XMaS

NEWSLETTER

2015

CONTENTS

On the cover: XAS chamber (left image, p. 14). Thumbnail images (from left to right): mounted piezoelectric sample (p. 8), GISAXS rail (p. 4) and SLCam detector (p. 10).

Welcome to our 2015 Newsletter!

Thanks to our users, XMaS continues to go from strength to strength with over 20 publications published in the last year, several of which appeared in very high impact journals. Our staff continue to ensure that the beamline has also been performing at a high level. Over the past year we have maintained an up-time of the facility of over 96% and welcomed over 100 individual researcher visits from 52 UK and 11 international research groups. Of these visits we hosted 40 new users and 55 users who were either students or post-doctoral researchers.

As can be seen in the enclosed highlights, the research on the beamline spans the full remit of materials science (**Fig. 1**) with projects covering fundamental studies to device applications. For the first time in many years we have also resurrected the white beam capability (see the article by Lichtenegger *et al.* p. 10). The arrival of the new GISAXS rail allows rapid switching between SAXS/WAXS and XRR and gives new enhanced capacity and opportunities for the soft-matter community. The growing number of users in the area of catalysis and energy research is enabling XMaS to reach into new material challenges. In the past year we also welcomed our first commercial users conducting proprietary research.

The offline facilities (x-ray source and sample laboratory) are now fully operational providing additional capacity to the facility. Although primarily designed to support the beamline operations, by allowing preliminary alignment and characterization, independent research projects are also encouraged. Please see the website for information about how to apply.

In addition to our regular activities, we have also welcomed final year school students from the UK and Sweden to the beamline (**Fig. 2**) as part of the "XMaS Scientist Experience". These visits (covered in more detail in a separate article p. 3) were designed to highlight the career opportunities for females in science. We thank all of the staff involved from the ESRF, ILL and, of course, our team in helping to make this so successful that we will re-run the event this year.

We continue to engage with our users, running a user meeting in Liverpool in June. Feedback from our user community is the bedrock upon which we can develop and enhance the facility and we welcome any comments you may have. To facilitate greater engagement with new users we have also refreshed the webpage (www.xmas.ac.uk). The new page summarises access mechanisms, highlights latest developments and provides a showcase for the scientific outputs.

Looking to the future, further funding for XMaS will need to be secured in the coming year. We are confident that there is a strong case for XMaS to remain as a significant part of the UK infrastructure and we will be soliciting user input to the scientific case. Of course the situation is complicated by the ESRF upgrade plan which is now reaching its final technical design stage. As the bending magnets are being removed, our source characteristics and position will be changing. This opens up new opportunities but also comes with additional challenges. The new web-page will be regularly updated to keep you appraised as we develop our conceptual design review and then move into the technical specifications for the new facility.

We look forward to receiving your proposals and welcoming you onto the beamline in the near future.

Chris Lucas, Tom Hase and Malcolm Cooper
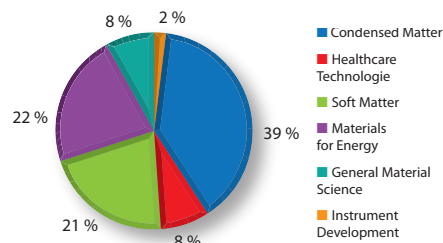
Fig. 1: XMaS Experiments by research category as reported by our users for the last year.

- Condensed Matter — 39 %
- Healthcare Technologie — 8 %
- Soft Matter — 21 %
- Materials for Energy — 22 %
- General Material Science — 8 %
- Instrument Development — 2 %
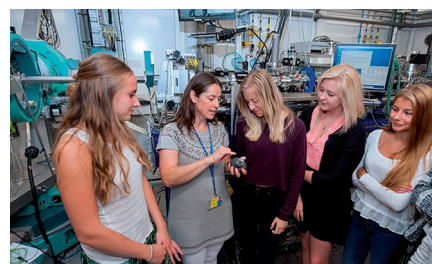
Fig. 2: School students visiting our staff at the ESRF.

UNIVERSITY OF LIVERPOOL

WARWICK
THE UNIVERSITY OF WARWICK

EPSRC
Engineering and Physical Sciences Research Council

XMaS scientist experience – Tackling gender inequality in physics

*K. Lampard – for more information contact
K. Lampard, Physics Department, University of
Warwick, Coventry, CV4 7AL, UK.*

kayleigh.lampard@warwick.ac.uk

The XMaS Scientist Experience is a competition open to first year A level female physics students to win a trip to XMaS, the ESRF and the ILL to see what life may be like as an international research scientist. We found that in this pilot year of the project we achieved so much more…

Worldwide, women remain seriously under-represented in the STEM* workforce and this is particularly so in the UK which has the lowest level in Europe. Despite women representing 46% of the overall UK labour force, they make up just 13% of those in STEM occupations [1]. Through the *XMaS Scientist Experience* project [2] we aimed to show female students that a career in STEM was both aspirational and attainable. Through introducing them to inspirational scientists and experiences we have broken down barriers and challenged their perceptions about pursuing careers in Physics or other scientific subjects.

The competition involved students writing an essay on *"What is the legacy of Dorothy Hodgkin, both on the study of structure on an atomic scale and for women in Science?"*. This question was selected to encourage the students to research an inspiring female scientist and for them to showcase their enthusiasm. The competition was launched in eight schools in the Coventry and Warwickshire area. From the entries 14 students won places on the trip (**Fig. 3**). With help to the XMaS team as well as staff at the ESRF and the ILL (**Fig. 4**), the incredibly successful trip took place from the 6th to the 9th April 2015. Thanks to air traffic control strikes the students got a bonus two days in France where they had the opportunity to revise for their upcoming A level exams with some extra help from the scientists at the ESRF!

"Speaking to the scientists here has helped me to see that hard work, determination and passion for physics are equally important and as long as I am willing to put the work in it was something that I could do" – S. Eastabrook.

"I am more likely to become a scientist because of this trip" – A. Couzens.

Following the trip the students presented what they had learnt to an audience at the University of Warwick.

The students have also been involved in engaging with younger audiences and sharing their experiences at STEM outreach events such as the Big Bang fair [3]. We are also collaborating with the University of Uppsala as they organise a similar trip for Swedish students.

Following this year's success, we were able to secure funding from the University of Warwick's Widening Participation Fund to continue the project for a further two years. The competition has now been launched again for a trip to take place in July 2016. The activity has been opened up nationwide and we are also extending our programme to include two Science Galas. These will be held in the physics departments of the Universities of Warwick on the 3rd February and Liverpool on the 10th February. These events, in partnership with our STEM collaborators [4], will be extravaganzas highlighting some inspiring careers as well as showcasing exciting science with hands-on demos. If you would be interested in presenting at, or attending, the events please get in touch.

[1] www.wisecampaign.org.uk/uploads/wise/files/not_for_people_like_me.pdf

[2] T.P.A Hase *et al.*, "XMaS inspiring women into scientific careers", Mater. Today 18, 7, 356 (2015).

