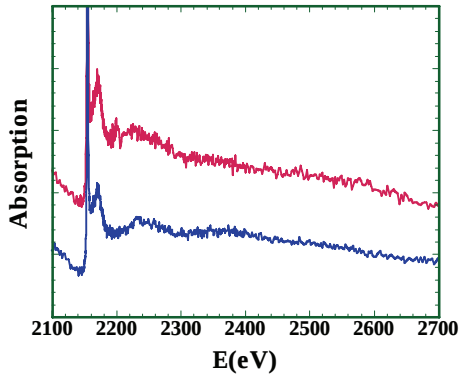

FIGURE 3. Phosphorus EXAFS data on a 5 μm grain taken with (bottom) and without (top) monochromator corrections.

While the beamline has been designed as a microspectroscopy facility, its use could be extended to different requirements. For instance the need in EXAFS spectroscopy to record spectra of model compounds has been recognized for a long time. Therefore a small experimental chamber with all the detection needs has been implemented upstream of the K-B set-up in order to run these references without dismounting the sample holder. The size of the beam amounts to about 1 x 1 mm^2. In the same spirit, and because the K-B mirrors bending is motorized, we foresee being able to remove the bend in order to obtain an alternate focus on the order of 20 micrometers, beyond the main chamber, where a special and oversized equipment could be installed.

The following section gives a few examples of applications, which have been conducted at the beamline since its general opening to the users, beginning of January 2005. To date most of the users have come from the Materials Science community, extended from Solid State Physics [2] to Environmental and Cultural Heritage studies. Other examples can also be found in the Proceedings of this Conference.

EXAMPLES OF APPLICATIONS

High Pressure Studies

Interest in a low energy microfocus beamline, which can reach K-edges of low Z elements of interest in materials science and geophysics already, has already been pointed out [3]. For that purpose, changes have to be made on the design and the use of the diamond anvil cell (DAC) in order to lower as much as possible the absorption of the environment (diamond anvils, gasket). Depending on the energy, transmission experiments through perforated diamonds will first be used (above 5 keV), then the fluorescence will be measured through a Be gasket (from 3 to 5 keV) and finally excitation and fluorescence collection will be carried out through a specially designed beryllium gasket. Obviously the quality of the result is strongly liked to the spatial stability of the focused beam on the sample which has typical dimensions of 20 x 20 μm^2.

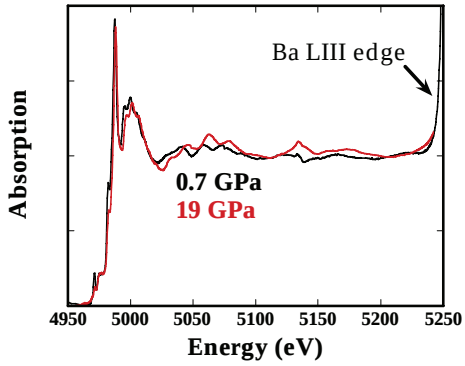

FIGURE 4. EXAFS spectra of $BaTiO_3$ at the titanium K-edge for different pressures.

Among the studies already performed on the beamline, the two following examples make use of these different configurations. On perovskites at the titanium edge, the transmission of the diamond is high enough (around 10^{-3}) to allow for a transmission geometry. Fig. 4 shows the EXAFS signal obtained for two different pressures in the case of $BaTiO_3$ at the Ti edge. The changes on the EXAFS structure reflect the decrease of the interatomic distances with pressure while the well known pre-peaks are drastically modified as the titanium atom goes back to a more centered position in the oxygen octahedron [3]. At the other energy limit, this transmission geometry is no longer applicable because of the absorption by the diamond anvils. Instead, the excitation is made through the beryllium gasket, and the fluorescence signal is also detected through this gasket. In order to increase the transmission of the gasket as much

as possible, it has been carved along the directions of the incoming and outgoing photons. Several other applications of x-ray absorption at high pressure at low energy edges can be found in the proceedings of this Conference.

