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Diamond is one of the world’s leading synchrotrons, providing its industrial and academic user communities with access to state-of-the-art analytical tools.

The resulting knowledge has wide-ranging impacts - scientific, economic, cultural and societal. The many high-impact peer-review publications we deliver attest to our scientific excellence. Equally important is the breadth and depth of engagement with industry and the resulting translation into economic impact, evidenced by over 125 companies paying for proprietorial access and an increasing number of companies engaging through partnerships with the many university groups who access Diamond. As we look to the future, the key challenge ahead will be to secure the investments in the facility that will ensure our continuing international leadership position. The Diamond Board will continue to use its influence to ensure that we maintain and enhance our leading global reputation.

Professor Sir Adrian Smith
Chairman of the Board of Directors

The many high-impact peer-review publications we deliver attest to our scientific excellence.
marked a double anniversary for Diamond: our 15th anniversary as a company and 10 years of research and innovation. This was marked by the official visit of HRH the Princess Royal last February - a tremendous accolade for everyone involved with Diamond.

Our facility is currently completing its final beamlines, which will see us close Phase II construction in 2019. We now have 31 operational beamlines, which are delivering an increasing number of high impact publications. This review presents some of the highlights of this science, illustrating both new insights we are providing in fundamental science, and the positive impact for the economy and society at large in partnership with our user community.

With over 9,000 user visits, a machine up time of 98.2%, and exceptionally dedicated staff supporting every aspect of our activities, our offer to the science community is second to none. All of this underpins outputs that grow from year to year, most readily illustrated by the number of peer-reviewed publications, numbering 6,525 in 2017 with 471 of the output linked to the life sciences. This is the result of our creating an integrated offer for our structural biology community, which is unique in the world. We now have six microscopes dedicated to the life sciences running seven days a week each delivering 220 days of science per year. We are becoming a one-stop shop to understand the origins of diseases at a molecular or cellular level and to both discover and develop drugs to treat them.

The physical sciences are blooming too, from multiprobe and operando studies of catalysts to new emerging technologies for ICT such as multiferroics, where electrical and magnetic functionality are coupled, so changing one can switch the other. As you will read in our Materials and Magnetism section, researchers from across the globe have used our I06 beamline to visualise this phenomenon and as the bas to new multifunctional devices that work well at room temperature, are opening up new avenues for creating new electronic storage devices. Engaging with industry is also an essential part of our mission and the past year has seen a record income from proprietorial access. An increasingly important part of this is the new embedded facilities for electron microscopy for both life and physical sciences at EBC and ePSIC, respectively. Diamond also provides crucial facilities for metrology, illustrated recently by work performed by RMB Oxford to test the performance of their manufactured components.

As taxpayers essentially fund 86% of the facility, we have kept our commitment to engage with the public. We offer regular open days and work with the media to communicate and create greater awareness of the ground-breaking science achieved here. With 5,635 visitors in the past year alone, of which 3,321 were school students and members of the public, we are continually making sure we present strong and diverse role models across all disciplines. We want to inspire as many young people as possible by the work we do and persuade as many of them as possible to choose STEM subjects as the path to their future careers.

With over 9,000 user visits, a machine up time of 98.2%, and exceptionally dedicated staff supporting every aspect of our activities, our offer to the science community is second to none.
Macromolecular Crystallography Group
Dave Hall, Science Group Leader

Diamond provides a range of techniques for academic and industrial researchers studying the machines of life. As one of those techniques, Macromolecular Crystallography (MX) reveals the shape and arrangement of biological molecules at atomic resolution, knowledge of which provides a highly accurate insight into function. This can be combined with complementary information from many other techniques available at Diamond alongside lab-based investigations to reveal the broader picture of molecular interactions and their effects.

MX is a core activity at Diamond with several beamlines dedicated to the technique alongside the APEX Hub, Membrane Protein Laboratory and XChem Fragment screening facility for the extensive UK structural biology community as well as researchers in Europe and beyond. The staff of the MX group are recognised as innovative world leaders in MX, moving the goalsposts of what is feasible for ‘conventional’ MX as well as developing techniques and beamlines that transform MX to the next level, enabling new experiments and methodologies. The group takes a long-term approach to enabling new capabilities at its suite of beamlines to meet the current and future demands of an exciting community of scientists; in 2017 this was no different, as can be seen by the exciting developments here.

In 2017 the Long Wavelength MX beamline (I23) (dedicated to solving the crystallographic phase problem directly from native protein) entered an exciting phase in its development, with a concerted push to facilitate user access alongside groundbreaking experiments with invited user groups. General user access to the technical tour of force was initiated in 2017 by its first call for users via the peer review proposal system for experiments in 2018 with great interest shown by the user community. Ongoing developments will continue on I23 to explore and exploit its potential to the full — we are entering a whole new world of what is possible with in-vacuum MX and the samples and technology that enable this.

Serial Synchrotron Crystallography (SSX) is another emerging method, in part, by the sample requirements imposed by X-ray Free Electron Lasers (XFELs). Serial techniques can also be exploited at synchrotrons, especially at microfocus beamlines, opening up many new opportunities. A number of approaches including fixed targets and extruders have been tried and tested at Diamond’s Microfocus MX beamline (I24) and are available for general users. Expertise at I24 is centred on Fixed Target Serial Synchrotron Crystallography (FT-SSX). FT-SSX is attractive as it potentially offers high hit-rates coupled with modest sample consumption. Furthermore, the same approach can be used almost without modification at both synchrotrons and XFELs.

Our fixed target approach makes use of silicon nitride ‘chips’ with the current generation of chip capable of holding more than 25,000 crystals. Chips are mounted on a high-speed, high-precision x-y stage mounted at the sample position (Fig. 1). This setup allows data collection from all 25,000 positions on a chip in less than 10 minutes.

2017 has seen the final touches to the capabilities of the dedicated in situ VMX beamline being commissioned and new workflows developed. The beamline is now at a state where regular user operation and further hardware/software refinement is continuing in parallel. Input from initial users has been invaluable in progressing the beamline development, and indeed the demand for acting as beta testers from users has illustrated the keen interest amongst the MX community for the new capabilities that the beamline now provides. Alongside the beamline development, the VMX team has also brought facilities together in a new central crystallisation laboratory located at the Research Complex (RCaH) next to Diamond. This facility is now open to users and can be used to prepare crystallisation experiments for the VMX beamline — as well as for the Membrane Protein Laboratory and the XChem facility. Furthermore, the beamline team is working with the Diamond-based XFEL Hub to develop serial crystallography functionality which will also become part of the beamlines future offering to the MX community.

The last phase III MX beamline, VMX, is progressing well. This beamline is designed to address the challenges of data collection from micron and sub-micron sized samples. With commissioning of the VMX optics batches essentially complete the end-station is now being assembled ready for commissioning and first experiments. First light into the experimental end-station was seen in early March 2018 when work began on commissioning the microfocus optics, Offline assembly and testing of the sample environment is underway for incorporation into the end-station in April/May ready for first user experiments.

Our more conventional MX beamlines also continue to evolve to provide new functionality as well as increased performance. Through 2017 significant changes were made to the sample positioning systems on beamlines I03 and I04. Both are now equipped with a high precision, fast Smartgon multi-axis goniometer (Fig. 2) coupled to high capacity BA&T sample robots. The goniometers enable optimised data collection methods on these high throughput beamlines and have brought high speed, high quality data collection, as developed for FT-SSX on I24, which enables the location of the smallest samples, best regions of samples and in automatic crystal X-ray centering methods. This latter use is part of a set of upgrades to all the MX cryogenic sample beamlines to bring automatic, open data collection to the user programme allowing expert systems to deliver the best data quality. The new goniometry set-up also allows I03 to switch to a fast, large format goniometer for ex-situ crystallisation plates for pathogenic samples or cornea experiments (Fig. 3). Standard I03 in-situ work is available on VMX and I24.

Finally, fragment screening at the XChem facility attached to beamline I04-1 is now fully integrated into Diamond’s user programme. Annually it hosts well over 30 screening experiments from academia and industry. In 2017, the programme contributed 35,000 of the more than 50,000 crystals shot at the beamline, but using less than one third of the total beamtime, illustrating the efficiency of the automated queue model. With the programme consistently oversubscribed, and demand from industry growing, the facility is expanding its capacity: a dedicated user support team is being assembled, with extra capacity and an increase in dedicated lab space. Additional beamtime has been agreed, given or provided for in the allocation period for 2018.

The progress made in 2017 for these facilities and their user programmes is underpinned by the dedication and expertise of all staff in the MX group working alongside support staff from across Diamond as well as collaborations built across the world. The same staff engage in outreach, teaching and training for users, students and the public to build a greater understanding of the capabilities and science of MX in the broader setting of integrated structural biology.
Endoglin (ENG)/CD105 is a mammalian glycoprotein that is found in the membranes of cells that line blood vessels. It is essential for healthy heart development and blood vessel growth, but conversely it is also involved in preeclampsia and can help tumours establish their blood supply. Additionally, ENG gene mutations cause hereditary hemorrhagic telangiectasia type 1 (HHT1), a genetic disorder characterised by complex vascular malformations that affect 1 in 10,000 individuals. Although ENG plays a crucial role in the vascular system and its inhibition can slow tumour proliferation, no high resolution structural data exist to show how it is organised and how it interacts with its binding partner, bone morphogenetic protein 9 (BMP9).

To gain the much needed structural insights on this protein, several hundred crystals were grown and screened for their diffraction properties. Just one yielded a usable dataset at 4.4 Å resolution using the Macromolecular Crystallography (MX) beamline (I02). Together with other structures, this showed that the N-terminal orphan region of ENG, which is responsible for its ligand-binding activity, consisted of two duplicated domains. Only the first of these domains recognised BMP9 through a hydrophobic interface. At the other end of the protein, the C-terminal region functioned as a scaffold that optimally positioned the binding site. Overall, ENG cradled BMP9 in such a way to effectively display it to other proteins involved in signalling pathways for blood vessel maintenance.

Endoglin (ENG)/CD105 is an essential endothelial cell co-receptor of the transforming growth factor (TGF)-β superfamily. This consists of extracellular type I and II serine/threonine kinase receptors that, upon interaction with structurally related ligands such as TGF-β and bone morphogenetic proteins (BMPs), regulate fundamental cellular processes by triggering a signal transduction cascade through cytoplasmic Smad proteins. Mutations of the human ENG gene are linked to hereditary hemorrhagic telangiectasia type 1 (HHT1), an autosomal dominant vascular disorder also known as Osler–Weber–Rendu syndrome, moreover, ENG has been implicated in preeclampsia and as highlighted by the observation that anti-ENG monoclonals can inhibit tumour angiogenesis – represents a promising target for cancer therapy. Therefore, structural knowledge of human ENG and its complexes constitutes a valuable framework to both understand the molecular basis of BMP-dependent signalling and shed light on its clinical implications.

ENG is a ~160 kDa homo dimeric type I transmembrane protein that consists of an N-terminal orphan region (OR) and a C-terminal zona pellica ria module (ZP). Extensive attempts to crystallise the full-length ectodomain of ENG failed likely because the flexibility of the linker between OR and ZP interferes with crystal packing. Therefore, ENG was divided into two fragments that spanned the ligand-binding OR and the homodimerisation-mediated ZP; respectively. These regions were expressed and crystallised separately using a novel mammalian fusion protein methodology. Furthermore, OR was crystallised in complex with BMP9, a physiological high-affinity ligand for ENG in endothelial cells.

The structure of OR reveals a monomer consisting of two β-helical-like domains (OR1/ OR2) with a common novel fold that also includes an α-helix (Fig. 1a and b). Structure-based sequence alignments show that OR2 is actually inserted after the second β-stand of OR1, suggesting that the OR fold originated by gene duplication and circular permutation (Fig. 1b-c).

To gain mechanistic insights into how ENG modulates BMP signalling by interacting with selected ligands, the structure of ENG OR complex with BMP9 was determined. Despite their perfect shape and high reproducibility, the OR-BMP9 crystals diffracted X-rays very poorly, so that efficient screening of hundreds of specimens using the ACTOR sample mounting robot at beamline I02 was essential to obtain a single usable dataset at 4.4 Å resolution. The structure of the complex reveals that the outer tip of the BMP9 β-sheets is recognised by an immunoglobulin grove on the OR1 domain of ENG (Fig. 1d). Notably, this binding region involves conserved ENG amino acids Ser278 and Phe382, mutations of which are found in patients suffering from HHT1; on the other hand, the structural data suggests that many other pathological mutations act indirectly, by interfering with proper folding of ENG. Remar kably, the BMP9-binding region of OR1 overlaps with the epitope of TRIC5/SIGK (Fig. 1d), a monoclonal antibody against ENG that is being clinically investigated for the treatment of solid tumours together with vascular endothelial growth factor inhibitors.

How does co-receptor ENG present the BMP9 ligand to other members of the signalling pathway, such as type I receptor, activated receptor-like kinase 1 (ALK1)? As mentioned above, the C-terminal half of the ENG ectodomain corresponds to a ZP module. This is a bipartite element that consists of a ZP-N and ZP-C domain and mediates protein-protein interactions in many other extracellular matrix components with unrelated biological functions. While it contains characteristic ZP-N domain features such as an immunoglobulin-like fold and two conserved disulphides, ENG-ZP-N is unique in that it includes an additional disulphide bridging two α-helices and opposes to the solvent a loop carrying an RGD motif associated with cell surface adhesion (Fig. 2). Interestingly, the immunoglobulin-like ZP-C domain is quite different from other Z-Ps. This is because the absence of an extended cysteine-carrying loop results in a minimal fold that is stabilised by one disulphide rather than the conventional three or four, leaving a single cysteine residue unpaired.

ENG lacks a conserved ZP-N tyrosine that is implicated in BMP9-mediated phosphorylation, as well as a consensus cleavage site in ZP-C whose processing is also associated with extracellular assembly, together with a short intradomain linker and an occluded ZP-N homodimerisation interface. These features explain why ENG is a non-polymerising ZP-module containing protein. Consistent with mutagenesis studies, the structure shows that coherent exposure of unpaired Cys516 within a membrane-proximal ZP-C loop allows it to covalently cross-link two molecules of ENG by forming an intermolecular disulphide with another copy of itself. Furthermore, it suggests that Cys282 - an additional cysteine not present in the ENG-ZP expression construct - would be located in the vicinity of Cys516, where it could form a second intermolecular disulphide. These observations result in a model wherein two disulphide-bonded copies of the ENG-ZP module would position the respective OR domains so that, together, they can embrace a BMP9 homodimer (Fig. 2).

The abundance of ENG, together with its nanomolar affinity for BMP9 and amyloid-folding antibody-like structure, allows the co-receptor to efficiently capture its ligand and retain it on the surface of endothelial cells. However, in order for the signalling cascade to initiate, ENG must deliver its cargo to the type I and type II receptors. Notably, the ENG-BMP9 interface is compatible with BMP9 recognition by ALK1, resulting in a model of the ternary (ENG-BMP9-ALK1) complex (Fig. 3). However, the same interface overlaps with the BMP9 binding site for type II receptor activated receptor type-2 (ALK2/RRF5), suggesting that signalling requires handing over of the ALK1-BMP9 complex from ENG to ALK2 (or alternatively bone morphogenetic protein type-1 receptor (BMPR1B), another type II receptor). Collectively, these observations bring detailed insights into the mechanism of BMP signalling and inform ongoing efforts to therapeutically target this essential cellular pathway.

**References:**
Gram-negative bacteria that are extensively resistant to multiple antibiotics are an ever-increasing global threat. Colistin is an antibiotic used as the last line of defence against highly resistant Gram-negative bacteria. However, in recent years bacteria have emerged with resistance to this crucial antibiotic.

Resistance to colistin is determined by an enzyme called ‘mobilised colistin resistance’ (MCR-1), which has rapidly disseminated worldwide and is found in clinical strains of E. coli and Klebsiella pneumoniae. MCR-1 modifies the outer membrane of Gram-negative bacteria, preventing it from interacting with colistin, but despite its huge importance, the mechanism by which this happens remains to be established.

To shed some light on the workings of MCR-1, the crystal structure was solved using the Macromolecular Crystallography (MX) beamlines 102, 103 and 104-1. MCR-1 was found to be a zinc metalloprotein, with an alkaline phosphatase fold containing three disulphide bonds. These high-resolution data provided a detailed view of the active site, identifying areas of the enzyme that were critical for function. Moreover, these results allowed a computational prediction of the mechanism of action, and that a single zinc ion may be sufficient for MCR-1 to function. Knowing these important details could enable the rational development of novel antimicrobials to effectively combat colistin-resistant bacteria in the future.

Bacterial diseases, particularly those caused by Gram-negative bacteria (GNB), are a serious and increasing clinical threat worldwide. Treatment of GNB infections is complicated by the intrinsic resistance to many antibiotic classes and the rapid acquisition of resistance to additional agents. There are now some bacteria for which there are few treatment options remaining, with only a handful of antibiotics that are considered reliable for therapy. The polymyxin colistin is one such key ‘last-resort’ antibiotic, used to treat infections by multidrug-resistant GNB pathogens. Colistin is a positively-charged polypeptide that binds to and disrupts the outer membrane of GNB by interacting with the negatively-charged lipid A headgroup. Until recently, resistance to colistin was considered rare, limited to changes in expression of chromosomal proteins that collectively modify the lipopolysaccharide, the component of GNB outer membranes. However, in November 2015 our team described colistin resistance mediated by MCR-1, a plasmid-encoded phosphoethanolamine (PEA) transferase.

Since this initial report, it has now been reported in over 40 countries, and is found in numerous bacterial strains, mainly E. coli and Klebsiella pneumoniae. In addition, a number of homologues have been identified, including MCR-2. MCR-1 has now been reported in bacteria producing other resistance determinants, such as carbapenemases, which can result in essentially untreatable bacterial infections. However, expression of MCR-1 seems to enhance virulence and result in decreased growth rate, cell elongation, and attenuation of virulence and resulting in decreased growth rate, cell elongation, and attenuation of virulence.

