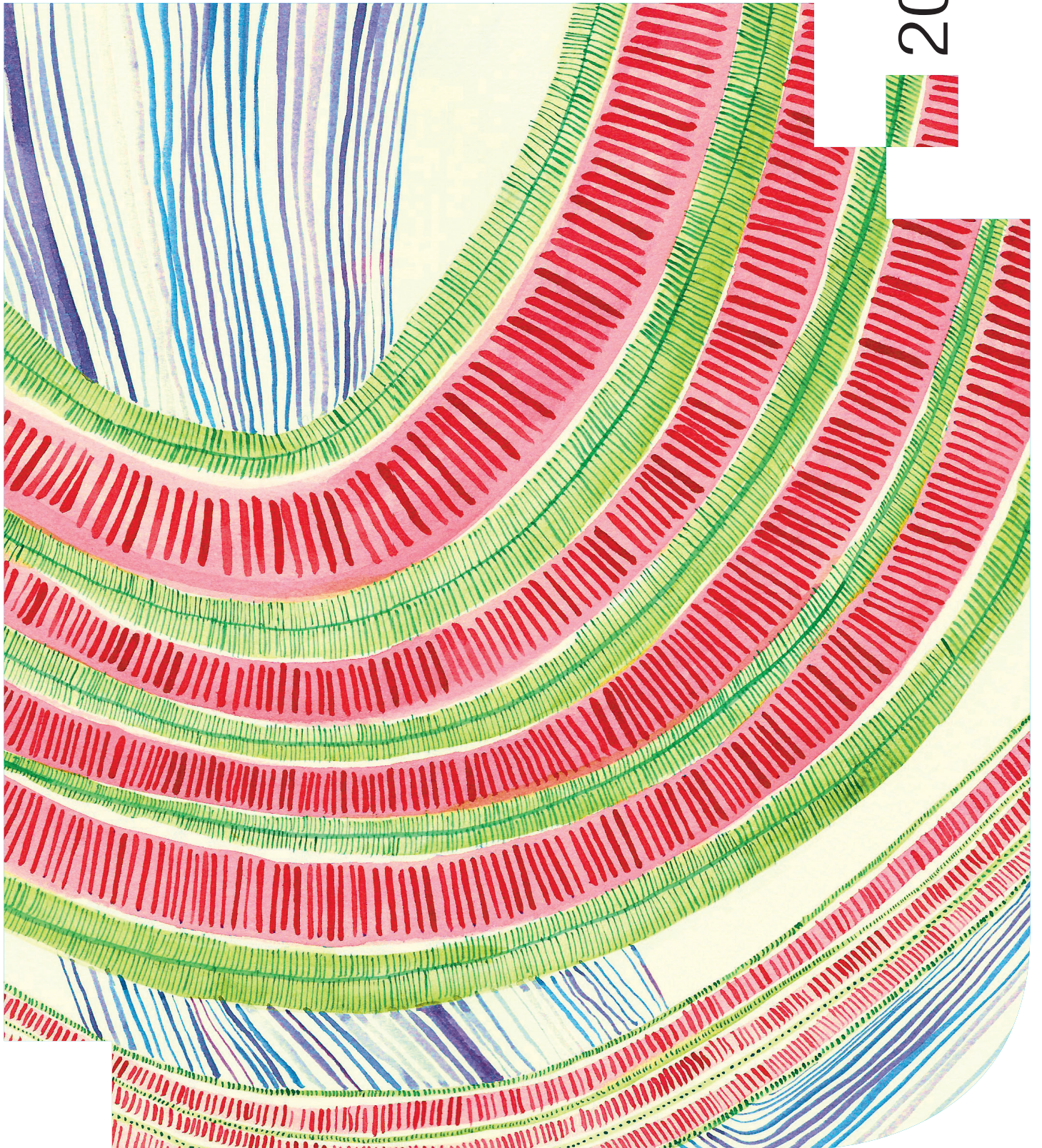


XMas

NEWSLETTER

2013





Status

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The XMaS beamline is now one year into its operation as an EPSRC mid-range facility. During the first year we provided 34 experimental shifts with an average up-time of 93.4%. The XMaS user community continues to cover a diverse range of scientific areas as shown in **Fig. 1**. We are excited by the new and growing user community interested in exploiting our low energy capabilities for EXAFS studies. This work is described in more details in the *Energy & Catalysis* section.

We thank our users for their feedback on how the mid-range facility is operating. We always value your comments and the information from the end-of-run survey is summarised in **Fig. 2**. We welcome any comments and/or feedback you have and will continue to strive to enhance and develop the facility. Further statistics and performance metrics can be found on the newly designed web-page:

<http://www.xmas.ac.uk>

As part of the on-going upgrades to the facility a number of technical developments and extension of the facility capabilities are currently in progress. In particular, we are extending our capabilities through the development of some “off-line” facilities that make wider use of the capital equipment that already exists and which can be used in parallel with the main beamline operations. These include a laboratory-based x-ray micro-source which is equipped with a diffractometer that is compatible with many of the sample environments used on the beamline. This instrument is scheduled to be available in the summer of 2014 and will be useable both for pre-alignment of samples prior to synchrotron beamtime and for “stand-alone” experiments. The instrument will be based in the rear cabin (previously the office of Paul Thompson). In addition, we can now offer a facility for the measurement of P-E loops. Currently this is available in the middle cabin at the beamline although it will soon be sited in a new purpose-built laboratory close

to the beamline. More details of these two facilities are given in the *Instrument Developments* section of this newsletter. We are pleased to announce that we have some additional funds to support a small number of users to make use of these facilities, but please contact us for more details if you think you may be interested in using them, as the synchrotron beamline takes priority on any equipment and staff resources.

Beamline developments include a new GISAXS setup for fast and automated switching between XRR, WAXS and GISAXS (delivery in Summer 2014) and the purchase of two new area detectors: a Maxipix (delivery by June 2014) and a larger 2D pixel detector (probably available by the end of the summer 2014). If you have an idea for an experiment that can make use of the XMaS beamline but requires some instrumental development in terms of sample environment then please don't hesitate to contact us, as funds may be available for such projects.

As announced in the 2012 Newsletter one of our main collaborative projects is now with the National Physical Laboratory as part of a European metrology programme. The laser interferometer for this project is due to be commissioned on the beamline at the end of February 2014 and can then be used both on the beamline and the “off-line” x-ray source. A two year postdoctoral research position is associated with this project (the advertisement went out close to Christmas 2013) and we hope to have somebody in post by April 2014.

In May 2013 the XMaS Annual User Meeting was held at the University of Liverpool and was attended by ~50 scientists. The meeting consisted of 8 user presentations which spanned the range of science performed at the beamline. The morning session highlighted studies of soft matter (organic and hybrid nanomaterials) and biomaterials. The first session in the afternoon was devoted to hard condensed matter physics, including

On the cover: artistic representation of self-assembled structures by surfactant/conducting organic oligomers by Becca Rose (see article p. 15)



charge density wave order in high magnetic fields and magnetic x-ray scattering from weak ferromagnets. Studies of electrically induced nanostrain in ferroelectric and magnetoelectric materials by means of synchrotron XRD and optical interferometry were also presented. The final session focussed on oxide materials with *in-situ* studies of corrosion in UO₂ single crystal thin films and strain mapping in In₂O₃ thin films and nanostructures. The meeting closed with an informal discussion and wine reception which was especially enjoyed by all of those who were not driving home. In 2014, the user meeting will take place at the University of Warwick. Please check the XMaS website to find more details.

In addition to our annual meeting, we have been involved in a number of workshops and meetings. As well as the third instalment of the multiferroic workshop series organised with the NPL (described in detail in this Newsletter) a one day workshop “*Surface Science with Synchrotron Radiation*” was held at the Royal Society of Chemistry in London on 22nd January 2014. The event, co-organised by XMaS, included a seminar by Jorg Zegenhagen, (Diamond Light Source), Chris Lucas (Liverpool

University), Georg Held (Reading University).

A workshop exploring the possibilities of using the XMaS beamline for EXAFS measurements down to x-ray energies of 2 keV will take place in Warwick sometime in early March 2014. If you would like us to help organise a focused event covering current or future opportunities on XMaS please get in touch as we have some funds available for these activities.

As many of you who have visited the ESRF will have noticed the site continues to have a considerable amount of construction work. Many of the laboratory buildings associated with the ESRF upgrade have been completed and there is now a brand new cafeteria area close to the site of the old one which was under the bridge between the ESRF experimental hall and the central building. The opening of a new main gate to the EPN campus is planned for the end of January 2014 (this is subject to the approval by the French Nuclear Safety Authority (ASN) for ILL and the end of works on the road junction by the City of Grenoble). Furthermore the operation of the extended tram line which will link the EPN campus to the centre of Grenoble is planned for September 2014 (the 34 bus

will stop running after that date). This will provide a regular service between the city centre and the EPN campus throughout the day until midnight which will greatly improve the options for eating both at lunchtime and during the evening. Note, this is strictly for those whose experiments are running so well that they can leave a long macro running while they go for a nice meal in town!

As part of the wider reorganisation of the ESRF main hall we are happy to announce that the beamline staff offices are moving back, closer to the beamline. The offices will be relocated in the area of the old XMaS PLUO now replaced by the Chartreuse Experiment Hall, on the mezzanine level.

Finally, congratulations to India Foster on the birth of her baby girl. Abigail Meadows has ably replaced India during her maternity cover but moving forward into 2014 this role will be covered by Kayleigh Lampard (Kayleigh.Lampard@warwick.ac.uk) who will be the principal administrator on the project at Warwick. All queries regarding expenses claims, meetings and other administrative issues should be directed to her.

Chris Lucas, Tom Hase and Malcolm Cooper

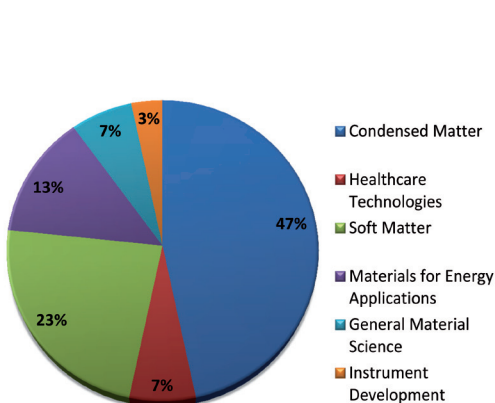


Fig. 1: Scientific areas as defined by our users in the end-of-run survey for the mid-range operational phase.

