Polycapillary based µ-XAS and confocal µ-XANES at a bending magnet source of the ESRF

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Abstract. Glass polycapillary optics are shown to be easy to use focusing optics for bending magnet XAS stations. These achromatic optics have acceptances of several mm horizontally and vertically, while their angular acceptances can be matched to the source divergence by the design of the polycapillary. A polycapillary half-lens based focusing system was successfully tested for transmission and fluorescence µ-XAS at the DUBBLE beamline (BM26A, ESRF) and the feasibility of confocal µ-XANES in fluorescence mode is presented. Transmission efficiencies of 25-45% with flux density gain factors of about 2000 and beam sizes of 10-20 µm were obtained in the 7-14 keV energy range. Although the polycapillary optic has a smoothly changing energy dependent transmission efficiency, the amplitude and shape of the EXAFS oscillations are not influenced by this. The focusing properties of the polycapillary lens cancel slight vertical motions of the incoming X-ray beam, resulting in a fixed µ-beam spot in the focal plane, making polycapillaries also suitable optic in combination with a non-fixed exit monochromator. In addition, by mounting a second polycapillary half-lens in front of an energy dispersive detector, a confocal set-up is obtained, which restricts the part of the sample seen by the detector to a microscopic volume of about 20×20×15 µm³ at the Fe K absorption edge for example.
1. Introduction
The majority of XAS (X-Ray Absorption Spectroscopy) instruments are built at bending magnet ports of synchrotrons, taking advantage of the broad energy range of these X-ray sources. Standard XAS experiments on homogeneous samples make use of mm-sized beams. However, in order to investigate microscopic inhomogeneous samples, beam sizes of micrometer dimension are required. At bending magnets very often horizontal focussing is achieved by dynamically bending the second crystal of a fixed-exit monochromator (sagittal focusing) and vertical focussing by reflection on a mirror after the monochromator. This sagittal focussing for example is used at the French CRG at the ESRF (FAME, BM30) giving beam sizes of about 150×200 µm² (V×H) [1]. Preliminary experiments at the FAME beamline by adding a Kirkpatrick-Baez (K-B) mirror system have shown that beam sizes of 10×10 µm² can be achieved [2].

An alternative µ-focusing system based on a half-lens glass polycapillary optic for µ-XAS on bending magnet stations is presented. Polycapillaries consist of a bundle of several hundred of thousand of small bent glass fibres all oriented towards the same focal point. X-rays entering the glass fibres are guided towards the glass fibres that focal point by repeated total reflections. This results in an achromatic optical element. The focal plane is typically several mm away from the exit of the optic. In contrast to KB mirror systems, half-lens polycapillaries have large acceptances, several mm horizontally and vertically, while the angular acceptance can be matched to the source divergence by the design of the polycapillary. These capillaries are easy to use and need only to be aligned along the incoming beam. No further alignment is needed when changing the energy of the incoming X-ray beam, even over several keV. Moreover, when used in combination with a non-fixed exit monochromator, the energy dependent vertical offset of the monochromator can be accounted for by a simple height optimisation of the focusing polycapillary. The achieved beam sizes are smaller than the above mentioned sagittal focusing systems. The performance of the polycapillary optic based µ-XAS set-up is verified by recording transmission EXAFS spectra from several standards, which show that the use of this optic does not distort the EXAFS oscillations.

By adding a second polycapillary optic in front of an energy dispersive detector in the fluorescence detection mode, a confocal detection set-up is obtained. The confocal detection restricts the probed fraction of the sample into an ellipsoidal volume allowing 3D resolved µ-XAS. The feasibility of this confocal µ-XANES is presented.

2. Experimental
The experiments were performed at the Dutch-Belgian CRG XAS beamline [3] of the ESRF (Grenoble, France). The 6 GeV electron storage ring was running at a uniform filling mode, typically yielding ring currents of 200 down to 160 mA during a synchrotron run. The DUBBLE XAS beamline is located at the soft edge of the bending magnet (magnetic field strength B=0.4 Tesla, critical energy $E_c=9.6$ keV) and receives a total of 2 mrad of the bending magnet radiation fan. The vertical and horizontal divergences of the source are 1.1 µrad and 103 µrad respectively. The beamline is equipped with a non fixed-exit Si(111) double crystal monochromator. The higher harmonics of the primary energy are suppressed by a vertical mirror after the monochromator which has a roughness of 1.5 Ångstrom rms and 1.5 µrad slope error and is placed under an angle of 2.8 mrad. This optical element can also be used for vertical focussing and can provide beamsizes of about 300 µm. However, for this set-up, this focusing capability was not used and in order to match the acceptance of the polycapillary half lens. The intensity of the incoming and transmitted X-ray beams were measured with ionisation chambers (Oxford Instrument). The fluorescence XAS spectra in the conventional µ-XAS mode were recorded with a LN$_2$ cooled energy dispersive (ED) nine channel monolithic Ge detector (ORTEC, EG&G) [4] with XSPRESS electronics [5]. The confocal µ-XAS spectra were collected with an Vortex-EM silicium drift detector.

