REPORT ON: FIRST APPLICATIONS OF A NEW XEOL MICROSCOPE FOR SPECTROELECTROCHEMISTRY

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Introduction

A new CCD microscopy instrument, x-ray excited optical microscopy 1 (XEOM 1) was deployed for the first time on the XMaS beam line following initial tests on DUBBLE in December 2010. XEOM 1 uses x-ray excited optical luminescence (XEOL) from 200 nm to 1 µm to acquire chemical maps of a sample with an ultimate lateral resolution of 1 µm. Because the microscopy is dependent on the optical system which collects the light, and not on the use of a scanned microbeam, 2048 x 2048 images can be collected in times from 0.5 s upwards, and (in this run) image stacks across the XANES edge were acquired in 400 s. (Note we used a 2048 x 506 CCD for test purposes, but the acquisition time is identical for 2048 x 2048 devices.) In the XMaS beam time we found an ideal configuration for XEOM 1 on the Huber goniometer, measured the first chemically differentiated images from test samples based on copper corrosion products and a topological insulator ($Cu_{0.2}Bi_2Se_3$), and acquired our first image stacks automatically synchronized with the monochromator scan (image spectra). In most cases XEOL imaging using a broadband back illuminated CCD was done in parallel with collection of the total XEOL signal (broadband photomultiplier (PM)) and the conventional x-ray fluorescent signal (APD photodiode). A cure for a serious acquisition problem noted on DUBBLE was tested and found to be successful, and thorough extended use of the camera, a few other problems were identified and probable solutions put in train.

Mounting XEOM 1 on the Huber goniometer

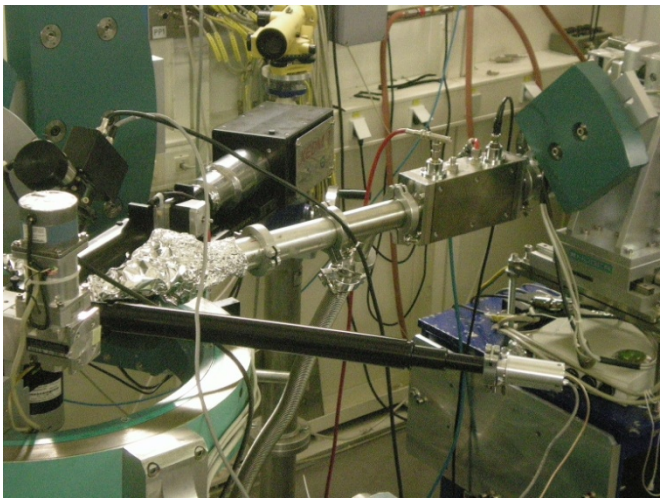

Figure 1: XEOM mounted on the XMaS Huber goniometer with the Chi circle horizontal

Several configurations were tried, but the best one, suggested by Paul Thompson the local contact was to position Chi circle of the Huber with its plane horizontal, and the microscope axis at 30° to the beam. (Fig. 1) This was very mechanically stable and also allowed for incident and take off angles for x-ray fluorescence XAS which avoided significant backscattering into the detector.

Tests of the imaging system

Initial tests of the imaging system were carried out using fluorescent paper with a 200 mesh (127 µm pitch, 100 µm holes)

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copper TEM grid mounted on it, and the beam heavily attenuated. The sample proved to be ideal for setting up and alignment, and several copies will be made.

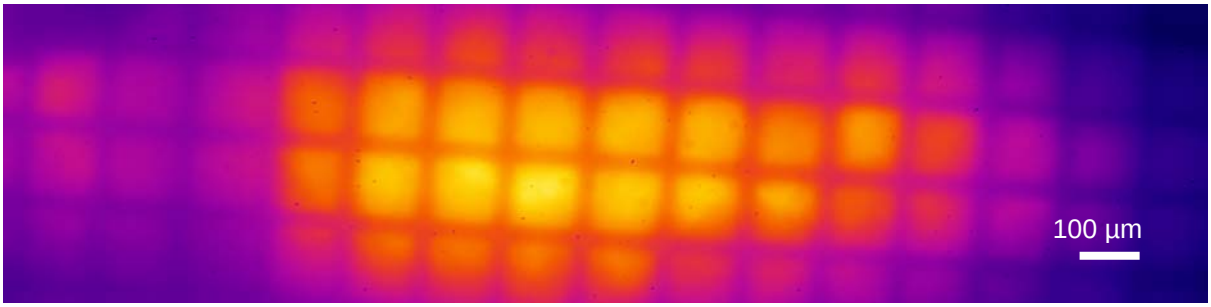

Figure 2: Ironbow false colour image of the alignment grid (200 mesh) backed by fluorescent paper.

First chemical maps of copper corrosion products

Cuprite (Cu_2O) was produced on the surface of a similar mesh and this was mounted on a copper coupon coated with nantokite (CuCl). XEOM was used to acquire images from this sample both sides of the Cu edge, and then image stacks synchronized with the monochromator scan. The two regions (cuprite mesh bars and nantokite holes) give good contrast in the image, and work is in progress to extract spectra from different regions of interest in the stack.

