

**Diamond Year 3
Outline Proposal 027**

XAS-3: A Versatile X-ray Spectrometer

XAS-3: A Versatile X-ray Spectrometer

Introduction

This proposal forms part of a coherent strategy for X-ray spectroscopy in the UK, based around three beamlines: a microfocus beamline (BL-13), a bending magnet beamline (BL-C) and a high flux beamline (XAS-3). The aim of XAS-3 is to provide a versatile, modular spectrometer that will set definitive standards for stability and beam quality at high flux.

This development will make feasible, those large classes of experiments, currently out of reach, that demand sample dilution, speed, combined-techniques and secondary spectroscopy.

This beamline will require a commitment to ongoing developmental effort in both beamline and detector technology, but offers immense rewards to science and the basic technology of SR.

Science

Ultra dilute systems. Trace levels of elements play a vital role in geology, environmental science, biology, chemistry and materials science. Cycling of elements in the environment requires information on speciation, especially on the mobile and reactive non-crystalline phases found in rivers, aquifers and waste sites within sediments and soils. Biological systems form an important component within element cycling and are key to phytoremediation. Although metallic elements have long been known to be an important component of enzymes (metalloproteins), structural studies have only been possible using concentrated systems. Many catalysts contain ppm levels of promoters or poisons that have a profound effect upon reactivity. In all of these areas, knowledge of the local structure is seen as the key step towards a better understanding of process. The current limits for XAS analysis are 1ppm for solutions and an order of magnitude higher in more strongly absorbing samples. In nature most toxic elements are present in concentrations below the current XAS detection limit. *We are seeking a beamline that will give an order of magnitude improvement in signal to noise compared with existing beamlines, and will permit study of samples in their natural state.*

Interfacial science Interfaces are an essential part of environmental and physical science. Data collection times are currently ca 1hour and this could be reduced to a few minutes or less. This would open the way for dynamical in-situ studies of electrode surfaces, electrocatalysis, corrosion and lubrication, and surface studies of catalysts. Surface XAS studies of sorption and desorption of toxic species will be possible in real time to gain understanding of mobility and bioavailability. *This beamline will be ideal for studies of small numbers of atoms and /or arranged in low-dimensional form.*

Time resolved XAS. The UK holds the world lead in energy dispersive XAS (EDE). It is feasible to reduce the readout time to 1 μ s. This will enable a complete spectrum to be recorded within the time period of a single bunch. Pump probe experiments will then be feasible with 50 ps

resolution. For dilute systems, scanning XAS or time-slicing is essential. On XAS-3 there should be sufficient flux to obtain complete scanning spectra in 1-2 seconds and good quality time-sliced data in milliseconds. *XAS-3 will permit study of transient intermediates in chemical and photochemical pathways.*

Combined techniques in SR have been pioneered in the UK to tackle systems where no single technique supplies a sufficient level of understanding. The core combination has been XAS/XRD. These two techniques provide information that spans changes of length scale and overcome problems of polydispersity. The improvement of flux provided by XAS-3 and provision of a pixellated area XRD detector will remove the compromises inherent in both techniques. This will permit collection of a complete structure dataset in seconds for complex materials. This combined approach is required for in the study of nucleation and crystallisation of ceramics, minerals, clays catalysts and bio-mineralisation. It will lead to the identification and elucidation of intermediate metastable phases in these systems. This facility will be ideal for experiments under extreme conditions such as HP/HT. High pressure melts are found in most planetary cores, but their properties are not well understood. Melts are an important component of industrial processes such as glass formation. These systems require the use of additional optical, electrical or magnetic probes. *XAS-3 will strive for 4π solid angle for x-ray and optical data collection and maximal information content.*

Secondary X-ray Spectroscopy (SXS) resolves the fluorescence / Raman scattered radiation with a second high resolution x-ray spectrometer. This gives two dimensional data that can supply site and / or spin specific local structural information via chemical shifts of emission lines or spin satellites. This can be exploited to unravel structural information from different charge states of the same element existing in a material. It has also been shown that mixed spin states, found in some transition metal compounds and in biological tissue can also be separated. X-ray magnetic circular dichroism spectra, are normally very surface sensitive because they are recorded using soft-x-ray techniques. SXS permits XMCD to be extracted at hard x-ray energies which enables experiments on bulk materials even under high pressure conditions. SXS can remove a large component of the lifetime broadening, and thereby go beyond the core hole lifetime limit. This makes it possible to reveal extra structure at the edge, in XANES, and in regions of multi-electron excitations. X-ray Raman scattering can also be measured to produce structural information on light elements such as B in borate like glass. Furthermore SXS can be exploited to examine the local structure of magnetostrictive materials, many of which have overlapping absorption edges. SXS is seen as a high priority area for technique development.

