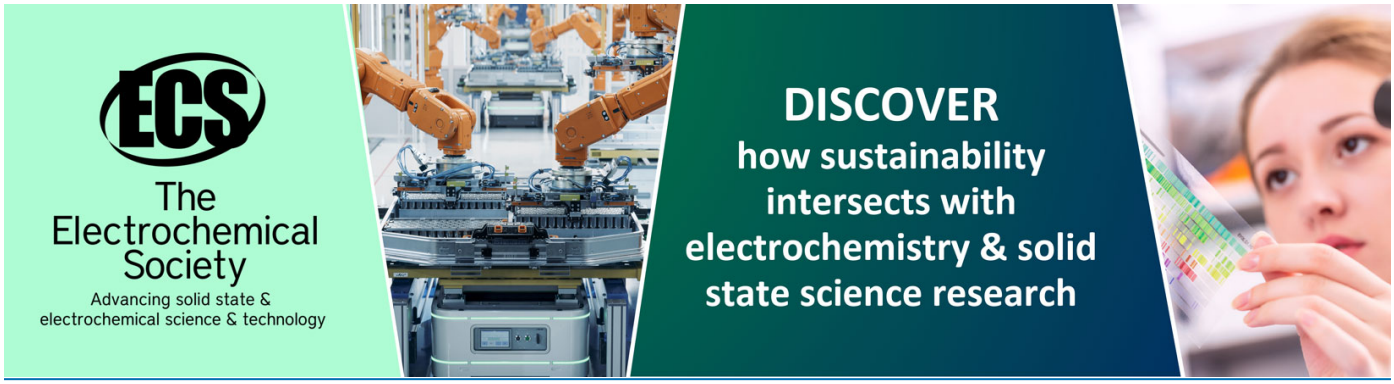
Novel XAFS capabilities at ELETTRA synchrotron light source



Journal of Physics: Conference Series **190** (2009) 012043 doi:10.1088/1742-6596/190/1/012043

Novel XAFS capabilities at ELETTRA synchrotron light source

Andrea Di Cicco[1,2,3], Giuliana Aquilanti[2], Marco Minicucci[1], Emiliano Principi[1], Nicola Novello[2], Andrea Cognigni[2], Luca Olivi[2]

[1]CNISM, Dipartimento di Fisica, Universitá di Camerino, I-62032 Camerino (MC), Italy;
[2]Sincrotrone Trieste, ELETTRA, 34012 Basovizza (TS), Italy;
[3]Institut de Minéralogie et de Physique des Milieux Condensés, UMR 7590, CNRS, Universités Paris 6 et Paris 7, Paris, France.

E-mail: andrea.dicicco@unicam.it

Abstract. The optical layout of the XAFS beamline at ELETTRA is presented along with its powerful capabilities for collecting XAFS spectra in a wide energy range 2.4 - 27 keV. Recent developments around the ensemble of available instruments made available different collection modes using various sample environments. In particular combined x-ray absorption and diffraction patterns can be collected even at high temperature using a special version of the l'Aquila-Camerino furnace and a MAR image-plate detector. An automated beamline control software allows us to perform successive measurements in different conditions without attending the beamline. Examples of XAFS and diffraction measurements, as well as single-energy temperature scans are presented showing the performances of the beamline for nanocrystalline systems and liquid metals under high temperature conditions.

1. Introduction

X-ray absorption spectroscopy (XAS) provides chemically specific short range structural information around the photoabsorber atom. Together with x-ray diffraction (XRD) that, on the other side, is sensitive at a longer range, XAS allows a full structural characterization of materials. For this reason several efforts have been made to develop experimental set-ups allowing the combined collection of XRD and XAS for different applications using both energy-dispersive and energy-scanning configurations[1, 2, 3, 4, 5, 6] . XAFS at ELETTRA is the Italian beamline dedicated to x-ray absorption spectroscopy. It is installed on a bending magnet source and it has been opened to users since 2004. It was designed to cover a wide energy range: from 2.4 to 27 keV meeting the needs of a large number of researchers in the area of conventional x-ray absorption spectroscopy. For this reason the research activity at the XAFS beamline at ELETTRA is quite diverse and ranges from catalysis to material and environmental science. In this paper we will show the novel capabilities recently developed at the XAFS beamline consisting in the installation of a special version of the l'Aquila-Camerino furnace that allows the combined recording of XAFS spectra up to 2000 K and the XRD patterns using an image plate detector mounted in an offset position. The potential of the XAS technique for measurements of disordered systems under high-temperature or pressure conditions was widely discussed in the recent literature (see for example ref. [7, 8]).