As colistin continues to spread, and more homologues are identified and disseminated, it is more crucial than ever to understand MCR-1 mechanism. These data, alongside our recently determined 1.12 Å resolution structure of MCR-2 from I04, will provide a starting point for more extensive investigations of MCR-1 mechanisms that can in turn be used for structure-based design of inhibitors for use in potential colistin-based combination therapies.

References:


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How does an inspector call: structures of UGGT, the eukaryotic glycoprotein quality control checkpoint.


Publication keywords: UGGT; Endoplasmic reticulum; Glycoprotein folding; UDP-glucose:glycoprotein glucosyltransferase; Eukaryotic secretion.

In all cells derived from animals, plants, fungi and protista a single protein called UGGT acts as a quality control checkpoint that inspects secreted glycoproteins. UGGT has fascinated scientists for many years as it has the capacity to check the quality of a huge array of glycoproteins, which come in many different shapes and sizes and folds. The way in which it screens such a diverse group of proteins is poorly understood, and no structures exist of UGGT. Furthermore, UGGT is implicated in human diseases as it can ensure that glycoproteins from viruses (such as influenza, hepatitis C, HIV and Zika) are folded correctly. By fully characterising UGGT, it is hoped that an inhibitor could be developed that may act as broad-spectrum anti-viral drug.

Using the Macromolecular Crystallography (MIX) beamlines (I02, I03, I04 and I04-1) and cryo-electron microscopy (cryo-EM) at the Electron Bio-Imaging Centre (eBIC), the structure of UGGT was solved. Four distinct crystal structures of a full-length UGGT revealed a novel seven-domain fold, with four thioredoxin-like domains arranged in a long arc, which terminates in two β-sandwich domains that tightly clamp the catalytic domain. Together, the cryo-EM map, the crystal structures and the biochemical data suggested that UGGT is highly flexible, a feature which enables it to check such a wide variety of glycoproteins.

A wonderfully efficient protein folding machinery in the Endoplasmic Reticulum (ER) of eukaryotic cells ensures that only correctly folded glycoproteins can exit the ER and proceed to the Golgi, and from the Golgi continue along the secretory pathway towards their individual cellular or extracellular destinations.

The stringency of ER Quality Control (ERQC) – while of great advantage to healthy cells – can lead to severe disease in patients carrying certain mutant glycoproteins: the latter are detected as incorrectly folded, and either retained in the ER or degraded by ER-associated degradation (ERAD). The enigma of the otherwise excellent ERQC machinery bears particularly unfortunate consequences when the mutation affecting the glycoprotein is mild, i.e. it impairs but does not abrogate its function ("responsive mutant"). In these cases, ERQC blocks mutated competent glycoprotein secretion – and disease ensues.

At the heart of ERQC is the glycoprotein folding quality control checkpoint, the enzyme UDP-glucose:glycoprotein glucosyltransferase (aka UGGT). The enzyme selectively re-glucosylates misfolded glycoproteins, promotes their association with ER lectins, and associated chaperones and prevents premature secretion from the ER. UGGT has long resisted structural determination and sequence-based domain boundary predictions. It is currently still a big mystery how the many UGGT substrate glycoproteins, each of which has a different size, shape and fold, can all be surveyed by UGGT alone.

Before our study, no full-length UGGT structures were known, nor to our knowledge UGGT inhibitors known (other than its product UDP). The protein sequence of UGGT does not resemble any other in the eukaryotic genome, so any structural details about the enzyme could shed light on UGGT function and inform ongoing efforts to develop UGGT inhibitors. We set out to characterise the UGGT structure both structurally by X-ray crystallography, SAXS, cryo-EM and biochemically.

Our crystal structures of a full-length UGGT revealed a novel seven-domain fold, with four thioredoxin-like (TRXL) domains arranged in a long arc, which terminates in two β-sandwich domains tightly clamping the catalytic domain. The presence of TRXL domains in the N-terminal part of UGGT brings to mind bacterial periplasmic disulphide isomerases and eukaryotic ER luminal chaperones binding misfolded proteins and/or peptides.

Together with the 15 Å cryo-EM map, the same UGGT crystal structures reveal pronounced inter-domain flexibility (Fig 1). Structure-based double cysteine point mutants that engineer extra inter-domain disulphide bridges rigidify the UGGT structure and exhibit impaired activity. Thus, UGGT enzymatic activity depends on inter-domain conformational mobility, suggesting UGGT’s intrinsic flexibility as a key requirement for the enzyme to be able to recognise and react with its many different misfolded substrates, flagging them for retention. By changing the relative orientations between its four TRXL domains, the enzyme could adapt its conformation to fit the particular glycoprotein it has bound and needs to re-glucosylate.

Structures of complexes of UGGT with substrate-misfolded glycoproteins would help verify these ideas, and we have started work towards biochemical purification and structural elucidation of such UGGT-misfolded glycoprotein complexes. In the meantime, in order to illustrate and communicate the novel hypothesis that the enzyme’s flexibility may be necessary to enable substrate promiscuity, we have generated a 10–protein molecular representation of UGGT, and assembled three distinct UGGT generic glycoprotein models, each of different size and shape, and bearing one jelly-baby ‘glycan’. Figures 2a–c show the 3D-printer UGGT model in three arbitrary conformations, with the TRXL domains (coloured purple, blue, cyan and green) grabbing hold of the LEGO glycoproteins. The latter are oriented in such a way that the jelly-baby ‘glycan’ is presented to the UGGT catalytic glucosyltransferase domain, coloured in red.

References:

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Structure of the surface layer surrounding Caulobacter crescentus bacteria


Publication keywords: Cryo-EM; X-ray crystallography; Tomography; Sub-tomogram averaging; Bacteria; S-layer

Many types of single-celled microorganisms such as bacteria are covered with a protective outer layer of proteins known as the S-layer. The S-layer defends the cell from the external environment and acts as a supportive scaffold. In fact for some species, the S-layer is the only component of the cell wall so its strong structure is paramount for protection.

The S-layer proteins are repeating units that fit together like chain mail to form the essential armour for the cells. Although these proteins have been previously imaged, their high resolution details have so far eluded scientists.

Two of the Macromolecular Crystallography beamlines (I03 and I04) were used to solve the crystal structure of the S-layer protein, RsaA, in a bacterium called Caulobacter crescentus. The X-ray structure was then combined with an electron cryotomography (cryo-ET) map garnered from living cells to determine the exact pattern of S-layer proteins on the surface of the bacterium.

The innovative combination of crystallography and cryo-ET in this study showed how the RsaA proteins coated and protected the bacteria, and also highlighted the small pores within the arrangement. This study demonstrates the merit of combining two techniques to explore a structure in living cells.

S-layer proteins (SLPs) are a diverse class of molecules found on many prokaryotes including Gram-positive and Gram-negative bacteria and the majority of archaea.1 SLPs assemble to form planar sheets called S-layers on the surface of cells, where they are anchored, usually through non-covalent interactions with other surface molecules such as lipopolysaccharide.2 The propensity of SLPs to form sheets in solution and their absence from early model organisms such as Escherichia coli has hampered high-resolution structural biological analysis of this abundant and important class of molecules.3 We turn to Caulobacter crescentus, a well-studied Gram-negative alphaproteobacterium with a characteristic architecture. The cell is completely enclosed by a S-layer that is continuous with the cell wall and the stalk (Fig. 1a). Cryo-ET imaging showed that the density corresponding to the S-layer of C. crescentus CB15 is almost perfectly hexameric (Fig 1a, inset) with a ~220Å repeat distance. Two discrete densities were observed in the S-layer, the outer highly connected S-layer lattice and the discrete inner domains located around the centres of the hexamers (Fig. 1b–c).

We purified the sole component of the C. crescentus CB15 S-layer, the ~98 kDa RsaA protein (Fig. 2a) directly from cells using a previously described S-layer extraction procedure that employs low pH. It was confirmed that the purified protein retained its characteristic polymerisation function by reconstituting S-layers in solution at physiological pH (Fig. 2b). Using the purified material, the crystals of RsaA with Ca$^{2+}$ were obtained and an extensive trimeric contact is also observed in the lattice. Ca$^{2+}$-ions are located near both the dimeric and trimeric interfaces in the lattice, possibly increasing the Ca$^{2+}$-dependency of S-layer assembly.

The structures explain the modular architecture and function of RsaA, the permeability barrier and serve function created by the S-layer and the strong Ca$^{2+}$-dependency of RsaA polymerisation since Ca$^{2+}$-ions are tightly co-ordinated within the RsaA fold or bound near the hexameric, trimeric, and dimeric interfaces.

Guided by the S-layer structure reported above, C. crescentus cells carrying mutated versions of the rsaA gene may be used for surface display of molecules for nanotechnological or antigen display applications and it will be possible to investigate S-layer biogenesis and its morphological changes during the cell’s life cycle at the molecular and atomic levels.
Bacteria utilise ATP-binding cassette (ABC) transporters to import nutrients and detoxify themselves. These transporters have been shown to exist in wide open conformations that permit the access of many substrates in the binding pocket. They alternate between an inward-open to an outward-open conformation much like a gate. One such ABC transporter, McjD, was previously characterised and was found to adopt a novel conformation that was distinct from others of its class.

In this study, McjD was trapped in two different conformations to provide further insights into its mechanism of action. Two of Diamond’s Macromolecular Crystallography (MX) beamlines, I23 and I04-1, were used to solve the structure of it both in the absence of a substrate or ATP and with just ADP-β-S, where (23) is the Long Wavelength MX beamline. Biochemical and biophysical measurements were also collected to complete the picture.

The structures showed that the transporter remained in an occluded conformation in the absence or presence of ATP/ADP. Additionally, the biochemical data showed that the transporter opened transiently to allow the release of its substrates from the binding pocket. This is the first time such a mechanism has been observed for ABC transporters and it is thought to be the root of its substrate specificity. By understanding how McjD works, it might be possible to understand how other ABC transporters acquire drug-resistance in bacteria.

**Figure 1:** Crystal structures of McjD in distinct conformations. McjD is shown in cartoon and nucleotides in red sticks. Each half transporter is colored in blue and green. Top panel is a side view along the plane of the membrane and bottom panel shows the NBDs for each state. The membrane is depicted in grey. (A) AMPPNP bounds outward-occluded conformation. (B) High-energy transition outward-occluded conformation (ADP-VO$_4$) and (C) apo inward-occluded.

Structural insights into the mechanism of bacterial ABC transporters

**Bacteria**

**Figure 2:** Electron density maps. (A) Clear |Fo|-|Fc| electron density map (green mesh contoured at 1.5 s) of McjD with anomalous difference maps used to place the VO$_4^{4-}$ ions. (B) Anomalous difference electron density map (pink mesh) around the vanadate, with data collected close to the vanadium K-edge, 2.26 Å. The map is contoured at 3 s. ADV-VO$_4$ and ADV-VO$_4$$_2$ are shown in green. In the absence of vanadate, the ADV-VO$_4$ site is occupied by a sulfate ion. The ADV-VO$_4$$_2$ site is occupied by a chloride ion. The ADV-VO$_4$$_2$ site is occupied by a chloride ion. The ADV-VO$_4$$_2$ site is occupied by a chloride ion.

**Figure 3:** Mechanism of antibacterial peptide export by McjD. ADV-VO$_4$$_2$ is shown in red and blue cartoons. The membrane is depicted in grey box. The nucleotides are shown as yellow spheres and Mg$^{2+}$ is shown as orange sphere. The vanadate and Mg$^{2+}$ are shown as dark grey.

**References:**


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Sweet Success: Crystal structure of the full-length GLP-1 receptor bound to a peptide agonist


Publication keywords: X-ray crystallography; G protein-coupled receptors

GLP-1 is an important hormone released from the gastrointestinal tract in response to food intake. Through its interaction with its binding partner, the glucagon-like peptide 1 receptor (GLP1R), GLP-1 promotes the release of insulin from the pancreas to regulate blood sugar. As a consequence, the stimulation of GLP1R is considered an attractive means of treating type 2 diabetes.

GLP-1 peptide analogues are effective in treating type 2 diabetes, but despite there being several medically approved variants on the market, they are expensive to produce and are administered by injection. Alternatives, such as small molecules or smaller peptides that could be taken orally would significantly simplify the treatment regimen for people with type 2 diabetes.

To design such small molecules, a detailed map of the interactions between GLP-1 and its receptor was needed. To obtain that information, the crystal structure of a truncated stabilised GLP-1 analogue bound to the receptor was solved using the Macromolecular Crystallography (MX) Microfocus beamline (I24). The structure revealed that the GLP-1 analogue adopted a very specific conformation and reached deep into the receptor’s binding pocket. It made numerous interactions with the receptor, the details of which enabled the design of a new GLP-1 analogue that were active in a mouse model of disease. These new smaller analogues could be the precursors of future diabetes treatments.

6 protein-coupled receptors (GPCRs) are cell surface transmembrane G protein-coupled receptors that transmit extracellular signals into intracellular signalling cascades. They are delicate molecular machines adapting multiple conformations states in response to specific hormonal and metabolic stimuli. One subfamily of GPCRs is the multi-domain class B secretin-like family, members of which are characterised by an extracellular domain (ECD) that binds peptide hormones juxtaposed to a transmembrane domain (TMD), and are validated drug targets for numerous diseases including osteoporosis, depression and anxiety and type 2 diabetes.

GPCR’s inherent flexibility, which is integral to their function, is the cause of their extreme instability when they are extracted from their native cell membrane environment. To obtain an X-ray structure of GLP1R the receptor had to be first thermolabileised using a radio-labelled truncated and modified form of the GLP-1 agonist peptide. The final thermolabileised (StaR) GLP1R contains eleven thermostabilising amino-acid mutations, which facilitated expression and purification of the receptor and trapped it in an active conformation. Peptide 5 was designed in-house and despite being just a third of the size of native GLP1R, activates the receptor with comparable efficiency.

ECL2 is tethered to TM3 through a disulphide bond. Additional electron density for an α-helix was observed in the intra-helical pocket of GLP1R and Peptide 5 was modelled into it with its N-terminus buried in the cavity of GLP1R. The GLP-1 agonist peptide adopts a specific conformation and reaches deep into the TMD and its C-terminus directed towards the ECD (Fig. 1a). The TMD exhibits the canonical seven transmembrane helices (TM1-TM7) in a similar conformation with the ECD extending away from the TMD (Fig. 1a). The TMD contains the seven transmembrane helices (TM1-TM7) in a similar conformation with the ECD extending away from the TMD (Fig. 1a). The TMD and ECD are validated drug targets for numerous diseases including osteoporosis, depression and anxiety and type 2 diabetes.

The structure reveals which residues in GLP1R are key in Peptide 5 binding and agrees with a wealth of previously published mutagenesis data characterising the binding of GLP-1 to GLP1R. The interaction surface between Peptide 5 and GLP1R is extensive with the N-terminal natural and unnatural residues of Peptide 5 interacting mainly with residues in TMs 1, 2, 3 and 7 and the C-terminal structural residues lying in hydrophobic pockets formed between TM1 and TM2 and ECL2 and the ECD (Fig. 2). Despite being shorter than GLP-1 and interacting less extensively with the ECD, Peptide 5 still binds with very high affinity to GLP1R. The reason for retaining such high binding affinity is likely due to the hydrophobic interactions involving the C-terminus of the peptide. These Peptide 5-specific interactions are also responsible for orienting the ECD differently when bound to GLP-1 (Fig. 2). The interaction between Peptide 5 and GLP1R is extensive with the N-terminal natural and unnatural residues of Peptide 5 interacting mainly with residues in TMs 1, 2, 3 and 7 and the C-terminal structural residues lying in hydrophobic pockets formed between TM1 and TM2 and ECL2 and the ECD (Fig. 2). Despite being shorter than GLP-1 and interacting less extensively with the ECD, Peptide 5 still binds with very high affinity to GLP1R. The reason for retaining such high binding affinity is likely due to the hydrophobic interactions involving the C-terminus of the peptide. These Peptide 5-specific interactions are also responsible for orienting the ECD differently when bound to GLP-1 (Fig. 2).

Comparison of the Peptide 5-bound GLP1R structure to that of another class B GPCR, GCGR, bound to an agonist molecule (Fig. 1b) reveals changes in the positions of the extracellular portions of TM2, TM3, TM7 and TM9 and the extent of TM8 which swings away from the central axis of the TMD. Similar changes have been observed when comparing agonist- (active) and antagonist- (inactive) bound structures of class A GPCRs suggesting that the Peptide 5-bound GLP1R structure is more akin to an active conformation. This observation also indicates a common activation mechanism across class A and B GPCRs where specific and concerted movements of TMs lead to a substantial repositioning of TMs and the consequent opening up of the intra-cellular surface of the receptor permitting docking of the G-protein transducer.

Diabetes and obesity are serious public health concerns which put great pressure on healthcare systems across the globe. Developing effective and affordable drugs to treat these conditions remains a pressing need. With the GLP1R structure in hand, the peremnent historical lack of success in developing small molecules that adequately target and activate GLP1R can now be explained by the extent and complexity of interactions between hormone and receptor (Fig. 2). Guided by the structure, we have rationally designed a series of truncated peptide agonists (Fig. 3) with improved pharmacokinetic properties and important improvements in activity, as demonstrated through in vivo diabetic mouse models. Reducing the size of these peptides drop the manufacturing costs, making them more affordable and easier to administer. Increasing their half-life and bioavailability prolongs their activity and consequently reduces the frequency with which they need to be delivered. To conclude, this landmark structure not only added the development of new peptide agonists against GLP1R but also considerably increased our understanding of the general mechanism of activation of the class B secretin group of GPCRs which includes many other important drug targets.