[3] http://nearme.thebigbangfair.co.uk

[4] www.xmas.ac.uk/impact/scientistexperience

* STEM: Science, Technology, Engineering and Mathematics

Fig. 3: *The 14 winners of the first* XMaS Scientist Experience *competition on their way to the ESRF.*
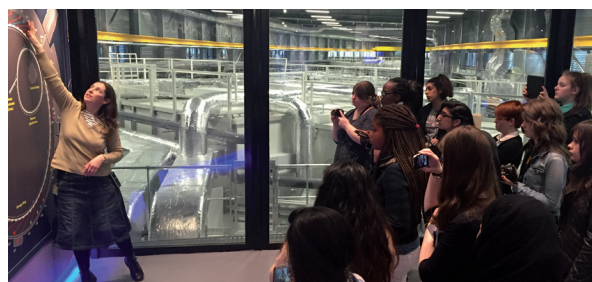
**Fig. 4:** *Students in the ESRF visitor centre being shown how the synchrotron works by Dr Laurence Bouchenoire.*

Improving the (GI)SAXS/WAXS capabilities

A combined XRR/(GI)SAXS-WAXS* setup is now available and functioning in the beamline experimental hutch. This new setup — designed and built by the company Nominal Ingénierie, based in Noyarey (France) — allows simultaneous SAXS and WAXS experiments to be performed and facilitates fast switching between SAXS and XRR configurations. The SAXS detector stage is motorised in the two directions perpendicular to the beam. The MAR165 or PILATUS3 300K can be mounted on the stage. The sample-to-detector distance can be changed manually from ~150 to 1400 mm. A set of PVC tubes and cones that follow the ISO K-200 Standard has been manufactured and are easily mounted and dismounted. These PVC tubes are filled with helium to reduce the background. Beamstops can be placed inside the tube and their position is adjusted by two perpendicular motorised translations. Photodiodes can also be placed on the beamstop to measure the transmitted beam intensity. The beamstops are held on the exit window with small magnets and can be exchanged straightforwardly. The lateral translation of the PVC tubes is motorised. In this way, the tubes can be removed from the beam and the detector arm of the diffractometer can be brought down to perform XRR measurements. A photo of the new setup is shown in **Fig. 5**.

The new setup is compatible with the 4 T magnet and thus, magnetic SAXS or WAXS experiments are possible. The nose of the conical tubes fits into the magnet aperture. For WAXS experiments, very short cylindrical tubes can be placed between the magnet exit aperture and the detector (**Fig. 6**). The superconducting magnet can provide fields up to ±4 T. This setup may be combined with phase-plates to control the incoming x-ray beam polarisation and perform measurements on chiral systems, for example.

* XRR: x-ray reflectivity
(GI) SAXS: (grazing incidence) small angle x-ray scattering
(GI) WAXS: (grazing incidence) wide angle x-ray scattering
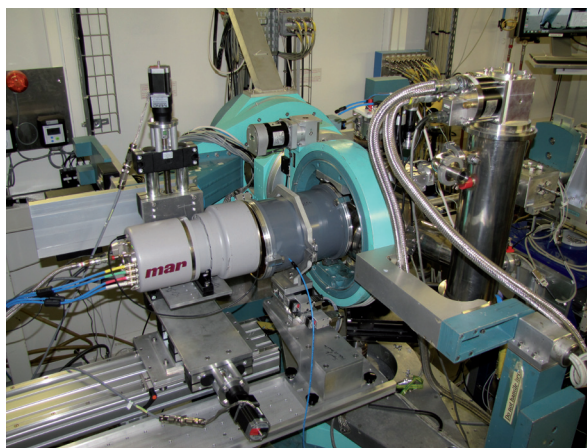
Fig. 6: *Magnetic WAXS setup using the XMaS 4 T superconducting magnet. The magnetic field can be applied horizontally and orthogonal to the x-ray beam direction or vertically and orthogonal to the x-ray beam. The magnetic field can also be applied parallel to the x-ray beam direction but the narrow opening of the magnet restricts the accessible angular range.*
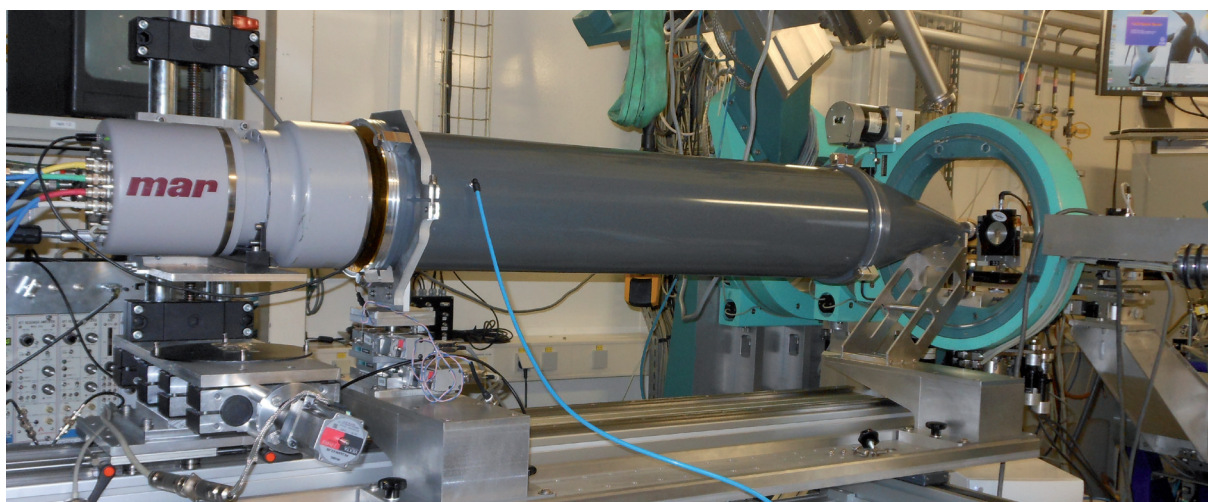
Fig. 5: *The new XRR/GISAXS setup installed in the beamline experimental hutch.*

Offline facilities

The x-ray laboratory source and the sample characterisation laboratory are now available to the user community.
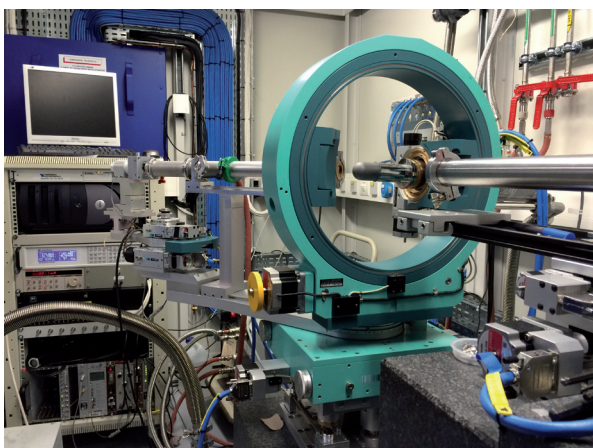
X-ray laboratory source

Pre-alignment and characterisation of samples prior to scheduled experiments is now possible and is strongly encouraged for a more efficient use of the synchrotron beam time. The offline source has the same Huber cradle as the main diffractometer allowing most of the same sample environment (cryostats and furnaces) to be mounted there. Temperature dependent XRD on single crystals or powder samples is thus possible (**Fig. 7**). Characterisation of thin films and multilayers by means of specular reflectivity can also be conducted. Electric field and laser interferometry capabilities will be identical to the main instrument. Application of magnetic fields will be restricted to 0.2 T in a reflectivity type configuration. The main detector is an avalanche photodiode detector (APD). A mount for our 2D pixel detectors (Maxipix and PILATUS3 300K) will be ready early in the year. We are hoping to develop a GISAXS setup similar to the one recently installed in the synchrotron hutch but testing is still to be conducted to see if it is feasible and what q-range can be accessed.

The x-ray laboratory can be used as a separate facility and offers an excellent opportunity for training students prior to synchrotron beam time.

Sample characterisation laboratory

The offline sample characterisation laboratory is also ready to use. It is located just opposite the beamline. Electrical characterisation (PE* loops and resistivity) as well as magnetoresistance measurements as a function of magnetic field angle (**Fig. 8**) are possible.

