Dispersive XAS on a High Brilliance Source: Highlights and Future Opportunities

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Abstract. Energy Dispersive X-ray Absorption Spectroscopy is a now a well-established method which has been applied to a broad range of applications. Ten years from the construction of beamline ID24 at the ESRF, the first dispersive XAS spectrometer using undulator radiation on a third generation source, we report an overview of recent results in very diverse fields of research, ranging from automotive catalysts to magnetism at extreme conditions. We also illustrate how pushing the instrument to its limits has opened new opportunities, such as an enhanced sensitivity to detection of tiny atomic displacements and the potential for micro-probe redox and speciation imaging.

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INTRODUCTION

Energy Dispersive X-ray Absorption Spectroscopy (EDXAS) is a now a well-established method which has been applied to a broad range of applications [1] (for a recent review see reference 1 and references therein). The energy dispersive spectrometer employs a bent crystal to focus and disperse a polychromatic X-ray beam onto the sample. The beam passing through the sample then diverges towards a position sensitive detector, where beam position is correlated to energy [2]. Major advantages of this scheme are: i) an intrinsic stability in focal spot position and in energy scale, since there are no moving components and ii) a high acquisition speed, where all energy points are aquired rigorously in parallel.

In general, the spectrometer is installed on a divergent synchrotron source (often a bending magnet). The latter source naturally yields the large horizontal divergence (typically a few mrads) necessary to obtain, with reasonable radii of curvature of the polychromator crystal, an energy dispersion making it possible cover a whole EXAFS spectrum. At the European Synchrotron Radiation Facility, we have adopted a non-conventional optical scheme (Fig.1) allowing to take maximum advantage of a high brilliance undulator source [3]. The required horizontal divergence is obtained by inserting a strongly focusing mirror (HFM) upstream the polychromator (PLC). This mirror also performs a first important demagnification of the source making this optical scheme more suited for microfocus/high brilliance applications.
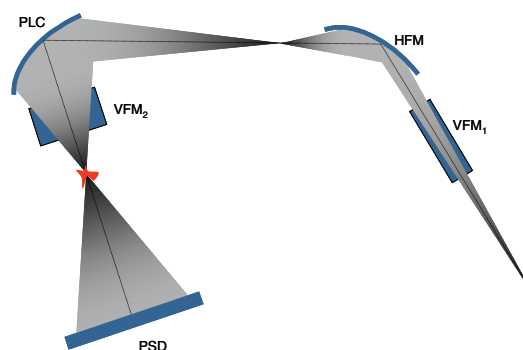

FIGURE 1. The complete optical scheme adopted on ID24, consisting in a pair of mirrors in a Kirkpatrick Baez geometry (VFM1 and HFM) and the polychromator (PLC). A second vertically focusing mirror (VFM2) downstream the polychromator is used to refocus the beam on the sample.

Drawbacks of EDXAS are related to the fact that i) the spectrum is obtained from a 2D image and ii)

energy – direction correlation of the diffracted X-rays needs to be preserved between the polychromator crystal and the detector. The first point makes EDXAS on high brilliance sources very sensitive to surface finish of optical elements, due to the relatively high spatial coherence of the beam, and to source instabilities, which amplify coherence related artifacts on the image. The second point puts strong demands on the nature and quality of samples, to avoid diffusion and small angle scattering.

In the ten years since the construction and start of operation of ID24 [4,5] a constant optimization program was carried out, starting with the stabilization of the source [6], followed by the implementation of new methods for data acquisition [7], through to an upgrading of the optical scheme [8] and finally in the complete refurbishment of the major optical elements [1].

We report here an overview of recent results from this instrument, in very diverse fields of research, ranging from automotive catalysts to magnetism at extreme conditions. We also illustrate how the synergy between source optimization, upgrades in optics and in detection methods and systems have opened new opportunities for EDXAS at high brilliance sources.

Three areas of application of X-ray absorption spectroscopy have shown to take maximum advantage of the intrinsic characteristics of high brilliance EDXAS: time resolved XAS studies, differential XAS techniques (i.e. X-ray Magnetic Circular and Linear Dichroism), and 2D μ-XAS mapping. The first area was historically the first to take advantage of EDXAS instruments to track rapid changes in the local and electronic structure of absorber atoms in disordered systems in the fields of biophysics, chemistry and materials science [9-13]. In the second area, EDXAS was found to be well suited in the detection of very small "difference" signals, such as XMCD, thanks to the intrinsic stability of the technique (no moving components) which helps reduce sources of non-statistical noise. EDXAS played an important role in extending XMCD to applications at extreme conditions [14]. 2D μ-XAS mapping is on the other hand a novel application of EDXAS, that fully exploits the acquisition speed to record thousands of spectra for constructing maps where each pixel contains full XAS information [15,16]. This is now possible with micron spatial resolution, thanks to the small spot size recently obtained on ID24 (5 x 5 μm^2) [1].