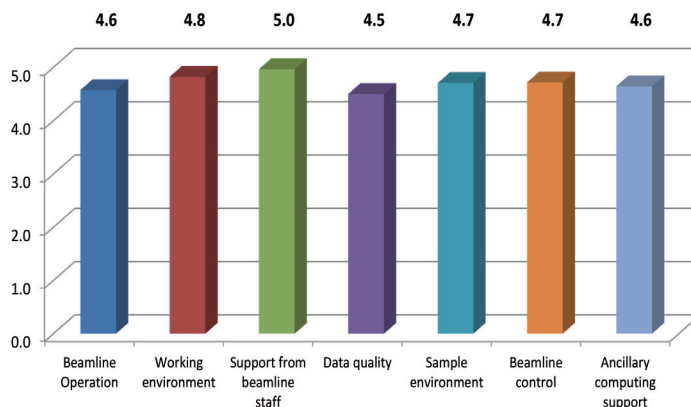


Fig. 2: Performance metrics for the beamline for the first year of operation.



X-ray & Neutron Scattering in Multiferroic and Ferroelectric Materials Research III

This third workshop in the series, co-hosted by the UK's National Physical Laboratory (NPL) and XMaS, was held at NPL in London on 14th November 2013 [1]. It was kindly co-sponsored by NPL, XMaS, the Institute of Materials, Minerals and Mining, the Universities of Oxford, Liverpool and Warwick, EPSRC, National Measurement System and the European Training Network "Nanomotion". This event has been steadily growing over the years and was again very successful in bringing together experts from the worldwide multifunctional materials community as well as users from both neutron and synchrotron facilities. The latest experimental and theoretical results were presented and new *in-situ* capabilities at central facilities across Europe and the USA discussed. Live video streaming from the NPL laboratories as well as pre-recorded video segments from XMaS highlighted the practicalities of conducting various metrologies on real samples.

As in the previous meetings, a highlight of the meeting was the discussion forum held during the afternoon to examine and disseminate the best practices, common problems and state of the art experiments for the study of this class of materials. This has fed into the good practice guide on how to conduct ferroelectric measurements which is also available online [2].

Due to the overall success of this and previous meetings, the series will continue with the next event scheduled to be held at NPL during the autumn of 2015.

[1] www.npl.co.uk/science-technology/functional-materials/research/x-ray-and-neutron-scattering-in-multiferroics-research

[2] <http://interactive.npl.co.uk/multiferroics/>

[3] www.nanostrain.eu

EMRP Nanostrain project

XMaS is pleased to be involved as a partner of the exciting new European Metrology Research Programme (EMRP) **Nanostrain** [3]. This programme is a collaboration between Europe's world-leading metrology experts, instrument scientists and global industry leaders including IBM, working together to develop innovative tools to measure strain accurately in piezoelectric materials at the nano-scale. The ultimate goal is to drive innovation in the next generation electronics devices.

This three year project will develop traceable measurements and characterisation of nano-strain under industrially relevant conditions such as high stress and electric fields. This will help deliver cheaper and more reliable energy efficient technology. For example, piezoelectric effect based transistors have the potential to be orders of magnitude better than existing technology because they circumvent the speed/power bottleneck of current technology (CMOS). This new generation of transistors will consume about a hundred times less power than today's devices. At the same time, simulations show achievable clock-speeds of about one order of magnitude larger (~30 GHz) than today's CMOS equivalent. However progress in delivering these devices depends on the development of traceable measurements using new metrology techniques to better understand how materials strain on the nano-scale in real-time and at high speeds. This is being developed on XMaS with the results then being openly available to support new emerging technologies. One hopes for ground breaking increases in chip processor speed, faster internet connections and huge energy savings worldwide.

For more information you can contact Carlo Vecchini (carlo.vecchini@npl.co.uk) or Markys Cain (Markys.Cain@npl.co.uk), National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK



Fig. 3: Delegates at the 3rd X-ray & Neutron Scattering in Multiferroic and Ferroelectric Materials Research workshop at NPL.

As well as providing access to a state-of-the-art synchrotron facility, the XMaS mid-range facility is also pleased to provide access to an increasing range of off-line facilities which are managed in parallel with the beamline.

Please consider using these in conjunction with any beamtime proposal, or consider them for independent projects. The access mechanism is evolving, so please consult the web-page for the most up-to-date information on how to apply.

Offline x-ray facility

A laboratory based x-ray micro source has been purchased and will be installed in the end cabin of the beamline for off-line x-ray measurements. A Huber 4-circle diffractometer was inherited from the University of Liverpool with an Eulerian cradle identical to the present Huber cradle on the beamline instrument. This means that all of the sample environment, detectors, etc. available on XMaS will fit onto this new refurbished instrument. The new lab source will use existing spare equipment (such as slits, monitors, electronics, detectors, etc.). This additional facility will be available to users to characterise, align and possibly pre-cool their samples in a cryostat prior to their experiment, potentially saving days of beamtime. The new facility will also allow high resolution diffraction studies as a function of temperature and can easily perform x-ray reflectivity measurements, using the comprehensive XMaS sample environments. The system is also designed to allow SAXS experiments using the MAR and new 2D detectors. Additionally, the facility could

be used as a “test bed” for new sample environments and beamline instrumentation projects.

Axo Dresden GmbH will supply the x-ray source and optics (**Fig. 4**). The source can be operated in two different modes: (1) Low resolution, high flux containing Cu $K\alpha_1$ and $K\alpha_2$ radiation. The post multilayer mirror flux will be $\sim 10^8$ photons/s in a spot size of ~ 1.5 mm x 1.5 mm at the sample position, (2) High resolution monochromatic beam using a Ge (022) channel cut monochromator to separate out the Cu $K\alpha_1$. This mode will provide a flux of $\sim 10^7$ photons/s with a spot size of ~ 1.0 mm x 1.0 mm at the sample position. The diffractometer will be mounted on an x-z translation table to allow easy switching between modes.

Offline P-E loop facility

The use of the off-line electrical characterisation facility has been growing rapidly over the last few months. More details about the facility are available on the web [1,2]. Initial tests have been made using lead zirconium titanate (PZT) standards supplied by the National Physical Laboratory to ensure that the system is correctly calibrated. The facility enables groups to measure resistivity and also ferro-electricity by PE loop measurements, using the complex sample environments currently available at XMaS. The system can also be integrated with the off-line x-ray source.

[1] www2.warwick.ac.uk/fac/cross_fac/xmas/description/sample_environments/#Electric_fields

[2] <http://interactive.npl.co.uk/multiferroics/index.php/Instrumentation>

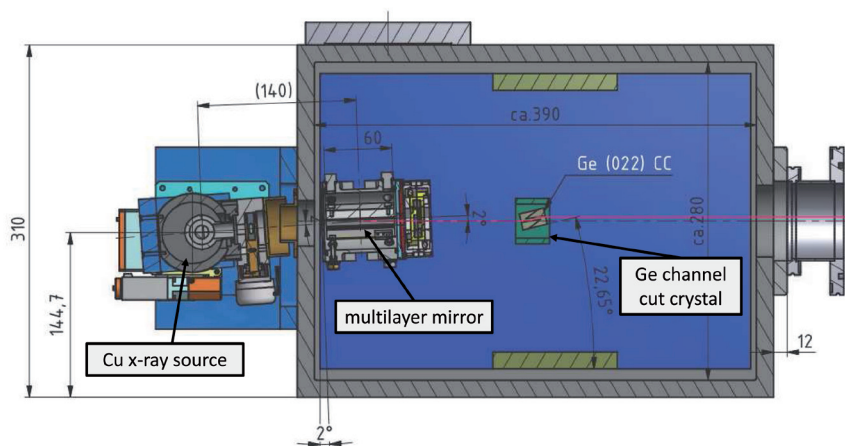


Fig. 4: Drawing of the x-ray laboratory source housing showing the Cu source, the multilayer mirror and the Ge (022) channel cut crystal. Image, courtesy of Axo Dresden GmbH.

Combined x-ray diffraction and interferometry measurement of dynamic strain in nano-scale materials

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This work forms part of the EMRP Nanostrain project described on page 4. The XMaS contribution to this project is to develop a new metrology tool combining x-ray diffraction with laser interferometry to measure displacements in piezoelectric materials. A summary report of the project is also available on-line [1].

Structural studies are routinely carried out with synchrotron x-rays with a resolution down to the atomic level (pm). Optical interferometry is a laboratory based technique used to measure micro- and nano-scale displacements. Combining these two techniques on XMaS in a simultaneous measurement is quite a feat of engineering and has not previously been attempted. It will allow us to establish a direct comparison between atomic displacement of the unit cell (pm range) and macroscopic changes of the sample length (mm range). By incorporating our electric field capabilities we will be able to measure simultaneously lattice changes, displacements and electrical polarisation responses to an applied electric field on a range of technologically relevant materials.

One challenge facing this project is that interferometry is very sensitive to external vibrations and other environmental factors. X-ray measurements are typically performed in a very noisy environment (vacuum pumps, moving parts with motors, etc.) which gives rise to a lot of vibrations that can adversely affect the interferometry results. In order to combine these techniques together, vibrations must be reduced or corrected for. Building a rigid sample-reference surface-interferometer system is the first step in reducing the background vibrations. In addition, we are currently measuring very accurately the vibrations in and around the diffractometer during and after axis movements to firstly identify the origin of any noise and then take steps to reduce or correct for them. These studies are being

conducted in conjunction with the National Physical Laboratory, UK and the project is scheduled to be commissioned during the first half of 2014. **Fig. 5** shows the schematic of the interferometer mounted on the XMaS diffractometer together with the newly designed and built sample holder.

By establishing a metrology that enables piezoelectric material properties to be measured across a range of length scales, the project will help industry and academic researchers to develop new types of microelectronic devices such as piezoelectric effect transistors that could provide a solution to the stagnating speed of modern computer processors. Not only will this research help us understand the effect of electrically induced strain on these materials but it will also look at the effect of other external stimuli such as temperature, magnetic field and electric field frequency.

This new metrological facility builds on a previous very successful NPL-XMaS collaboration which developed the tools needed for simultaneous measurement of high resolution XRD data and electric polarisation [2]. The finished system will be available as part of the standard suite of XMaS sample environments for the investigation of ferroelectric but also magnetoelectric materials. The new setup will also fit in the off-line x-ray laboratory currently being developed at XMaS.