Currently, XMaS offers an electric field capability of ±2 kV with temperatures down to 2 K in a ±4 T magnetic field. A separate sample environment supplies ±5 kV down to 10 K in a ±1 T field. The article on p. 9 by Vecchini *et al.*, entitled "Ferroelectric characterization of PZT ceramics as function of temperature" illustrates how their work benefited from the available offline facility.
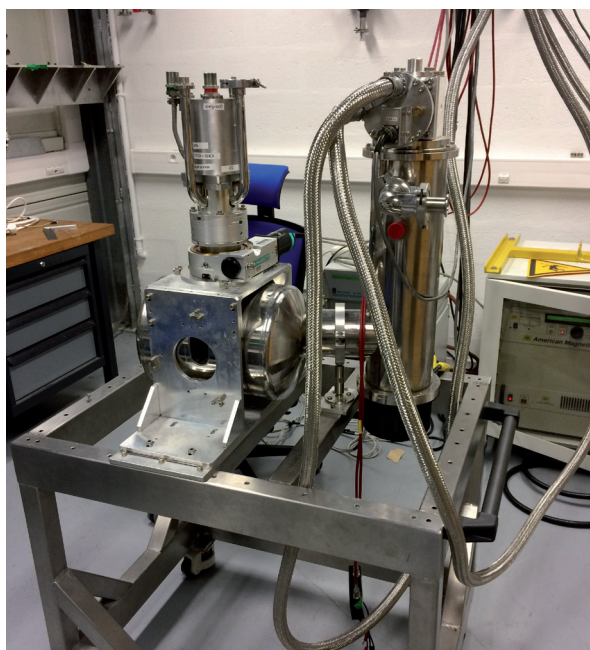
Both offline facilities are controlled using SPEC, the same control system as the one employed on the beamline.

How to apply for access time?

The application form for requesting time on the offline facilities can be found directly on our web site (www.xmas.ac.uk). The access procedures are still evolving. In this early stage please contact us directly with access requests. We will be moving to an application procedure similar to that of the synchrotron facility with proposal deadline 4 times a year. We stress that priority in staff time and resources will be given to supporting the synchrotron beamline. Further details will be posted to the web-page.

XMaS can support users to access the offline facilities and we encourage you to apply to use our expanded capabilities.

* PE: Polarisation-Electric Field

** Anisotropic Magnetoresistance

Fig. 7: *X-ray lab source diffractometer showing the XRD temperature setup with flight tubes installed.*

Fig. 8: *New AMR** setup to measure electrical parameters as a function of magnetic field, azimuth and temperature is now available.*

Complex modulated magnetism in PrPtAl

G. Adbul-Jabbar, D.A. Sokolov, C.D. O'Neill, C. Stock, D. Wermeille, F. Demmel, F. Krüger, A.G. Green, F. Lévy-Bertrand, B. Grenier and A.D. Huxley – for more information contact A.D. Huxley, School of Physics and CSEC, University of Edinburgh, Edinburgh EH9 3FD, UK.

a.huxley@ed.ac.uk

The transition between ferromagnetism and paramagnetism is one of the simplest examples of a continuous phase transition. Interesting behaviour is expected when the transition temperature becomes small because incoherent fluctuations above the transition temperature then exist to low temperatures. Ultimately, for lower transition temperatures, either the transition must become first order or new forms of order must appear to satisfy the third law of thermodynamics. A new theory known as "order-by-disorder" [1] clarifies how the fluctuations associated with different competing ground states may stabilise new forms of order under these circumstances. Our findings on PrPtAl provide the first concrete vindication of one of the predictions of this approach: the formation of modulated magnetic structures [2].

Our diffraction study at XMaS has allowed us to characterise complex magnetic states discovered in PrPtAl at the boundary between ferromagnetism and paramagnetism. Much of the observed behaviour is consistent with the predictions of the order-by-disorder theory, including a change from ferromagnetism to a modulated state whose modulation vector increases with temperature. Surprisingly, the phase diagram is also more complex. Rather than this modulated state changing directly into the paramagnetic state as the temperature is further increased, it changes to a doubly modulated state before paramagnetism is finally attained. This second modulated state is very unusual, having two simultaneous collinear incommensurate ordering vectors. We focus below on the first modulated state, which has only one incommensurate vector (together with a strong third harmonic) (see **Fig. 9**).

A temperature dependent modulation vector above a jump from ferromagnetism is also found for the rare earth elements Tb and Dy. Differences in other physical quantities however, indicate a new mechanism is at play in PrPtAl. Hexagonal Tb and Dy inherently "want" to form helical magnetic structures (owing to their band structure and the RKKY interaction). However, the anisotropy energy, which grows extremely strongly with the magnitude of the ordered moment, pushes them into a ferromagnetic state at low temperature. The conjecture for PrPtAl is the opposite: PrPtAl "wants" to be a ferromagnet but the extra-fluctuations available for a modulated structure stabilise modulations close to the Curie temperature. In order to tell these two cases apart experimentally, one possibility is to consider how the modulated state changes the electronic density of states and magnetic fluctuations. In the first case (Tb and Dy) the gapping of the Fermi-surface decreases the fluctuations where they are the strongest. This contrasts with the order-by-disorder mechanism in which the dominant fluctuations are centred on $q=0$, rather than at the spin density wave (SDW) ordering vector and the formation of the SDW actually increases their strength. This should have consequences for the heat capacity and electrical conductivity: the order-by-disorder theory predicts that they will be enhanced in the modulated state if order-by-disorder is at play, but reduced otherwise. This is indeed what we observed experimentally.

[1] G.J. Conduit *et al.*, Phys. Rev. Lett. 103, 207201 (2009).

[2] G. Abdul-Jabbar *et al.*, Nat. Phys. 11, 321 (2015).
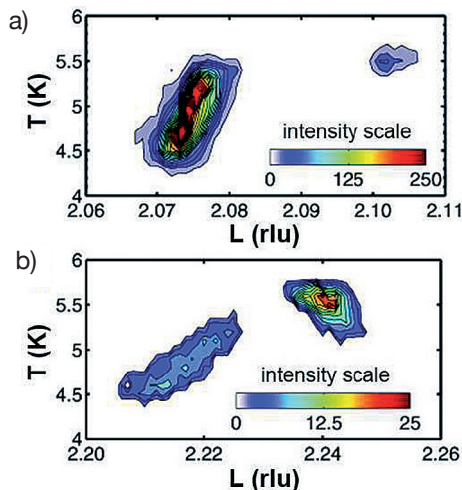
Fig. 9: *The figure shows intensity maps around satellites at (00L) close to the (002) Bragg peak as a function of temperature for PrPtAl measured at the Pr L_{II} edge. At lower temperature a single modulation wavevector q≈0.07 (rlu) (a) and a third harmonic (b) are seen. The change of wavevector with temperature and the strong third harmonic are well explained by the "order-by-disorder" theory. Just before 6 K, two new vectors appear at q≈0.1 (rlu) (a) and 0.24 (rlu) (b).*

Copper oxide layers are odd

*E.M. Forgan, E. Blackburn, A. Holmes, A. Briffa,
J. Chang, S. Hayden, R. Liang, L. Bouchenoire and
S. Brown – for more information contact E.M. Forgan,
School of Physics & Astronomy, University
of Birmingham, Birmingham B15 2TT, UK.*

e.m.forgan@bham.ac.uk

It is now nearly 30 years since High-T_c "cuprate" superconductors were discovered, but we are still finding out totally new things about them and still do not understand properly the cause of the superconductivity or what controls the upper limit on the superconducting transition temperature T_c.

It is clear that superconductivity (SC) resides in the CuO_2 layers found in all cuprate High-T_c materials, but these layers can also be insulating and antiferromagnetic or exhibit a "pseudogap" – which behaves somewhat like a superconducting gap, but without superconductivity. Which phenomenon is observed depends on the doping of holes in the CuO_2 layers. In $YBa_2Cu_3O_{7-x}$ (YBCO), the first superconductor discovered with a T_c above the boiling point of liquid nitrogen, the doping is varied by changing the oxygen content.