TIME RESOLVED XAS

Examples of present and future opportunities for time-resolved studies on ID24 can be found in references [17-22]. These include the investigation of

catalysts under *operando* conditions, where several methods and techniques are coupled and synchronized to EDXAS at the millisecond regime. For the study of heterogeneous systems in the solid-gas phase, these are Diffuse Reflectance Infrared Spectroscopy (DRIFTS) and Mass Spectrometry (MS), whereas for homogeneous systems in the liquid phase, Stopped-flow and UV-Visible Spectroscopy (UV-Vis).

In the field of heterogeneous catalysis, besides fundamental and applied research carried out by academia, ID24 has also attracted the interest of automotive industry. Industrial groups carry out proprietary research to elucidate the dynamical behaviour of their catalysts "in-situ" and under real working conditions [23,24]. An overview of the time-resolved XAS facilities available for industrial users on ID24 can be found in reference [25].

To give an example of the work devoted to the optimization of three way catalysts used in automotive industry we report recent data on the investigation of the behaviour of a supported catalyst system, Rh/γ-Al_2O_3, and its interaction with NO [26, 27]. Due to the key role Rh plays in the removal of NO_x gases in three way catalysts, the fundamental chemistry of Rh surfaces and of Rh in a nanoparticulate form has been widely studied.
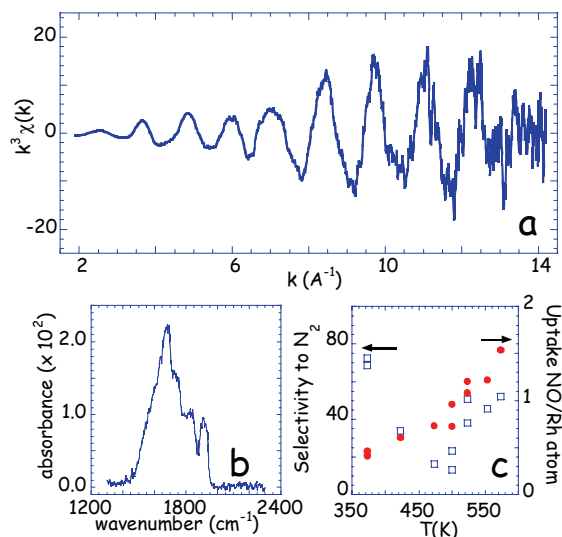

FIGURE 2. a) k^3 weighted Rh K-edge EDXAS and b) DRIFTS spectra derived from 5wt% Rh/Al_2O_3 after 50 seconds of exposure to 5%NO/He at 373 K. Each spectrum was acquired in ~ 60 msecs. c) Mass spectrometry derived variation of the net uptake of NO and net selectivity (N_2/(N_2 + N_2O)) toward N_2 as a function of sample temperature.

Understanding the manner in which Rh behaves under reaction conditions and from structural, reactive and kinetic viewpoints is of central importance to the development of such useful catalytic processes. For

this reason, structure, function, and reactivity need to be studied simultaneously.

We show in Fig. 2a and Fig. 2b representative k^3 weighted Rh K edge EDXAS and DRIFTS spectra (all aquired in ~ 60 msec) derived from 5wt% Rh/Al_2O_3 after 50 seconds of exposure to 5%NO/He at 373K. Fig2c shows mass spectrometry derived variation of the net selectivity ($N_2/(N_2 + N_2O)$) toward N_2 and net uptake of NO observed during 50 seconds of 5%NO/He exposure as a function of sample temperature. Analysis of the complete synchronous data set (EDXAS, DRIFTS and MS) for samples of different concentration and at different temperatures, for both the oxidation and reduction cycles, permit the elucidation of the structural-reactive role of the differing Rh-nitrosyl species that may be supported by the Rh component as a function of its degree of oxidation within these processes [26].

Currently this new methodology is being implemented on ID24 for the use of the wider research community, and further experiments utilising transmission infrared measurement are forseen.

DIFFERENTIAL XAS

The intrinsic stability and speed of EDXAS can be exploited to increase the detection sensitivity to small differences in XAS spectra, by making rapid comparative measurements in samples subject to a periodic external perturbation, such as a temperature gradient, or the rotation of a magnetic field. X-ray Magnetic Circular Dichroism (XMCD) is a well known example of "differential XAS" technique, measuring the difference in absorption between two helicity states of the photon, or, with fixed helicity, between two opposite directions of magnetization.