The paper is organized as follows: in section 2 the layout of the beamline is described. In section 3 we describe the novel sample environments and the setup for the combined XAS and XRD measurements; moreover we describe also the capabilities of the new beamline control software, allowing us to perform successive measurements in different conditions. In section 4 we will present several results obtained exploiting the novel capabilities described above showing the potentialities of this instrument for nanocrystalline systems and liquid metals.

2. Beamline layout

The XAFS spectrometer is built in the direction of the tangential fan of the bending magnet 11.1 of the ELETTRA synchrotron light source. The optical layout is shown in Fig. 1. A mask is placed at 13.3 m downstream the bending magnet source. It consists of a copper support with two 20 mm wide rectangular slots defined by tungsten alloy blades of 0.2 and 2 mm height. The two slots are used respectively to align and define the correct shape of the x-ray beam before the next optical element. The second optical element is a mirror placed 16.5 m from the source. The mirror provides vertical collimation and consists of a silicon ingot with platinum coating. It has an optically active length of 1000 mm and width of 60 mm respectively and it is positioned at 3 mrad respect to the direct beam. The mirror is water cooled and is operated under ultra high vacuum conditions. Although the contribution from L edges of Pt (11.5 - 14 keV) may have an impact on the x-ray absorption spectra, systematic tests have shown no noticeable features on the XAFS signal by the Pt coating when the detectors of the x-rays intensity before and after the sample operate in optimal conditions of linearity. Two pairs of entrance W alloy slits define the shape of the beam impinging on the monochromator. The monochromator, placed at 21.7 m from the source is a double flat crystal double cam Kohzu apparatus. The energy range 2.4 - 27 keV can be covered using interchangeable under vacuum pairs of Si(111) and Si(311) crystals. Two successive Bragg reflections, with an inherent energy resolution given by the Darwin angular width directs photons of the desired energy parallel to the incoming beam direction, but offset upward by 25 mm. The fixed exit is achieved by the rotation and translation of the first crystal along the two cams. The detuning of the second crystal provides harmonic rejection at working energies below 9 keV. Downstream the monochromator a second set of W alloy slits are used to define the beam on the sample.

Any specialized sample environment set-up is mounted on a wide motorized table (1.5 x 1 m^2) positioned at 26.2 m from the source, remote controlled and constructed for a load of 800 kg. Initial sample environment configurations were limited to a cell for in-situ studies of catalytic materials and to simple sample holders for XAS measurements at liquid nitrogen or at room temperature. The special cell for the study of catalytic materials has been developed in collaboration with the CNR unit of Milan. This allows in situ measurements of catalytic materials in reducing and oxidizing atmosphere. A specially designed fuel cell was also used to study metal nanocatalysts under operating conditions, using fine alignment procedures[9, 10]. The standard set-up allowed only transmission mode with ionization chambers for beam intensity measurements. These are filled with optimal He, Ne2, Ar, Kr gas mixtures at a total pressure of 2 bars and are operated at a field of 2kV per 30 cm of length. The ionization chambers signals are amplified by Keithley picoamperomers and digitalized by a voltage to frequency converters before being finally read by the counters of the data collection PC. The typical photon flux at the sample for standard beam size and ring current is in the 10^{10} photon/s range. The noise level contribution due to the photon statistics in the normal transmission geometry can be therefore limited below the 10^{-4} level.