[1] www.euramet.org/fileadmin/docs/EMRP/JRP/JRP_Summaries_2012/Industry_JRPs/IND54_Publishable_JRP_Summary.pdf

[2] J. Wooldridge *et al.*, *J. Synchrotron Rad.* 19, 710 (2012).

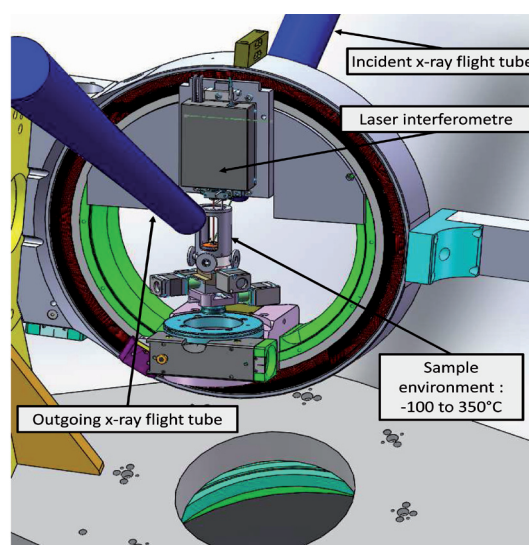


Fig. 5: Interferometer and sample holder fitted on a Huber diffractometer. Image, courtesy of NPL and Huber Diffractionstechnik GmbH.

Combined XRR/GISAXS setup

In small angle scattering experiments, due to the large sample-to-detector distance, flight tubes of different lengths are often used to reduce stray scattering and absorption. Some experiments require both wide and small angle information (i.e. short and long length scale information) from the same sample and sometimes even simultaneously. In the current setup for (GI)SAXS, the flight tubes have to be placed/removed manually when switching between SAXS and WAXS or x-ray reflectivity (XRR) configurations. Moreover, the existing setup is not optimal for simultaneous SAXS and WAXS experiments as some angular areas cannot be accessed.

To address these issues a new design is being implemented on the beamline (**Fig. 6**) which will allow for a smoother, remote controlled exchange between configurations. A rail will support the area detector (e.g. MAR165) and will allow for an easy manual change of the sample-to-detector distance. A motorised girder will be used to move the flight tubes in and out of the beam. The back of the tubes will have an additional x-z translation to allow for fine tuning of the beamstop position.

The beamstop will be inside the tube and easily exchangeable (manually). Different cone shapes are foreseen in order to access simultaneously SAXS and WAXS information, minimising the “blocked” areas. The design work is in an advanced state and the completion of the new setup is expected by early summer 2014.

Purchase of 2D Detectors

As part of the ongoing upgrade programme to the beamline hardware, a Maxipix 2x2 pixel detector has been ordered from the ESRF. The delivery of the device is, however, not expected before early summer mostly due to a nine month lead time to deliver the actual 2x2 Medipix2/Timepix chips to the ESRF. The purchase of further wide area 2D pixel detector with a larger sensitive area than the Maxipix and being able to operate below 3 keV is also underway. A call for tender has been launched with a closing date in February. In addition, we remind our users that they continue to have access to other detectors such as the Maxipix 1x1 (**Fig. 7**) and the Pilatus 300K-W from the ESRF loan pool which are available on request.

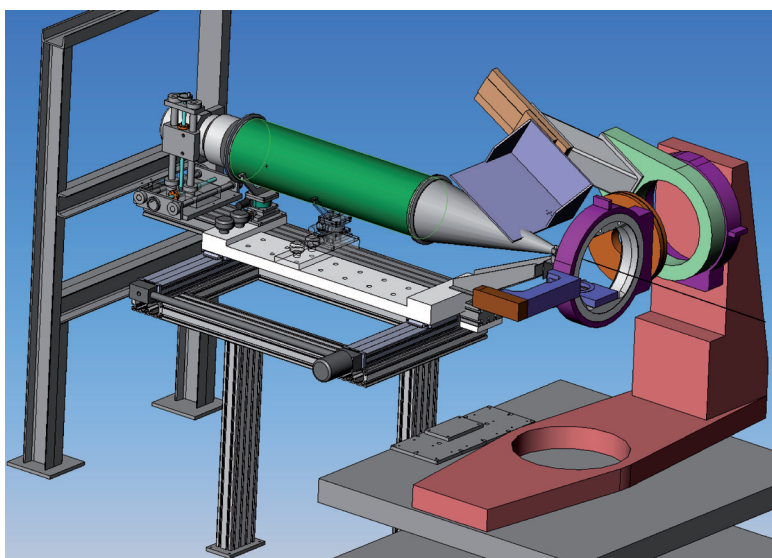


Fig. 6: General view of the combined XRR/GISAXS setup. The flight tube is displaced laterally to change from one configuration to the other. Image, courtesy of Nominal Ingénierie.



Fig. 7: Maxipix is a fast readout, photon-counting pixel detector system developed by ESRF and based on the Medipix2 readout chip developed by CERN and the Medipix2 collaboration. Image, courtesy of the ESRF-ISDD.

The malleability of uranium

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Almost all metallic elements have simple crystal structures (*fcc*, *bcc*, *hcp*, *dhcp*) at ambient pressure and temperature [1]. There are exceptions, of course, such as Mn and Hg, but the most exotic structures are found with the early actinides Pa, U, Np, and Pu. These latter four elements display a remarkable structural diversity that arises from the interplay of the partially occupied *5f* and *6d* states [2,3].

Unique to the elements, uranium in its ambient pressure, ambient temperature, “ α ” phase, is orthorhombic; it has highly anisotropic coefficients of thermal expansion and at low temperatures exhibits a minimum in atomic volume, that coincides with a charge density wave (CDW); $T_0 = 43$ K [4]. It is now understood that the key parameter in this transition to the CDW state is the electron-phonon interaction in the [100] direction [5], so changing the length of the *a*-axis is predicted to have a profound effect [6]. Clearly, being able to manipulate the *a*-axis is an attractive route to understand the behaviour of electron-phonon coupling and consequently, the CDW condensation in uranium.

The strain induced in high quality, single crystal, epitaxial films through interaction with a substrate allows for both compressive and tensile strains to be engineered. For example, α -U grown on Nb has a (110) orientation due to a slight compression (−0.35%) of *a*. On the other hand, when grown on W (which is smaller than Nb by 4%) a (001) orientation film under tensile strain is produced [7].

In earlier experiments, the onset temperature of the CDW in the U/Nb system [8] was shown to be suppressed. In the U/W system however, the tensile strain stretches the *a*-axis and reveals some intriguing physics. In addition, the form of the CDW is simpler in U/W as it is associated with a doubling of the *a*-axis resulting in diffraction at the non-allowed (1.5 0 3) position giving a unique probe of the CDW properties.

We show in Fig. 8, results from a recent experiment at XMaS where the tensile strain results in a 250%

change in T_0 . Diffraction data recorded as a function of temperature from a 150 nm epitaxial film of α -U/W are shown in Fig. 8. They reveal that a change occurs in both the *a* lattice parameter (Fig. 8a) and atomic volume (Fig. 8b) determined from structural Bragg peaks. These changes accompany the formation of the CDW as measured at the (1.5 0 3) position (Fig. 8c). During the creation of the CDW, the system thus enters a mixed phase region (high-T and low-T) whose *a*-lattice parameters continually evolve as a function of temperature across the transition (Fig. 8a).

These experiments demonstrate the incredible malleability of uranium; it is the ideal system in which to study the interplay of structure, electron-phonon coupling and the CDW state.

- [1] J. Donohue, "The Structures of the Elements", John Wiley & Sons Inc. (1974).
- [2] K.T. Moore and G. van der Laan, *Rev. Mod. Phys.* 81, 235 (2009).
- [3] P. Söderlind *et al.*, *Nature* 374, 524 (1995).
- [4] G.H. Lander *et al.*, *Advances in Physics* 43, 1 (1994).
- [5] S. Raymond *et al.*, *Phys. Rev. Lett.* 107, 136401 (2011).
- [6] J. Bouchet, *Phys. Rev. B* 77, 024113 (2008).
- [7] R.C.C. Ward *et al.*, *J. Phys. Cond. Matt.* 20, 135003 (2008).
- [8] J. Chivall, Thesis submitted to UCL (unpublished) (2011).

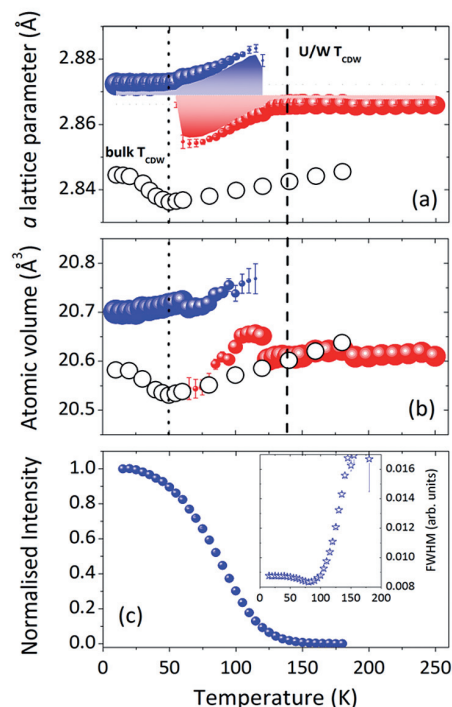


Fig. 8: Experimental quantities from a 150 nm film of α -U/W with the (001) orientation. **(a)** Length of *a*-axis: high-T (red) and low-T (blue) forms, bulk. **(b)** Atomic volume in film and bulk. **(c)** Intensity and FWHM (inset) of the (1.5 0 3) satellite from the CDW.

Multiple wave DAFS on BaTiO₃

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Diffraction anomalous fine structure (DAFS) is a powerful technique for obtaining absorption spectra from specific crystalline phases, such as a buried strained layer, in the presence of other material containing the same element. Analysis of DAFS data is very complex since, unlike absorption, which sees only the imaginary part of the scattering amplitude, diffraction signals include contributions from both the real and imaginary parts. Untangling the two is challenging but can be done in centrosymmetric crystals where the phase arising from the crystal structure takes on a very simple form. In non-centro-symmetric systems, which include crystals of most biological materials and ferroelectrics, the situation is even more complicated.