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Membrane Protein Laboratory (MPL)

Andrew Quigley, MPL Facilities Coordinator

The Membrane Protein Laboratory (MPL) is a well-established, state-of-the-art facility that provides a pipeline from protein production to high throughput protein crystallisation. The MPL was the world’s first membrane protein laboratory to be based inside a synchrotron, and its close proximity to the beamlines allows MPL staff and users to collaborate closely with beamline staff, creating a highly productive working environment.

The MPL was established to assist researchers investigating proteins that are embedded in the membranes that coat thousands of cells in the body. These proteins make up around 30% of the human genome. We have over 7,000 membrane proteins in our bodies and many of these are important drug targets; over 50% of currently approved drugs target membrane proteins.

Crystallising membrane proteins is an essential, and extremely difficult step towards solving their structure. Having a dedicated laboratory with cutting edge equipment, close to the experimental stations where membrane protein structures can be solved, greatly enhances scientists’ ability to successfully crystallise membrane proteins and further our understanding of these important drug targets.

The MPL is open to user applications from anywhere in the world, and proteins crystallised here have been used in experiments in other facilities. A forthcoming paper will describe the successful Xfel data collection at SACLA-Japan from the MPL team, Diamond (I24 and XFEL team) and Oxford collaborators (Department of Biochemistry).

Recently published work details a collaboration between Brazilian scientists and the MPL, which investigated the role that two mitochondrial pyruvate carrier subunits, MPC1 and MPC2, play in the active transport of glycolytic pyruvate across the inner mitochondrial membrane. Diseases such as cancer, Alzheimer’s disease, and diabetes are known to be pyruvate-related, and a greater understanding of these membrane proteins will aid in the development of small-molecule- and antibody-based therapeutics that specifically target MPC1 or MPC2 in pyruvate-related diseases.

Over the last decade, data collection and data processing landscape in X-ray crystallography for biomolecules has changed significantly. Improvements include faster readouts from silicon pixel detectors, ubiquitous presence of robotic arms and related cryogenics, new types of set-up for single and multiple crystal mounting, fast data transfer and larger capacity for data storage, new processing software and continued introduction and update of process pipelines. One consequence of these changes is the ability to create complete datasets from several crystals, rather than a single crystal.

Also in collaboration with the MPL research published in the journal Crystallography and Crystal Cathedral, discussions how the use of multiple crystals has become an accepted methodology in structural biology, with synergies including technology, hardware and software to make the technique routinely accessible to users. Diamond’s automated VMXi beamline is a prime example; handling large and multiple crystal mounting, fast data transfer and larger capacity for data storage, new processing software and continued introduction and update of process pipelines. One consequence of these changes is the ability to create complete datasets from several crystals, rather than a single crystal.

Research conducted elsewhere has proposed that MPC2 and MPC2 function together via the formation of an oligomeric structure. However, in this new research works provided an unprecedented in vitro demonstration that human MPC2 functions independently of MPC1 to induce pyruvate transport. They used synchronisation radiolysis circular dichroism (SRCD) analysis, on beamline I23, to investigate the secondary structure composition of human MPC2, and to gauge the conformational changes due to binding of substrate and inhibitor. The significant changes in the secondary structure content of MPC2 that they detected support the interaction between the protein and ligands.

These results are the first successful, large-scale, recombinant production and functional reconstitution of the family of soluble carriers in an artificial lipid bilayer. It opens up a discussion concerning pyruvate import regulation by at least two different molecular entities in human mitochondria: heterotypic MPC1:MP2 and homotypic MPC2:MP2, and has immediate implications for the development of small-molecule- and antibody-based therapeutics that specifically target MPC2 in pyruvate-related diseases.

The XFEL Hub at Diamond

Allen Orville, XFEL Hub Group Leader

The XFEL Hub at Diamond is funded by the Wellcome Trust and the Biotechnology and Biological Research council (BBSRC) to provide expertise and support to the UK community engaged in XFEL related research in the life sciences. This includes all aspects of various XFEL experiments from conception to beamtime proposals through sample preparations and testing, to XFEL data collection, analysis and publication.

Over the past year, members of the XFEL Hub have visited and/or conducted serial femtosecond crystallography (SFX) and time-resolved SFX (tr-SFX) experiments at all five XFEL facilities: i) the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory in Menlo Park, California, USA; ii) Spring-8 Anogram Compact free electrons Laser (SACLA) in Hyogo, Japan; iii) the European XFEL in Schenefeld Germany; iv) The Pohang Accelerator Laboratory XFEL (PAL-XFEL) in Pohang Korea; and v) The Swiss XFEL at the Paul Scherrer Institute in Wilisau Switzerland. Six out of eight, and eight out of 11 experiments conducted at either LCLS, SACLA or the European XFEL included UK research groups in 2017 and the first half of 2018, respectively. The XFEL Hub also provided travel awards to several UK research groups that were granted XFEL beamtime at these three facilities.

The XFEL Hub, through its membership in the SFX Consortium, is working to supply an on-demand droplet sample injector for the downstream interaction region of the SFX/SXIF1 instrument. One of our goals is to support SFX and tr-SFX by delivering ~30 picolitre droplets of microcrystal slurries directly into and synchronized with the XFEL beam pulses. At the end of this year or early next year, we anticipate testing sample delivery at 10 kHz within each pulse train to yield a 60 Hz overall data collection rate. Longer-term goals include 100 kHz sample delivery within a pulse train, which will produce SFX data at 600 Hz overall. Although MHz sample delivery rates are likely to require fast jets, an advantage of on-demand acoustic methods is that they are more efficient with samples since none is wasted in the gap between the X-ray trains.

The XFEL Hub continues methodological R&D to support on-demand acoustic sample delivery methods for SFX and tr-SFX. Three complement fixed target strategies developed by the UK and I23 teams at Diamond. We have also formed a new Beamtime Access Group (BAG) at Diamond titled, Dynamic Structural Biology at Diamond & XFELs, which emphasises serial data collection strategies at ambient temperature and pressure using slames of microcrystals. The new BAG consists of Diamond’s I23 beamline directors, IC and VR, and other members.

In autumn 2017, Dr Allen M. Orville, group leader of the XFEL Hub, participated in the first, and directed the third, set of user-assisted SFX commissioning experiments at the SFX/SXIF1 instrument at the European XFEL. Following the wishes of the facility, both peer-reviewed proposals were open to the whole community, highly collaborative, and attracted more than 100 interested scientists from around the world. The distribution lists for these early experiments span 1/4 time zones.

The European XFEL delivers X-ray pulses in a discontinuous train structure that repeats at 10 Hz and with a ‘dark period’ or ‘idle time’ between each train. For example, a 600 ms pulse train is followed by a 99.4 ms gap. The maximum intra-train repetition rate is 4.5 MHz with 27 MHz X-ray pulses per train, but it can also operate slower by integer divisions. During the user-assisted commissioning studies, the facility delivered 60 ms pulse trains at 10 Hz with an intra-train frequency of 1.1 MHz.

These characteristics require sample delivery methods that replenish samples very quickly and clear the debris from the interaction region. To this end, the teams used flow-focusing gas dynamic virtual nozzles operating at approximately 10 – 100 Hz. These first results demonstrated that ground-state SFX structures collected in the MHz regime can produce high quality atomic structures of macromolecules. This suggests that when the European XFEL detector speed, sample delivery, and data analysis is fully optimised for maximum rates, then one might expect complete SXIF data sets to high resolution in approximately one minute.

During the 19 March 2018 ceremony at the UK embassy in Berlin, representatives for the UK government, the German federal government, and the European XFEL signed documents to bring the UK into the European XFEL Convention. The agreement stipulates that the UK will contribute about 2% annually to the operations budget as well as €62M to the construction costs of the facility. The Science and Technology Facilities Council (STFC) is a shareholder and will represent the interests of UK scientists and citizens in the European XFEL.

The XFEL Hub, through its membership in the SFX Consortium, is working to supply an on-demand droplet sample injector for the downstream interaction region of the SFX/SXIF1 instrument. One of our goals is to support SFX and tr-SFX by delivering ~30 picolitre droplets of microcrystal slurries directly into and synchronized with the XFEL beam pulses. At the end of this year or early next year, we anticipate testing sample delivery at 10 kHz within each pulse train to yield a 60 Hz overall data collection rate. Longer-term goals include 100 kHz sample delivery within a pulse train, which will produce SFX data at 600 Hz overall. Although MHz sample delivery rates are likely to require fast jets, an advantage of on-demand acoustic methods is that they are more efficient with samples since none is wasted in the gap between the X-ray trains.
The recent Science Division reorganisation has resulted in a rationalisation of the beamlines that were originally members of the Surfaces & Interfaces village. The new Structures and Surfaces Group consists of four beamlines, I05 (Angle Resolved Photoelectron Spectroscopy – ARPES), I07 (Surface and Interface X-ray Diffraction), B07 (Versatile Soft X-ray Scattering – VERSOX) and I09 (Surface and Interface Structural Analysis – SISA). There will be a much closer working relationship within this new structure, including more extensive internal collaborative research and improved offline facilities to serve the user community. The alignment has extended beyond just the science division and we are now able to work much more closely with engineering colleagues and software developers that are aligned with the new groups, leading to common solutions across the beamlines. Obvious overlap in the science programmes will be developed, such as Angle Resolved Photoelectron Spectroscopy (ARPES) on I05, B07 and I09, who have also been offering hard X-ray Photoelectron Spectroscopy (NARPES) for studying bulk electronic structures. Beamlines I07 and B07 will strengthen the programme in areas of non-ultrahigh vacuum (non-UHV) studies including catalysis and electrochemistry. The new structure will also encourage cross-group developments and we expect strong interactions with the Magnetic Materials Group, Spectroscopy beamlines and the Soft Condensed Matter Group in a number of science areas such as energy materials or catalysis. The grouping will enhance our ability to work more closely with user groups, offering a comprehensive range of techniques to non-specialists that will aid understanding of their science problems.

The beamlines within the group continue to develop through a number of upgrade projects, both major and minor. VERSOX (B07) is in the process of bringing its second branch online, which will enable high throughput X-ray Photoelectron Spectroscopy (XPS) measurements on multiple samples and Near-edge Extended X-ray Absorption Fine Structure (NEXAFS) in a non-UHV environment. Together with the Near Ambient Pressure XPS experiments on the existing branch, this provides excellent opportunities to study the electronic and structural properties of different samples of relevance to a range of science areas including atmospheric chemistry, pharmaceuticals, catalysts or cultural heritage amongst others. Beamline I09 is adding new capabilities to its end station provision, a HarAXES system to enable studies of the electronic states of buried interfaces and a momentum microscope to produce images of the electron band structure directly in momentum space. Beamline I05 has two branches, one of which is the high resolution facility that has proven to be a very successful addition to the suite of beamlines, since it became operational in 2014. Many experiments make use of the in situ cleaving techniques to study novel crystal structures, whilst there is also a fully equipped molecular beam epitaxy (MBE) system attached to the end station that can be used to produce samples in situ, as demonstrated by the successful growth of Goldblum doped europium oxide (EuO) thin film structures. The Nano-ARPES branch has been attracting an increasing number of users that want to understand not only the electronic structure on a macroscopic scale but also to establish the dimensionality of those states. This year’s science highlights cover two specific areas from this broad range of applications, namely understanding the mechanism by which ozone reacts with organic molecules in seawater and two highlights on understanding materials related to spintronics. Jones et al. used I07 to highlight the unexpected result that rather than ozone attacking organic molecules at the surface of a water layer, it seems to produce radicals in the liquid that then attack the structure of the layer. This result will cause a rethink in understanding the mechanisms occurring in atmospheric chemistry and interactions in seawater. More conventional surface science studies were undertaken on I09, where Prinzelli et al. have demonstrated the role of dimensionality in affecting the electronic structure in important spintronic materials. Dilute magnetic semiconductor (GaMnAs) and strained strontium doped lanthanum manganite (LSMO) samples were studied by photoelectron spectroscopy (PES) at different energies, to establish the changes in electronic structure with depth by relating specific peaks to carrier mobility in the materials. ARPES measurements on beamline I05 by Suzuki et al. studied the spin-orbit splitting in the layered oxide compounds PdCoO$_2$ and PtCoO$_2$ both terminated with CoO. The surprisingly large spin splitting is unexpected but can be explained by large inversion-symmetry breaking related to the top surface layer. The CoO$_x$ layer has oxygen atoms above and below the Co atoms and it is the movement of electrons through these two different routes (caused by the different environment at the surface) that produces the large asymmetry.

The diversity of the science programme is a strength of this group with studies ranging from the observation of novel electronic states in complex crystals to experiments on the structure of liquid layers at the air-liquid interface. This year’s science highlights cover two specific areas from this broad range of applications, namely understanding the mechanism by which ozone reacts with organic molecules in seawater and two highlights on understanding materials related to spintronics. Jones et al. used I07 to highlight the unexpected result that rather than ozone attacking organic molecules at the surface of a water layer, it seems to produce radicals in the liquid that then attack the structure of the layer. This result will cause a rethink in understanding the mechanisms occurring in atmospheric chemistry and interactions in seawater. More conventional surface science studies were undertaken on I09, where Prinzelli et al. have demonstrated the role of dimensionality in affecting the electronic structure in important spintronic materials. Dilute magnetic semiconductor (GaMnAs) and strained strontium doped lanthanum manganite (LSMO) samples were studied by photoelectron spectroscopy (PES) at different energies, to establish the changes in electronic structure with depth by relating specific peaks to carrier mobility in the materials. ARPES measurements on beamline I05 by Suzuki et al. studied the spin-orbit splitting in the layered oxide compounds PdCoO$_2$ and PtCoO$_2$ both terminated with CoO. The surprisingly large spin splitting is unexpected but can be explained by large inversion-symmetry breaking related to the top surface layer. The CoO$_x$ layer has oxygen atoms above and below the Co atoms and it is the movement of electrons through these two different routes (caused by the different environment at the surface) that produces the large asymmetry.

The members of the Structures and Surfaces Group are committed to continuing the high quality scientific output from the beamlines, through enhanced interaction with our user community. Please contact us, if you would like to discuss any of the techniques or possible experiments and how the synchrotron studies could help in your research.
Achieving maximal spin splitting at a crystal surface


Publication keywords: Spin-orbit coupling; Rashba; Spin-splitting; Delafossite; ARPES

The surfaces of materials can host unique electronic properties, where the electrons behave very differently from the interior. All electrons possess a magnetic moment, their spin, but in most non-magnetic materials electrons with different spins behave in the same way. This may not be the case at surfaces, where a splitting of states of opposite spin may be observed. This leads to novel electronic phases, an interesting area of fundamental research but also for potential applications in spin-controlled devices. For spin-splitting to be useful in electronic devices, it is often necessary to maximise the size of the splitting.

Researchers from the University of St Andrews and the Max Planck Institute for Chemical Physics of Solids in Dresden investigated the origin of large spin-splitting on cobalt-based delafossite oxides. They used high-resolution angular resolved photoemission measurements on the dedicated beamline (I05), which has a small light spot, high flux and excellent manipulator control that makes it ideal for measurements on small samples.

Their results show that spin-splitting in delafossite oxides reaches as much as the full strength of the spin-orbit coupling of the relevant orbitals. This highly surprising result is a consequence of unusually strong symmetry breaking at the surface, enabled by the crystal structure. This insight could be used to design new materials exhibiting record-breaking spin-splitting.

![Figure 1](image1.png) (a) Crystal structure of PdCoO$_2$. In the bulk, triangular P$_2$ layers (red) are separated by insulating CoO$_2$ (green). PdCoO$_2$ is an example of the CoO$_2$ block (Fig. 1a). The platinum and palladium based delafossite metals have a single, fast Pt/Pd based band crossing which triangularly coordinated noble metal (A, A=Pt,Pd) layers are separated as 0.13 Å, comparable to 0.1 Å in BiI$_3$ and 0.26 Å in Au$_2$Pd$_3$ surface alloy.

![Figure 2](image2.png) (b) Fermi surfaces of PdCoO$_2$, measured by angle-resolved photoemission. In addition to the bulk Fermi surface, two semicircular Fermi surface components are clearly observed. Expected values of spin polarization on the six electrons as a function of momentum is shown in the figure. The measurement shows switching of spin polarization between the two hole surfaces, indicating Rashba-like spin splitting.

![Figure 3](image3.png) Spin-split surface states of PdCoO$_2$ and PdRhO$_2$. (a) indicating a spin splitting that scales with the SOC strength of the Dirac cone. Metal. The splitting retains the strength of the atomic SOC of the transition metal even as the strength is increased by a factor of approximately 2.1 by moving from Co to Rh. (b) Maximum spin splitting at the Fermi level, which is clearly visible in the energy distribution curves shown in (b) and (c). The key point is the structure of the top Co$_2$ layer (Fig. 1b). Electrons can hop from one Co to another either via the oxygen in the layer above (O1), or via the oxygen in the layer below (O2). In the bulk these two paths are equivalent, however the top oxygen has no noble metal above it. This causes an on-site energy shift between the two oxygens, and makes the hopping path through the surface oxygen much more likely. The inversion symmetry breaking is no longer a small perturbation of the dominant kinetic Hamiltonian; rather the kinetic Hamiltonian itself becomes asymmetric. This asymmetry of hopping integrals is estimated to be about 40%, or about 150 meV. This is more than twice the atomic spin-orbit coupling of cobalt, allowing the gap splitting to assume the full atomic spin-orbit coupling strength, as observed.

What is more, this kinetic mechanism of inversion symmetry breaking has a potential for achieving truly large spin splitting scales in compounds containing heavier atoms with larger spin-orbit coupling. Usually increasing the atomic spin-orbit coupling causes the splitting to be limited by the smaller inversion symmetry breaking scale, however the kinetic inversion symmetry breaking is proportional to the bandwidth, and will also grow as heavier atoms with larger orbitals are used. This suggests a route to stay in the ‘strong inversion symmetry breaking’ limit even when the absolute size of spin orbit coupling is large. A proof that this is indeed possible is found by measuring the surface electronic structure of previously unstudied PdFeO$_2$. Similar surface states are observed to the cobalt-based compound, but the energetic spin splitting in the regime reaches ~2-3 times larger value of 150 MeV, a record for an oxide, reflecting the 2.5 times larger atomic spin-orbit coupling. This confirms an electron energy-coupled inversion symmetry mechanism.