3. Advances in the experimental set-up and beamline control

Several advances in the experimental set-up and beamline software were carried since early 2007 in the framework of a collaboration between the XAS group based at Camerino University

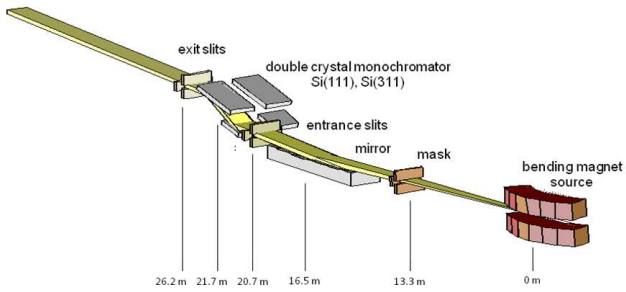


Figure 1. The basic optical concept of the XAFS beamline at ELETTRA. The mask define the size of the beam upstream the mirror. This one collimates the beam vertically before the double crystal monochromator in order to obtain the intrinsic energy resolution.

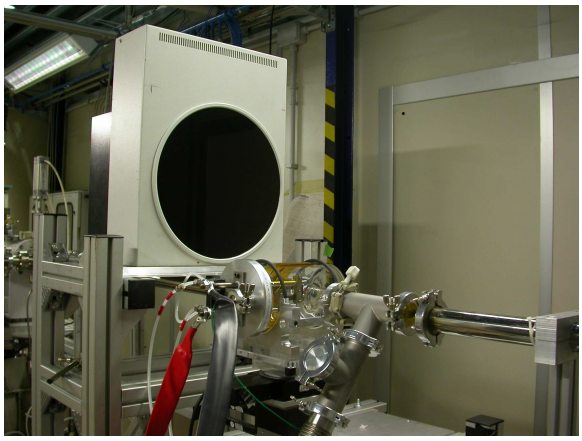


Figure 2. The high temperature L'Aquila-Camerino glass furnace for combined x-ray absorption and diffraction (custom version installed at XAFS@ELETTRA) and the vertical configuration for MAR image-plate detector.

and the XAFS staff at ELETTRA. The aim of those longstanding scientific proposals was to perform XAS experiments under non-standard conditions improving and extending the beamline capabilites for the users of the XAFS beamline.

The main upgrades regarded the sample environment capabilities and control and the beamline software for data acquisition. A special version of the L'Aquila-Camerino furnace[11, 12] has been designed for operation on the XAFS beamline. The furnace operates under high vacuum conditions in a wide range of temperatures 300-2500 K, measured by means of a thermocouple or by a pyrometric probe. The furnace is controlled remotely by the beamline control system allowing for temperature cycles with continous collection of the temperature. The furnace is designed to operate with the window for x-ray diffraction oriented vertically, in order to take advantage of an extended horizontal dimension of the x-ray beam in the range of 10 mm without reducing the angular resolution, determined mainly by the vertical aperture and by the sample thickness when using the image-plate without collimation devices. The experimental set-up including the furnace and the MAR image-plate detector arranged vertically is shown in Fig. 2. The sample environment now is going to include also a He cryostat with remote temperature control, developed within a loan agreement with the Camerino XAS group, for which single-energy temperature scans and fluorescence data collection will be possible. The plan for extending the sample environment possibilities include also the installation of a large-volume high-pressure cell, for which we are preparing the necessary development of the set-up based on our previous experience[12]. Very recently, a large-area Si drift detector for fluorescence measurements has been purchased (KETEK GmbH AXAS-M with an assembled 80 mm^2 SSD). The FWHM is < 160eV for the MnKa line and count rates up to > 100kcps can be achieved without significant resolution degradation. The new detector is being tested and installed on the beamline as a standard device for fluorescence measurements. Significant efforts were also devoted to improve the beamline control and automation system for different data collection modes. The software of the beamline was originally developed using LabView, using separated ambients for the alignment, beamline and detector setting and optimization, and for data-collection. The need for a more automated and simplified running of the beamline came both from the new sample environment possibilities and from the extended and new data collection