A large acceptance polycapillary lens with an entrance diameter of 5 mm, an optic length of 50 mm, an exit diameter of 1.6 mm and a focal distance of 3.6 mm, manufactured by XOS (X-ray Optical Systems, USA), specifically designed for the beam characteristics of BM26A (i.e. with respect
to source size/divergence, source-sample distance, bending magnet energy range) was used. The X-ray absorption data were recorded using a collimated incoming beam with a size of 0.5×2 mm² (V×H) with or without polycapillary focusing. The polycapillary is placed in between the first ionisation chamber and the sample. A strongly focusing polycapillary with a focal distance of 2.2 mm was put in front of the Vortex-EM detector to achieve confocal detection.

In order to determine the position of the focal plane and the vertical and horizontal beam sizes, a Gold wire (thickness: 180 µm) was scanned through the X-ray beam. Knife-edge scans were obtained by recording the transmitted X-ray intensity, \( I_t \), with the second ionisation chamber as function of the scanning distance. The full-width-at-half-maximum (FWHM) of a Gaussian fit to the derivative of the knife-edge scan was taken as the vertical and horizontal FWHM beam sizes. In addition to the knife-edge scans, X-ray images of the focused X-ray beam in the focal plane were taken using a SensiCam CCD (PCO Imaging, Germany, pixel size: 0.67 µm).

The transmission EXAFS spectra of Cu and Cu₂O powder were recorded with and without the polycapillary focusing optics, to verify that no systematic errors were introduced due to the use of the polycapillary optics.

All samples were measured in air at ambient conditions. The EXAFS data reduction and analysis were performed with the XDAP software [6]. The pre-edge background was subtracted using a modified Victoreen curve [7] and the atomic background, \( \mu_0 \), was subtracted using a cubic spline routine [8]. The pre-edge background subtracted spectra were normalised to the edge jump, which was taken to the value of the atomic background at 50 eV above the edge position.

3. Conventional μ-XAS

3.1. Focusing polycapillary μ-beam

The variation of the μ-beam full-width-at-half-maximum (FWHM) as function of distance from the polycapillary optic exit window is given in Figure 1. The focusing optic has a depth of focus of about 200 µm. A 2-dimensional image of the focused beam in the focal plane at 9 keV is also given in Figure 1. Although the beam at the entrance of the polycapillary has a rectangular shape of 0.5×2 mm (V×H), a symmetric focused beam with a binormal intensity distribution is obtained in the focal plane. At 9 keV, a FWHM of about 17 µm is obtained for the focused beam. The beamsize decreases as function of increasing X-ray energy, and is typically between 10 and 20 µm in the 7 to 14 keV energy range [9]. In this energy range, transmission efficiencies of 45-25% and an overall flux density gain of 2000 were obtained [9]. The estimated flux for the unfocused beam for the slit dimensions used (0.5×2 mm² (V×H)) at 14 keV is \( \sim 10^9 \) photons/s. With the observed transmission efficiency of about 25%, this results in an estimated flux of \( \sim 2 \times 10^8 \) photons/s. The polycapillary lens delivers a stable focused beam spot position in the focal plane. Vertical shifts of the beam at the entrance side of the lens, induced by the synchrotron beam, optics vibrations or due to the use of a non-fixed exit monochromator [9], have little influence on the focused beam spot position.