For these classes of material, more information is required in order to determine the scattering phase. Here, we have combined multiple (three-beam) diffraction to observe interference between overlapping reflections, to provide scattering intensities that are extremely sensitive to the x-ray scattering phase. We performed multiple wave

diffraction anomalous fine structure (MDAFS) experiments on a 200 μm thick ferroelectric barium-titanate single crystal (BaTiO₃) [1]. The goal of this method is to extract DAFS information in a direct manner from non-centrosymmetric crystals. MDAFS, which is a combination of DAFS with multiple-beam diffraction, allows extraction of the fine structure function by measurements of the triplet phase via Renninger scans at different energies around an absorption edge.

The XMaS six-circle diffractometer was used in horizontal diffraction geometry in order to perform Renninger scans of the (110) reflection at energies around the Ti K absorption edge. Therefore, the ϕ - and Ψ -circles were used to align the reciprocal lattice vector of (110) reflection onto the ω -axis, which was then used for the Renninger scans. High-quality diffraction data (Fig. 9) were then used to reconstruct the real and imaginary parts of the absorption spectra.

The resulting absorption spectrum extracted from the Renninger scans is shown in Fig. 10. This experiment demonstrated the technical suitability of the beamline for further intense multiple wave DAFS studies.

In the future we expect this technique to be applied to studies of more complex ferroelectric materials, including buried layers.

[1] Y.-R. Lee *et al.*, Phys. Rev. Lett. 97, 185502 (2006).

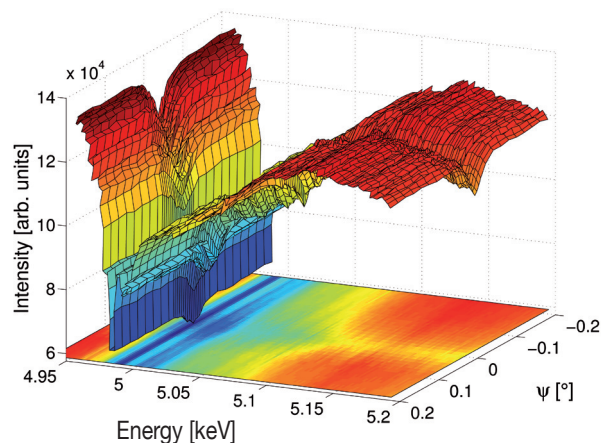


Fig. 9: Renninger scans around the Ti K absorption edge as a function of energy.

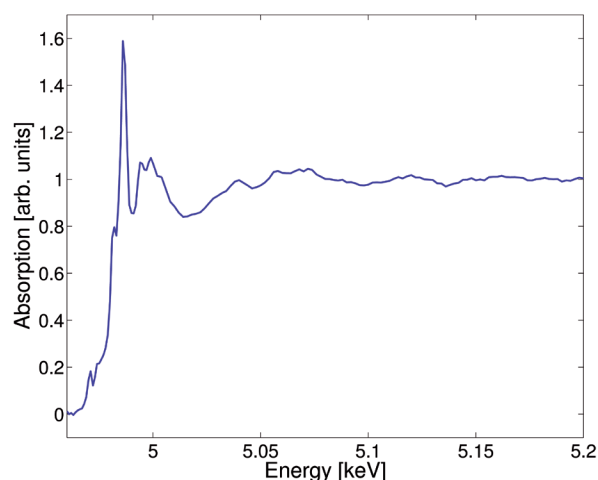


Fig. 10: Ti K absorption spectrum from BaTiO₃ extracted from the Renninger scans shown in Fig. 9.

Quantitative determination of quadrupole transitions at the L-edges of rare-earths

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The aim of this experiment was to evaluate a new technique for the quantitative measurement of quadrupolar transitions (E2) and to compare results to those obtained previously for dipolar transitions (E1) at the L edges of the heavy rare-earths. Previous work involved x-ray resonant interference scattering (XRIS) between resonant charge (E1) and resonant magnetic (E1) complex scattering amplitudes [1]. These measurements were performed in horizontal scattering geometry (i.e. π incident polarisation) with a reversible magnetic field applied orthogonal to the scattering plane. Quantitative results for E1 XRIS were obtained for the ferro(ferri)magnetic phases of the heavy rare-earths Gd to Tm. Due to the fact that our results appeared to contradict the accepted wisdom, firstly regarding the existence of an E1 contribution at the E2 energy and secondly regarding the overall sign of these signals and the effect of matrix elements, objections were raised [2,3]. It is therefore imperative to clarify the energy positions of the E1 and E2 contributions as observed in an XRIS experiment, where the signs of the E1/E2 contributions are visible. The existence of low energy E1 contributions in Ho, Tb, Er and Tm have been confirmed in studies of their antiferromagnetic phases through x-ray resonant magnetic scattering (XRMS). However, these measurements employed polarisation analysis which can introduce quantitative errors due to resolution/analyser uniformity effects as well as being prone to absorption correction errors. Additionally, XRMS measures the modulus squared of the complex magnetic scattering amplitudes and thus has no overall sign sensitivity.

Through close examination of the resonant scattering cross section, we have a method for sensitizing the XRIS spectra not to the E1 contribution, but rather to the E2 signal, simply by switching the scattering plane from horizontal to vertical (another technique capable of emphasising E2 signals is Borrmann

spectroscopy [4] but this requires near perfect crystals and is unsuitable for metal crystals).

The results are shown in Fig. 11. The E1 signal was measured in horizontal scattering geometry and the E2 in vertical. For the horizontal E1 geometry, the signal is enhanced by a factor of $\tan(2\theta)$ and so the E1 data have been divided by this factor to allow direct comparison of signal amplitudes. For similar reasons, the E2 spectrum has been divided by $\sin(2\theta)$, reflecting the E2 cross-section. Also, the appropriately scaled E2 contribution to the spectrum obtained in horizontal scattering has been subtracted to provide a pure E1 spectrum. It is clear that asymmetry ratios of the order of 0.1 % can easily be resolved using the new method.

[1] S. D. Brown *et al.*, Phys. Rev. Lett. 99, 247401 (2007).

[2] A. I. Goldman *et al.*, Phys. Rev. Lett. (Comment) 102, 129701 (2009).

[3] S. D. Brown *et al.*, Phys. Rev. Lett. (Response) 102, 129702 (2009).

[4] R.F. Pettifer *et al.*, Nature 454, 196 (2008).

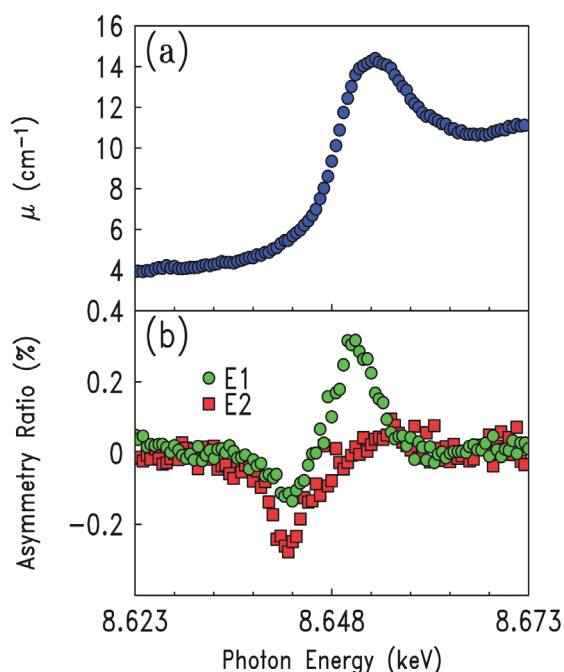


Fig. 11: (a) Tm L_3 edge absorption. (b) Pure E1 (circles) and E2 (squares) asymmetry ratios for Tm (200) at the L_3 edge. All angular dependences have been compensated to allow comparison.

Interface magnetism in rare-earth superlattices

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Multilayers (ML) consisting of a ferro(i)magnetic and a non-ferromagnetic layer exhibit new, interesting and crucially controllable properties that can be exploited in both basic and applied research. The system properties can be controlled, in part through finite size effects but also through manipulation of the interface where structural and magnetic modifications with respect to the bulk arise. Magnetic MLs are now a main stay in current technology finding applications in many sensors based technologies. Further exploitation of these material systems may become possible through the control of the magnetic properties via a direct manipulation of the spin dependent chemical potentials that arise through interface proximity effects and morphology.

Over the last decade, progress in characterisation techniques allows a more systematic and detailed study of the induced ferromagnetism in thin multilayer structures. In addition, new simulation software and high performance computation now allow for a rapid quantitative determination of the layer moments, their spatial profile and morphology [1].

Rare-earth superlattices such as Gd/Y are an interesting sub system of metallic MLs that can be used to explore low dimensional and confined magnetism, as well as spin waves [2] and complex

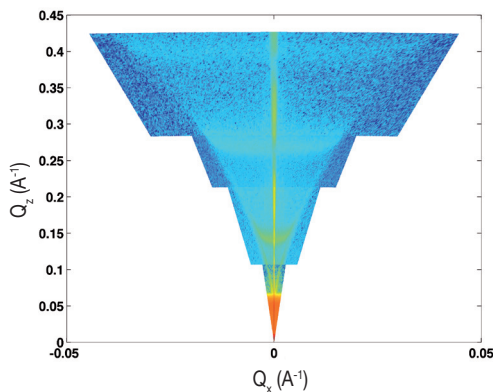


Fig. 12: Reciprocal space map of a Gd/Y superlattice ($\lambda=1.5418 \text{ \AA}$). The broad diffuse Bragg sheets reveal that the interface morphology is correlated vertically through the superlattice stack.

magnetic textures [3]. Two important and inter related questions relating to the role of the interface remain unanswered: the exact layer structure of these rare-earth samples has been only addressed partially with most of studies concentrating on the crystal structure; secondly the exact mechanism of the inter layer coupling between the Gd layers remains unclear. It is assumed to be a modified RKKY type but is much stronger and extending over a much longer spatial distance (up to 70 \AA) than that seen in the more widely studied transition metal multilayers such as Cu/Co and the cause of this is unclear.