High Temperature Studies

For these studies it is also mandatory to use a very well focused beam, in order to limit the amount of sample to be heated and to obtain the best homogeneity of the sample temperature. The furnace is made of a platinum or tungsten wire on an assembly otherwise used at higher photon energies [4]. A small crystal or a small amount of powder is inserted into a hole in a flat part of the heating wire. The signal can be detected by fluorescence, provided that the detector is protected from infrared radiation by a beryllium cap, which keeps the silicon diode at its normal temperature. Sample temperatures as high as 2000 K can be then obtained. An example of T dependent Al K-edge data on $Ca_3Al_2O_6$ is shown in Fig. 5.

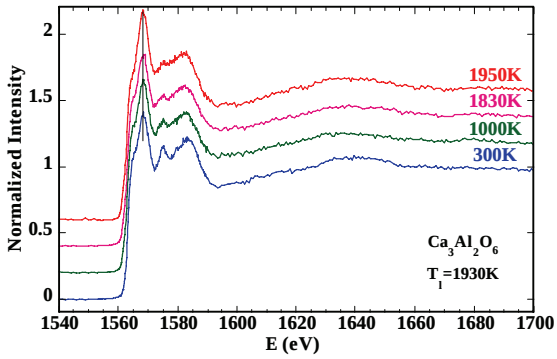

FIGURE 5. EXAFS spectra of $Ca_3Al_2O_6$ at the aluminum K-edge for different temperatures up to the melting point.

The obvious changes when the temperature increases can be analyzed in terms of a loss of long-range order and an increase in the disorder parameters with temperature. Other elements of great interest for the understanding of the behavior of the earth's crust at high temperatures have also been studied, in particular silicon and calcium in alumino-silicate compounds (see results in this Conference proceedings). These studies show that the melting process is not completely identical for all these compounds and seems to depend on the degree of organisation of the elemental units in the solid. Because of the very small size of the beam spot, the overall dimension of the whole assembly could be downsized in order to study various samples that are difficult to obtain in large amounts, or to study the behavior of one particular area of interest inside a larger compound.

Environmental and Heritage Studies

Environmental sciences is an area where the coupling between imaging techniques and spectroscopy is very useful. Indeed, in most cases the samples are highly heterogeneous and contain a large variety of elements present in a small area. The interplay between these elements can be of a fundamental importance. As an example, it is now recognized that the risk assessments of metal contaminated soils must not only be based on total or extractable metal concentration but also on the spatial distribution and chemical speciation of metal contaminants in soils that affect their mobility and bioavailability. Another application of x-ray absorption and fluorescence for environmental science can be found in the proceedings of this Conference. It deals with the understanding of the processes controlling the mobility and availability of phosphates in a lake environment. Phosphorus is a growth limiting nutrient for microorganisms and plants thus this knowledge could significantly contribute to agricultural land and freshwater lake management.

Archaeological studies also benefit from this microscopy, as the goal is to understand the effect of aging and/or weathering on artefacts on a micrometer sacle. For instance, in studies of the degradation of ferrous artefacts (Fig. 6) the superficial layer has to be studied at a scale of a few micrometers in both directions in order to determine and to describe the corrosion paths [5]. Speciation of iron and chlorine on a ferrous artefact by coupled cartography and spectroscopy experiments.

In very recent studies of the corrosion of ancient glasses, like stained glass windows of several cathedrals, low energy and microbeams were used together since the glass corrosion affects the superficial layer, and involves element constitutive of the glass like sodium, potassium or manganese. Magnesium also appears to be of great interest. For more details on these studies, refer to the proceedings of this Conference.