To conclude, it has been shown here that a ‘tropic’ for achieving large spin-splitting is to use heavy elements with large atomic spin orbit coupling and large orbital overlaps in a structure where the preferred hopping paths are out of plane. Due to the loss of bonding at a surface such kinetic energy will become asymmetric, and introduce a large spin-orbit coupling energy scale, allowing the full spin-orbit coupling energy to be utilised in spin-splitting surface states.

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Using X-rays to investigate cloud chemistry


Publication keywords: Atmospheric aerosol; Sea-water; Thin film; Heterogeneous oxidation; Ozone; OH radical; X-ray reflectivity

Atmospheric aerosols critically affect the Earth’s climate by directly scattering and absorbing solar radiation and indirectly through their involvement in cloud formation and their influence on cloud radiative properties. Numerous aerosols are coated in a thin organic film, which affects their physical properties and therefore their contribution to the Earth’s climate. As the atmosphere is an oxidizing medium, it is likely that an aerosol will be oxidized in its lifetime, which will also affect the physical properties of the aerosol such as its ability to uptake water and whether it will act as a cloud condensation nuclei (CCN), the precursor to a cloud droplet. Therefore, it is important to study oxidation reactions of atmospheric aerosols coated in a thin film to better understand aerosol contribution to cloud formation and cloud radiative properties and thus the Earth’s climate.

An X-ray reflectivity experiment was conducted on I07 at Diamond to study the oxidation of real organic films at the air-water interface with common atmospheric oxidants (gas-phase ozone and the aqueous phase radicals, hydroxyl and nitrate). The thickness and scattering length density of the film were monitored throughout the experiment using X-ray reflectivity. Scattering length density provides information on the chemical composition and amount of material present at the air-water interface. I07 was used because a good signal-to-noise ratio can be obtained up to high reflection angles and because of the availability of fast acquisition times.

Atmospheric aerosol samples were collected at Royal Holloway University of London using filter samplers and sampling cartridges. The site is close to central London and some of the UK’s busiest motorways. The sampling cartridges contained cotton desiccants to remove any ambient gaseous ozone to prevent the oxidation of the material collected on the filter prior to the oxidation experiment. Surface sea-water samples were collected at Wold Bay-on the south coast of England using a long reach sampler. In all cases, organs were extracted and stored at 4°C until use.

X-ray reflectivity studies were performed on monolayer films of atmospheric or sea-water material at the air-water interface formed on a Langmuir trough. A custom trough was set up on an anti-vibration table on the I07 beamline and reflectivity of the film was monitored before and during addition of an oxidant.

Figure 2. X-ray reflectivity profile for a model of atmospheric aerosol film material exposed to the aqueous phase hydroxyl radical.

As a reaction was observed with the aqueous phase hydroxyl radical and no reaction was observed with gas-phase ozone, it suggests that the organic film material in both atmospheric and sea-water samples contains a lack of unsaturated material. Unsaturated material contains double bonds which ozone would cleave resulting in the formation of smaller molecules that would either partition to the gaseous or aqueous phase resulting in a decrease in the amount of material at the air-water interface. Aerosol react by abstraction of a hydrogen atom and can therefore react with material that contains no double bonds. Similarly no reaction was observed between sea-water film material and gas-phase ozone, however, a reaction was observed (decrease in the amount of material at the air-water interface) between sea-water film material and the aqueous phase nitrate radical.

Atmospheric aerosol and sea-water samples were also analysed by mass spectrometry techniques. No unsaturated material was detected, which could mean that the concentration of unsaturated material in the samples is very low and could even be below the detection limit of the technique, or that the samples contain a much greater proportion of saturated material. In support of the lack of reaction observed with gas phase ozone, a number of studies in the literature have shown that unsaturated material exists in much lower concentrations compared to saturated material in atmospheric aerosol samples.

In conclusion, organic material extracted from real atmospheric aerosol and sea-water samples forms stable films at the air-water interface. The oxidation of these films has been studied using X-ray reflectivity and shown that such films are unreactive to gaseous ozone and can be modelled as a constant amount of material at the air-water interface. It is proposed that the samples rather do not contain unsaturated material or contain it in very low concentrations, which is supported by multiple studies in the literature which propose that unsaturated material in atmospheric aerosol is present in very low concentrations when compared to saturated material. As reflectivity has shown that a thin organic film extracted from atmospheric aerosol does react with the aqueous phase hydroxyl radical and a thin organic film extracted from sea water does react with the aqueous phase nitrate radical. Therefore heterogeneous oxidation by gas-phase ozone may not be important in the atmosphere, whereas radical oxidation appears to be important. Thus it is recommended that future proxy studies focus on radical oxidation of saturated organics. Future studies of real aerosol samples collected at different stages throughout an aerosol lifetime are also recommended to determine whether gas-phase oxidation by ozone is important at specific times.

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Understanding the behaviour of electrons in spintronic materials

A team of researchers led by a group from National Research Council (CNR) Trieste developed a technique to reliably and precisely detect variations in electronic structure with depth. They used the Surface and Interface Structural Analysis beamline (I09), which allows photoelectron spectroscopy at tunable probing depths by changing the photon energy. The researchers applied their technique to two prototypical spintronic materials, and advanced theoretical modelling allowed them to attribute the results to the ability of carriers to move freely through the solid, and to precisely define the depths at which such variations take place. This is a step towards achieving the necessary precise control of spatially-confined spintronic materials.

Complex materials at the focus of modern research display unusual characteristics, often termed as quantum properties. In many cases, these exhibit a critical dependence on small variations of external parameters such as temperature, electric and/or magnetic field, photoexcitation and strain. Spintronics is a highly active field, exploiting quantum properties to achieve new approaches, providing new features to devices.

The integration in nanoscale components, however, favors spintronics with the challenges of surface confinement. Lateral distortions, stoichiometry changes, surface states and orbital population rearrangements alter the electronic structure when the crystal is interrupted. The uncontrolled configuration is recovered only in the bulk. The introduction of a long-range crystal interruption: films below these thicknesses do not possess the desired magnetoresistance.

A high-mobility electron gas at the LaAlO

Di femtoseconds. Such a problem indeed requires the resolution of uncontrollable processes. This possibility is offered by the combination of hard and soft X-ray photoelectron spectroscopy respectively HARPS and SX-PES in consistent experimental conditions at Diamond’s Beamline I09. It was applied to a prototypical spintronics system: the rare-earth-doped manganese, Sr

3-x

MnO

3

(FM); and ferromagnetic state.

Figure 2: (a) Photon energy dependent Mn 2p core level spectra of LSMO (measured with linear polarisation at T = 200 K). The spectra are shifted vertically for ease of comparison after integral background subtraction. The arrows indicate the position of the well screened satellites for each spin-orbit partner. (b) Expanded view of the Mn 2p peak around 640 eV. The evolution the peak fit component reproducing the LBEES structure is shown as a function of screening photon energy. Note that at E = 100 eV the well screened intensity is clearly present in GMA, albeit absent for LSMO.

order parameter such as magnetic alignment adds a further characteristic spatial scale that can be probed by changes-driven interactions to create an intricate picture.

Evidence is accumulating that critical thicknesses are encountered frequently when assessing properties such as two dimensional conductivity, magnetoresistance and ferromagnetism. The term indicates the region of the solid in which radical changes in the electronic structure are produced by the crystal interruption: films below these thicknesses do not possess the desired emergent properties (although they may bear other ones).

Often difficult to understand whether critical thicknesses arise from intrinsic effects, controllable by interface engineering, or from extrinsic, uncontrollable processes. Such a problem indeed requires the resolution of the electronic structure of a single system, and virtually a single sample, by a technique of intrinsic probing depth tunable across the surface region.

Figure 3: Illustrated panel: relative amplitude of LBEES plotted as scatter plots for LSMO (circles) and GMA (squares). The vertical inner-Area is 10% of the MNP. The horizontal axis is obtained by propagation of uncertainty in peak fittings parameters. The curves show the mass functions, derived directly from the data points. The grey lines labelled peaks define the emergence threshold for GMA (LBSM). The plot evidences that the solid state is quasiparticle reproduces the relative intensity of the LBEES to LSMO (circles), thus confirming the area and zero peak (red) to the maximum in the 0-0.8 eV range. A box-plot shows the evolution of the theoretical hybridisation parameter.

An effective approach has been achieved by the study of core-level satellites in photoelectron spectroscopy (PES)\(^{11}\). Indeed, during the photoemission process, photoemitted atoms are projected in a set of final states depending on the mechanisms available to screen the core charge, giving rise to satellites. A subset of these, observed at lower binding energy than the main line (low binding energy satellites, LBSM), is sensitive to carrier mobility. Cluster model calculations\(^{12}\) define such sensitivity with the hybridisation parameter, which quantifies the contribution of mobile states to the equilibrium electronic structure.

In complex materials, LBSM are encountered (or disappear altogether) when the probing depth of PES is increased to deeper regions below the surface. Indeed, by increasing the excitation photon energy from 800 eV to 6 keV, the depth probed by PES extends from 1 nm to 10 nm, thus spanning the transition from surface to bulk properties. In order to use this approach to confirm or disprove interpretations, however, it must achieve quantitative precision.

This possibility is offered by the combination of hard and soft X-ray photoelectron spectroscopy respectively HARPS and SX-PES in consistent experimental conditions at Diamond’s Beamline I09. It was applied to two prototypical spintronics systems: the rare-earth-doped manganese, Sr

3-x

MnO

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(FM); and ferromagnetic state.

The evolution of the intensity of the LBEES versus photon energy could be determined by a line shape analysis (Fig. 1b, Fig. 2b), respectively were measured for GMA (40 nm film, Mn doping 13%, respectively grown on GaAs(100) substrate) and LSMO (40 nm film, caxis 33%, respectively grown on LaAlO

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substrate), as a function of increasing photon energy, i.e. with increasing probing depth. The LBEES features were clearly observed.

The evolution of the intensity of the LBSM versus photon energy could be determined by a line shape analysis (Fig. 1, Fig. 2b), allowing for the development of a quantification procedure (Fig. 3). The relative amplitude of the LBSM component was plotted, for each photon energy, against the corresponding inelastic mean free path (IMFP) of the electrons, defining the corresponding probing depth. The resulting plot was fitted by considering an exponential attenuation of the LBSM through the surface layer, where thickness of the fitting parameter. A value of c=1.2 mm was found for GMA and d=4 mm was obtained for LSMO. LSMO was also measured in three strain states induced by substrate mismatch, finding no detectable modifications in d.

The relative energy distance between the LBSM and the main line also provided a precise method to compare experiments with state-of-the-art cluster model calculations, and thus to create (Fig. 3) a vertical scale of the variation of the hybridisation parameter, which, consistently, changed more drastically within the thickness in both materials.

In conclusion, it has been demonstrated that the combination of SX-PES and HARPS can be used to quantify the characteristic scale of the modifications of the electronic structure produced by the surface in complex materials. Such an approach paves the way for methodical discrimination between competing models of the effects of vertical confinement. Finally, precise means to draw a comparison with calculated scatter has allowed reliable attribution of the bulk properties to the increased hybridisation of the ground state with high mobility states.

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Magnetic Materials Group
Samjeet Dhesi, Science Group Leader

The newly formed Magnetic Materials Group concentrates on emergent phenomena in quantum materials using the capabilities of beamlines I06, I10, I16 and I21. The research encompasses a variety of challenges and opportunities at the frontiers of condensed matter physics and materials science ranging from topological states of matter, superconductivity, spintronics, two-dimensional systems, skyrmions and multiferroics. The key insights made by researchers exploit the high sensitivity of polarised X-ray spectroscopy, microscopy and scattering available across the beamlines. For instance, polarised soft X-rays combined with the PhotoEmission Electron Microscope (PEEM) on the Nanoscience beamline (I06) have visualised the domain dynamics underpinning antiferromagnetic spintronic materials while the resonant soft X-ray scattering on the BLADE X-ray Dichroism and Scattering beamline (I06) has been used to understand the topological properties of skyrmions. On the Materials and Magnetism beamline (I16), interference effects in hard X-ray scattering have led to a deeper understanding of long-range magnetic ordering in canted antiferromagnets. The Ionised X-ray Scattering beamline (I21) is in a commissioning phase, but has had already performed ground breaking experiments measuring orbital excitations, magnon dispersion and electron-photon coupling in several highly-correlated systems. In this inaugural contribution to the annual highlights we present research from our user community that uniquely demonstrates how polarised X-ray science can uncover dramatic changes in the magnetic properties of materials from subtle changes to the geometric and electronic structure.

The origins of many complicated magnetic structures arise from short-range and long-range interactions. The understanding of long-range order arising from the Dzyaloshinskii-Moriya interaction (DMI) is, therefore, fundamental to developing new devices based on magnetoelectric effects. Building on previous work that determined the sign of the DMI for the weak ferromagnet, FeBO$_3$, researchers on beamline I16 have gone a step further and unraveled the relationship between band filling and the sign of the DMI by studying a series of isostructural weak ferromagnetic carbonates. The change in sign of the DMI is correlated to the electronic structure using first-principles calculations and is a dramatic demonstration of how magnetic properties, that can be determined using polarised X-rays, are influenced by subtle changes to the electronic structure.

When inversion symmetry is broken using interface engineering in trilayers, the spin-orbit interaction leads to the spin-orbit torque (SOT) effect that can then be used to switch the magnetisation of a thin magnetic film. The use of the SOT depends sensitively on interface properties, but can also be tuned by altering the resistivity of the materials in the trilayer using ion sputtering during growth. On I10 researchers have employed this approach to relate the changes in the resistivity of a Pt layer, in a Pt/Co/AlO$_x$ trilayer, to changes in the Co spin and orbital moments determined using X-ray Magnetic Circular Dichroism (XMCD).

In terms of technical developments across the beamlines we start with the latest addition to the suite of Diamond beamlines, I21. I21 is a polarised soft X-ray beamline covering the energy range 259 eV to 3000 eV and dedicated to Resonant Inelastic X-ray Scattering. In the past few months the beamline team have started user operation and welcomed eight international research groups for first experiments. The novel collection geometry on I21 means that the beamline leads the world in detection efficiency and can perform scans in a fraction of the time that would otherwise be possible. The beamline has already achieved a resolution of 13.8 ± 0.2 meV at the O K-edge (Fig. 1) and is now pressing ahead with further developments to reach higher photon energies covering the 4d and 5d transition metal 3p and 4p edges respectively, provide polarisation analysis of the scattered X-rays and install more efficient detectors. I16 has also made important steps in installing a new electromagnet facility, to complement the existing low-temperature 14 T magnet, for fast XMC measurements and is also installing a new versatile electromagnet in the RASOR diffractometer. I06 is completing the refurbishment of the beamline, which will permanently house the vector magnet and time-resolved soft X-ray diffraction systems. Beamline I06 has also started the process of installing a new Medipix3RX quad detector for the PEEM with a higher quantum efficiency with respect to the existing detector. In the coming year, I06 will also upgrade the PEEM manipulator to reach lower temperatures using liquid He making researchers to explore the phase diagrams of, for instance, multiferroics and superconductors. I10 have upgraded the polarisation analyser to house an area detector and are continuing to develop versatile polarisation control of the incoming X-rays. The main upgrade to the B16 Test beamline has been the design and development of a pink beam compatible X-ray camera system, which overcomes the challenges of the high flux of white beams, including degradation of image quality due to accumulated contamination on the scatterer during intense X-ray exposure. This camera system will facilitate fast imaging on B16 using pink-white beams. Furthermore, in the B16 science highlights, a novel approach to selecting a single bunch using surface acoustic waves is generated.

Figure 1. Combined energy resolution at the Oxygen K-edge using the 2000mm HPM3 beamline grating and the 2700mm SVLS2 spectrometer grating on beamline I21.

By depositing thin films of BiFeO$_3$ on vicinal surfaces researchers on beamline I06 were able to grow single ferroelectric domain samples leading to deterministic and robust room-temperature control of the magnetic orientation of a Co overlayer. BiFeO$_3$ is a multiferroic with a DMI that leads to a spin cycloid structure with a ~63 nm period. At first glance it might seem that such a complicated magnetic structure would have little effect on a Co overlayer. However, the combined use of Neutron Diffractions, at the nearby I5S facility, and the PEEM on beamline I06 demonstrated that the interface region of the BiFeO$_3$ structure has a canted antiferromagnetic component that, upon reversal of the BiFeO$_3$ electric polarisation using a bias voltage, is able to reproducibly switch the Co film magnetisation direction. These nanoscale insights into the interface region of single domain thin film BiFeO$_3$ are only possible using the PEEM combined with polarised soft X-rays and show how controlling film structure can lead to new and robust functionality.

The Magnetic Materials Group will continue developing the beamlines and off-line laboratories for the research community and would welcome input on how we can maintain the world-leading facilities developed at Diamond. In the long term we are also working on the development of the facilities ready for an upgrade to high-repetition rate Diamond X-Machne. Our aim is to reduce a family of polarised X-ray beamlines with intuitive software, underpinned by advanced on-site sample characterisation facilities and supported by state-of-the-art data visualisation tools.
Magnetic Materials Group  Beamline I06

Imaging exchange coupling in multiferroic, multifunctional devices


Publication keywords: Multiferroics; Exchange: Spinning patterns

The data storage on which our smartphones, tablets and computers rely works via electrical fields (e.g. flash drives) or magnetic fields (e.g. hard drives), but research into magnetoelectric materials could lead to a new generation of multifunctional devices that use a combination of the two.