We have used molecular beam epitaxy (MBE) to grow Gd/Y superlattices varying the Y-spacer thickness. Our work has focused on characterising the interfaces in such structures using x-ray reflectivity (**Fig. 12**) and extracting the magnetic profile using x-ray magnetic scattering (XRMS) (**Fig. 13**). XRMS data were collected at the Gd L_3 edge by passing the linear σ polarised light through a phase retarder to produce left or right circular polarised light. The asymmetry ratio was then determined by reversing the magnetic field and/or helicity to return the charge magnetic inference term which can be modeled to elucidate the magnetic profile.

Detailed x-ray scattering data of this kind gives a deeper insight into the interfaces properties of rare-earth superlattices and their influence on their related magnetic properties.

- [1] www.genx.sourceforge.net. GenX differential evolution algorithm for fitting x-ray and neutron reflectivity data.
 [2] A.T.D. Grünwald *et al.* Appl. Phys. Lett. 96, 192505 (2010).
 [3] V.V. Tamavich *et al.*, submitted to Phys. Rev. B (2013).

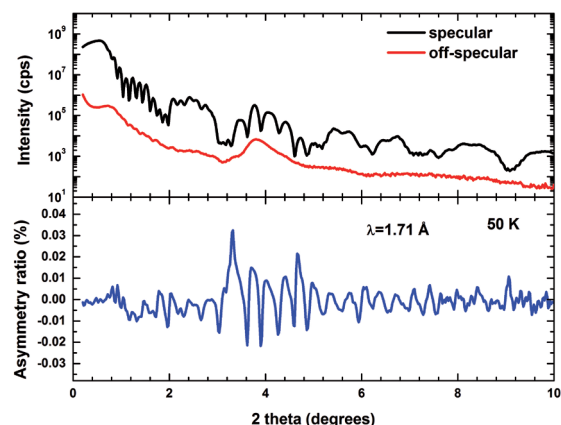


Fig. 13: (top) Specular and off-specular x-ray scans from a superlattice of 5 Gd MLs and 5 Y MLs measured at the Gd L_3 edge. The peaks at high scattering angle come from the buffer layer. (bottom) Recorded XRMS asymmetry ratio for the same sample.

Epitaxial ferromagnetic MnSb for semiconductor spintronics

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Spintronic devices exploit both the spin and charge of electrons. Perhaps the most famous example is that of a hard disk read-head sensor, which uses tunnelling magnetoresistance (TMR) to measure tiny fluctuations in magnetic fields whilst scanning over the ferromagnetic bits on the disk surface. There is huge interest in taking spintronics beyond such passive devices into the realm of *semiconductor spintronics* and exploit spin-polarised currents (or even pure spin currents, where no charge actually flows) within semiconductor devices. In principle, spin states can be manipulated at a far lower cost in energy than charge states, leading to much lower power requirements in memory and processing. However, a major challenge for semiconductor spintronics is injecting and detecting spin-polarised currents into ordinary non-magnetic semiconductors. This generally requires very high quality interfaces, which can be achieved through epitaxial growth of new materials.

We have used molecular beam epitaxy (MBE) to grow thin films of MnSb [1,2] and related materials [3] onto semiconductor substrates. MnSb is a ferrimagnetic material with a high Curie temperature ($T_C \approx 590$ K). Furthermore, we have been able to stabilise substantial thicknesses (~ 10 nm) of a cubic polymorph of MnSb [4]. This cubic structure is especially interesting for spintronic applications as c-MnSb is predicted to be a *half-metallic* material (100% spin polarisation at the Fermi level) at room temperature allowing high efficiency spin injection.

Our work on XMaS has focused on structural characterisation of MnSb/semiconductor thin-film systems using x-ray diffraction (XRD). As well as conventional out-of-plane XRD, we exploited the flexible diffractometer to measure crystal truncation rods (CTRs) and perform in-plane grazing incidence XRD to extract strain states and identify polymorph orientations for a range of different MBE-grown samples. An example reciprocal space map (RSM) is shown in Fig. 14, for a 70 nm MnSb(0001) thin film grown on GaAs(111). Non-optimal initial growth of

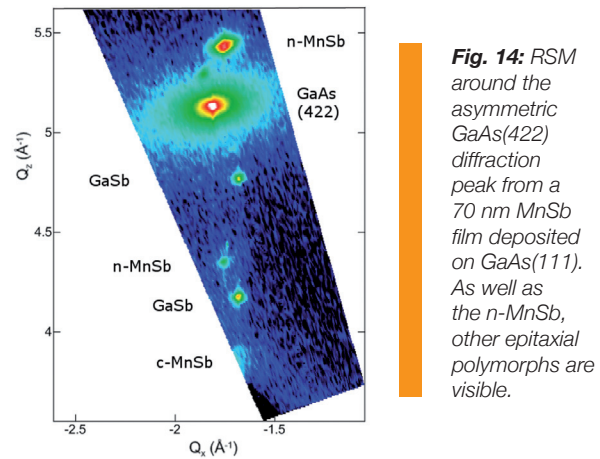


Fig. 14: RSM around the asymmetric GaAs(422) diffraction peak from a 70 nm MnSb film deposited on GaAs(111). As well as the n-MnSb, other epitaxial polymorphs are visible.

the MnSb gives rise to GaSb(111) at the interface, while highly strained c-MnSb(111) inclusions exist in the bulk of the film. Fig. 15 shows a waterfall plot of in-plane XRD curves as a function of grazing incidence angle. The arrows highlight features due to (A) ordinary hexagonal n-MnSb, (B) and (C) c-MnSb polymorphs. Small features to the left of A at very grazing angles are likely to arise from crystalline Mn surface oxides. Mn oxide formation can be avoided by capping with semi-crystalline Sb, which improves the magneto-transport properties of the MnSb films. XRD data of the kind shown here give a detailed view of the depth-dependent structure and allow the epitaxial relationships, strain and near-surface structures of these complex polymorphic thin films to be determined. The results will allow us to further refine our MBE growth, which in turn facilitates new spintronic applications in systems with carefully tailored interfaces.

This work is funded through two EPSRC-supported collaborations (EP/K032852/1 and EP/J003263/1) and an EPSRC Overseas Travel Grant (EP/I00114X/1).

- [1] S.A. Hatfield & G.R. Bell, *Surf. Sci.* 601, 5368 (2007).
- [2] S.A. Hatfield *et al.*, *Appl. Surf. Sci.* 255, 3567 (2009).
- [3] J.D. Aldous *et al.*, *J. Crystal Growth* 357, 1 (2012).
- [4] J.D. Aldous *et al.*, *Phys. Rev. B* 85, 060403(R) (2012).

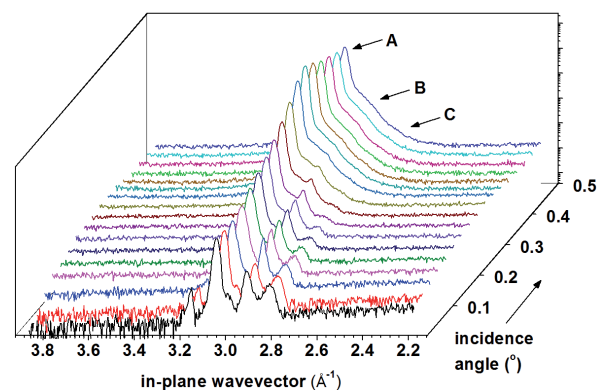


Fig. 15: XRD curves for 150 nm MnSb on GaAs(111) with varying grazing incidence angle.

A view of highly oriented In_2O_3 nanorods from reciprocal space

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There is a growing interest in the development of functional devices such as field effect transistors and gas sensors based on one-dimensional (1D) nanowires or nanoribbons of semiconducting materials, particularly wide-gap metal oxide semiconductors. Most of the well-established vapour deposition techniques for the preparation of semiconducting oxide nanowires or nanobelts lead to a tangled mass of interpenetrating ribbons with no control over their orientation. We have recently developed a new approach to the growth of highly oriented In_2O_3 nanorods on the intrinsically anisotropic (110) surface of cubic Y-stabilised ZrO_2 (YSZ) substrates using oxygen plasma assisted molecular beam epitaxy [1]. The key to the development of highly anisotropic structures such as those shown in Fig. 16 lies in the large anisotropy of the surface energies, γ , for the low index terminations of In_2O_3 , where density functional theory calculations show that $\gamma(001) \gg \gamma(110) > \gamma(111)$. Growth of rods with high aspect ratios oriented uniaxially along the [1-10] direction allows development of favourable low energy (111) side facets.

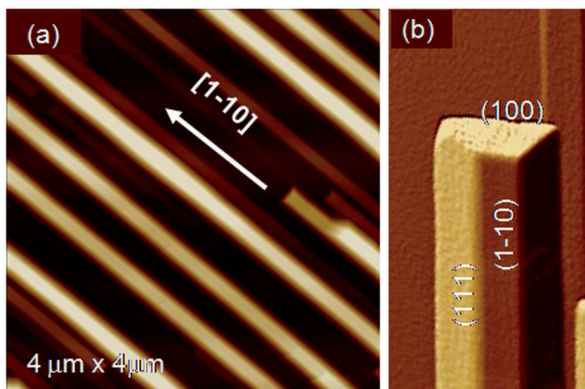


Fig. 16: Atomic force microscopy (AFM) images of In_2O_3 nanorods grown on YSZ(110) substrates at a substrate temperature of 1000 °C by oxygen plasma assisted molecular beam epitaxy. (a) is a $4 \mu\text{m} \times 4 \mu\text{m}$ topographic image, while (b) shows an expanded 3D deflection image. Low energy (111) side facets are apparent in (b).

The optical and transport properties of epitaxial nanostructures are strongly influenced by internal strain, which amongst other things may lead to significant changes in the bulk bandgap. We have therefore embarked on detailed study of our nanorod structures using synchrotron based x-ray reciprocal space mapping on XMaS, with typical results such as those shown in Fig. 17 [2].

The most obvious feature of the maps for the specular (880) reflection shown above is that the anisotropy in real space evident in Fig. 16 is matched by a corresponding anisotropy in reciprocal space. A more detailed analysis of these maps and similar ones for off axis reflections reveals that the rods are coherently strained along the long-axis [1-10] direction but remain almost fully relaxed in the short-axis [001] direction. This surprising result is apparently a consequence of marked anisotropy in elastic constants which makes stretching along the [1-10] direction much easier than along [001]. Our ongoing work in this area is aiming both to explore the impact of strain on the functional properties of the rods and to obtain more complete 3D reciprocal space data using 2D area detectors.