Figure 1: (left) Measured vertical FWHM (µm) of the polycapillary focused microbeam as a function of the distance to the polycapillary exit window for an incident X-ray energy of 9 keV, (right) two-dimensional X-ray image at the focal plane. Incoming beam size: 0.5×2 mm (V×H).
3.2. Transmission EXAFS

Transmission XAS spectra on Cu foil and Cu$_2$O powder were recorded under ambient conditions with and without focusing polycapillary are given in Figure 2. The pre and post edge regions of the absorption spectra taken with polycapillary focusing have different slopes compared to the unfocused case. This is due to the combined effect of the smoothly changing transmission efficiency of the polycapillary with X-ray energy and the vertical shift of the incoming beam as function of X-ray energy due to the non-fixed exit monochromator, as the transmission efficiency of the polycapillary lens is optimal on axis. However, the EXAFS and Fourier Transforms spectra are not influenced by this energy dependent transmission efficiency, as shown in Figure 2.

3.3. Application: Ni speciation on air filter

A 2-dimensional elemental $\mu$-XRF map for Ni-k$\alpha$ fluorescence radiation recorded on atmospheric particulate matter (PM$_{10}$) collected on a filter in the proximity of iron works is given in Figure 3. The Ni K XANES spectra taken with a large unfocused beam and a focused beam on the Ni hotspot (corresponding to an air particle not larger than 10 $\mu$m) in the map are compared in Figure 3, the corresponding illuminated areas are indicated on the Ni map. The shoulder on the low energy edge of the Ni hotspot spectrum is due to a larger fraction of metallic Ni and/or Ni sulphides. This example illustrates the spatial resolution of presented the polycapillary based $\mu$-XAS setup on a real live application.
Figure 3: left: Ni Kα fluorescence map on atmospheric particulate matter (PM$_{10}$) collected on a filter air filter, the red and blue areas indicate the irradiated areas for the conventional and focused XANES respectively given on the right; right: normalised Ni K fluorescence conventional XANES and µ-XANES spectra.

4. Confocal µ-XANES

4.1. Confocal detection volume

In the conventional detection mode considered above, the probed volume is determined by the intersection of the focused beam and the sample. The probed volume can be further reduced by adding a second polycapillary in front of the energy dispersive detector in the fluorescence detection, in this way a confocal detection mode is obtained. The sensitive volume is now limited to the intersection of the foci of both polycapillary lenses. Taking into account the binormal intensity distribution for both the focusing and confocal polycapillary optics, this sensitive volume then results in an ellipsoid. The FWHM of the horizontal axes of this ellipsoid are determined by the beam size ($s_B(E)$) of the focusing polycapillary and the acceptance ($s_A(E)$) of the confocal polycapillary respectively. The vertical axis ($s_V(E)$) is given by $s_V(E) = (1/s_B^2(E) + 1/s_A^2(E))^{1/2}$. The measured FWHM dimensions of the confocal detection volume at the Cu K edge were 18×12×10 µm$^3$.

Figure 4: Confocal Fe K µ-XANES spectrum recorded on a mineral inclusion inside a natural diamond compared with hematite (Fe$_2$O$_3$).
4.2. Confocal Fe-K μ-XANES on a mineral inclusion in natural diamond.

Most natural diamonds are formed under extreme conditions several hundred of km deep inside the Earth. During the growth of the diamond mineral inclusion can be formed. These enclosed minerals are then shielded from the environment during the exhumation of the diamond preserving their original capture composition. Inclusions in sub-lithospheric natural diamonds can therefore provide direct information on the physical and chemical conditions in the deep Earth down to the upper interface of the lower mantle [10,11]. In order to study the mineral inclusion inside the diamond and due to the high X-ray scatter power of the diamond host, a confocal detection is needed.

The confocal Fe K μ-XANES spectrum obtained on a mineral inclusion inside a natural diamond is given in Figure 4. The measured FWHM dimensions of the confocal detection volume at the Fe K edge were $21 \times 19 \times 14 \, \text{µm}^3$. The strong similarity with hematite confirms the feasibility of the confocal μ-XANES and allows the identification of the Fe mineral in the inclusion.

5. Conclusions

Polycapillary based μ-XAS and confocal μ-XANES are shown to be feasible on a third generation synchrotron bending magnet station. Reduction of the sample setup vibration will further improve on the data quality in the confocal detection mode.

6. Acknowledgements

We kindly thank the staff of DUBBLE for the technical support. Dr. G. Silversmit is supported by a postdoctoral fellowship from the Research Foundation-Flanders (FWO-Vlaanderen, Belgium). This research was performed as part of the Interuniversity Attraction Poles (IAP6) programme financed by the Belgian Government. FWO-NWO are thanked for making the beamtime on the DUBBLE beamline available. We like to thank Felix Kaminsky for providing the diamond sample.

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