An important area of research on ID24 deals with XMCD studies at high pressure using the diamond anvil cell [28]. A large number of experiments currently deals with investigations of the pressure evolution of the magnetic moment on 3d metals [29], compounds [30,31] and oxides, where the XMCD signal at the K-edge of the 3d metal is only of the order of 10^{-3}. In some cases it has been possible to follow simultaneously the evolution of the local structure (from XANES) and of the magnetic moment (from XMCD) during a pressure induced structural and magnetic phase transition, such as the well known bcc-hcp transition in Fe at around 13 GPa [29, 32].

Recently, we were successful in measuring the much weaker X-ray Linear Dichroism (XLD) over an extended energy range, to detect tiny atomic movements [33, 34]. Displacements of atoms from their equilibrium distance, which are of the order of femtometres, are common in a variety of effects. For example, magnetostriction involves tiny mean atomic displacements that add up to give a macroscopically measurable quantity. Magneto-striction can be sensed as the buzz of a transformer, and used in under-water acoustic generation. We have measured the mean atomic displacement for atoms undergoing magnetostriction in an FeCo alloy by employing the subtle changes observed in the XAS spectrum when the relative orientation between the photon polarisation vector and the sample magnetisation vector is changed [33]. These results show that EXAFS sensitivity can be extended to include atomic displacements of the order of 0.00001Å, well within the range of thermal expansion over a temperature of one degree, piezo-effects, strictive-effects and elastic phenomena. All of these phenomena with the exception of piezo-effects are manifested in amorphous materials where the power of XAS as a structural technique is maximal.

Fig. 3 shows recent differential XAS data collected at the Fe K- on a thin amorphous ribbon of $TbFe_2$, undergoing periodic strain due to a 0.5T magnetic field rotating in the plane perpendicular to the propagation of the linearly polarized X-rays. Absorption spectra were recorded with the magnetic field parallel and perpendicular to the electric field direction and the differential signal was averaged over a large number of pairs. The amplitude of the differential signal is only of the order of 10^{-4}.
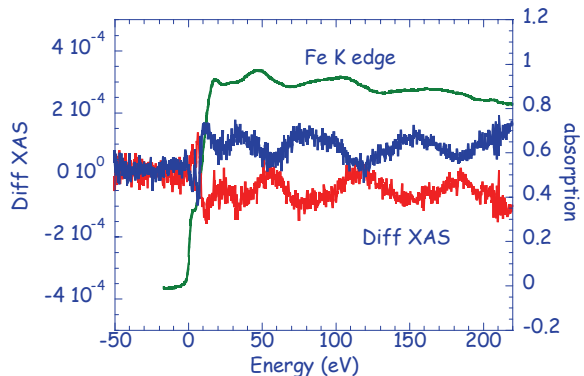

FIGURE 3. Fe K-edge XANES on a thin amorphous $TbFe_2$ ribbon (green). Normalized differential XAS: the two curves (red and blue) correspond to different starting positions of the magnet (parallel and perpendicular).

Rare Earth - Transition Metal (RE-TM) Laves phase compounds, such as $TbFe_2$, $DyFe_2$, and $TbDyFe_2$, exhibit very large room temperature magnetostriction, which, together with the large magnetic anisotropy energy, is thought to be associated to the asymmetry of the RE. When the magnetisation is rotated, the non-spherical RE ions are thought to be capable of producing important strain in their surroundings. In totally disordered amorphous alloys magnetic anisotropy and magnetostriction may

arise at the atomic level or as a stress induced long range order. While the microscopic origin of the anisotropy in amorphous alloys is debated, the existence of long range ordering is evident from the appearance of a magnetic domain structure. The possibility to measure local magnetostrictive strain, with chemical selectivity (i.e. in Tb-Fe and Dy-Fe in $TbDyFe_2$), will help in further understanding the role played by the asymmetry of the RE.

Further examples of areas to potentially benefit from differential XAS include piezo-electric materials with complex unit cells, elasticity of materials, and non linear phenomena, such as phase transitions[34].

2D MICROXAS MAPPING

The advantages of an energy dispersive spectrometer, that features no movement of optics during acquisition leading to an enhanced stability of energy scale, spot size and position, combined with a micron sized spot [1] and the option of fluorescence detection [7], have made possible to address 2D mapping with micron resolution on heterogeneous samples, providing full XAS information on each pixel. It is worth noting that due to the absence of mechanical scanning of the monochromator, the spatial resolution is not affected by the energy scan and remains fixed to the dimensions of the probe. Moreover, the dwell time per pixel is short enough to make it practically possible to acquire 100 x 100 pixel images in a few hours in fluorescence (less than 1 hr in transmission).

The information collected, intrinsically complete, is also too complex to be directly visualized. The extraction of the relevant information, spanning from simple oxidation state identification (from XANES) to local structural parameters (from EXAFS), requires specific software developments for data reduction, image reconstruction and visualization, providing a targeted reduced XAS information on each pixel.