In the past few years, yet another behaviour of the CuO_2 layers was discovered in underdoped YBCO [1, 2], and was later found to be generic. This is a "charge density wave" (CDW), which is associated with minute displacements of atoms from their equilibrium positions, modulated with a period of about 3 atomic spacings. We found that the CDW and SC compete – if one is strong, the other is suppressed [2] – so understanding the CDW is important for understanding the SC.
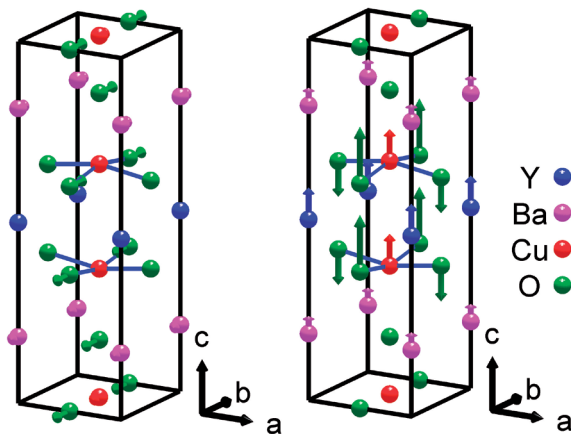
We decided to try to determine the precise structure of the CDW, by measuring a large number of x-ray diffraction satellites from the CDW and then fitting their intensities to a set of atomic displacements. This was no easy task, since the CDW signals are about 10^6 times weaker than the crystal Bragg peaks and might be hidden by background or spurious signals. (These factors explain why CDWs took so long to discover.) However, the excellent background suppression by the in-vacuum "tube-slits" on the ingoing and outgoing beams at XMaS, and the suppression of fluorescence by the energy resolution of the silicon drift Vortex detector allowed us to measure hundreds of satellite intensities.

Then came the difficult part: fitting the results. There are 11 atoms in the YBCO unit cell, which might be displaced in the basal plane or c-direction, and the copper oxide layers are actually bilayers of CuO_2. However, we were able to reduce the potentially large number of fitting parameters by symmetry arguments to show that there were two possible models, each with 13 displacement parameters.

The "most obvious" model was one in which the CDW had compressive displacements, equal in the two halves of a bilayer. These would set up periodic charge densities which might disrupt both the electronic band structure and the superconductivity. This would not fit, and after much effort, we tried a model which had shear displacements, which break the mirror symmetry of the bilayers (**Fig.10**). This was clearly the correct model. The data were good enough to show also that the displacements of the four oxygens around each copper in a layer had a fascinating "butterfly" pattern, with head and tail displaced downwards while wings went up. These results recently published in Nature Communications [3] are leading to new understanding [4] of CDWs and "Fermi surface reconstruction" which changes the carriers from holes to electrons in underdoped SCs.

[1] G. Ghiringhelli *et al.*, Science 337, 821 (2012).

[2] J. Chang *et al.*, Nature Physics 8, 871 (2012).

[3] E.M. Forgan *et al.*, Nat. Commun. 6, 10064 (2015).

[4] A. Briffa *et al.*, *arXiv*/1510.02603 (2015).

Y ● Ba ● Cu ● O ●

Fig. 10: *The "butterfly" motif of atomic displacements (exaggerated) in a CDW in YBCO. This motif is modulated with a period of about 3 unit cells in the b-direction. A similar CDW along the a-direction coexists with it. There are large displacements in the c-direction, shearing the bilayers, combined with small basal-plane displacements that are $\pi/2$ out of phase. The perturbation due to the CDW has odd symmetry about the centre of the bilayer.*

Dynamic magnetoelectric analysis at XMaS

S.R.C. McMitchell, C. Vecchini and P. Thompson – for more information contact S.R.C. McMitchell, XMaS – The UK-CRG, ESRF, Grenoble, 38000 France.

sean.mcmitchell@esrf.fr

New capabilities at XMaS now allow deep insights into dynamic magnetoelectric mechanisms. The developments are part of the Nanostrain project, which is an EMRP project **[1]** based around a consortium of academic and industrial entities such as IBM and the UK National Physical Laboratory (NPL). This project aims to progress the fundamental materials science of technologically important materials under device-like conditions, as well as to develop ties between physical properties and structural changes; all of which will feedback in to the real-world device engineering such as the piezoelectric effect transistor (PET) patented by IBM.

The new analysis suite represents an extension to the existing in situ strain measurement setup **[2, 3]** that allows the simultaneous collection of data from diffraction, laser interferometer and electric polarization under AC electric fields. This allows separation of intrinsic (crystallographic) and extrinsic (domain related) components of the piezoelectric response. In addition to faster ADC electronics, increasing the possible applied electric fields from 1 kHz to 1 MHz, the application of AC magnetic fields (up to 0.1 T) simultaneously to electric fields will be available. This offers the opportunity to study not only the piezo/ferroelectric response and magnetic response of magnetoelectric/multiferroic materials but also the coupling between electric and magnetic orders.

The two XMaS offline facilities compliment these synchrotron-based methods perfectly. Temperature dependent polarization measurements can elucidate ferroelectric transitions in advance of beamtime and the lab x-ray diffractometer is available for basic crystallographic analysis. Furthermore, the offline source has the same Huber circle as the main beamline diffractometer allowing cryostats with electric feedthroughs to be mounted there too. In addition to the offline ferroelectric testing, a new magnetoresistance setup allows the mapping of anisotropy by measuring sample resistance as a function of magnetic field angle.

This new characterisation suite offers an exceptionally powerful tool in the understanding of these technologically important magnetoelectric and multiferroic materials, especially in thin film form. Not only will these new capabilities be a huge benefit to fundamental materials science but will also feed into the nanoscale engineering of novel technologies such as the PET.

[1] www.nanostrain.eu

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

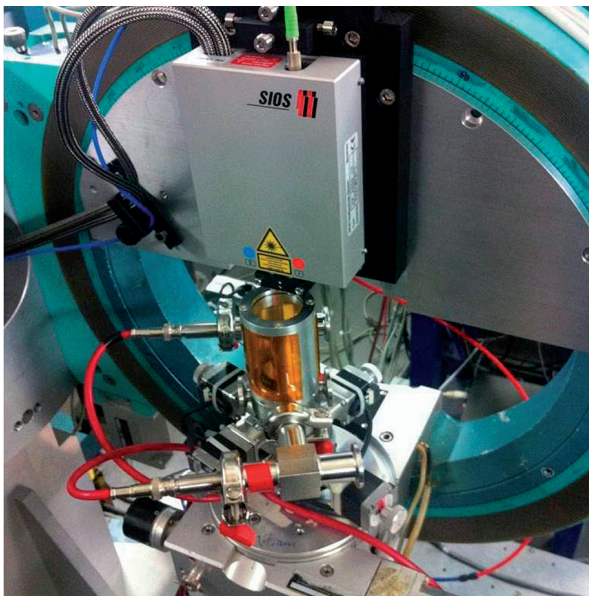[3] C. Vecchini *et al.* Rev. Sci. Instrum. 86, 103901 (2015).