modes. The possibility of performing series of experiments modifying various experimental conditions with a set of standard commands (*macro* set of instructions) is certainly a pre-requisite for performing routine experiments combining various techniques (XAS, XRD, single-energy scans) under extreme or non-standard conditions. The strategy for improvement has been to improve and simplify the existing software, reducing also the existing dead times, implementing new subroutines for the management of new devices (furnace, temperature readout, cryostat, sample and cell holders), improving some of the existing routines (slits control, sample holder and slit control and scanning capabilities, energy mesh), and introducing new collection modes (single-energy temperature[13] scans). Presently, it is possible to perform complex temperature loops measuring the x-ray absorption at a well-defined energy near an absorption edge. Multi-column data files are conceived to include all the necessary information about the experiments and can be visualised directly during the experiment using both open-source and home-developed graphic software. All of the various subroutines can work as stand-alone programs or within a set of commands to be executed within a command file. The present beamline control system includes a simplified version for standard XAS experiments and a more sophisticated interface allowing for complex experiments requiring more detailed control of sample environment and scanning capabilities.

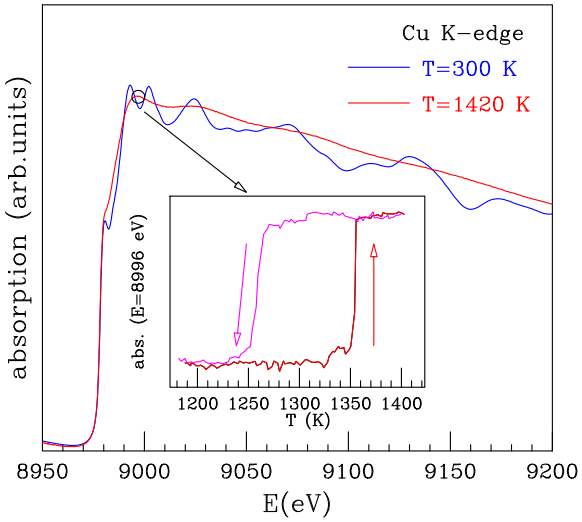


Figure 3. Cu K-edge spectra of pure solid (blue on-line, 300 K) and liquid (red on-line, 1420 K) copper collected at the XAFS beamline at ELETTRA. The single-energy temperature scan showing a large hysteresis loop (undercooling) is shown in the inset (upward stroke is red on-line).

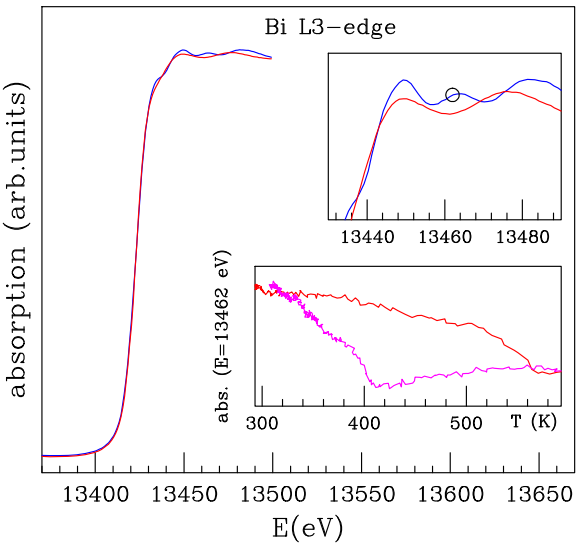


Figure 4. Bi L_3 edge near edge spectra of nanocrystalline Bi (embedded in SiO2) at 300 K (blue on-line) and 600 K (red on line). The high-quality spectra showing clear differences are magnified in the upper inset. The lower inset shows the temperature scan (upward stroke is red on-line) which is typical of a nanocrystalline system: broadened melting point and huge undercooling.