Magnetoelectric materials have both electrical and magnetic functionality, and changing one induces a change in the other – it’s called ‘cross-coupling’. Developing an understanding of cross-coupling involves studying how the magnetic properties change when an electric field is applied, but most magnetoelectric materials have very complicated structures. Researchers simplified the process by simplifying the material itself, developing a unique process for making a simpler magnetoelectric material.

They then used I06’s X-ray PhotoElectric Microscope (XPEEM) to image – in real-time – how changing the electric properties results in a change in the magnetic state. Their results are an important step towards exploiting cross-coupling to make new multifunctional devices that work well at room temperature, opening up new directions for creating spintronic devices that make use of an electron’s spin, as well as its charge.

We find ferromagnets and ferroelectrics all around us: our latest credit cards can both make a magnetic stripe and a ferroelectric memory chip on it. Yet usually they are of different materials on separate planes, like on the card. Multiferroics are materials in which both magnetic and ferroelectric properties exist intrinsically in the same material, and offer the possibility to combine normally spatially-separated functions into a single device with multiple functions, as well as to drive new device paradigms. This could drastically increase the performance and reduce the size of future circuits. The biggest challenge is to understand just how these properties are internally coupled and then how to exploit this coupling to design new multifunctional devices.

On Diamond Light Source’s I06 Nanofacility beamline, researchers have made an important step to show how magnetoelectric coupling can be exploited to make a new, robust multifunctional device working at room temperature. Using monodomain epitaxial thin film heterostructures of the most promising multiferroic, I06’s X-ray Photomicroscopy (XPEEM) has imaged how the ferroelectric properties can deterministically control the magnetic orientation of an epitaxial overlayer only a few atoms thick.

Switching the BiFeO$_3$ ferromagnetic state between ‘up’ and ‘down’ controlably and reproducibly initiates the ferromagnetic orientation of the overlayer by 90$^\circ$. This opens up new directions for creating fast, low power ‘spintronics’ devices (microelectronic devices that use the electron’s spin as well as its charge) by exploiting the multiferroic properties of BiFeO$_3$.

Staying ahead of Moore’s Law – which predicts a doubling of the number of transistors in microelectronic circuits every two years – is driving the search for new device functionalities, which in turn require the discovery of materials with new properties that can be controlled by applying a voltage or current.

Multiferroic materials, especially ‘magnetoelectrics’ that showed coupled magnetic and ferroelectric properties in the same phase, offer great promise to satisfy these requirements. These films are necessary for any device that should eventually be integrated into a large-scale circuit, and optimal growth of films also offers the opportunity to control and even improve certain properties of a material as compared to bulk counterparts. For example, in silicon films the electron mobility can increase under certain conditions of optical stress (i.e. squeezing or stretching the crystal in two directions, leaving the third direction free to adjust), thus allowing higher operating speeds. Optoelectronic materials can also improve the properties of ferromagnetic films influenced by the size and distribution of domains, adjacent volumes in which the polarization points in different directions. For BiFeO$_3$, the deleterious effect of multiple domains was eliminated by growing large-area BiFeO$_3$ films processing only a single ferromagnetic domain – ‘monodomain’ films, with the desirable property that there is only one, well-defined direction of the polarization in either the ‘up’ and ‘down’ states.

In magnetoelectric BiFeO$_3$, the magnetic organization of spins on the Fe sites is antiferromagnetic, i.e. moving from one Fe to the next, the magnetic spins point in opposite directions. In bulk BiFeO$_3$, the spins have the added complexity that they rotate slightly going from one site to the next, completing a full rotation over a distance of about 6 Å in bulk (the period of the so-called ‘spin-cycloid’). The cycloid is expected to create problems for any BiFeO$_3$, but monodomain devices, since over large areas there is no single direction of the magnetization, as there is in single crystalline antiferromagnets. To complicate matters even more, in BiFeO$_3$, crystals that are possible ferromagnetic domains, each with 3 cycles of different orientations – 24 different configurations in all, making multimdomain BiFeO$_3$, a complex material difficult to incorporate in a well-behaved, deterministic magnetic device.

One of the building blocks of spintronics is an ‘exchange-coupled’ bilayer, based on an effect discovered in the 1950s but still not well understood, in which the spins in a spin antiferromagnetic layer are coupled to the spins in a ferromagnetic overlayer.

Since the spins in a collinear antiferromagnet is fixed, exchange coupling across the interface serves to effectively fix the direction of the ferromagnetic layer. New functionality can be introduced by creating a magnetoelectric exchange-coupled bilayer, in which the spins axis L in the ferromagnetic overlayer is rotated when the ferroelectric polarization is switched; then exchange-coupling between L and the spins in the ferromagnetic overlayer would cause the ferromagnetic spins to rotate as well, in a deterministic and controllable way.

Precisely this new type of magnetoelectric exchange coupling is demonstrated by the XPEEM data (Figs. 1-3). Several improvements to the samples constructed for these experiments were crucial to achieving unambiguous interpretation of the data. Most important is the use of monodomain BiFeO$_3$ films under epitaxial strain: neutron diffraction indicates that each ferromagnetic monodomain is a single-antiferromagnetic domain even after hundreds of ferromagnetic switching cycles. Thus, monodomain BiFeO$_3$, films eliminate the 24 different polarization–cycloid configurations mentioned previously for bulk BiFeO$_3$. In the presence of a strong exchange coupling to the ferromagnetic overlayer, the stability of the monodomain ensures a single one-to-one correlation between the BiFeO$_3$, ferromagnetic state and the overlayer spin orientation and (b) deterministic control over the spin orientation of the overlayer.

Ferromagnetic switching of the monodomain BiFeO$_3$, between ‘up’ and ‘down’ states was accomplished inside the XPEEM by installing the Ferroelectric (FEM) microscope at the (a) ‘down’ to (b) ‘up’ and back to (c) ‘down’ state continuously (scale bar 10 µm). The pola polarization was monitored at the (a) ‘down’ state (b) ‘up’ state and back to the (c) ‘down’ state.

The BiFeO$_3$, ‘down’ state was switched successfully at room temperature more than 1000 times, a breakthrough result for multifunctional devices. This suggests that the strain engineering of heterostructures is a promising path for the realization of practical, new multifunctional devices.

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Engineering platinum resistivity to enhance spin-orbit torque


Publication keywords: Spin-orbit torque; Spin Hall angle; Magnetic memory

Spin-orbit torque (SOT) arises from spin-orbit coupling in heavy metal/ferromagnet bilayers, and can be used to control the magnetisation direction. It is of considerable interest as a way to efficiently switch the magnetisation of spintronic devices, which have advantages over traditional electronic devices, including non-volatile memory and logic applications. In order to engineer materials with enhanced SOT, for lower power consumption, scientists are investigating the microscopic origin of SOT.

A team of researchers based in Korea and the UK used X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements on Diamond’s BLADE: X-ray Dichroism and Scattering beamline (I10) to investigate the relationship between the resistivity and the spin-Hall angle of platinum. They found that the SOT strength increases with heavy metal resistivity. Their results are expected to provide an efficient route for material engineering towards improved SOT-based spintronic devices.

The manipulation of the magnetisation by in-plane current utilising spin-orbit torque (SOT) has been receiving a great deal of attention due to its possible applications in spintronic devices such as magnetic memories and spin logic devices. For wider applications of spintronic devices, it is essential to find an efficient way to switch the magnetisation. In this respect, many attempts are being made in order to improve the SOT efficiency, for instance, by finding heavy metal (HM) electrodes with high spin Hall angle.

In order to efficiently engineer materials with large spin Hall angle, it is important to address the so-far unanswered question concerning the microscopic origin of the SOT. One of these questions is the relation between the resistivity of the HM layer and the spin Hall angle. In this work, the effect of the resistivity on the spin Hall angle was investigated using Pt(5 nm)/Co(0.8 nm)/AlOx (1.8 nm) structures (Fig. 1a), in which the resistivity of Pt is modulated by varying Ar deposition pressures ranging from 3 to 50 mTorr. The resistivity of the Pt layer shows a gradual increase with Ar pressure and reaches a value of almost 1.6 times larger for Pt deposited under 30 mTorr than that grown under 3 mTorr (Fig. 1b). This is expected because the reduced kinetic energy of sputtered atoms under a higher pressure leads to imperfections in the crystal structure.

Next, the effect of the Pt resistivity on the spin Hall angle and resultant SOT is investigated by measuring SOT-induced effective magnetic fields and the critical current for SOT-induced magnetisation switching. The effective magnetic fields are measured using a harmonic lock-in technique: the measurement of the first and second harmonic Hall voltages with respect to the in-plane magnetic fields, allowing us to extract the effective spin Hall angle (\(\theta_{\text{SH,eff}}\)). Figure 1c shows that the \(\theta_{\text{SH,eff}}\) increases ~3 times while the resistivity of Pt layer increases by a factor of 1.6. The increase in \(\theta_{\text{SH,eff}}\) is confirmed by SOT-induced switching experiments where the magnetisation direction was monitored by measuring the anomalous Hall resistance (\(R_A\)) while sweeping a pulsed driving current up to ±0.25 mA. The results, shown in Figure 1d, demonstrate deterministic SOT-induced switching of perpendicular magnetisation and show a reduction in the switching current (\(I_{\text{sw}}\)) for a larger Pt deposition pressure or a larger Pt resistivity. The decrease in switching current, or enhancement in the switching efficiency (Fig. 1e), is in good agreement with the enhancement in \(\theta_{\text{SH,eff}}\) obtained by the harmonic lock-in technique.

It has been experimentally shown that the \(\theta_{\text{SH,eff}}\) of Pt increases with the Pt resistivity, while the enhancement factor of the spin Hall angle is 3.0 while the enhancement factor of the Pt resistivity is 1.6. This may imply that there is a significant interface contribution to the enhancement in \(\theta_{\text{SH,eff}}\) since more current flows near the Co/Pt interface as the Pt resistivity increases. To account for this additional contribution to the SOT, the interface contribution needed to be experimentally addressed, which is related to the spin-orbit coupling-induced band splitting originating from the inversion-symmetry breaking at the interface. X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements were performed to verify whether the interface spin-orbit coupling is influenced by the Pt resistivity. Two quantities associated with the spin-orbit coupling of the Co atoms were obtained: the branching ratio (\(B\)) and the orbital-to-spin magnetic moment ratio (\(m_{\text{L}}/m_{\text{S}}\)) using the XAS and XMCD spectra and their integrated intensities for Pt(5 nm)/Co(0.8 nm)/AlOx (1.8 nm) samples (Fig. 2ab). The obtained values of \(B\) and \(m_{\text{L}}/m_{\text{S}}\) show a gradual increase with Pt resistivity indicating that the spin-orbit interaction of the Co indeed increases with the resistivity of the Pt layer. These results are in good agreement with the theoretical prediction \(\theta_{\text{SH,eff}}\) which emphasises the important role of interfacial spin-orbit interaction that contributes to the increase in \(\theta_{\text{SH,eff}}\). Therefore, our result, the efficient control of \(\theta_{\text{SH,eff}}\) and hence of SOT by controlling the HM resistivity, opens up a novel way to improve the switching efficiency in SOT-active devices.

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**Magnetic Materials Group**  
**Beamline I16**

**Adding electrons to switch magnetic chirality**


**Publication keywords:** Dzyaloshinskii-Moriya interaction; Weak ferromagnetism; Resonant X-ray diffraction

The Dzyaloshinskii-Moriya interaction (DMI) was first introduced in 1957 to explain 'weak ferromagnetism'. It causes a twisting of the pattern of atomic magnets, and is now considered to be the driving force behind the exotic magnetic vortices called Skyrmions. A predictive theory hadn't been developed, however, as until now a detailed study of the amplitude and sign of the DMI hadn't been carried out.

A team of researchers has used the Materials and Magnetism beamline (I16) to carry out a systematic study of the DMI in a series of magnetic crystals. I16 offers the very high X-ray flux needed to observe the tiny signals associated with magnetism. Even more importantly, it has the space and versatility to allow the development and testing of novel techniques. For these experiments, the researchers installed a moveable magnet to drag around the whole magnetic pattern without moving the sample, yielding data of much higher quality than traditional scans. Their novel technique could be applied to small crystal grains, with one of the samples (NiCo$_3$) being around 50 microns in size.

Their results showed a spectacular change in the magnitude and sign of the DMI as electrons were added to 3d shells, confirming theoretical calculations and a simple model based on the number of electrons carried by the magnetic ion. The study brings us a step closer to systematic prediction of important magnetic properties. The possibility of controlling and changing the sign of the DMI is an essential step towards finding suitable materials for spintronics applications.

Magnetic order at the atomic scale is readily exchange interactions, which are mostly symmetric upon exchange of the spins. In 1957, Dzyaloshinskii introduced an antisymmetric part to explain the weak ferromagnetism observed in some crystals. This new term, known as the Dzyaloshinskii-Moriya interaction (DMI), is a key ingredient in many modern magnetic phases, such as multiferroics and skyrmions. Despite the intense research effort on these materials, the DMI still lacks a simple understanding at the microscopic level, in particular because many experimental studies on the DMI address only its magnitude, not its sign. The sign of the magnetic twist is accessible in a handful of long-period magnetic structures, with complex phase diagrams that defy systematic investigations versus band filling.

Weak ferromagnets with the carbonate structure offer an opportunity to perform such a systematic study NiCO$_3$, FeBO$_3$, CoO$_3$, and NiO are the same crystal structure and the same low temperature magnetic ground state ferromagnetism due to a small canting of the spins away from the collinear antiferromagnetic arrangement (Fig. 1). The main difference is the nature of the transition metal ions, which carry the magnetic moment, and it is expected that the number of valence electrons has a large influence on the DMI. The sign of the DMI in these crystals is directly connected to the direction of the canting of the spins with respect to the antiferromagnetic sequence (Fig. 1), but the determination of this direction is not straightforward. Specifically, the canting direction can easily be drawn in any direction of the basal plane by a small magnetic field, which is convenient to ensure a single magnetic domain in the sample, but the phase of the antiferromagnetic structure is needed to extract the sign of the DMI.

A new diffraction method was developed for this purpose. Magnetic scattering encodes the magnetic structure, but the measurement of pure magnetic reflections cannot capture its phase and therefore the pattern of stacking of the canted moments. Interference was needed with a reference wave, independent of the magnetic structure: here Resonant Elastic X-ray Scattering (REXS) is used, which contributes to the same crystallographically forbidden reflections as the antiferromagnetic structure. The sign of the REXS amplitude must of course be known. Despite the rather exotic nature of the REXS amplitude in this case (pure electronic quadrupole scattering), it can be reliably modeled with a modern X-ray spectroscopy software.

The measurements were performed at beamline I16, with a monochromatic X-ray beam tuned to the K absorption edge of the transition metal of each sample. The ‘spacegroup forbidden’ 009 reflection, allowed for the antiferromagnetic structure and quadrupole moment scattering, was measured in the low temperature magnetic phase. In order to exploit the interference effect, a weak magnetic field was rastered in the basal plane of the sample, dragging the whole magnetic structure without moving the sample. The interference intensity varied in proportion to sin(ψ), where ψ is the angle of the DMI and η is the azimuthal angle of the magnetic field in the basal plane. The simple scan yields directly the signs of the DMI, as shown in Figure 2, characterized by the deviation of the measured intensity toward η = 90° or η = 270°, i.e., whether the red rings in Figure 2 go up or down. The results are remarkably clear: the sign of the DMI is the same in FeBO$_3$, NiO, and NiCo$_3$, which are both opposite to CoO$_3$ and NiCo$_3$. Moreover, the canted canting angle is negative (Fig. 1), FeBO$_3$, and positive (Fig. 1) in CoO$_3$, NiCO$_3$, and NiO. These signs represent the missing information from the absolute values of the canting angles that are reported in the literature and complete our knowledge of the relative strength of the DMI in this series of materials.

The experimental signed values of the canting angles are in agreement with state-of-the-art first-principle calculations within local density approximation taking into account the on-site Coulomb interaction U and spin-orbit coupling (LDA+U+SO).

The results show a nearly monotonic variation of the canting angle (and the DMI) as a function of the filling of the 3d band, with a change of sign between FeBO$_3$ and CoO$_3$. This can be understood with a simple model based on inter orbital contributions to the DMI (QDMI), following the superexchange-based approach developed by Moriya: considering two interacting ions, one considers each of the partial contributions for DMI between one orbital of one ion and one orbital of the other ion. By changing the occupation of the 3d states we change the balance between empty and fully occupied channels for the 10-DW. It results in a change of sign and magnitude of the total DMI.

This work, relying on a novel diffraction method, provides thus a simple microscopic understanding of the DMI in insulator systems.

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Fast Active Optics for Synchrotron Radiation


Publication keywords: Surface acoustic waves; Optics; Pulse picker

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ynchrotron light sources produce a strong and stable pulsed beam, for which the pulse sequence is dependent on the circumference of the storage ring. Many experiments only require some of the pulses, including ‘pump and probe’ experiments that activate a process and then measure it. Experiment hutchs are equipped with pulse pickers that are used to select which pulses reach the sample. Currently, pulse pickers rely on mechanical systems rotating at high velocities, such as crystals or mirrors. They are limited by their rotation speed, and other design factors.

To overcome these limitations, a team of researchers has developed a new type of pulse picker, based on an active optic system that uses surface acoustic waves (SAW) rather than mechanical components. It provides a flexible method of selecting pulses, via electron modulation of the amplitude of the acoustic waves.

For their experiments they used B16, which is equipped with the special optics needed to focus the beam onto the detector. Having successfully demonstrated that this new type of pulse picker is feasible for pulses separated by at least 120 ns, the team has plans to install a second one at the BESSY II facility in Germany.

X-ray time-resolved experiments allow the investigation of the dynamics of chemical reactions or physical phenomena. Various pump-probe experiments can be conceived, and the studied processes span different time scales from picosecond to millisecond. In pump-probe experiments, a fast change in the sample is triggered by external activation (pumping). A short time after the activation, an X-ray pulse is used to measure the state of the studied sample (probe). Ideally, no additional X-ray pulses should reach the sample.