[1] K.H.L. Zhang *et al.*, *Nano Letters* 10, 3740 (2010).

[2] A. Regoutz *et al.*, *Nanoscale* 5, 7445 (2013).

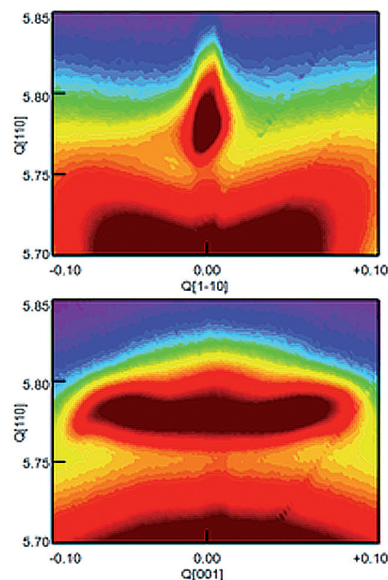


Fig. 17: 2D reciprocal space maps around the epilayer (880) reflection for the nanorod structures shown in Fig. 16. Longitudinal wavevector transfer along the [110] direction and transverse wavevector transfer along orthogonal [1-10] and [001] directions are given in reciprocal lattice units of the YSZ substrate. The lattice parameter for YSZ is just over one half of that for the epilayer, which is therefore under tensile strain.

XRR characterisation of the active bifunctional layer for self-assembled monolayer field-effect transistors

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Self-assembled monolayers (SAMs) of organic molecules such as silanes, carboxylic acids (CA) or phosphonic acids (PA) have been intensively investigated as functional molecular layers in organic thin film transistors due to their excellent properties [1-3]. They can be easily deposited from solution, tailored to a desired functionality in order to tune the device performance and are applicable to flexible substrates. Although they are often utilized as gate dielectrics, their application surpasses pure dielectric functionality. It has been demonstrated that bifunctional molecules consisting of semiconducting moieties, insulating alkyl chains and an anchor group can be deposited forming self-assembled monolayer field-effect transistors (SAMFETs) [4-8]. SAMFETs based on fullerene (C_{60}) functionalized alkyl phosphonic acids have been proved to be effective N-type transistors [6]. The major issue with SAMFETs is the alignment of the semiconducting moieties to obtain effective $\pi\pi$ -stacking and a dense packing of the insulating alkyl chains.

Here we report on a novel approach towards the self-alignment of multifunctional, complex molecules in a mixed SAM enhancing the semiconducting performance (channel formation of the SAM) and insulating properties (ordered n-alkyl chains across the SAM) of the layer. We use the difference in binding strengths of CA and PA, respectively, to an oxidised aluminium gate electrode which enables a (partial) replacement of a CA-SAM by immersion of

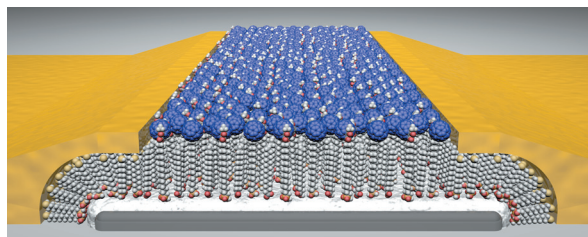


Fig. 18: Cartoon illustration of a self-assembled monolayer field-effect transistor consisting of C_{17} -CA partially exchanged by $C_{60}C_{18}$ -PA.

the substrate into a PA solution [8]. By substituting CA molecules of a dense octadecanoic acid (C_{17} -CA) SAM with C_{60} functionalised PA molecules (C_{60} - C_{18} -PA) an upright alignment of the PA molecules can be enforced (Fig. 18). We propose that this exchange process takes place until the C_{60} - C_{18} -PA forms a densely packed C_{60} head layer.

The structure perpendicular to the surface of the partially exchanged SAM was investigated via x-ray reflectivity (XRR) at a photon wavelength of 1.55 Å. The scattering length density profile ($SLD = \rho_e \cdot r_e$, where ρ_e is the electron density and r_e is the classical electron radius) indicates a densely packed C_{60} head layer (Fig. 19). CA molecules remain on the substrate underneath the C_{60} moieties preventing the fullerenes from touching down onto the gate electrode and pushing them into a confined layer (~ 22 Å) on top of the CA-SAM (reduced SLD close to the surface). This leads to enhanced charge transport and a strongly reduced leakage current since a dense carboxylic acid remains underneath the voluminous C_{60} head of the functionalized molecules. Compared to pure C_{60} - C_{18} -PA SAMFETs, strongly increased drain currents (factor of 10 higher than in previous n-type SAMFETs [6]) and on/off-ratios (up to 10^3) were found.

- [1] M. Halik *et al.*, Nature 431, 7011 (2004).
- [2] H. Klauk *et al.*, Nature 445, 7129 (2007).
- [3] S.A. Di Benedetto *et al.*, Adv. Mater. 21, 14 (2009).
- [4] E.C.P. Smits *et al.*, Nature 455, 7215 (2008).
- [5] S.G.J. Mathijssen *et al.*, Nat Nano 4, 10 (2009).
- [6] M. Novak *et al.*, Nano Letters 11, 1 (2011).
- [7] T. Schmaltz *et al.*, Adv. Mater. 25, 32 (2013).
- [8] T. Lenz *et al.*, Langmuir 28, 39 (2012).

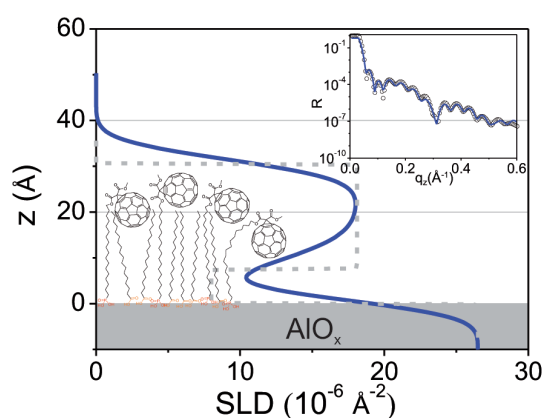


Fig. 19: Best fit SLD profile from XRR measurements on a C_{17} -CA SAM after an exchange reaction with $C_{60}C_{18}$ -PA; z represents the distance to the aluminium oxide substrate. The measured reflectivity data (points) and fit (line) are shown in the inset.

Quiescent bilayers at the mica–water interface

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Using a home-built x-ray reflectometry (XRR) liquid cell that employs a simple “bending mica” method [1], we have obtained the structural details such as the absorbed layer thickness, surface coverage and interfacial roughness [2] of self-assembled layers of a series of *quateryary alkyl ammonium bromide* surfactants (C_nTAB where n denotes the number of hydrocarbons in the surfactant tail).

Our studies reveal different morphologies to those determined in previous experiments performed using atomic force microscopy (AFM). The AFM studies observed a variety of aggregate morphologies which ranged from surface micelles to cylinders. We suggest that this discrepancy is due to our surfactant films being *quiescent*, i.e. they are unperturbed compared with a layer under a scanning AFM nano-probe. In addition we have observed that the bilayer thickness, surface coverage and the chain tilt angle all depend on the surfactant concentration and surfactant hydrocarbon chain length, and that the bilayer thickness exhibits a maximum value at approximately the critical micellisation concentration (cmc) for all the C_nTABs investigated (Fig. 20a). Our results suggest that the surfactants form partially interdigitated bilayers below cmc due to relatively fluid and disordered chains. At ~1 cmc, the surface sites of mica become densely and fully occupied, and surfactant molecules tilt with respect to the surface normal in order to satisfy the packing constraints set by the area of the mica surface site (Fig. 20b). Such observations are consistent with previous near edge x-ray absorption fine structure (NEXAS) and molecular dynamics (MD) simulation studies. Surprisingly, the tilt angle θ_t is observed to increase with n. We have explained this by correlating θ_t with the chemical potential of micellisation per molecule, $\Delta\mu = k_B T \ln(\text{cmc})$. That is, the chains become more densely packed as the hydrophobic driving force increases with the surfactant chain length. Thus, the chains have to tilt more to satisfy the above

surface-site packing constraint. As the surfactant concentration further increases above 1 cmc, we suggest that some surfactant molecules desorb from the surface and consequently the bilayers recover some fluidity and in turn revert to their interdigitated structure. These experimental data are consistent with the thermodynamic model of Evans and Wennerström [3].

The suggestion of *quiescent bilayers* has fundamental implications to processes such as lubrication, self-assembly under confinement, detergency and wetting, where the morphology and structure of surfactant layers at the solid-liquid interface is an important consideration. It is also generally relevant to self-assembly of soft materials, e.g. of surfactants and conducting organic oligomers [4] (artistically shown on the front cover).

[1] W.H. Briscoe *et al.*, *Soft Matter* 8, 5055 (2012).

[2] F. Speranza *et al.* *Soft Matter* 9, 7028 (2013).

[3] F. Evans, *The colloidal domain: where physics, chemistry, biology, and technology meet*. Second ed., New York: Wiley, 632 (1999).

[4] T.G. Dane *et al.*, *Soft Matter* 9, 10501 (2013).

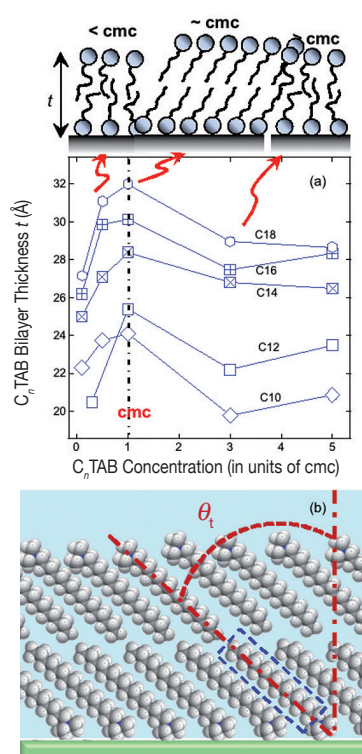


Fig. 20: (a) C_nTAB surfactants bilayer thickness t as a function of surfactant concentration (in units of cmc). All C_nTABs exhibit a maximum t at ~1 cmc. The proposed structures in three different concentration regimes are shown schematically above the figure. (b) Surfactant tails tilt at ~1 cmc.