4. Results

Here we show a couple of examples of high-temperature experiments carried out at the XAFS beamline using the new set-up described above. In Fig. 3 we show the Cu K-edge spectra of solid and liquid Cu, measured at 300 K and 1420 K respectively (temperature measured by

a pyrometer). Details about sample preparation and results obtained in a similar experiment carried out at BM29, ESRF can be found in ref. [14, 15]. We notice that the quality of the collected data at ELETTRA is particularly high, with noise levels below 10^{-4}, confirming the potential of this facility especially in an intermediate energy range (roughly 4∼12 keV) both because of the low harmonic content and for the high flux obtainable. In the inset of Fig. 3 we report a single-energy temperature scan (energy indicated by a circle) showing the large undercooling of about 100 K associated with the distribution of micrometric Cu droplets composing the sample (obtained reducing a mixture of CuO and BN grains[15]). The observed sharp melting and freezing processes indicate that our sample consists of a narrow size distribution of very pure Cu droplets (see ref. [14, 15, 16]).

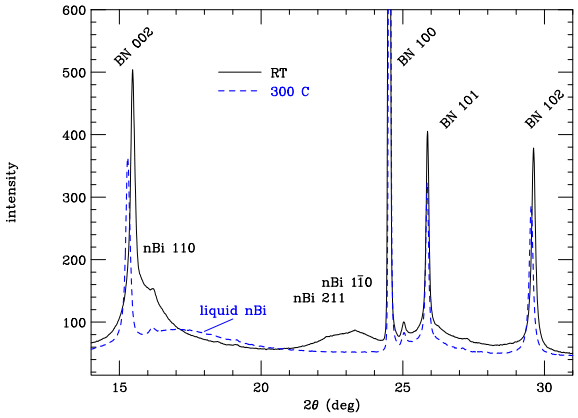


Figure 5. Angular dispersive X-ray diffraction pattern of nanosized bismuth (nBi) confined in a glassy inert matrix and dispersed in BN powder. Broad Bragg peaks associated with the Bi nano-crystal (solid line) are observed between 15 and 25 degrees. Bragg peaks are not observed at 573 K (300 ^{o}C, dot-dashed line) indicating the melting of the Bi nanoparticles.

Another interesting example of application of these techniques is shown in Fig. 4. The sample has been prepared by reducing a mixture of Bi oxide, silica and other oxides thus obtaining a nanometric Bi powder confined in a glassy inert matrix (sample nBi). This procedure (see [17] and ref. therein) has been found to be reliable for preparing large quantities of metallic Bi nanoparticles (the estimated average size is around 10 nm) although the size distribution is quite broad and the sample homogeneity may be not optimal (thus affecting the quality of the XAS measurements). The sample has been mixed with BN, then the final mixture has been pressed in a pelletter. The pellet has been positioned in the furnace shown in Fig. 1 close to a small pellet composed by micrometric metallic Bi and graphite (see [18] and ref. therein). Temperature was measured and recorded during x-ray measurements by a K-type thermocouple inserted between the two pellets and close to the x-ray beam. We then performed XAS and XRD experiments on nanosized and micrometric Bi particles under the same temperature conditions just moving the position of the furnace at the appropriate positions. In this way we are sure of the differences in melting/freezing temperatures and undercooling properties between bulk-like and nanosized Bi. Again, the quality of the XAS measurements on nBi is very high, as shown in Fig. 4 (see in particular the upper inset where Bi L_3 absorption spectra are magnified). A typical single-energy temperature scan (energy indicated by a circle in the upper inset) for such nanosized system is shown in the lower inset of Fig. 4. The hysteresis loop shown here is very different from that obtained in a bulk-like system (see Fig. 3 and ref. [18]). Here, the broad melting and freezing curves are mainly related to the reduced dimensions and scattered size distribution. Due to the grain size dimensions in the nanometer range, crystallization along the downstroke begins around 400 K, but nucleation occurs in the 400-300 K for smaller particles. The XRD patterns of nBi at room temperature and above the melting point, collected using the setup described above, are shown in Fig. 5. The observed diffraction patterns confirm the nature of the observed transitions. The broad Bragg peaks related to the nanosized Bi grains are easily identified in a background basically associated with the BN powder, and those peaks

disappear above the melting point (XRD patterns are shown in Fig. 5 at 300 and 573 K).