This beamline will ensure the secure development of XAS at Diamond into new and promising areas, as well as challenging, area. and will give the UK a unique tool for future scientific discovery.

Primary optics: summary

The applications described above require data of the highest accuracy, either because the signal/background level is very low, or because data are collected extremely quickly. Therefore, the principal requirements for these applications of XAS are maximal flux and beam purity, maximal stability and minimal noise. The flux requirement can only be satisfied by a MPW, since only this source will give the broad and stable energy range. It is mandatory for QEXAFS and EDE.

We propose a robust versatile spectrometer which covers a wide spectral range giving a focussed beam for $E < 35\text{KeV}$, and an unfocussed beam for energies above this value.

Primary optics: details

1. In order to utilise efficiently the vertical aperture of radiation offered by an MPW without degrading energy resolution, the first optic is required to be a mirror. This will produce a collimated beam and reduce the heat load on the primary monochromator. This will impose a maximum energy cut-off; proposed to be 35keV so that all elements are covered. However consideration will be given to make the mirror removable to extend the energy range.
2. A twin axis monochromator with cryogenic cooling is proposed. The power loading on the monochromator (750W/mrad) will necessitate a development program, but this is already under active consideration at a number of other SR facilities. A 4-bounce system will reduce monochromator tails, reduce the heat loading problem, and produce a constant height exit beam without the use of any translational motion.
3. A design study is required to establish the best strategy for horizontal and vertical focussing. Alternatives are: one fixed mirror + sagittal 4th crystal, two fixed mirrors, toroidal second mirror. These are not entirely exclusive options.
4. Consideration will be given for a small two/four mirror harmonic rejection device.

Output Beam Characteristics: scanning monochromator

Energy range 4-35 keV, with energy resolution less than 1/4 of the core-hole lifetime limit. Instrument function approaching rectangular shape to eliminate thickness distortion. Beam size $\sim 50\mu\text{m}$ (v) $\times 1700\mu\text{m}$ (h) FWHM. Flux $1\times 10^{14}\text{ s}^{-1}$ with Si(111) at 10keV (compare ESRF: ID26 10^{13} , SRS: MPW6.2 10^{13} , SRS:16.5 10^{12}). Harmonic content 10^{-5} - 10^{-6} at all energies, to facilitate studies with thick samples and samples in absorbing containers. Absolute energy calibration will be incorporated into normal practice. A polarisation monitor will be available.

Cooled Laue and Bragg energy dispersive monochromators

A detailed design study for the EDE monochromators will be required, since cooling the monochromator will

present a very serious challenge. However EDE on this beamline would offer a larger k -range, and higher flux than ID24 at the ESRF and potentially be more stable because a secondary source point is not required.

Energy range: 6-35 keV, resolution $\Delta E/E$ 1×10^{-3} ; photon flux $3\times 10^{13}\text{ s}^{-1}$ with Si(111) at 10keV (ID24 2×10^{12} , 9.3 5×10^{11}), beam size $\sim 50\mu\text{m}$ (v) $\times 30\mu\text{m}$ (h) FWHM.

Detectors and secondary optics specification

Subsystem detectors and secondary optics will be designed as modules that may be readily exchanged. Located on a kinematic mount with 10micron precision, modules will be optimised and prealigned offline, in order to maximise beamline throughput.

Detectors: For many samples, beam damage will limit the duration of experiments. In these circumstances, improvements to data quality will rely upon the development of more efficient detectors. For fluorescence measurements, multilayer Bragg filters are emerging as viable alternatives to solid state detectors, but CCLRC's strong lead in the latter area indicates that within the next few years a pixellated Ge or GaAs detector with $<500\mu\text{m}$ pixels and > 1000 channels is not unreasonable. For X-ray Diffraction a 1D curved compact μ -strip detector and a 2-D pixellated detector are proposed. High throughput, high resolution (2 eV) imaging solid state detectors should be investigated. For EDE, XSTRIP2 will offer a 1024 channel PSD with $<1\mu\text{s}$ minimum integration time. A design study will be required to define the characteristics of an optimum secondary x-ray spectrometer.