In-situ soft XAS of catalysts

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Elements such as P, S, and Cl are found in a wide range of functional materials such as catalysts. They may often constitute coordinating elements for ligands in homogenous catalytic situations whereas in heterogeneous catalyst formulations and processes they are most often (though not exclusively) thought of as undesirable, poisoning the desired catalysis. Understanding the roles these elements play in determining the nature of a catalytic system is therefore of considerable interest. Indeed, interest in these elements goes well beyond catalysis as they are ubiquitous in many areas of soft condensed matter, geosciences, and biology.

K-edge x-ray absorption spectroscopy (XAS) provides a means to access, in a chemically specific manner, the speciation and bonding of these elements. Recently XMaS has successfully started a process of optical optimisation to cover the 2-4 keV energy range and therefore a “new” facility for UK spectroscopists has arisen to complement and add to those few spectroscopy resources already active in this area. Using the 4 bunch operational mode of the ESRF we have started to explore this new capacity using a prototypical heterogeneous catalyst system – that of Rh/Al₂O₃ derived from a Cl containing precursor.

Fig. 21 shows *in-situ* Cl K and Rh L₃ edge XAS from a 0.5 wt% Rh/Al₂O₃ catalyst ca. 10⁻² mbar H₂ at 298 K (red curves). Subsequently the sample was heated to 373 K (blue), 573 K (green), and 613 K (black) whilst maintained under an H₂ atmosphere. From simple inspection of these (and other) results a number of important aspects of the behaviour of this system may be readily obtained. Firstly, the level of Cl retention in these systems is found to be a significant function of the Rh loading. Secondly, the degree to which Cl is removed during reduction process is very dependent on the starting Rh content. Indeed the Cl is shown to be far more tenacious than previously thought [1] and this persistence is significantly enhanced as the Rh loading is decreased to levels (<1 wt%) that would be considered most relevant to real world application.

Further, the Cl K-edge XAS from these samples, as well as a variety of standards, shows variable pre-edge structure. This pre-edge structure arises due to mixing of Cl “p” and Rh “d” orbitals and therefore studies of the pre-edge region open a new window into more detailed assessments of Cl symmetry and bonding. It is hoped, therefore, that data of this nature will permit us to specify the exact nature of the modes of Cl coordination present in systems of this type, how they change with reactive circumstances and to eventually understand how and why species such as Cl modify the behaviour of catalysts as they do.

In this sense, and no doubt many others, the extension of the operational capacity of XMaS to the 2-4 keV energy regime could provide a much needed additional UK resource for a host of chemically oriented research communities.

[1] A. Suzuki *et al.*, *Angew. Chem. Intl. Ed.* 42, 4795 (2003).

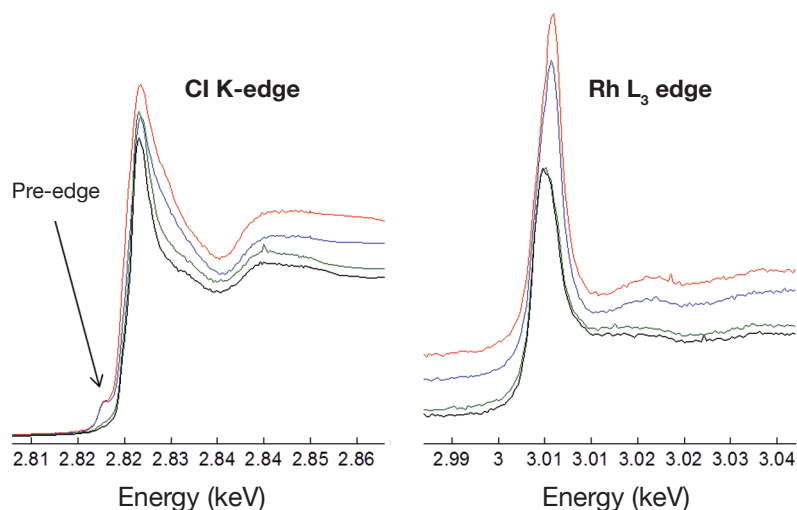


Fig. 21: Cl K (left) and Rh L₃ (right) edge XAS for a 0.5wt% Rh/Al₂O₃ sample observed during *in-situ* reduction – from 298 K (red) to 613 K (black) under 10⁻² mbar H₂.

Immobilised transfer hydrogenation catalyst: mystery of the disappearing chlorides

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Immobilisation of successful homogeneous catalysts to solid supports through ligands often suffer from metal leaching, which irreversibly deactivate the catalyst. A new approach, linking the multi-dentate ligand 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) with polystyrene has proven highly effective in stopping leaching of iridium in transfer hydrogenation reactions [1]. Reversible deactivation, however, is significant after an unprecedented length of thirty uses and the catalyst can be reactivated by treatment with dilute acid. Understanding these deactivation/reactivation processes is crucial to further improving the catalyst for pharmaceutical and fine chemical industries [2].

The work highlighted here took advantage of the recently developed capability of XMaS for low energy x-ray absorption fine structure (XAFS) spectroscopy. Fluorescence spectra were collected at Cl K-edge of the catalyst after different number of uses and after reactivation. This allows direct probing of the metal catalyst on support, which is extremely difficult to characterise and monitor changes using other, more traditional, techniques.

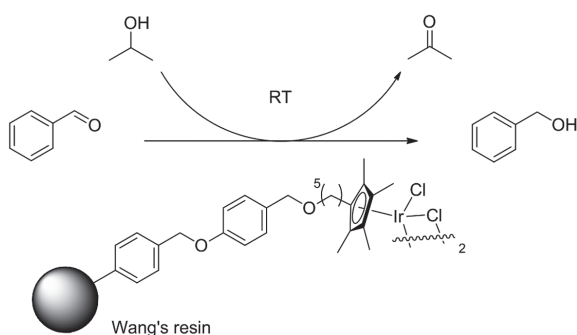


Fig. 22: Immobilised catalyst and transfer hydrogenation.

Initial data showed rapid loss of about one third of the chloride after the first three uses despite no loss in catalytic activity. This was followed by a steady loss of chloride until significant loss of catalytic activity and of chloride on iridium (Fig. 23). The normalised spectra, however, does not indicate drastic changes in the average Cl coordination sphere. Curiously, the reactivated catalyst, i.e. after treatment with aqueous hydrochloric acid, showed a very different spectrum.

Spectra collected at Ir L₃ edge for the same samples (at B18, Diamond Light Source) corroborated the loss of Ir-Cl signals as the catalyst was deactivated. However, no Ir-Cl signal was detected after the reactivation with hydrochloric acid. The chlorine signal observed at the Cl K-edge therefore must come from a species not directly bonded to the iridium catalyst, for example as a chloride counterion.

These results have significant implication on the identity of the true catalytic species and the mechanism of this type of transfer hydrogenation, which is still not reported in the literature. The data supports a loss of chloride from the pre-catalyst via exchange with solvent or substrate to give the catalytic species. Complete loss of chloride, however, results in unreactive Ir species, possibly due to formation of stable iridium alkoxides. Treatment with dilute acid can help remove the alkoxide ligands, restoring the activity of the catalyst. Further study of this catalytic system under turnover conditions is in progress.

[1] P.C. McGowan *et al.*, *Chem. Commun.* 49, 5562 (2013).

[2] T. Ikariya & A.J. Blacker, *Acc. Chem. Res.* 40, 1300 (2007).

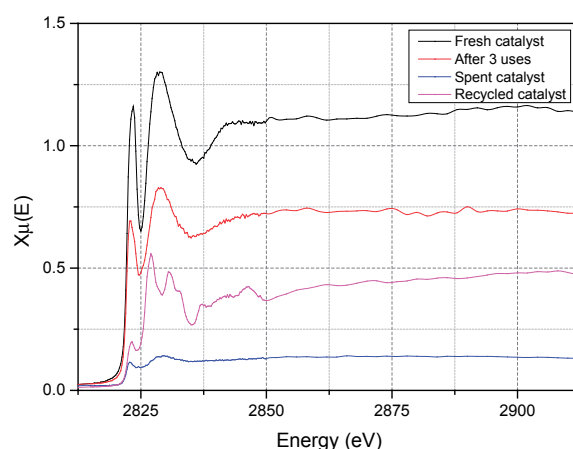


Fig. 23: X-ray absorption near edge structure (XANES) spectra of fresh, used, spent and reactivated immobilised Ir catalysts across the Cl K-edge.

NEXAFS to probe the electronic structure of ionic liquids

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Ionic liquids, salts composed entirely of mobile cations and anions, have potential applications as solvents, e.g. for dissolution of metal complexes [1] and catalysts [2]. For such applications, knowledge of the influence of the ionic liquid solvent on the solute is vital. The electronic properties of solutes in solution are relatively hard to study, as most techniques probing electronic structure require ultrahigh vacuum (UHV), meaning specialist apparatus is required to study liquid solutions [3]. Ionic liquids can be studied in UHV at room temperature using standard apparatus due to their very low vapour pressure [4, 5].

Near edge x-ray absorption fine structure (NEXAFS) spectra were recorded across the sulfur K-edge for six different ionic liquids at room temperature. Detection was achieved using both drain current and fluorescence yield, with a system pressure of $\sim 10^{-7}$ mbar. No problems with sample charging over time were observed; hence, a metal sample holder is sufficient for ionic liquid samples, without the need for charge neutralisation (often used in x-ray photoelectron spectroscopy, XPS). The sample holder used (Fig. 24) was capable of holding up to four ionic liquids at a time.

The fluorescence spectra for all six ionic liquids gave sharp, reproducible peaks (Fig. 25). Peak positions and relative peak intensities within each spectrum can be compared, whilst peak intensities cannot be compared between different ionic liquids, as there are too many experimental variables (e.g. the sample volume could not be controlled and therefore was different for all ionic liquids). The most intense peak for all six ionic liquids was in the range ~ 2.480 – 2.484 keV. The six ionic liquids can be classified into two groups, those containing CF_3SO_2 functional groups (Fig. 25a), and those containing OSO_3 functional groups (Fig. 25b). Currently, time-dependent density functional theory (TDDFT) calculations are being carried out by our collaborators to provide detailed insights as to the identity of the unoccupied orbitals. Overall, these

results demonstrate the viability of studying ionic liquids using NEXAFS, with minimal sample and apparatus preparation required.