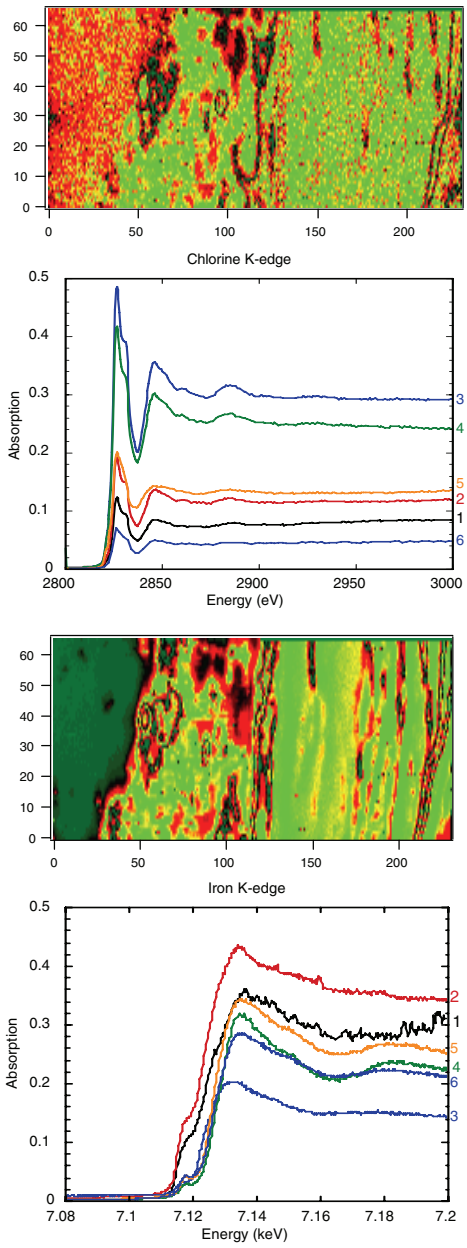

FIGURE 6. Speciation of iron and chlorine on a ferrous artefact from Glinet 16th century AD archeological site by coupled cartography and spectroscopy experiments. The scale of the maps is in micrometers. Numbers correspond to different Points of Interest.

PERSPECTIVES

The key point of the beamline is to offer a variety of users communities the possibility of performing x-ray absorption experiments at the micrometer scale, with access to absorption edges of very light elements (the K edge of sodium) up to the actinides (using the M edges as a signature), with a very versatile sample environment: oxygen and water sensitive samples can be introduced in the chamber without any contact with the atmosphere, and special thin window cells may be used for liquid samples. The extended energy domain allows studying the samples at the same beamline when a wide variety of elements are present in the system.

Future developments in the next few months are planned in two different directions:

1) Exploit the flexibility of the focusing system to focus beyond the present experimental chamber at the expense of spot size. For instance the focus can be set outside the experimental chamber at the expense of its size - which will increase to about 20 x 20 μm^2 - in order to provide a high photon flux for special experimental environments, like ultra high vacuum chambers for surface studies. This geometry will be used soon for Resonant Inelastic X-ray Scattering experiments where the x-ray spot on the sample is the source of the fluorescence crystal analyzer.

   In a different perspective, setting a Fresnel Zone Plate beyond the K-B system could provide us with a sub-micron photon spot for ultra-fine cartographies, probably at the expense of a full EXAFS data collection energy range.

2) X-ray spectroscopy has been recently coupled in-situ with several other characterization techniques, like Raman spectroscopy. Therefore micro-Raman will be implemented in the next future on the experimental chamber and these two structural techniques will be performed simultaneously on the same area of the sample.

CONCLUSIONS

The new LUCIA beamline is now commissioned and most of the results obtained are fully in line with the specifications, and are even in excess, like the energy range (thanks to the high quality of the undulator). Therefore, the low energy x-ray user community now has the added option of microspectroscopy. But apart from experimental aspects, the problem of the data analysis remains. The fields of soft x-ray spectroscopy and low Z-elements still require different theoretical approaches, related to the validity of some basic approximations of the models (the muffin-tin approximation for instance, or the multiple scattering model). This means that there is still room for improvements in this area of spectroscopy.

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