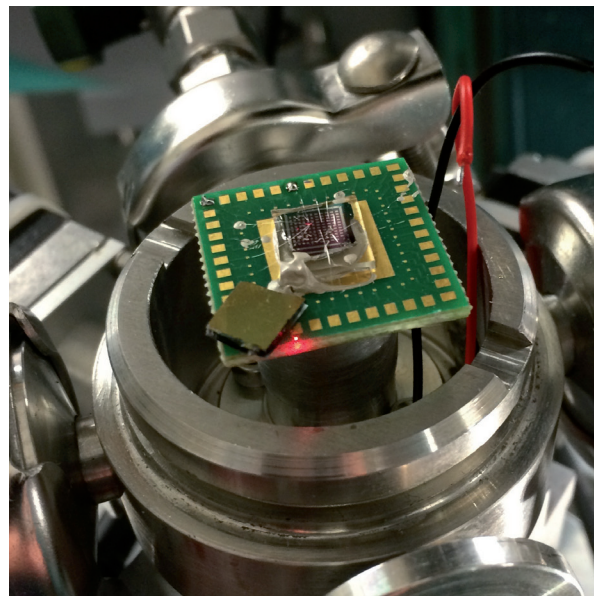**Fig. 11:** *Piezoelectric setup at XMaS.*

Fig. 12: *Mounted sample with electrical contacts.*

Ferroelectric characterization of PZT ceramics as a function of temperature

C. Vecchini, P. Thompson, O. Gindele, M. Stewart, A. Kimmel and M.G. Cain – for more information contact M. Stewart, National Physical Laboratory (NPL), Teddington, TW11 0LW, UK.

Mark.Stewart@npl.co.uk

PZT (Lead Zirconate) ceramics are widely used in many applications including, for example resonators, fuel injectors, actuators, gyroscopes, sensors and ultrasound transducers. However, very little is known about their electrical and mechanical properties away from a small range of temperatures around ambient conditions. The large variety of compositions, doping and stoichiometries used in commercial PZT makes their classification extremely hard. While it is nowadays standard and accepted practice to investigate these functional materials in static or quasi-static conditions, their usage requires dynamic applications of external stimuli. This is applicable not only to PZT, but to other ferroelectric and emerging functional materials, such as lead-free piezoelectrics, multiferroics and magnetoelectrics, ferroelastics as well as magnetostrictive materials. Recently, great effort has been made by several groups to extend the quasi-static functional properties measurements to dynamic investigations [1, 2]. These measurements are often very challenging, especially when combined with extreme temperatures. Attempts to measure dynamical ferroelectric properties have generally been attempted in the engineering temperature range.

Taking advantage of the developments performed within the EMRP Nanostrain Project [1, 3], we have used the XMaS sample characterisation laboratory (see p. 5 for more information) to investigate the dyna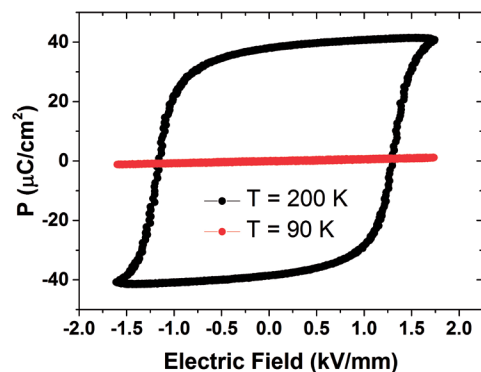mical electrical response of PZT ceramics from room temperature down to 10 K (**Fig. 13**). A cryostat has been fitted with high voltage feedthroughs and connected to the PE loop facility available on the beamline (which has been developed by a joint effort between NPL and the XMaS team). The observation of an apparent suppression of ferroelectric response at about 100 K (**Fig. 14**) has been found in agreement with the only low temperature study of ferroelectric properties available in literature [4]. However, the NPL and XMaS team proceeded to investigate further these compounds as a function of electric field parameters by changing both the frequency and magnitude of the applied electric field. The data showed a frequency as well as a voltage dependence of the "transition" temperature.

Further investigations at large electric fields show that the apparent disappearance of the ferroelectric response is only due to an exponential increase of the coercive field with lowering temperature in PZT compounds with compositions close the tetragonal phase in the MPB (Morphotropic Phase Boundary). This observation has been successfully reproduced by NPL's theoretical modelling group, which used a molecular dynamic approach based on the shell-model. The theoretical work, developed to model the response of ferroelectric materials to applied electric field gives new insight on both the local environment and on the strain dependence with the strength of electric fields, which relates to composition [5].

[1] C. Vecchini *et al.*, Rev. Sci. Instrum. 86, 103901 (2015).

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

[3] www.nanostrain.eu

[4] http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19980236888.pdf

[5] C. Vecchini *et al.*, in preparation.

Fig. 13: *Example of PZT sample mounted on the XMaS cryostat. The bottom electrode is mounted on a sapphire plate.*

Fig. 14: *Polarization – Electric field data collected at 0.3 Hz and 200 K (black) and 90 K (red), showing the apparent suppression of ferroelectric response.*

Area detector diffraction goes 3D

H.C. Lichtenegger, T. Grünewald, W. Bras,
H. Rennhofer, L. Vincze, P. Tack and J. Garrevoet
– for more information contact H.C. Lichtenegger,
Institute of Physics and Materials Science, BOKU
Wien, 1090 Vienna, Austria.

helga.lichtenegger@boku.ac.at

Laue diffraction is the oldest method to determine crystal structures and has – as of today – been largely replaced by monochromatic x-ray Bragg diffraction. Specifically the development of large area detectors has led to very convenient measurement protocols allowing one to acquire 2D information in one shot, whilst full 3D information still requires a sample rotation. Only recently, with the advent of very intense whitelight synchrotron radiation sources, has Laue diffraction received an exciting revival with collection of the diffraction patterns from single molecules a good example of its application. A new approach using an energy dispersive area detector now allows energy dispersive Laue diffraction (EDLD). In this way the conventional 2D information as available from area detectors is complemented by an energy spectrum recorded in each pixel, thus effectively using the energy as a third dimension **[1]**. This approach can be developed into a particularly promising method for polycrystalline samples with preferred orientation. Sample rotation in order to access 3D information is no more necessary, as all the information can be acquired in one shot.

For this purpose we used a white beam at XMaS and an energy dispersive area detector (SLcam). In order to access maximum information in 3D we devised a novel setup that allowed us to access large scattering angles requiring an extremely tight configuration of beam shaping, sample, beamstop and detector (**Fig. 15**). We applied our new experimental approach to assemblies of carbon fibres.

Carbon fibres are known to yield strong 002 reflections normal to the graphite planes which exhibit preferential orientation along the fibre axis and different radial distributions depending on the fibre type. By simultaneously collecting 2D diffraction patterns at different energies and at every measurement point in the sample, we obtained 3D information. **Fig. 16** shows an example of diffraction patterns at one single sample spot but at different energies. The different intensity distribution about the azimuth at different energies is immediately obvious. It allowed us to extract the multiple fibre orientations present in one sample.

We think that our approach holds great potential for a variety of complex materials, especially for intricately structured fibrous samples **[2, 3]**. Due to the white beam energy dispersive setup it also provides chemical information together with 3D structural information through simultaneous fluorescence information at the elemental absorption edges and diffraction information collected by the same detector in one shot.

[1] S.A. Send *et al.*, J. Appl. Cryst. 45, 517 (2012).

[2] H. Lichtenegger *et al.*, J. Appl. Cryst. 32, 1127 (1999).