Synchrotron radiation facilities provide strong and stable X-ray beam pulses that can be used for time-resolved measurements. Since at synchrotron light sources many experiments are served simultaneously, a pulse picker is preferably implemented in each experimental station.

Modern pulse pickers are mechanical choppers rotating at high velocities. Depending on the design, mechanical bunch pickers can select X-ray pulses separated by at least several nanoseconds. Another limitation common to most of the pulse pickers actually in use is the low repetition rate, in the kilohertz region. However, synchrotron sources commonly operate with a repetition rate in the meghertz region.

In 1989 Kézuka et al. formed the possibility of using the surface acoustic wave (SAW) to manipulate an X-ray beam, and in 1991 Takahashi et al. presented a different kind of pulse picker based on X-ray diffraction from a multilayer modulated by SAW trains. The SAW induces a sinusoidal deformation on the multilayer surface, which acts as a grating. When illuminated by X-rays it produces diffraction satellites. The SAW propagates with a constant velocity, usually between 2000–5000 m/s.

The time resolution is defined as the time that the SAW train needs to enter and leave the X-ray beam footprint. To be of practical value for Diamond, the time resolution has to be smaller than the 400 ns wide ion clearing gap.

In this highlight a feasibility test for an X-ray pulse picker built taking advantage of an SAW was performed at the BESSY II facility in Germany.

The substrate was a Y cut of Lithium Niobate (LiNbO3), a piezoelectric material. The X-ray energy of 8 keV was selected, and the SAW wavelength was 12 μm. The propagation velocity was 3468 m∕s.

The SAW is off (left). The two small peaks (arrows) are the m=1 diffraction satellites due to the scattering on the SAW grating (right). They are separated from the main peak by 3.5 degrees. The SAW is on (middle). A short time after the SAW has stopped, the two small peaks are no longer present due to the interaction with the multibunch. The SAW on (right). The two small peaks are again the m=1 diffraction satellites. In the comparison (right) the SAW was emitted with 100 ns duration.

In the SAW camera images (Fig. 2) the peaks are well separated, even though they are not entirely decoupled from each other. The integrated intensity of the satellites was correlated to the delay time. The integration area in the CCD image was automatically selected by a pulse picker, the integrated intensity from the satellites was correlated to the delay time. The integration area in the CCD image was automatically selected by a pulse picker, and then measured. The satellite intensity decreases when the delay time increases, while the intensity is maximal when the delay is such that the SAW train reaches the footprint during the ion gap, and it has a relative maximum in the middle of the gap due to the interaction with the single bunch.

X-ray diffraction from a SAW-modulated Si∕B4 C multilayer was studied in a two-circle diffractometer at the B16 beamline at Diamond. The X-ray energy of 8 keV was selected, and the SAW wavelength was 12 μm. The propagation velocity was 3468 m∕s.

In this high intensity test for an X-ray pulse picker built taking advantage of an SAW, the X-rays were modulated by a surface acoustic wave (SAW). The SAW is off (left). The two small peaks (arrows) are the m=1 diffraction satellites due to the scattering on the SAW grating (right). They are separated from the main peak by 3.5 degrees. The SAW is on (middle). A short time after the SAW has stopped, the two small peaks are no longer present due to the interaction with the multibunch. The SAW on (right). The two small peaks are again the m=1 diffraction satellites.
Imaging and Microscopy Group
Paul Quinn, Science Group Leader

Imaging and Microscopy is a newly formed science group, which brings together eight experimental facilities (I08, I10, I11, I12, I13-1, I13-2, I14 and ePSIC) with a new imaging group leader to coordinate and drive the group’s activities. These facilities use electrons and X-ray images under different experimental conditions across a diverse range of length scales and time scales. Different contrast mechanisms allow for imaging of sample properties such as elemental composition, density and structure and this ability to extract image sample properties in minute detail lends itself to a wide range of scientific areas from chemistry and catalysis to environmental science, materials science, biology, medicine, and cultural heritage.

The Scanning X-ray Microscopy (SSM) beamline (I08) is for morphological, elemental and chemical speciation on a broad range of organic-energetic interactions in a 20 - 4900 eV photon energy range. And sample investigations under ambient or cryogenic conditions. I08 has a range of applications including biological and biomedical science, earth and environmental science, geochemistry, and materials science. During the reporting period, the performance for lower photon energies on I08 was improved significantly, in particular for carbon Near Edge X-ray Absorption Fine Structure (NEXAFS) spectromicroscopy. I08 faced its first major upgrade as a result of the Scanning and Mapping projects. This upgrade is now finalised and offers superior performance in data collection and software interfaces to the user community. The design and construction of a soft X-ray spectroscopy and tomography beamline (I09) progresses according to plan. This instrument is expected to be available for experiments in the second half of 2019.

The Dual Imaging and Diffraction (DIAD) beamline (K11) will be the first beamline to offer two X-ray microscopy techniques (imaging and diffraction) applied synchronously with a switching time of a few milliseconds. This enables in situ structural characterisation experiments taking advantage of both techniques simultaneously. DIAD is being built to use light from a free-polar magnet wiggle. The diffraction technique is conducted using monochromatic light, whereas the imaging technique can be performed with monochromatic or polychromatic (“polar”) beam. The X-ray energy can be chosen separately for both techniques in the range from 7 - 38 keV. The beamline is under construction and is expected to start commissioning activities in the middle of 2019. First users can now routinely perform ptychography as a standard user experiment, enabling the beamline’s ambition for multi-scale imaging. A large number of pilot experiments are currently underway, many of which previously used the imaging branch but can now explore higher resolution ptychographic imaging. Examples are the study of battery failure, the origin and structure of particles from the Fukushima accident, or the micro- and nano-structure of insects.

I12, the JEEM beamline, performs mainly in-line phase contrast tomography with a strong emphasis on dedicated sample environments. Failure of lithium batteries, material cracks, the structure of ice crystals, bones under load, the storage of CO₂ in brine, and dendritic growth are some examples of the studies conducted under realistic conditions. Two projects are currently under development for submicron and phase-sensitive imaging. A new full-field microscope will perform z-axis phase contrast imaging over a field of view of 50 - 100 µm and a resolution of 50 - 100 nm. The use of fast direct electron detectors has improved image quality, measuring the absolute phase and providing small angle information allowing us to identify nano-sized structures from micrometer resolution X-rays. The highest spatial resolution of 5 nm has been achieved on the interference branch with ptychographic imaging. Our most important development is that we are now able to use the EXCALIBUR photon counting detector at 50 Hz/frames rate which has reduced position-tomography scans from days to a few hours. We can now routinely perform ptychography as a standard user experiment, enabling the beamline’s ambition for multi-scale imaging. A large number of pilot experiments are currently underway, many of which previously used the imaging branch but can now explore higher resolution ptychographic imaging. Examples are the study of battery failure, the origin and structure of particles from the Fukushima accident, or the micro- and nano-structure of insects.

In the imaging and coherence beamline aims for multiscale imaging in the energy range of 6 - 30 keV. The achievable resolution ranges from several microns to some tens of nanometers with two branchlines operating independently for this purpose. The Diamond-Manchester imaging branchline performs mainly in-line phase contrast tomography with a strong emphasis on dedicated sample environments. Failure of lithium batteries, material cracks, the structure of ice crystals, bones under load, the storage of CO₂ in brine, and dendritic growth are some examples of the studies conducted under realistic conditions. Two projects are currently under development for submicron and phase-sensitive imaging. A new full-field microscope will perform z-axis phase contrast imaging over a field of view of 50 - 100 µm and a resolution of 50 - 100 nm. The use of fast direct electron detectors has improved image quality, measuring the absolute phase and providing small angle information allowing us to identify nano-sized structures from micrometer resolution X-rays. The highest spatial resolution of 5 nm has been achieved on the interference branch with ptychographic imaging. Our most important development is that we are now able to use the EXCALIBUR photon counting detector at 50 Hz/frames rate which has reduced position-tomography scans from days to a few hours. We can now routinely perform ptychography as a standard user experiment, enabling the beamline’s ambition for multi-scale imaging. A large number of pilot experiments are currently underway, many of which previously used the imaging branch but can now explore higher resolution ptychographic imaging. Examples are the study of battery failure, the origin and structure of particles from the Fukushima accident, or the micro- and nano-structure of insects.

In its optimisation phase and over the coming year the spatial resolution will improve to ~10-100 nm and new techniques, and facilities such as ptychography, cryogenic sample handling and in situ sample environments will be rolled out for routine use.

In 2017 the Electron Physical Sciences Imaging Centre (ePSIC) at Diamond welcomed its first users. The two transmission electron microscopes which make up the centre, a JEOL ARM 200 and a JEOL GRAND ARM 300, were brought to Diamond through collaboration with Johnson Matthey and Oxford University. The ARM 200 is a state-of-the-art probe-corrected analytical microscopy capable of atomic resolution electron energy loss and X-ray spectromicroscopy. The ARM 300 is a dedicated imaging instrument aligned across a wide range of applications. It has a high spatial resolution over a field of view of 100 - 3000 nm and is equipped with a fast direct electron detector (operating at up to 2000 fps). These combined capabilities make this a unique resource for electron microscopy within the UK. With an in-situ sample holder, users at ePSIC can perform variable temperature measurements from 100 to 1600 Kelvin to directly image the atomic structure of materials during thermally driven transitions. This in-vita capability will be expanded upon over the coming year. As-failed instruments EID detectors has been added to the ARM 200 to allow combined X-ray spectromicroscopy and high-resolution imaging. The state of the art instrumentation available at ePSIC has attracted both established electron microscopists looking to develop new techniques and scientists with limited previous electron microscope experience interested in the atomic structure of their samples. The collaboration of the expert staff at ePSIC with this range of users is helping to bring cutting edge microscopy techniques to the wider material science community.
Iron (Fe) is abundant in the Earth's continental crust but only exists in low concentrations in the ocean. Rivers are important suppliers of Fe to the ocean. It is mainly transported as particles spanning a range of size, mineralogy and speciation, which together determine their reactivity. Chemically reactive Fe-bearing particles are characterised by poorly-crystalline mineral nanoparticles (e.g. ferrihydrite, lepidocrocite). These natural nanoparticles settle onto the continental shelf and are a source of dissolved bioavailable Fe and Fe surfaces that separator and transport organic carbon (OC). Globally, organic carbon associated with reactive Fe on continental shelves is 2900–6000 times the amount of carbon in the atmospheric carbon pool. Reactive Fe therefore plays an important role in regulating the carbon cycle on Earth's surface.

Large Arctic rivers (Yenisei, Ob, Lena, Vuoksa, Kuzonets river) are important suppliers of Fe to the continental shelf in the Arctic Ocean. These rivers drain areas of permafrost (ground that remains at or below 0°C for more than two consecutive years) that preserves a vast stock of organic matter (OM) (Fig. 1). The Arctic is subject to severe climate change and higher surface temperatures are increasing the thickness of the summer active layer (the upper surface of the permafrost that thaws every summer), possibly increasing the supply of organic matter to the continental shelves\(^1\). The capacity for reactive Fe to mobilise, transport and sequester organic carbon in the Arctic remains poorly understood, and so the aim of this study was to quantify and characterise Fe-bearing particles and their relationship with OM in a large Arctic River, the Lena River in northeastern Russia.

The Lena River basin contributes the second largest discharge to the Arctic Ocean, supplying a substantial portion of particulate material to the Laptev Sea estuary and continental shelf\(^2\). Water samples were collected from stations along the Lena River and in major tributaries during the post-spring flood period. These stations span a wide range of topography, permafrost and latitudinal extent. Fe was separated into different size fractions (particles > 0.22 μm, colloids < 0.22 μm – 1 μm, aquares < 1 μm: Fe). The particulate fraction contained the highest proportion of Fe (6.7–70%), and the aquaeric fraction contained the highest proportion of OC (50–60%), in all samples. Transmission Electron Microscopy (TEM) and synchrotron-based Scanning X-ray Spectromicroscopy (SXSM) on beamline I08 were performed on particles from the main channel and tributaries, to characterise the size, mineralogy, Fe speciation and association with organic carbon. TEM images of a 150 nm long aggregate composed of 20–50 nm particles (a). The nanoparticles are sub-randomly arranged as amorphous to poorly-crystalline structure and the SXSM pattern shows two broad peaks at 15.0 nm and 19.5 nm (b), and the TEM data shows the nanoparticles to be composed of Fe (c), alongside minor elemental concentration. The Cu signal comes from the underlying copper grid.

Reactive Fe-bearing particles were present as poorly crystalline particles (200 nm – 1 μm) composed of aggregates of smaller (< 10 nm) spherical nanoparticles (Fig. 2a). The Selected Area Electron Diffraction (SAED) patterns with two broad peaks at 15.0 nm and 22.0 nm (Fig. 2b) and Energy Dispersive X-ray (EDX) peaks of Fe and O (Fig. 2c), indicate a composition of 2-Fe hydroxide. Poorly-reactive Fe-bearing particles were identified as clay particle aggregates (80–500 nm in size) and crystalline iron oxides (hematite, 100 to 200 nm), that are not readily available for biological uptake or surface complexation with OM. Organic matter structures were identified using TEM as micron-sized web-like networks of fibres (Fig. 3a) and micron-sized bacteria cells (Fig. 3b). No ferrihydrite ‘inclusions’ were observed within these structures and these were analysed using SXSM on beamline I08. TEM and SXSM were applied on the same particles, enabling novel comparison between the mineralisation and speciation of Fe associated with organic matter. X-ray fluorescence (XRF) imaging on Beamline 10B at the ESRF was optimised to mapapat particles at a 50 nm resolution and can distinguish between carbon (C), nitrogen (N) and iron (Fe) in the particulate material. Maps in Figures 3c and 3d show that Fe is indistinguishable from discrete nano-size particles amongst C and N-rich regions, suggesting that these OM structures trap and transport Fe in the Lena River basin.

A key study was used to analyse the distribution state Fe in the nanoparticles associated with the organic matter structure. Beamline I08 was optimised for this task due to the 280 – 4400 eV photon energy range and spectral resolution of 4000 over the photon energy range. Stacks of SXSM images were acquired at different photon energies, and were used to make Fe L-edge NEXAFS (Near Edge X-ray Absorption Fine Structure) spectra with a spatial resolution of 50 nm (Fig. 3e). The acquired spectra were compared with spectra of Fe-bearing colloids in Southern Ocean waters\(^3\), and corresponded with Fe(III)-rich particles (Fig. 3e). The combined use of TEM and SXSM shows that organic fibres trap discrete Fe(III) particles, composed of Fe-bearing nanoparticles associated with networks of OM in the Lena River basin, with no evidence of Fe-OC, complexation or a reduced mixed valence Fe. Hence, larger particles of reactive Fe and organic carbon are transported together in large Arctic rivers.

In this study, SXSM and TEM imaging were used to characterise Fe-bearing particles and colloids in the Lena River and major tributaries. Chemically reactive Fe(III) identified as ferrihydrite, that accounts for 70–15% of the total suspended Fe in the Lena River. Aggregates of ferrihydrite (Fe(III) oxide) were deposited in estuarine and shelf sediments and contribute to organic carbon degradation or traps and sequester organic carbon in Arctic shelf sediments. Nanoscale ferrihydrite associated with networks of OM or attached to the surface of clay minerals (Fig. 3); will be transported further across the continental shelf, preserving a source of bioavailable Fe to the Arctic Ocean. The Arctic is subject to severe climate change threatening to alter terrestrial and ocean biogeochemical cycles. We demonstrate that the Lena River, a major Arctic River, is an important contributor of reactive Fe to the continental shelf of the Arctic Ocean. This work places constraints on the present day supply of Fe from a large Arctic river to the Arctic Ocean.
Investigating lithium ion battery failures


Publication keywords: Li-ion batteries; High-speed X-ray imaging; Thermal runaway

The 18650 cylinder is the most widely used lithium ion (Li-ion) cell geometry, powering everything from laptops to electric vehicles. Its capacity has been steadily increasing, and now more than ever, the safety of Li-ion batteries is of the utmost importance. Cell failure is extremely rare during normal operation, but under abusive conditions the active materials within Li-ion batteries break down exothermically, generating large amounts of heat that can lead to a positive feedback loop, fire and even explosions – a phenomenon known as thermal runaway. Rupture of 18650 cells during thermal runaway is one of the most hazardous types of failure, and yet the stages leading to rupture are not well understood. Researchers are investigating the cause of rupture to further our understanding of failure mechanisms and to guide the development of safe next-generation Li-ion cells. To capture the dynamic sequence of events with enough detail, they need to use Diamond’s high-speed X-ray imaging capabilities. The I12 JEEP beamline offers a large field of view for high speed and high energy imaging of Li-ion battery failures. Their results show that the introduction of a bottom vent on commercial cells can help reduce the risk of rupture and improve the safety of the cell.

High-energy density lithium ion batteries are used for a wide range of applications, from portable electronics and medical devices to aerospace and manned spaceflight. Maintaining a high standard of safety for lithium ion cells is more important now than ever before particularly since high-energy density cells are expected to operate under challenging conditions for applications that are often ‘mission critical’. For example, when a battery pack for the auxiliary power unit caught fire on a Boeing Dreamliner in 2014, the entire fleet of aircraft was grounded for several months due to passenger safety concerns.

Catastrophic failure of lithium ion batteries stems from the occurrence of thermal runaway where, at a critical temperature, a series of exothermic reactions cascade throughout the cell. This process generates a lot of heat and produces large amount of product gas, both of which present significant safety challenges to mitigate hazards. For example, the rapid generation of heat and gas inside an 18650 cell can lead to violent rupture and fires. One of the most violent failure mechanisms occurs when the pressure inside cylindrical 18650 cells reaches a critical point where the cell bursts and generates projectiles from its ejection contents. The ejected contents consist of hot, electrically conducting, reacting material that can lead to propagation of thermal runaway to neighboring cells or heat dissipation or short circuiting elsewhere. Identifying the cause of rupture is crucial for manufacturers to carry out an informed approach to engineering safer cell designs. However, in a previously study, igniting was shown to occur in less than 0.01 s, which along with the events occurring inside a steel casing, makes the dynamic occurrences particularly challenging to capture and characterise.