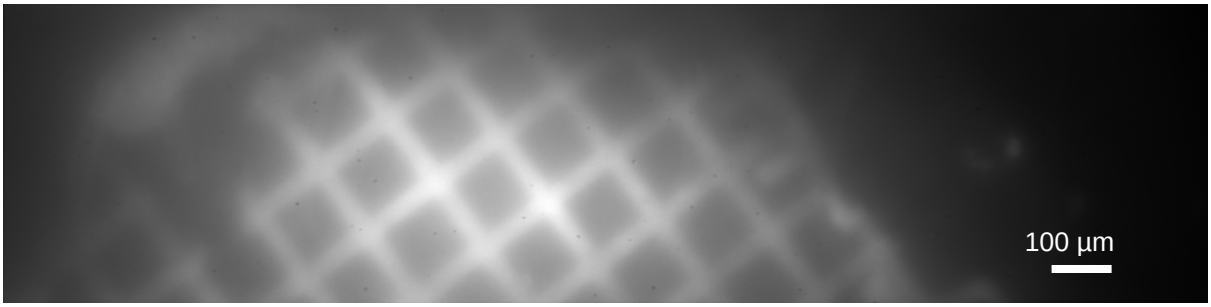

Figure 3: XEOL image of a cuprite grid (200 mesh) on the surface of a nantokite coated coupon (9.907 keV, last image in a stack of 400).

Acquisition of image spectra

A macro was written by ESRF software support (Laurent Claustre) to synchronize the acquisition of CCD images by our XEOM control system with the stepping of the monochromator, using a TTL timing pulse output by the XEOM control system (a self-contained acquisition system for imaging and spectroelectrochemistry running from a user laptop). In this way it became straightforward to acquire stacks of images (image spectra) across absorption edges and into the EXAFS

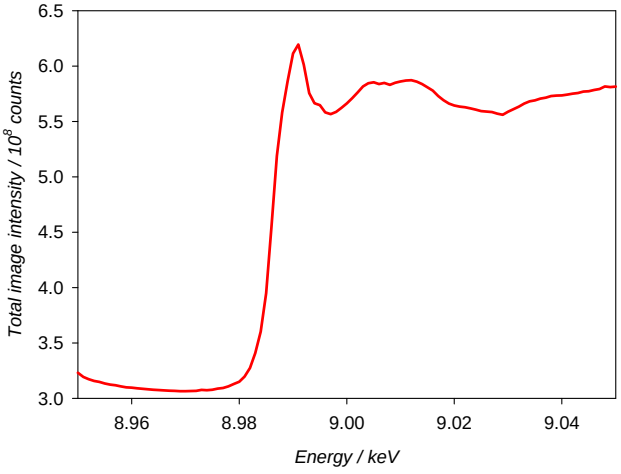

Figure 4: Total XEOL-XANES from the stack in Fig 3.

region (Fig. 4). A minor problem with this system was that around 0.5 monochromator steps per 100 images were skipped at random for reasons which are unknown at present, but which might be due to large volumes of traffic on the Ethernet.
However, because our images are independently stamped with both time and energy. we can use our software to identify the skiped point(s) and properly match the SPEC record with the image stack (see esaProject development below).

Problems solved and arising

1. On DUBBLE it was found that the high background x-ray flux in the hutch could enter our CCD camera and cause the electronics to flush images after a few 10s of seconds. Before the XMaS run, the camera mounting tube was sheathed in 0.5 mm thick self-adhesive lead sheet and a similarly lined box was constructed to contain the camera. These measures proved entirely successful.

2. Almost all images contained luminous arcs running from top to bottom. After a lot of investigation at ESRF and subsequently, these have been correlated with ripples in the surface of the CCD itself or a surface coating designed to extend its UV response. One explanation is that these act as focussing mirrors, reflecting a fraction of the incident radiation onto the inner surface of the fused silica window in front of the CCD chip. From there it reflects back onto the CCD surface. Discussions with the camera supplier (Finger Lakes Industries) and the CCD manufacturer (Hamamatsu) are in progress but it appears that the Hamamatsu CCD chip is faulty.

3. Parallel collection with the CCD and the photomultiplier tube revealed that not all surfaces emitting high fluxes in the visible produced CCD images. The bandwidth of the CCD is somewhat larger than that of the PM (and extends 250 nm farther into the IR according to its specification) and the quantum efficiency is up to a factor of 10 better across the range. Despite this, the PM often detected visible emission from surfaces, modulated by the XANES/EXAFS information, when this was not apparent in the CCD images or even the total count therein. At first it was thought that the PM tube was detecting x-rays, augmenting its signal. The direct line of sight is already blocked to x-irradiation (at 9 keV) by a 15 mm thick fused silica lens, and shielding the PM and its mounting tube in lead made no difference. In any case, the same phenomenon was observed when the PM was moved to the fully shielded CCD camera port. Investigation of this problem is under way.