[3] M. Ogurreck, *et al.*, J. Appl. Cryst 43, 256 (2010) & 46, 1907 (2013).
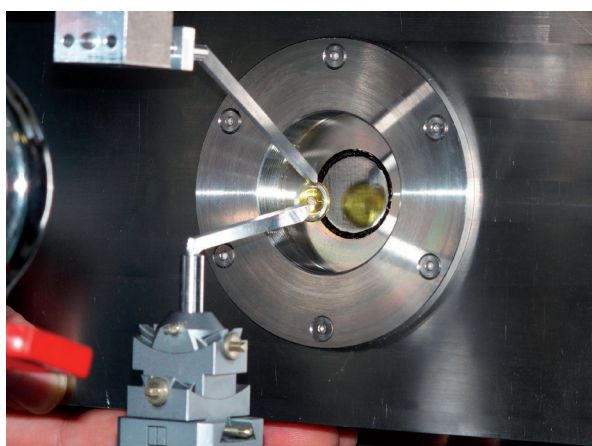
Fig. 15: *Experimental setup showing the SLcam detector, beamstop, sample and collimator.*
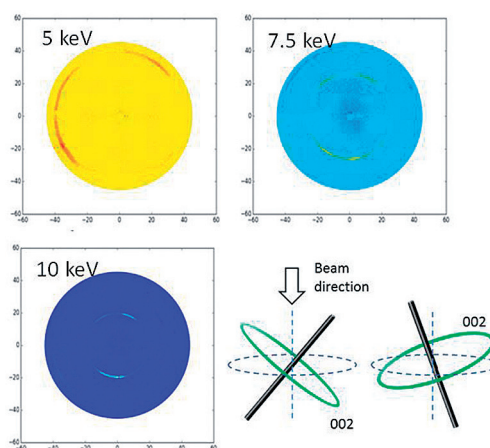
Fig. 16: *Scattering patterns of C fiber sample (002 reflection) at different energies. Extracted orientation information for carbon fibers.*
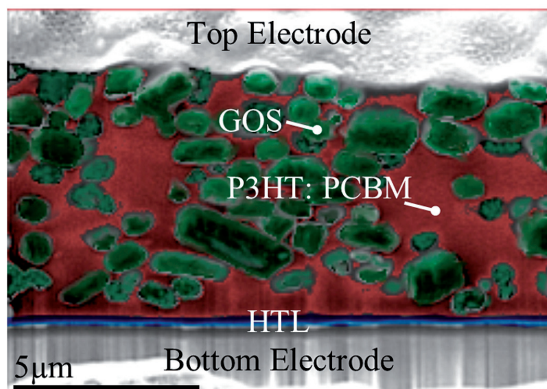
Organic-inorganic x-ray detectors

S.Lilliu and P. Büchele – for more information contact S.Lilliu, Masdar Institute of Science and Technology, Abu Dhabi 54224, UAE or P. Büchele, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany.

samuele_lilliu@hotmail.it, patric.buechele@gmx.de

Radiography is an essential diagnostics branch in medicine. In projection radiography the human body is exposed to x-rays and their transmitted intensity is captured by a detector. For decades radiologists have employed detecting photographic paper. In spite of the introduction of solid state x-ray detectors, their full adoption has been hindered by the high cost. Researchers are trying to develop low-cost and high-resolution flat-panel detectors for the energy range between 20 and 120 keV. Today's digital x-ray detectors mainly consist of a scintillator layer that converts x-rays into visible light and an imaging sensor that converts light into electrical signals. Apart from the high manufacturing costs, these detectors also have the disadvantage that the generated light propagates isotropically as it passes through the scintillator layer. As a consequence, the light hits a large number of adjacent pixels instead of hitting only one pixel of the image sensor. This results in a loss of spatial resolution.

In the hybrid approach proposed by Büchele *et al.* **[1]** this problem is solved by embedding the scintillator directly into a blend of organic semiconductors (bulk-heterojunction), which acts as a photodiode converting light into electrical charges **(Fig. 17)**. This gives the emitted light no opportunity to become

widely spread and a high spatial resolution is obtained. Manufacturing costs are kept low thanks to effortless and effective spray deposition.

Grazing incidence wide angle x-ray scattering (GI-WAXS) measurements performed at XMaS played an important role in understanding the device physics. **(Fig. 18)** shows diffraction images of P3HT: PCBM: GOS films at different concentrations. We observe a structural interplay between P3HT and GOS during thermal treatment. The amount of P3HT face-on lamellae increases with GOS concentration, which explains the increase in mobility measured by x-ray induced charges probed by x-ray charge carrier extraction by linearly increasing voltage (X-CELIV).

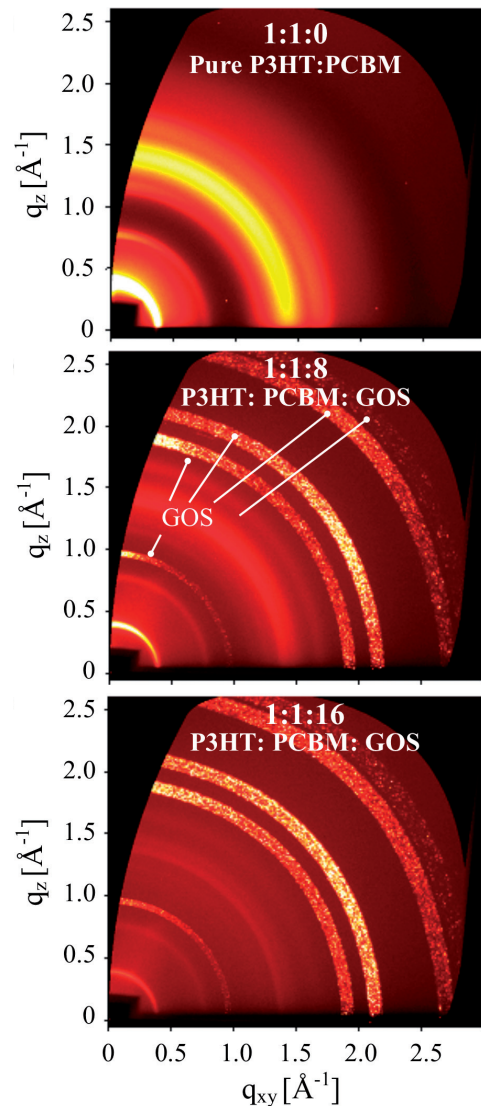[1] P. Büchele *et al.*, Nat. Photon. 9, 843 (2015).

Fig. 17: *Scanning electron microscopy (SEM) image of the device cross-section in false colour showing scintillating terbium-doped gadolinium oxysulfide (GOS: Tb) macroparticles (green) embedded in poly(3-hexylthiophene-2,5-diyl)) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) bulk-heterojunction (red). HTL is the hole-transporting layer.*

Fig. 18: *GI-WAXS images of thermally annealed P3HT: PCBM: (GOS:Tb) films at different concentrations.*

Model membrane systems for studying nanoparticle cellular entry mechanisms

B. Sironi, C.M. Beddoes, R. Sorkin, J. Klein
and W.H. Briscoe – for more information contact
W.H. Briscoe, School of Chemistry, University of Bristol, UK.

wuge.briscoe@bristol.ac.uk

Nanomaterials are increasingly found in consumer products, ranging from children's cuddly toys to food additives. Nanoparticles (NPs) also have great potential in the biomedical field, particularly for drug delivery, biosensors and theranostics. However, their impact on human health and the environment is not well understood. NPs can enter the human body via the dermal, respiratory, ocular or gastrointestinal systems. While this can be exploited for medical treatments, it also poses concerns about the detrimental effects of NPs on living systems [1].

The activity of NPs in contact with biological systems is unpredictable, and can vary from being highly carcinogenic to regenerative. Much of the knowledge in this area has come from phenomenological *in-vitro* and *in-vivo* studies of cells and animal models, which show that direct cellular entry of NPs is one of the mechanisms for them to impart toxicity. Researchers are therefore focusing on rigorous and quantitative physicochemical methods to study the interactions between nanoparticles and model cell membranes.