High energy and high flux synchrotron X-ray sources such as Diamond Light Source hold the exceptional capability of carrying out high-speed and high-resolution X-ray imaging with a high energy beam. One of the most rapid failure mechanisms of lithium ion batteries can be captured in detail and the interaction between the mechanical design of commercial cells and the rapid internal structural dynamics during thermal runaway can be examined. In this study, high speed X-ray imaging at up to 4000 frames per second (fps) was used to elucidate the stages that lead to violent rupture of 18650 cells. The failure mechanisms of different commercial cell designs (Fig. 1) were characterised and compared with respect to safety and merits associated with their respective designs. Failure mechanisms were characterised into four different types: controlled explosion, cell bursting, top bottom puncture and escape of internalmund. The unprecedented spatial and temporal resolution achieved at I12 allowed the distinct stages that lead to each type of failure to be classified (Fig. 2). For example, across all cell designs, three consistent steps provided violent rupture and ejection of cell contents. First, the spin-groove extended (see labelling of components in Figure 1), followed by the electrode assembly shifting and clogging the vent, and finally, the top-fold straightened out and released the header components leading to ejection of the entire electrode assembly.

The shift of the electrode assembly towards the vent that led to clogging, is thought to have resulted from an insufficient gas flow being able to pass through the core of the assembly from the base of the cell. This led to the electrode assembly shifting in the direction of the escape path towards the vent, hindering the flow of escaping gas, and leading to a rapid pressure rise within the caving of the cell. A practical application of this result was then explored by introducing a second vent on the base plate of an 18650 cell. The simultaneous relief of pressure from the top and bottom of the cell was shown to drastically reduce the risk of violent rupture and ejection, most notably by improving the relief of generated gas and avoiding the shift of the electrode assembly that previously caused clogging.

The insights achieved in this work indicate that to achieve a high standard of safety for next generation lithium ion batteries, cell designs must evolve to not only restrict the occurrence of thermal runaway to different commercial design but to also minimize the impact of the rapid internal structural dynamics of the cell. In this study, high speed X-ray imaging was used to link internal structural dynamics to external risks posed during thermal runaway, and demonstrates the potential of this diagnostic approach to be combined with other metrics of risk such as heat generation, gas generation, and internal temperature measurements.

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References:
Corrective glasses provide sharper X-ray vision

The intense X-ray light produced by modern synchrotron radiation sources and X-ray free-electron lasers (XFELs) allows the fine structure and dynamics of matter to be studied in exquisite detail. In principle, beams should be able to be focused to a few nanometres and below. Such small intense X-ray nanobeams are crucial to concentrate the radiation onto a given sample. However, the beam’s short wavelength places stringent requirements on today’s X-ray optics, which limit resolution due to refractive, diffusive, or reflective distortions (known as aberrations) of the resulting image.

To understand and correct these distortions, an X-ray microscopy technique known as Ptychography, was performed at Diamond Light Source’ s X-ray Imaging and Coherence beamline (I13), which offers a very flexible optics and sample environment, ideal for testing new X-ray optics. Using the Coherence Branchline (I13-1), built specifically to provide resolution beyond the limitations of X-ray optics and scintillator-detected X-rays, Ptychography elucidated the wavefield created by the X-ray optics with high spatial resolution and sensitivity. From this, wavefront errors from the optics alone were plotted in great detail to design appropriate corrective glasses. Capable of correcting optics beyond current manufacturing limitations, the glasses consist of an X-ray phase plate placed on the optical path following the lens to achieve free performance and highest possible NA.

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Corrigenda for previous publications:

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With this novel scheme, many X-ray optics can be improved in performance beyond current manufacturing limitations. The principle is not only applicable to refractive optics as shown here, but can also be transferred to reflective and diffractive optics as well. As the glasses are very compact and easy to align, they can also be retrofitted to existing beamline optics. This benefits not only the resolution and sensitivity in classical X-ray microscopy schemes, but may also lead to new opportunities for refractive X-ray heating and non-linear X-ray optics at XFEL sources.
Imaging and Microscopy Group
Beamline I13 (Imaging Branchline I13-2)

Imaging multiphase fluid flow in permeable media


Publication keywords: Multiphase flow, Permeable media, Snap-off, Capillary trapping, Pore-scale displacement

Knowing how fluids move through micron-sized voids (or ‘pores’) in rock kilometres below the Earth’s surface is crucial information to help understand and optimise underground carbon dioxide (CO₂) sequestration, oil recovery from reservoir rocks, and other host processes. Oil and gas can be trapped in pores as water flows through the rock, with strong trapping beneficial for CO₂ storage and weak trapping preferable for efficient oil recovery. However, the exact nature of trapping at the pore scale is not well-understood, with inhibiting viscous and driving capillary forces both thought to play an important role in controlling flow during trapping events.

To illuminate this process, an innovative flow apparatus was engineered to replicate the high pressures and temperatures seen in reservoirs. With the Diamond Manchester Imaging Branchline (I13-2) within the X-ray Imaging and Coherence beamline (I13) at Diamond Light Source, fluid flow was carried out at 50 MPa in a tilted, micrometre-scale, and with a time resolution around of a few minutes. I13-2 offers photon flux over a million times higher than that of a laboratory X-ray source, perfect for studying rapid dynamic processes like fluid displacement. As a result, the time-resolved imaging provided pore-by-pore analysis of the local capillary pressure during trapping events. Results reveal that water pushes oil into pore spaces in approximately 10 minutes – orders of magnitude slower than the opposite process when oil pushes out water from the pore space. After trapping, the oil rearranges in the pore space to find a new position of minimum energy and the capillary pressure increases rapidly. These new insights provide useful information to build novel models predicting how these fluids flow and how much oil or gas is trapped.

Multiphase fluid flow in permeable media is a complex pore-scale phenomenon, which has many applications in natural and industrial processes, such as water infiltration in soils, oil recovery from reservoir rocks, gas-sequestration of supercritical CO₂, to address global warming, and subsurface non-aqueous phase liquid contaminant transport. At the pore scale, the two most important processes that compete during the displacement of a non-wetting (hydrophobic) fluid by a wetting (hydrophilic) fluid are pore-filling or piston-like displacement and snap-off; this latter process can lead to trapping of the non-wetting phase. The trapping of the non-wetting phase is important for CO₂ storage, a maximum trapping efficiency is desired whereas for oil recovery, less trapping is preferable for efficient production. Although, there are several studies reported on two-dimensional visualisation of fluid displacement and trapping, the dynamics of injection processes (displacement of a non-wetting fluid by a wetting fluid) leading to snap-off have not been investigated in such details in realistic three-dimensional geometry. The time-dependent information is important to stabilise models of pore-scale displacement and to quantify how the balance of viscous and capillary forces controls the trapping process.

We conducted dynamic flow experiments in a 3.0 mm diameter and 10 mm long Ketton limestone sample. The sample was first saturated with brine. The system was pressurised to 10 MPa, followed by injection of oil (a high-slip, low-surfactant aqueous brine solution) through a non-wetting (hydrophobic) fluid by a wetting (hydrophilic) fluid to a pressure gradient of 50 kPa. The sample was imaged in three dimensions continuously during drainage using a pink beam (with photon energy of 17 keV) and with a time resolution of 10 ms. When the brine-oil interface reached the end of the oil-filled throats, the sample was imaged during steady-state drainage. The drainage processes were photographed using a pink beam (with photon energy of up to 30 keV) at beamline I13-2. We used a voxel size of 3.2 μm and a time-step of 10 s between each three-dimensional data collection. After the completion of the drainage process (identified when there was no longer any visible change in fluid saturation), the flow was reversed by injecting brine (imbibition process) from the base of the sample at a pressure gradient of 22 kPa. The sample was imaged continuously during imbibition.

Figure 1 shows the oil phase at various time steps during drainage (Fig. 1a) and imbibition (Fig. 1c-h). The residual oil at the end of imbibition contains a number of disconnected ganglia (trapped phase), represented by different colours (Fig. 1c). A complete three-dimensional image sequence of drainage and imbibition processes is shown in videos (Videos 1 and 2).

In this study, our aim was to obtain a complete understanding of various pore-scale displacement and snap-off events that result in trapping of the non-wetting phase in the pore space. Figure 2 shows snapshots of one of the pore-filling and trapping events during imbibition. The complete three-dimensional sequence of the oil displacement process is shown in the video (Video 3). During brine injection, the brine-oil interface moves from pore to pore in a piston-like displacement without oil trapping, until it reaches the pore space marked by the red circle (Fig. 2e). Here, the brine (not shown for effective visualisation) in the adjacent oil-filled throats starts to swell. The brine layers in the throat continue to grow until the brine-oil interface is no longer stable, resulting in snap-off of the interface and trapping of the oil.

To explain the snap-off process quantitatively, we analyse the local capillary pressure (calculated from the Young-Laplace equation, P_c = -σ cosθ/ r, where P_c is the capillary pressure, σ is the interfacial tension between oil and brine, and θ is the total curvature estimated from an analysis of the segmented image). A sequence of time and injected brine volume during the pore-filling and snap-off events observed in Figure 2A for the capillary pressure, time and normalised oil volume is shown in Figure 3. Here, the ganglion and connected side represent the values measured on the left and right side of the X-X section respectively (shown in Fig. 2a). The X-X section was selected in the throat where the snap-off occurred (Fig. 3b). From Figure 3a, we observe that the capillary pressure on both sides decreases approximately linearly with injected brine volume and time. The brine-oil interface migrates from left to right without any trapping (representing pore-filling events). At point A (Fig. 3b), we observe a rapid increase in the oil volume in the subset near the throat (open symbol in Fig. 3b corresponding to the red box in the most picture). This is linked to the capillary pressure gradient, caused by a sudden decrease in the local capillary pressure in the ganglion side (Fig. 3a), which drives the brine flow towards the throat. Then after 46 minutes, we observe a pore-filling event that occurs between points A and B where the capillary pressure remains approximately constant (Fig. 3c) while locally the oil saturation decreases rapidly (Fig. 3d). This type of pore-filling behaviour, however, has not been seen or hypothesised hitherto in drainage as we see rapid changes in capillary pressure at a constant saturation.

Beyond point B (Fig. 3), there is an apparent disparity in capillary pressure across the system, which drives brine in layers to flow from the ganglion to the connected side. This represents a swelling of wetting layers in the throat, as can be seen by an incremental reduction in oil volume in the throat subset in Figure 3b (open symbols). Eventually at point C (Fig. 3a, 3c), we see snap-off, resulting in the trapping of all ganglion in the pore body. When this happens, there is a rapid rise in capillary pressure in the ganglion-side, indicating a lower energy configuration. The remarkable feature of this analysis is that the swelling of wetting layers proceeds over approximately 14 minutes. This is many orders of magnitude slower than the sub-millisecond filling observed during a drains jump in drainage.

We have investigated three different snap-off events for different pore topologies and fluid configurations, which are reported in Singh et al. The time-scale for brine layer swelling in all the studied events are of the order of tens of minutes, followed by instantaneous snap-off processes. After snap-off the local pore-scale capillary pressure rise as the ganglion realigns to find a lower energy configuration.

In conclusion, the time-resolved X-ray micro-tomography provides new insights into pore-scale fluid displacement in three-dimensional porous media. This has led us to investigate the pore-filling and snap-off events that lead to the trapping of the non-wetting phase. These findings have important implications in many fields such as oil recovery, CO₂ sequestration and remediation of oil-contaminated sites.

References:

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State-of-the-art electron microscopy offers clarity on diamond defects


Publication keywords: Type Ia diamonds; Platelet defects; STEM; TEM; EELS

Flawless diamonds are extremely rare and expensive. Most diamonds contain defects, and for scientific and industrial applications, the defects are very important. In a naturally-formed diamond, the presence and structure of defects can be used to accurately determine the geological environment in which it was formed. The defects also shape the electronic and optical properties of diamonds, and exploiting these properties in synthetic diamonds could lead to next-generation optical storage devices, high-frequency field-effect transistors (FETs) and high-power switches.

Research into the nature of diamond defects has uncovered more than a hundred different optically-active types, many of which have an unknown atomic configuration. For more than 50 years, researchers have been investigating the platelet defect. A number of theoretical structure models have been proposed, but imaging techniques were unable to give experiments the atomic-resolution necessary to confirm or discard them.

Now a team of researchers have made use of recent advances in electron microscopy, at the state-of-the-art electron Physical Science Imaging Centre (ePSIC), to solve the mystery of the platelet’s structure. They used a combination of atomically-resolved scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) to uncover the structural details of a natural diamond, and confirm the correct structural model. Further studies could shed light on how the platelet defect is formed, or structures of other types of defect, and this remarkable step forward could bring new opportunities for tailoring optical and electronic properties of diamond.

The nature of defects in diamonds has attracted considerable scientific interest, mainly due to their role in shaping electronic and optical properties. They may well hold the key to next-generation devices, including optical storage, high-frequency field-effect transistors and high-power switches.

Over 100 different types of optically-active defects have been identified, and in a natural diamond the presence and structure of defects plays an important role in defining colour and quality, and can be used to accurately determine the geological environment in which it formed.

Nitrogen is a common impurity in diamond, forming several different types of defect. The presence and quantity of nitrogen-related defects is fundamental to diamond classification (Fig. 1). Type Ia diamonds have a high concentration of nitrogen, and related absorption bands in their spectra. They are further classified depending on whether nitrogen is present in an aggregated form (type ia), or in isolated substitutional sites (type b). Diamonds with a low concentration of nitrogen, which do not show the absorption bands, are classified as type Ib.

In natural type Ia diamonds, nitrogen aggregates occur with and within extended defects on {100} planes, called platelets. Platelets have a typical diameter of tens to hundreds of nanometers. They are optically active in the infrared, with a frequency that depends upon the size of the platelet. Platelet defects are common in both natural and synthetic diamonds, but their exact atomic configuration has been a mystery for more than 50 years.

In 1940, Raman and Nikanikant used X-ray diffraction to make the first observations of platelets in diamonds, and these were characterised by Evans and Phaal in 1962 using TEM. A number of theoretical structural models were proposed, but until now these could not be tested experimentally.

Using STEM and TEM to image carbon materials is particularly challenging, as the light atoms show a low contrast and are easily displaced by electron irradiation. The interatomic distances that need to be resolved are shorter than most other elements, and it is only now that recent advances in aberration-corrected electron microscopy at low voltage have made it possible to image platelets with sub-Angstrom spatial resolution and sufficiently high contrast.

Using atomically-resolved scanning STEM, TEM and EELS, a team of researchers from the UK and South Africa have imaged the atomic structure and local chemistry of platelets in a natural type Ia diamond.

Previous work found evidence of a strong link between nitrogen and platelets, suggesting that nitrogen may play an important role in the formation and structure of these defects. EELS spectra from the core of several platelet defects revealed the presence of a nitrogen K-edge, and subsequent studies (also predominantly using EELS) confirmed the detection of measurable quantities of nitrogen in platelets. However, the quantities detected are generally too low to support a nitrogen-only platelet structure; the presence of carbon is also necessary.

The new study presents aberration-corrected high-resolution STEM images, which show the atomic arrangement in the platelet core. Its findings are supported by EELS data from the core, which enable a complete description of the platelet structure.

The team used aberration-corrected STEM imaging in high-angle annular dark field (HAADF) mode, together with EELS spectrum imaging, to study the atomic structure and chemical composition of platelets in greater detail (Fig. 2). They also recorded high-resolution TEM (HREM) images, and then qualitatively compared HREM and STEM images to simulated images generated from the various theoretical structural models.

High spatial-resolution EELS spectrum imaging was used to investigate the presence, distribution and coordination environment of nitrogen in the platelets, taking care to use sufficient flux for accurate signal detection while avoiding progressive electron-beam induced damage of the platelet structure. The results showed clear evidence for the presence of nitrogen within the defect.

The change in the EELS structure of the carbon K-edge at the defect core, and its similarity to the nitrogen K-edge, indicates that the defect core contains both atomic species in an integral arrangement. The presence of a pre-edge feature in both carbon K- and nitrogen K-edges indicates trigonal distortion of the lattice with the consequent coordination environment of the nitrogen atoms being three-fold rather than four-fold.

The experimental results favour one particular structural model, the ‘jiggag’ model, in which interstitials of carbon or nitrogen are arranged at alternating (jagged) sites. They also confirm earlier studies showing that the platelet is primarily composed of carbon, with a small fraction of nitrogen.

It is still unclear how these platelet sites form and the role of nitrogen in their formation, and further studies at different stages of platelet formation could further our understanding. However, this is a remarkable step forward in characterising a challenging material, and it is hoped that these new imaging capabilities will also shed light on other diamond defects with unknown structures. A new level of clarity on the atomic structure of these defects will offer up new opportunities for tailoring the optical and electronic properties of diamond.

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Platelet A

Platelet B

Figure 1: Atomic characteristics of platelets in diamond. (a) Bright-field STEM image of a platelet in diamond. The platelets are 200 pm and 500 pm planes are wavenet edge-on and top-down respectively. [110] planes are also visible. (b) High-resolution STEM image showing a single platelet. The beam direction is parallel to <110>. The diameter of tens to hundreds of nanometers is visible. (c) HAADF STEM image of diamond viewed along an beam direction showing the nitrogen K-edge at the platelet structure.