First images of topological insulator

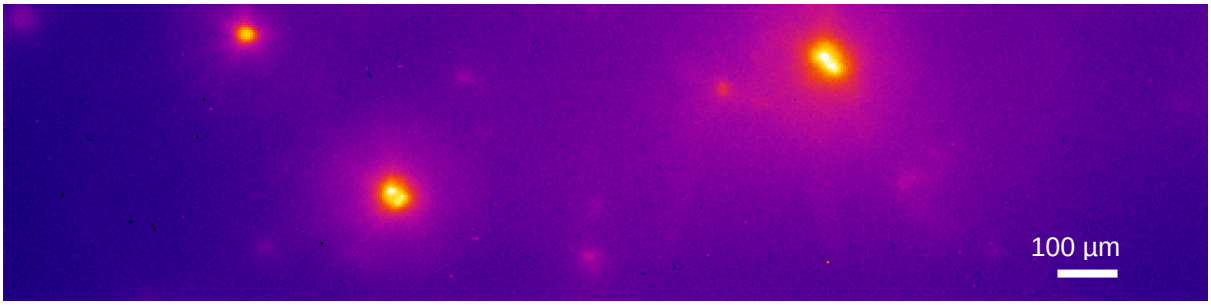

Figure 5: XEOL difference image. An image taken just pre-edge (8.95 keV) has been subtracted from a just post edge image (9.00 keV) so that the intensity is representative of the Cu edge height. Image 4 x 4 binning, 2000 s per image acquisition time.

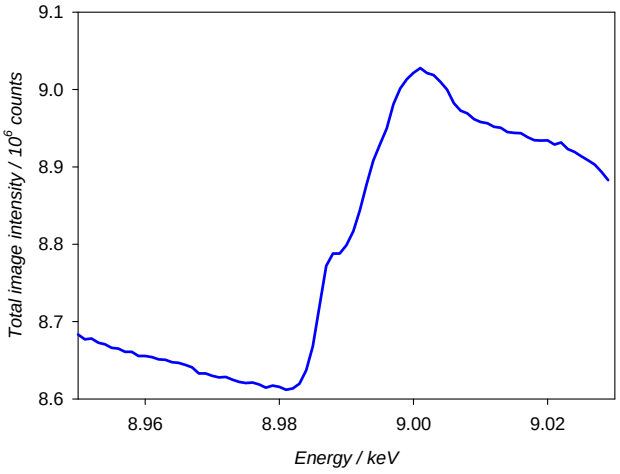

Figure 6: Raw XEOL-XANES extracted from a bright region on the copper bismuth selenide topological insulator of figure 5.

A $Cu_{0.12}Bi_2Se_3$ topological insulator grown at Warwick was added to the sample list. In this material, the superconducting properties are believed to be controlled by atomic-scale planes of copper intercalated between planes of bismuth selenide. However, the exact conditions for producing intercalated copper, rather than substitutional copper are not well known. XEOM images of this sample taken by subtracting a pre-edge image from a post edge image showed regions several microns across apparently enriched in copper (Fig. 5), and image stacks revealed a very distinctive XANES spectrum (Fig.6) which requires further investigation.

Work in progress

Following experiments with FITS and similar formats we have devised a much simpler system which meets our requirements for storing both XRD and XANES images. It consists of an indefinitely extendable text header containing parameters (as text) linked to keywords which identify the parameter (e.g. TITLE), followed by a binary representation of the image which may be in one of five standard IEEE number formats (INT16, UINT16, INT32, UINT32, and BINARY64). Upon read, the software supplies defaults for any missing keywords, and so the system is entirely reverse compatible on file structure. This allows us to store highly processed images with a large dynamic range, as well as raw camera images, all in the same format. esaProject, our data analysis package has been extended to extract spectra from user-defined regions of interest in image stacks. It can already mine SPEC files for various types of information such as the beam monitor signal, and associate these correctly with XRD data from the XMaS Mar CCD camera, and this ability is being added to the XEOM image processing at the time of writing this report.

Deferred experiments

We had proposed to examine an idea for a compact beam monitor following problems using ion chambers where monochromator glitches could not be normalized out of the XEOM data. However, provided that the ion chamber is the last component before the sample in the beam line (i.e. any apertures come before the ion chamber), the method is much more successful (clearly, mono glitches are accompanied by small angular movements of the beam, and if the apertures are between the ion chamber and the sample, some unmonitored modulation of the beam intensity on the sample occurs. We therefore deferred these experiments until beam time in May in order to focus more fully on working with XEOM 1.

Conclusions and Future Work

Successful operation of a spectromicroscope which can offer micrometre-scale chemical mapping on a bending magnet beamline with mm-scale focussing has been demonstrated.
The coupling of XEOM 1 to an operating electrochemical/environmental cell is a key part of our experimental strategy. Beam time has been granted in May 2011 for us to examine the effect of the x-ray beam on the cell window and electrolyte as previous experiments have suggested that their optical constants are temporarily modified by the passage of the beam. Applications for further time in 2011/2012 will focus on developing applications for XEOM 1.