- [1] A.P. Abbott *et al.*, *Green Chem.* 13, 471 (2011).
- [2] V. I. Parvulescu *et al.*, *Chem. Rev.* 107, 2615 (2007).
- [3] B. Winter *et al.*, *Chem. Rev.* 106, 1176 (2006).
- [4] K.R.J. Lovelock *et al.*, "Ionic Liquids UnCOILed: Critical Expert Overviews", eds. N. V. Plechkova and K. R. Seddon, John Wiley & Sons, 251 (2012).
- [5] K.R.J. Lovelock *et al.*, *Chem. Rev.* 110, 5158 (2010)

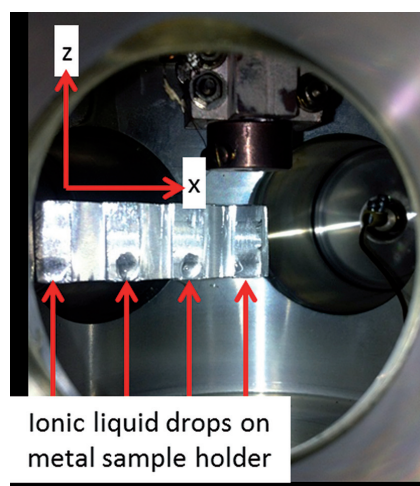


Fig. 24: Photograph of the sample holder used during the NEXAFS experiments.

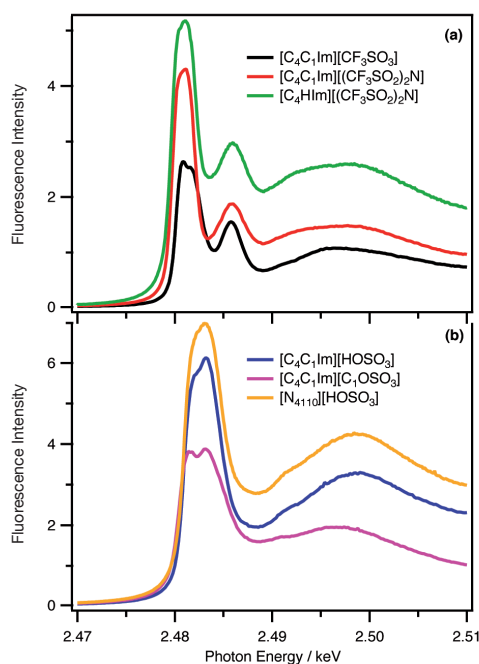


Fig. 25: Sulfur fluorescence intensity across the S K-edge for six sulfur-containing ionic liquids: (a) CF_3SO_2 -based ionic liquids, (b) $\text{OSO}_3\text{CF}_3\text{SO}_2$ -based ionic liquids.

➡ Please note

Some of the experimental reports in the previous pages are as yet unpublished. Please email the contact person if you are interested in any of them or wish to quote these results elsewhere.

➡ Our web site

This is at: www.xmas.ac.uk

It contains the definitive information about the beamline, future and past workshops, press articles, Key Performance Indicators (KPIs). You can also follow what happens on the beamline every week on Twitter [@XMaSBeam](https://twitter.com/XMaSBeam).



➡ Living allowances

These are €70 per day per beamline user – the equivalent actually reimbursed in pounds sterling. XMaS will support up to 3 users per experiment. For experiments which are user intensive, additional support may be available. The ESRF hostel still appears adequate to accommodate all our users, though CRG users will always have a lower priority than the ESRF's own users. Do remember to complete the "A-form" when requested to by the ESRF, as this is used for hostel bookings, site passes and to inform the safety group of attendees.

➡ Beamline people

Beamline Responsible – Simon Brown (sbrown@esrf.fr), in partnership with the Directors, oversees the activities of the user communities as well as the programmes and developments that are performed on the beamline.

Beamline Coordinator – Laurence Bouchenoire, (bouchenoire@esrf.fr), is in charge of Beamline Operations and can provide you with general information about the beamline, application procedures, scheduling, etc. Laurence should normally be your first point of contact.

Beamline Scientists – Simon Brown (sbrown@esrf.fr), Oier Bikondoa (oier.bikondoa@esrf.fr), Didier Wermeille (didier.wermeille@esrf.fr) and Laurence Bouchenoire (bouchenoire@esrf.fr) are Beamline Scientists and will provide local contact support during experiments. They can also assist with queries regarding data analysis and software.

Technical Support – Paul Thompson (pthompso@esrf.fr) is the contact for instrument development and technical support. He is assisted by John Kervin (jkervin@liverpool.ac.uk), who is based at Liverpool University, provides further technical back-up and spends part of his time on-site at XMaS.

Project Directors – Chris Lucas (clucas@liverpool.ac.uk) and Tom Hase (T.P.A.Hase@warwick.ac.uk) continue to travel between the UK and France to oversee the operation of the beamline. Malcolm Cooper (M.J.Cooper@warwick.ac.uk) remains involved in the beamline operation as an Emeritus Professor at the University of Warwick. Kayleigh Lampard (Kayleigh.Lampard@warwick.ac.uk) is now the principal administrator on the project and is based

in the Department of Physics at Warwick. All queries regarding expenses claims, etc. should be directed to her. Linda Fielding (Linda.Fielding@liverpool.ac.uk) is the administrator at the University of Liverpool.

➡ The Project Management Committee

The current membership of the committee is as follows:

- Peter Hatton (chair) (University of Durham)
- Andrew Boothroyd (University of Oxford)
- Robert Cernik (University of Manchester)
- Karen Edler (University of Bath)
- Brian Hickey (University of Leeds)
- Chris Nicklin (Diamond Light Source)
- William Stirling (Institut Laue-Langevin)
- Simon Crook (EPSRC)

meeting twice a year. In addition to the above, the directors, the chair of the PRP and the beamline team are in attendance.

➡ The Peer Review Panel

The current membership of the panel is as follows:

- Sean Langridge (chair) (ISIS)
- Geetha Balakrishnan (University of Warwick)
- Wuge Briscoe (University of Bristol)
- Steve Collins (Diamond Light Source)
- Carsten Detlefs (ESRF)
- Paul Strange (University of Kent)

In addition either Chris Lucas or Tom Hase attends their meetings.

➡ Housekeeping!!

At the end of your experiment samples should be removed, tools, etc returned to racks and unwanted materials disposed of in appropriately. When travel arrangements are made, therefore, please allow additional time to effect a tidy-up.

➡ PUBLISH PLEASE!... and keep us informed

Although the list of XMaS papers is growing we still need more of those publications to appear. We ask you to provide Laurence Bouchenoire with the reference. Note that the abstract of a publication can also serve as the experimental report!

➡ IMPORTANT!

When beamline staff have made a significant contribution to your scientific investigation you may naturally want to include them as authors. Otherwise we ask that you add an acknowledgement, of the form:

"This work was performed on the EPSRC-funded XMaS beamline at the ESRF, directed by C.A. Lucas, T.P.A Hase and M.J. Cooper. We are grateful to S.D. Brown, O. Bikondoa, D. Wermeille, L. Bouchenoire and P. Thompson for their invaluable assistance, and to K. Lampard and J. Kervin for additional support."

How to apply for synchrotron beam time ?

→ Beamline Operation

The XMaS beamline at the ESRF, which came into operation in April 1998, has some 174 days of beam time available each year for UK user experiments, after deducting time allocated for ESRF users, machine dedicated runs and maintenance days. During the year, two long shut-downs of the ESRF are planned: 4 weeks in winter and 4 weeks in summer. At the ESRF, beam is available for user experiments 24 hours a day.

→ Applications for Beam Time

Two proposal review rounds are held each year. **Deadlines for applications to make use of the mid-range facility (CRG) time are normally, 1st April and 1st October** for the scheduling periods August to end of February, and March to July, respectively. Applications for Beam Time must be submitted electronically following the successful model used by the ESRF. Please consult the instructions given in the ESRF web page:

www.esrf.eu

Follow the links: «**User Portal**» under «**Quick Links**»

Enter your surname and password
and select: «**Proposals/Experiments**»

Follow the instructions carefully — you must choose «CRG Proposal» and «XMAS-BM28» at the appropriate stage in the process. A detailed description of the process is always included in the reminder that is emailed to our users shortly before the deadline — for any problems contact Laurence Bouchenoire (bouchenoire@esrf.fr).

Technical specifications of the beamline and instrumentation available are described in the new XMaS web page (www.xmas.ac.uk).

When preparing your application, please consider the following:

- Access to the mid-range facility time is only for UK based researchers. Collaborations with EU and international colleagues are encouraged, but the proposal must be lead by a UK based principal investigator and it must be made clear how the collaborative research supports the UK science base. Applications without a robust link to the UK will be rejected and should instead be submitted directly to the ESRF.
- All sections of the form must be filled in. Particular attention should be given to the safety aspects, and the

name and characteristics of the substance completed carefully. Experimental conditions requiring special safety precautions such as the use of electric fields, lasers, high pressure cells, dangerous substances, toxic substances and radioactive materials, must be clearly stated in the proposal. Moreover, any ancillary equipment supplied by the user must conform with the appropriate French regulations. Further information may be obtained from the ESRF Experimental Safety Officer, tel: +33 (0)4 76 88 23 69; fax: +33 (0)4 76 88 24 18.

- Please indicate your date preferences, including any dates that you would be unable to attend if invited for an experiment. This will help us to produce a schedule that is satisfactory for all.

- An experimental report on previous measurements must be submitted. **New applications will not be considered unless a report on previous work is submitted.** These also should be submitted electronically, following the ESRF model. The procedure for the submission follows that for the submission of proposals — again, follow the instructions in the ESRF's web pages carefully. **Reports must be submitted within 6 months of the experiment.**

- The XMaS beamline is available for one third of its operational time to the ESRF's user community. Applications for beamtime within that quota should be made in the ESRF's proposal round - **Note: their deadlines are earlier than for XMaS! - 1st March and 1st September.** Applications for the same experiment may be made both to XMaS directly and to the ESRF. Obviously, proposals successfully awarded beamtime by the ESRF will not then be given beamtime additionally in the XMaS allocation.

→ Assessment of Applications

The Peer Review Panel for the UK-CRG considers the proposals, grades them according to scientific excellence, adjusts the requested beam time if required, and recommends proposals to be allocated beam time on the beamline.

Proposals which are allocated beam time must in addition meet ESRF safety and XMaS technical feasibility requirements.

Following each meeting of the Peer Review Panel, proposers will be informed of the decisions taken and some feedback provided.



is an EPSRC sponsored project

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