A number of preliminary experiments were carried out on ID24 to explore the practical feasibility of complete 2 dimensional mapping of natural samples, such as metamorphic rocks. In such systems, the challenge is to date back to P and T conditions of the formation of rocks that have been subducted to great depth. This would provide key information to help in understanding the formation of mountain belts and the geodynamics of convergent zones at the lithospheric scale. Estimates of these so-called P-T maps have never been successfully achieved because they critically rely on the quantitative knowledge of redox and speciation within the crust, at least in two dimensions.

We performed a first test experiment at the Fe K-edge on a natural rock thin section (30 µm thick sample glued on a 1 mm thick glass plate). This complex geological sample, where chlorite, phengite and quartz minerals were thought to coexist, was an excellent candidate because of (1) the high variations of iron content, and (2) the expected variations of iron redox and speciation. About 3000 spectra were collected in ~100 min using TurboXAS in fluorescence mode [7], with 5 µm resolution, to cover an area of about 200 x 400 μm^2.

2D maps of iron content, Fe oxidation state and Fe speciation were obtained by extracting values of the absorption jump, edge energy position and absorbance at a defined energy, respectively [16]. Quantitative values of Fe redox were extracted by analysis of the pre-edge region.

These results were in excellent agreement with independent methods, such as Electron Microanalysis (for the Fe content) and thermodynamical calculations (for the Fe oxidation state variations) [15]. This method therefore opens the way to validation of theoretical models for estimating P,T conditions of formation of metamorphic rocks in subduction zones.

Very recently we tested 2D mapping in transmission mode to perform "in-situ" investigations in the Diamond Anvil Cell. Maps of redox and speciation at extreme conditions of pressure and temperature yield information on possible phase transitions and/or chemical reactions that occur at P and T conditions in the interior of planets. As test sample, we chose a major component of Earth's mantle, ringwoodite [γ-$(Mg,Fe)_2SiO_4$]. We aquired Fe K-edge XANES maps at different pressures, up to ~ 40 GPa, before and after laser heating, covering for each map an area of 200 x 200 μm^2 at 5 µm resolution.

Fig. 4 illustrates maps of normalized absorbance at a defined energy (E = 7125 eV) at 26 GPa (top) before (left) and after (right) laser heating. Analysis of the modifications in the spectra from the hot spot region will allow to extract Fe speciation at high P and T, yielding key information for modelling Earth's mantle processes.

This method is still in a development phase, and there is a large margin for improvement. The next obvious step is to exploit the EXAFS region with quantitative mapping of local structural parameters, such as bond distances and coordination numbers. The implementation of simultaneous elemental mapping using analysis of fluorescence lines is also foreseen.
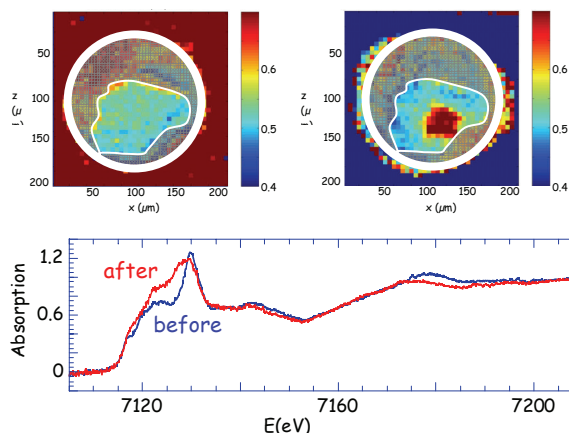
FIGURE 4. Top: Maps of Fe K-edge normalized absorbance (at E=7125 eV) on (γ-(Mg,Fe)$_2$SiO$_4$) at 26 GPa before (left) and after (right) laser heating. The sample occupies the unshaded zone. Bottom: Single pixel Fe K-edge XANES at the center of the hot spot (before and afer laser heating).

CONCLUSIONS

Ten years from the start of operation of beamline ID24, some fields of application of XAS fully exploit EDXAS at a high brilliance source.

In the conventional area of time resolved XAS, for example, recent heterogeneous catalysis work shows that the combination of EDXAS and complementary techniques yielding structure, function, and reactivity information simultaneously, allows to tackle more and more complex processes.

We also identify two novel areas of application of EDXAS. The first, in the study of tiny local atomic perturbations, where a sensitivity to atomic displacements of ~ 0.00001 Å has been reached using differential XAS. The second, in 2-dimensional chemical mapping of heterogeneous samples on the micron scale, where each of the thousands of pixels composing the image provides full XAS information.

Further advances in detection systems and in optics, combined to the high brilliance of the new synchrotron sources, should allow to make further breakthroughs is both these areas: atomic displacement sensitivity can be improved by one order of magnitude before reaching the statistical limit, and the spatial resolution can approach the 100 x 100 nm^2 regime with a modified design of the beamline allowing for higher demagnification.

ACKNOWLEDGMENTS

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