Sample modules and offline facilities

XAS-3 will adopt a modular design for sample environments, to provide a platform common to all of the XAS beamlines. This will maximise exchangeability of sample environments between beamlines, and minimise the time lost between experiments. A wide variety of sample environments will be provided, in collaboration with user groups. These include cells capable of operating at high and low temperatures and pressures (HT, LT, HP, LP) equipped for simultaneous XRD measurements and Raman, optical, electrical resistivity and magnetic properties, utilising as much as possible the 4π solid angle for x-ray and optical beam delivery and for data collection. Process monitoring will be available for reacting systems. The data acquisition system will allow seamless integration of user-defined sample environments and ancillary data collection into the experiment. This will ease automation of tasks such as setting up, control of multiple techniques and remote access for monitoring. Offline facilities will permit initial alignment and sample characterisation to be undertaken. These facilities would be shared with BL-13 and BL-C.

List of Supporting Groups

This proposal is the result of merging two proposals (XAS-2a and GPXS) that were submitted in Round 2. It is hoped that this proposal encompasses those aspects of both that were the most challenging. In the intervening period, support for this proposal has grown from new environmental and microbiological groups in the UK.

Abrahams I	Chemistry Department	Queen Mary College London
Chadwick A V	Chemistry, School of Physical Sciences	University of Kent
Anderson J A	Physical and Inorganic Chemistry	Dundee University
Barnes P	Crystallography, Birkbeck College	University of London
Bayliss S	Molecular Sciences	De Montfort University
Benfield R	Physical Sciences	University of Kent
Berry F J	Chemistry Department	Open University
Blundy J	Department of Earth Sciences	University of Bristol
Burch R	Department of Chemistry	Queens University, Belfast
Collins S.P.	CLRC	
Doherty S	Department of Chemistry	Queens University, Belfast
Evans J	Department of Chemistry	Southampton University
G. Gadd	Biological Sciences	University of Dundee
Greaves G N	Physics Department	University of Wales, Aberystwyth
Hardacre C	Department of Chemistry	Queens University, Belfast
Harris K D M	Department of Chemistry	Birmingham University
Harvey I	Daresbury Laboratory	CLRC
Henderson C M B	Earth Sciences	Manchester University
Irvine J	Chemistry Department	University of St. Andrews
James S	Department of Chemistry	Queens University, Belfast
van der Laan G	Daresbury Laboratory	
Lambert R M	Department of Chemistry	Cambridge University
C Langdon	Soil Science	Reading University
Linford R G	Chemistry Department	De Montfort University
Mosselmans F	Daresbury Laboratory	CLRC
Murphy L	Daresbury Laboratory	CLRC
Ormerod M	Department of Chemistry	University of Keele
Parker E	Department of Physics	Warwick University
Patrick R A D	Earth Sciences	Manchester University
R.F. Pettifer,	Department of Physics	University of Warwick
Rayment T	Department of Chemistry	Cambridge University
Robinson J	Department of Physics	Warwick University
Russell A E	Department of Chemistry	Southampton University
Russell M	Isotope Geology Unit	SUERC, Glasgow
Sadler P J	Edinburgh	Edinburgh University
Sankar G	Faraday Research Laboratory	Royal Institution
Sapelkin A	Molecular Sciences	De Montfort University
Saunders G	Department of Chemistry	Queens University, Belfast
Seddon K	Department of Chemistry	Queens University, Belfast
Sermon P	Chemistry Department	University of Surrey
Slater P R	Department of Chemistry	Surrey University
Dr Ian Thompson	Centre for Ecology and Hydrology	Oxford, NERC
Vaughan D	Earth Sciences	Manchester University
Wall T	Department of Physics	Warwick University
Walton R I	Department of Chemistry	Exeter
Went M J	Chemistry, School of Physical Sciences	University of Kent
Young N A	Department of Chemistry	University of Hull

This document was prepared by T.Rayment, A Dent, R Pettifer, A. Sapelkin, S Bayliss, with help from F.Mosslemans and I. Harvey