A central pre-requisite for this approach is detailed structural characterisation of model membranes systems. A simple but unique method developed at XMaS for studying soft nanofilms at the mica-water interface [2] has allowed us to characterise a number of different model membrane structures over the past few years. Using x-ray reflectivity (XRR) lipid bilayers, multilayers and interfacial liposomes have been studied. Depending on the lipid concentration and chain length, liposomes at the solid-water interface can undergo rupture forming bilayers or retain their spherical structure. In **Fig. 19**, curves D and E show intact distearoylphosphatidylcholine (DSPC) liposomes and dimyristoylphosphatidylcholine (DMPC) bilayer, in respective 0.42 mM aqueous liposomes dispersion. XRR of dioleoylphosphatidylcholine (DOPC) multilayers

prepared by drop-casting its liposome dispersions on mica reveals a well ordered lamellar structure with domains formed by over 50 bilayers of 4.6 nm each, as indicated by sharp equidistant Bragg peaks (**Fig. 19**, curve A). When positively charged 4 nm generation 4 (G4) polyamidoamine dendrimers are intercalated in the multilayers, the overall lamellar structure is retained, but the order diminishes: Bragg peaks are still present, consisting of domains with ~20 layers of 4.5 nm lamellae. Also, the surface morphology changes, as indicated by the absence of "negative" peaks in the reflectivity curve (**Fig. 19**, curve B). When neutral and negatively charged polyamidoamine dendrimers are added, the final sample retain the lamellar structure; whereas addition of dendrimers with hydrophobic surface groups in a wide range of DOPC/dendrimer number ratio ($5 \times 10^2 - 5 \times 10^4$) disrupted the multilayer structure. Loss of order is also observed when 20 nm negatively charged polystyrene NPs are added. They do not intercalate in the DOPC lamellar structure but disrupt the order of the sample, with no Bragg peaks observed (**Fig. 19**, curve C). This may be attributed to the large size of the particles, inhibiting them from intercalating between two lipid bilayers.

Taken together, these results show the effects of nanoparticles on the model membrane structures and on the energetic process of membrane fusion in endocytosis. The major task ahead is to understand the correlation between the physical parameters that characterise nanoparticles and their interactions with model membrane systems [3]. These include nanoparticle geometry, surface charge and surface chemistry, and designing membrane systems that mimic the structural and compositional sophistication of cell membranes. This also represents opportunities for contributions to understanding nanotoxicity from a physicochemical perspective using x-ray techniques.

[1] C.M. Beddoes *et al.*, Adv. Colloid. Interfac. 218, 48 (2015).

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

[3] B. Sironi *et al.*, ms in preparation.
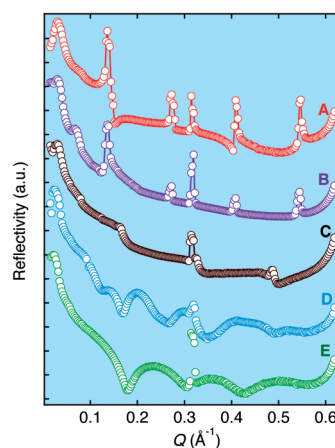
Fig. 19: *XRR curves collected at room temperature in air for DOPC lipid multilayers (A); with addition of DOPC/ G4NH$^+$ dendrimers ($\varnothing_{NP}$ = 4 nm, number ratio v = 5x10^3) which retained the lamellar structure (B); and with the addition of DOPC/polystyrene NPs ($\varnothing_{NP}$ = 20 nm, v = 10^{-4}) showing no order (C); and for DSPC interfacial liposomes (D) and DMPC bilayer (E), both in aqueous liposome disperions.*

Potential hazards of long-term nuclear waste storage

S. Rennie et al. – for more information contact
S. Rennie, Interface Analysis Centre, School of Physics, University of Bristol, Bristol, BS8 1TL, UK.

sophie.rennie@bristol.ac.uk

Nuclear power is a reliable, readily available energy resource that presents an attractive solution to the increasing demand for low-carbon energy technologies. Today, more than 400 commercial nuclear reactors operate in 31 countries, providing 11% of the world's electricity. Together, these facilities produce 12,000 tons of high-level radioactive waste each year, highlighting the need to develop a safe and efficient storage strategy for this material.

The long-lived radiation fields that result from highly radioactive fission products require spent nuclear fuel to be stored over timescales of tens of thousands of years. This presents a very real possibility that the fuel will come into contact with water over the course of its storage lifetime. The predominant component of nuclear fuel, uranium dioxide (UO_2), is insoluble in its stable state, however, once the fuel has been used during reactor operation, the radiation fields generated by fission products are able to cause radiolysis of the water [1]. This process yields highly oxidising species that are able to transform UO_2 into the readily soluble UO_2^{2+} ion. In other words, this mechanism has the potential to corrode the spent fuel, causing the release of harmful radionuclides into the environment [1].

Detailed studies of the structure of spent fuel in such an extreme environment are prohibitively complicated, but there are other experimental routes that might shed light on fuel behaviour. We have used an intense, monochromated beam of x-rays to mimic the radiation fields generated by spent nuclear fuel, with the aim of investigating their effect on a UO_2 / water interface [2]. This was first achieved on XMaS in a joint project carried out between XMaS and Diamond Light Source, by exposing single crystal UO_2 thin films to ultra-pure water in the presence of a 15 keV x-ray beam. As well as initiating radiolysis, the beam was also used to measure x-ray diffraction and reflectivity profiles, to probe the crystalline structure, surface morphology, oxide layer density and, ultimately, the dissolution of UO_2 as a function of exposure time. Modelling the reflectivity data and the UO_2 (002) Bragg peak diffraction spectra reveals a loss of crystalline UO_2, an increase in the UO_{2+x} hyperstoichiometric layer, a surface roughening, and eventually a loss in material due to dissolution.

These measurements can help to refine predictive models of the spent fuel/water interface. Using engineered interfaces that are particularly sensitive to any change in surface structure, for instance, it is possible to investigate the role of individual variables. This information is important to the validation of theoretical models that attempt to predict the behaviour of fuels in contact with ground water over long timescales.

[1] D.W. Shoesmith, J. Nucl. Mater. 282, 1 (2000).

[2] R.S. Springell *et al.*, Faraday Discuss. 180, 301 (2015).
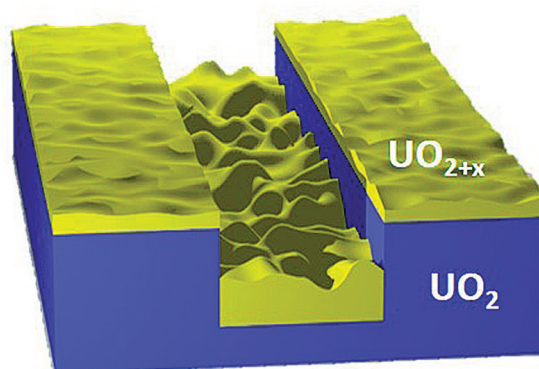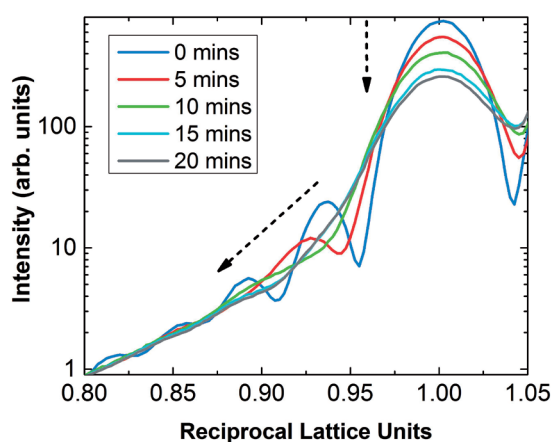
Fig. 20: *Significant changes to the UO_2 diffraction profile are observed on exposure to water and x-rays (left). The data allows us to model the surface (right): along the beam path, we find a loss of UO_2 (blue) and a growth of the hyperstoichiometric surface layer (UO_{2+x}) (yellow), concurrent with radiolytic species causing oxidation and dissolution of the sample surface.*