Conclusions

The optical layout and experimental set-up of the XAFS beamline at ELETTRA are described in this paper along with the new possibilities for combined x-ray absorption and diffraction experiments under extreme or non-standard conditions. The new experimental possibilities associated with sample environment (furnace and cryostat), detectors, and scanning modes are discussed in details. In particular, the advances concerning the beamline control and the sample environment are shown to allow us performance of high-temperature experiments under controlled conditions. The possibility of performing x-ray diffraction, x-ray absorption and single-energy absorption temperature scans using a high-temperature furnace is emphasized. Results for the melting and freezing of bulk Cu and nanosized Bi at high temperatures are discussed showing the quality of the measurements and the potential of these techniques for studying and understanding phase transitions of crystalline, nanocrystalline and liquid systems.

References

[1] Dent A J, Wells M P, Farrow R C, Ramsdale C A, Derbyshire G E, Greaves G N, Couves J W and Thomas J M 1992 *Rev. Sci. Instr.: Proceedings of the 4th international conference on synchrotron radiation instrumentation* vol 63 (AIP) pp 903–906
[2] Filipponi A, Borowski M, Bowron D T, Ansell S, Di Cicco A, De Panfilis S and Itié J P 2000 *Rev. Sci. Instr.* **71** 2422–2432
[3] Sapelkin A V, Bayliss S C, Russell D, Clark S M and Dent A J 2000 *J. Synchr. Rad.* **7** 257–261
[4] Grunwaldt J D and Clausen B S 2002 *Topics in Catalysis* **18** 37–43
[5] Filipponi A, Giordano V M, De Panfilis S, Di Cicco A, Principi E, Trapananti A, Borowski M and Itié J P 2003 *Rev. Sci. Instrum.* **74** 2654–2663
[6] Aquilanti G, Crichton W A and Pascarelli S 2003 *High Pressure Research* **23** 301–305
[7] Di Cicco A and Filipponi A 1996 *Journal of Non-Crystalline Solids* **205–207** 304–311
[8] Filipponi A 2001 *J. Phys.: Condens. Matter* **13** R23–R60
[9] Principi E, Di Cicco A, Witkowska A and Marassi R 2007 *Journal of Synchrotron Radiation* **14** 276–281
[10] Witkowska A, Principi E, Di Cicco A, Dsoke S, Marassi R, Olivi L, Centazzo M and Albertini V R 2008 *J. Non-Cryst. Sol.* **354** 4227 – 4232 ISSN 0022-3093 functional and Nanostructured Materials, 4th Conference on Functional and Nanostructured Materials
[11] Filipponi A and Di Cicco A 1994 *Nucl. Inst. & Methods in Phys. Res. B* **93** 302–310
[12] Di Cicco A, Gunnella R, Marassi R, Minicucci M, Natali R, Pratesi G and Stizza S 2006 *J. Non-Cryst. Sol.* **352** 4155–4165
[13] Filipponi A, Borowski M, Loeffen P W, De Panfilis S, Di Cicco A, Sperandini F, Minicucci M and Giorgetti M 1998 *J. Phys.: Condens. Matter* **10** 235–253
[14] Di Cicco A, Trapananti A, Faggioni S and Filipponi A 2003 *PRL* **91** 135505–1–135505–4
[15] Di Cicco A and Trapananti A 2007 *J. Non-Cryst. Sol.* **353** 3671 – 3678 ISSN 0022-3093 liquid and Amorphous Metals XII - Proceedings of the 12th International Conference on Liquid and Amorphous Metals, 12th International Conference on Liquid and Amorphous Metals
[16] Di Cicco A 1998 *Phys. Rev. Lett.* **81** 2942–2945
[17] Witkowska A, Rybicki J, Trapananti A, Principi E and Di Cicco A 2005 *Physica Scripta* **T115** 474–476
[18] Principi E, Minicucci M, Di Cicco A, Trapananti A, De Panfilis S and Poloni R 2006 *Phys. Rev. B* **74** 064101 (pages 7)