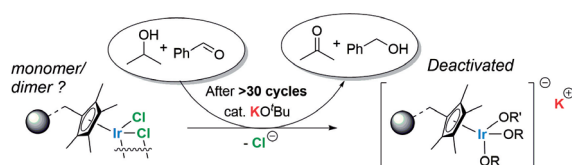# Activation and deactivation of an immobilised transfer hydrogenation catalyst

G.J. Sherborne, M.R. Chapman, A.J. Blacker, R.A. Bourne, T.W. Chamberlain, B.D. Crossley, S.J. Lucas, P.C. McGowan, M.A. Newton, T.E.O. Screen, P. Thompson, C.E. Willans, and B.N. Nguyen – Institute of Process Research and Development, School of Chemistry, University of Leeds, LS1 4EE, UK.

bao.nguyen@leeds.ac.uk

We previously reported a series of *ex-situ* measurements to investigate a slow, non-leaching deactivation process of a commercial immobilised $Cp*IrCl_2$ catalyst on Wang resin. The catalyst was reported [1] to be highly robust and can be recycled 30-80 times although deactivation ultimately settles in. Traditional characterisation techniques, *e.g.* MAS NMR, ICP, IR, failed to shed light on such process. Initial results from Ir L-edge EXAFS and Cl K-edge XANES of *ex-situ* samples suggested that deactivation is linked to the complete loss of chloride ligands (**Fig. 22**) from the iridium centre.

Treatment of the deactivated catalyst with dilute HCl temporarily restores some catalytic activity however XAS data showed no increase of Cl content in the catalyst. The Cl XANES spectrum of the "deactivated" catalyst was confirmed to be that of KCl, formed by reaction of HCl with the deactivated form $[Cp*Ir(OR)_3]K$ of the catalyst. In this study, the deactivation/reactivation process is observed in an *in-situ* experiment at the K and Cl K-edges. Structural changes detected by multi-element XAS are directly linked with measured catalytic activity in the same fixed-bed spectroscopic flow-cell, which decreased over the same timescale (**Fig. 23**).

Based on these results and stoichiometric experiments with KO^tBu (**Fig. 23b**), a sensible deactivation and reactivation mechanism has been proposed (**Fig. 24**) [2]. These findings have led to further studies into improved reactivation protocols which will improve the value of this and similar catalysts. The results also have significant implication on the identity of the true catalytic species and the mechanism of this type of transfer hydrogenation, both of which are still unknown in the literature.

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

[2] B.N. Nguyen *et al.*, J. Am. Chem. Soc. 137, 4151 (2015).

Fig. 21: XAS study of an immobilised $Cp*IrCl_2$ catalyst for transfer hydrogenation at *Ir L-edge, Cl K-edge* and *K K-edge*.
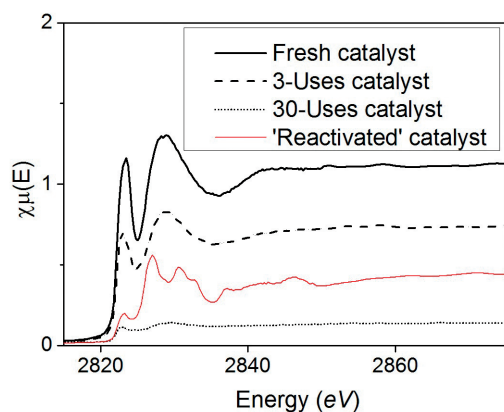
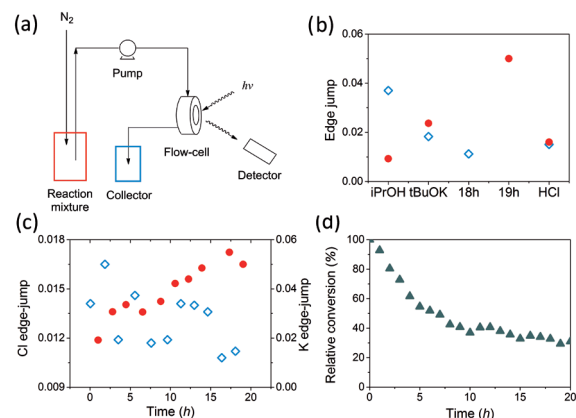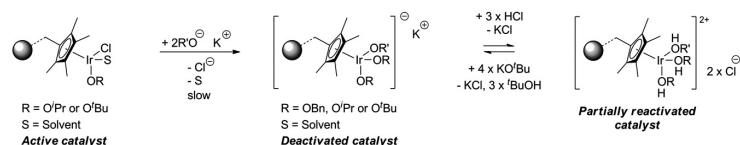**Fig. 22:** Ex-situ Cl K-edge spectra of immobilised $Cp*IrCl_2$ at various stages of deactivation.

Fig. 23: In situ XAS experiment monitoring Cl and K K-edges of immobilised $Cp*IrCl_2$ catalyst during catalytic reaction.

Fig. 24: Mechanism of deactivation and reactivation of the immobilised Cp*Ir catalyst for transfer hydrogenation.

➡ 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 can be found at: **www.xmas.ac.uk** and 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** 🐦

➡ 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. He is also the beamline Safety Representative.

● **Beamline Coordinator –** Laurence Bouchenoire, (bouchenoire@esrf.fr), looks after 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.

● **Postdoctoral Research Associate –** Sean McMitchell (sean.mcmitchell@esrf.fr) is associated with the Nanostrain project (www.piezoinstitute.com). He provides support for *in situ* interferometry and electrical measurements on the beamline and on the offline facilities.

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

● **Project Directors –** Chris Lucas (clucas@liv.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@liv.ac.uk) is the administrator at the University of Liverpool.

The Project Management Committee

The current membership of the committee is as follows:
- P. Hatton (chair), University of Durham
- S. Crook, EPSRC
- A. Boothroyd, University of Oxford
- R. Cernik, University of Manchester
- K. Edler, University of Bath
- B. Hickey, University of Leeds
- R. Johnson, University of Oxford
- S. Langridge, ISIS, Rutherford Appleton Laboratory
- C. Nicklin, Diamond Light Source
- W. Stirling, Institut Laue Langevin

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

➡ The Peer Review Panel

The current membership of the panel is as follows:
- R. Johnson (chair), University of Oxford
- E. Blackburn, University of Birmingham
- W. Briscoe, University of Bristol
- S. Corr, University of Glasgow
- C. Detlefs, ESRF
- Y. Gründer, University of Liverpool
- J. Quintanilla, University of Kent
- R. Walton, University of Warwick
- J. Webster, ISIS

In addition either Chris Lucas or Tom Hase attends the meetings in an advisory role.

➡ 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!

It is important that we acknowledge the support from EPSRC in any publications. 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:

"XMaS is a mid-range facility supported by EPSRC. We are grateful to all the beam line team staff for their 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 synchrotron 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 L. Bouchenoire (bouchenoire@esrf.fr). Technical specifications of the beamline and instrumentation available are described in the XMaS web page (www.xmas.ac.uk).

■ When preparing your application, please consider that 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 to 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. **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.** Please also remember to fill in the end of run survey form on completin of your experiment, which is available on the website.

■ 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 10st 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 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.

XMaS
the UK-CRG

is an EPSRC sponsored project

XMaS, ESRF – The European Synchrotron, CS 40220, 38043 Grenoble Cedex 9, France
Tel: +33 (0)4 76 88 25 80 – web page : www.xmas.ac.uk – email: bouchenoire@esrf.fr