Figure 2: High-resolution HAADF STEM image of two platelets viewed edge-on along <110> directions showing the atomic structure at the platelet core. (a) Image of platelet A, (b) Image of platelet B. Reprinted by permission from Springer Nature. [Olivier EJ et al. doi:10.1038/s41563-018-0024-6 (2018)].
Crystallography Group
Heribert Wilhelm, Science Group Leader

The Crystallography Science Group comprises beamlines I11, I15, I15-1, and I19, members of the former Engineering & Environment and the Materials Villages. The reorganisation of the beamlines into Science Groups will enhance the collaboration across Diamond.

Furthermore, the technical and scientific expertise within the Crystallography Science Group can be fully exploited to provide the basis for future development and pioneering experiments.

The Crystallography Science Group beamlines employ various X-ray scattering and diffraction techniques to study structural properties of crystalline, amorphous, and liquid materials at ambient and different non-ambient conditions. These powerful facilities are used for a wide range of science disciplines, from Condensed Matter Physics, Chemistry, Engineering, Earth and Materials to Life Sciences. Important research fields cover in situ studies of batteries, synthesis of new materials as well as structural studies at extreme temperature and/or pressure conditions. The high demand and productivity of the beamlines are reflected by the output of about 150 publications in 2017.

I11 Update

The High-Resolution Powder Diffraction Beamline (I11) uses monochromatic X-ray beams with high brightness and energies in the range of 6 – 25 keV for high-resolution and time-resolved powder diffraction experiments, either in the first experimental hutch (EH1) or for long duration experiments (LDE) in EH2. The beamline provides a suite of different sample environments for high-temperature studies of crystalline and amorphous materials. This includes an external furnace, a high-pressure high-temperature cell, and a high-temperature furnace. The high-temperature furnace is in operation only for a few years, is high in demand for studies on high-temperature materials and is a valuable tool for studying materials under extreme conditions.

I15-1 Update

The X-ray Pair-Distribution Function Measurements beamline (I15-1) employs three discrete energies – 40, 65, and 76 keV – of the X-ray spectrum, as well as an energy range of 5 – 25 keV to determine the structures of single-crystalline molecules or for the study of structural changes induced by a physical variable, such as high pressure (see highlight by E. Brechin) or gas exposure.

The transport of pre-mounted samples to Diamond and a cryogenic storage has been realised during last year. It ensures that the samples are stored under controlled conditions until they are loaded into the beamline immediately prior to beamtime. This has proved the way for remote-access operation of the beamline. Users from the North-East England BioSS have moved to operating the beamline completely remotely from the University of Newcastle – including sample exchange, data collection and processing. This mode of operating in the first experimental hutch (EH1) makes it possible to carry out chemical crystallography studies in a more responsive manner as beamtime can be scheduled in more regular and shorter periods.

An on-axis viewing camera has been installed in EH2 to improve the alignment of the crystals. The system also includes a spectrometer for in situ ruby-fluorescence measurements, needed for the determination of the pressure exerted to the samples contained within gas-membrane driven diamond-anvil cells. New forms of high-pressure structure determinations can be carried out without the need to remove the pressure cell from the diffractometer for each pressure change. Furthermore, a static liquid-cell has been developed in collaboration with the University of Edinburgh. It operates between a few hundred bar to several GPa of pressure, i.e. a pressure range of most interest to technological applications. It allows the pressure to be adjusted in fine steps and structural information to be obtained to a high degree of crystallographic detail.

Figure 7: The extreme conditions beamline (I11) provides poly- and monochromatic X-rays in the energy range of 10 – 20 keV for high-resolution and time-resolved powder diffraction experiments, either in the first experimental hutch (EH1) or for long duration experiments (LDE) in EH2. The beamline team, together with the controls and software groups, continues to make strides towards their vision of providing quality, automatically processed PDF data at the point of data collection. The database, which will store the required sample information, is complete. The collected two-dimensional scattering data are already automatically processed into one-dimensional PDF data in the PDF analysis software. PDF data processing within Diamond’s DARWIN software is undergoing further improvements before an anticipated release later in 2018.
Moving towards renewable raw material sources


Publication keywords: Decarbocation, Synchrotron X-ray diffraction, Zn/ZSM-5

The world currently relies on coal, oil and gas, not only for fuel but also as raw materials for the production of chemicals. With reserves of these fossil fuels running out, and a growing awareness of the CO₂ pollution their use causes, it is becoming increasingly important to develop sustainable carbon sources. One option is to use biomass, dry plant matter, and a team of researchers have demonstrated a new method for converting biomass into butene gas, which in turn can be processed into the chemicals used in the production of polymers and resins.

Their work uses Gamma-valerolactone (GVL), a chemical processed from biomass raw material, and the catalyst Zn/ZSM-5, and demonstrates that it is possible to use a renewable source material to produce benzene, toluene and xylene.

They used high-resolution X-ray powder diffraction (SRXD) on III to examine the structure of their samples, which yielded important information about the reaction mechanism. This was the first time that SRXD had been used to investigate the structures of adsorbed structures of the Gamma-valerolactone GVL and immobilized Zn-species used in the research. The results are a step towards affordable, sustainable chemical prediction.

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Using high temperature and pressure to form novel materials

Chemistry drastically changes at very high pressures, allowing exotic types of chemical interactions leading to the formation of novel materials. For mixtures of iron (Fe) with a significant amount of nitrogen (N), theoretical calculations suggested that new Fe-N compounds could be synthesised at high pressures, and are expected to have enhanced properties such as increased hardness, superconductivity, or the ability to act as a catalyst.

A team of researchers used I15 to carry out this research, because this beamline provides an intense and highly focalised X-ray diffraction that allows investigation of the atomic structure of the compounds produced. A new laser-heating setup on I15 allowed the experiment to reach temperatures up to 1700°C and pressures of 128 GPa — more than a million times the atmospheric pressure — by employing a laser-heated diamond anvil cell.

Over the course of their experiments, the scientists saw the development of three compounds, ZnS-type FeN, Fe3N, and NiAs-type FeN, which they were able to characterise using X-ray powder diffraction. Above 17.7GPa, the FeN compound adopting a NiAs-type structure was formed, remained stable as the pressure was reduced, and could be removed for analysis of its physical and chemical properties. However, they did not observe the iron pernitride FeN2 that was predicted by the theoretical calculations. Their results will help to increase the accuracy of the theoretical calculations, and will lead to new insights into the intriguing chemistry of Fe-N compounds at high pressures.

The membrane diamond anvil cell (DAC) allows the generation of extreme pressures by squeezing a small sample in between two diamond anvils. The synthesis of new compounds in this hand-sized device can be noticed and characterised using synchrotron X-ray diffraction. Indeed, the interaction of energetic X-rays with a periodic atomic arrangement, such as crystals, produces an interference pattern (diffraction pattern) from which the periodic atomic lattice and some information about its integrity can be precisely determined. To help cross energy barriers impeding a possible chemical reaction towards the most stable compound at a given pressure, heating the sample up to 2000 K is vital and is achieved by focusing two high power infrared lasers on the sample. This complex, double-sided laser-heating setup was investigated by performing powder X-ray diffraction.

Below 12 GPa, laser-heating of the samples resulted in the synthesis of the previously discovered Fe4N compound.

The FeN compound was characterised by powder X-ray diffraction up to 128 GPa with frequent laser-heating but no further chemical or structural transformations were observed. The evolution of the FeN compound’s unit cell lattice parameters and volume with pressure is shown in Figure 2. Based on these measurements, valuable information regarding the compound’s equation of state, its compressibility as well as the evolution of the chemical interactions between the Fe and N atoms could be inferred. By fitting a third order Birch-Murnaghan equation of state to the data, the volume was found to increase with pressure. The bulk modulus of FeN is 13.7(2) GPa at ambient pressure.

The FeN compound in its NiAs-type structure proved to be retrievable down to ambient conditions after the complete release of pressure. However, a partial structural phase transition of FeN in its NiAs-type of structure into Fe3N in a ZnS-type structure was detected, with the latter being a phase previously produced exclusively in thin films. Interestingly, neither of these two phases are thermodynamically favored below 10 GPa, where the FeN compound, although of different stoichiometry, is energetically favored. This result underlines the large activation barriers impeding chemical reactions necessary for a change in stoichiometry (FeN → Fe3N) as opposed to an effortless structural transition (NiAs-FeN → Fe3N). With this conclusion in mind, the laser-heating of the FeN compound at high temperatures could very well result in the synthesis of yet another nitrogen-rich FeN solid, such as the theoretically predicted iron pernitride FeN2.

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Metal organic frameworks (MOFs) are crystalline materials, which are receiving a lot of interest due to their porous nature, which allows them to accommodate guest molecules within their structure. Potential applications include drug delivery, catalysis, and the capture or separation of gases. There are around 60,000 MOFs, and until very recently research had focused on their solid form.

For this new study, the team investigated the structure of ZIF-4 at Diamond, the Advanced Photon Source in Chicago and ISIS Neutron and Muon source, using their results to produce a computational model of the glassy state from which they could infer the structure of the liquid state. Their results show that this MOF retains its porous structure in its liquid form. This opens up a whole new area of research, investigating whether other MOFs also behave in this way, as well as discovering the properties and potential applications of liquid and glass MOFs.

Metal-organic frameworks (MOFs) continue to be of interest for a variety of applications such as gas sorption, separation, drug delivery, harmful waste storage and catalysis. The overwhelming majority of research concentrates on the retention of coordinative bonding between crystal and liquid phases. ZIFs, for example, exhibit liquid-like behaviour upon melting, resulting in a good fit to the experimental structure factors. To investigate the mechanism of melting, synchrotron X-ray diffraction data were collected at the Advanced Photon Source, USA (APS), to evaluate structural changes in the glass upon heating. The pair distribution functions (PDFs) contain the expected peaks at approximately 1.3 Å, 2 Å, 3 Å, 4 Å, and 6 Å, which correspond to C-C, C-N, N-N, N-C, C-N and Zn-N pair correlations, respectively. Constant temperature molecular dynamics simulations were also carried out, with the PDFs obtained showing similar trends to the experimental ones (Fig. 3). The high temperature experimental data on the liquid MOF phase at 865 K was modelled using NW-PM2, providing the first configuration for a liquid MOF (Fig. 3b). Simulations also provided the opportunity to build up a molecular picture of the melting process (Fig. 4), showing how it proceeds via dissociation of an imidazolate ligand from a Zn4 tetrahedron, followed by a different coordination environment.

![Image](https://via.placeholder.com/150)

**Figure 1:** (a) The construction from metal and linker of ZIF-4 tetrahedron, the basic building unit of ZIF-4 (b), imidazolate, Zn, green, N, blue, C, grey. (b) Representation of the cage topology adopted for ZIF-4, where each polyhedron corner corresponds to one Zif-4 tetrahedron. (c) Crystallographic structure of ZIF-4, (d) with the cations represented in orange.

![Image](https://via.placeholder.com/150)

**Figure 2:** (a) Experimental neutron structure factor (PDF) data and the fit from the configuration shown in (b). inset: X-ray data and fit. (b) Atomic configuration of the melt-quenched glass, gained from modelling synchrotron and neutron total scattering data.

![Image](https://via.placeholder.com/150)

**Figure 3:** (a) Experimental glass (top) and computational ZIF-4 (bottom) X-ray structure factors upon heating. (b) Atomic configuration of the ZIF melt, gained from reverse Monte Carlo modelling of the total scattering data collected at 856 K. Free volume is represented in orange, Zn atoms in green, N in blue, and C in grey.

![Image](https://via.placeholder.com/150)

**Figure 4:** Visualisation of a representative imidazolate exchange event. Zn, green; N (initially coordinated), light blue; N, blue; N (coordinated after exchange), orange; C, grey.
Putting the squeeze on Re$^{IV}$


Publication keywords: Rhenium; High pressure X-ray crystallography; High pressure SQUID magnetometry; Magnetic order

Materials that have long range magnetic order are fundamental to modern technologies, including data storage devices, space research, cancer therapy and biomedical imaging techniques. Future miniaturisation of these components depends on designing molecules that behave in the same way as larger magnets, and to do this we need an improved understanding of the connection between molecular structures and their resulting properties.

Although high-temperature- and high-magnetic-field-based studies are common in molecular chemistry, the effect of high pressures is less well explored. A team of researchers has therefore studied the effect of increasing hydrostatic pressure on rhenium(IV) compounds that exhibit long range magnetic order. They used small-molecule single-crystal diffraction on Diamond’s I19 beamline to provide high-precision measurements able to monitor small changes in the structure, and high-pressure magnetometry to explore the link between the structural changes and changes in magnetic behaviour.

Their results showed that applying pressure to single crystals of rhenium(IV) compounds shortens distances between molecules in the crystal, with corresponding changes to magnetic behaviour, including an increase in the temperature at which long range magnetic order occurs. (Re(Cl)$_2$(HNEt$_2$)][ReCl$_3$] (blue circles), and the strongest magnetic exchange interactions ($J$ = 60 K).

For the Re–Re distances shorter would be expected to increase the strength of the exchange and increase the ordering temperature, and one method of achieving this is to exert hydrostatic pressure. By combining high-pressure single-crystal X-ray crystallography and high-pressure SQUID magnetometry, in tandem with detailed theoretical analysis, the relationship between changing structure and changing magnetic behaviour can be extracted, and the underlying physical origins of the behaviour revealed.

Compounds 1 (Phme) and 2 (P$_2$(Z)$_2$) crystallise in orthorhombic space groups. For the 16$^{-}$ and 2$^{15}$, the metal ion occupying a distorted atabulad environment, bonded to two H-atoms and four halides. The extended structures display staggered zig-zag chains that propagate along the a-axis of the unit cell via interhalide dispersive interactions (Fig. 1). Under pressures of up to 4.30 GPa unit cell volumes decrease by 20% (T1) and 14% (T2), the principal component of compression occurring along the a-axis of the unit cell in both cases. 2 undergoes a phase transition between 1.91 GPa and 3.06 GPa to a monoclinic phase with space group $P2_1$ and when subjected to complete compression-decompression cycles to 4 GPa, both 1 and 2 return to their original ambient pressure unit cell space group. In addition, ambient pressure crystal structures solved at T = 4 K show both species retain their room temperature structures.

The most significant structural changes observed under pressure in T 2 occur in the intermolecular Re–Re–Re distances. For the Re–Re–Re distance shorter by 6.4 Å at 3.32(11) Å, while for the 2 the Re–Re–Re distance decreases by 0.3 Å to 3.57(2) Å.

High pressure SQUID magnetometry performed on monocrystalline samples of 1 and 2 in a tabbuckle diamond anvil cell, shows that the application of hydrostatic pressure leads to an increase in ordering temperature (Fig. 2). At the highest pressures measured, $T_c$ (determined from field cooled and zero-field cooled measurements as a function of temperature) reaches 28 K at 4.10 GPa for 1, and 42 K at 4.30 GPa for 2. For 1 this represents a four-fold enhancement, with the rate at which $T_c$ increases being 5.1 and 5.4 K GPa$^{-1}$ for 1 and 2, respectively. The phase transition observed for compound 2 does not affect the monotonous increase of the ordering temperature, and in both cases the changes in $T_c$ are reversible, recovery of the ambient pressure $T_c$ is observed when the pressure is released from the cell. Density functional calculations show that the shortest Re–Re–Re pathways generate the most efficient magnetic exchange interactions $J$ at all pressures, and that an increase in the magnitude of $J$ in 1 and 2 is obtained when external pressure is applied, in agreement with increasing $T_c$ in both systems. Indeed, the correlation between parameters is straightforward, external applied pressure produces a linear increase in $T_c$ and a linear increase in $T$ (Fig. 3).

The use of multiple high pressure techniques is a simple and efficient methodology for probing structure-property relationships. For synthetic chemists it has the added advantage of negating the need to make families of compounds that may differ electronically. In this instance, the pressure-induced enhancement of the magnetic ordering temperatures of two spin-canted Re$^{IV}$ systems can be directly correlated to changes in structure, specifically Re–X–Re distances, through the combined use of single-crystal X-ray crystallography and SQUID magnetometry, allowing unprecedented insight into the underlying physical origins of behaviour in a step-by-step manner.

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Organisms | Tissue | Cells | Organelles | Complexes | Proteins | Atoms
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**Computational Tomography**

- **1-2 mm**
  - Fluorescence Microscopy
  - Cryo-Soft X-ray Tomography
  - Cell Electron Tomography
  - Single Particle Electron Microscopy
  - X-ray Crystallography

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**B24 exploits cryo-soft X-ray tomography (cryo-SXT),** which is a powerful technique for imaging intact cells in their near native state to resolutions of 25–40 nm. The technique sits neatly in the resolution gap that exists between electron and light microscopes and its real power lies in its ability to provide 3D imaging of whole cells with little or no chemical or mechanical modification. A schematic of the various imaging techniques available to biologists and how B24 and cryo-SXT fits into this tool set is shown in Figure 1. Cryo-SXT provides a unique tool to aid biologists to understand many key cellular and disease processes. One of the first external user experiments at B24 applies illustrates the power of the technique where Halle et al used B24 to visualise red blood cells infected with the malaria parasite *Plasmodium falciparum*.

The user program at eBIC has continued to grow rapidly in 2017 with two new Titan Krios 300 KeV microscopes (Thermofisher) brought online, taking the total number of high-end microscopes to 4. eBIC is also heavily engaged in developing a user program for cellular studies and during 2017’s cryo focused ion beam scanning electron microscopy (cryo-SIM) has allowed correlative imaging with the B24 X-ray microscope to be developed and workflows are currently being optimised which allow users to take acryo-electron tomography (cryo-ET) at eBIC. The development of the facility is in joint collaboration with the advanced microscopy unit, MRC, at the University of Oxford. B24 is now in the final round of commissioning and optimisation with users and will enter full user operation in the summer of 2018.

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**eBIC is the first high-end cryo-electron microscopy (cryo-EM) facility worldwide to be embedded in a synchrotron and user operations have been set up to mirror the well-established synchrotron model. The centre is funded by the Wellcome Trust, the Medical Research Council (MRC) and the Biotechnology and Biological Sciences Research Council (BBSRC). eBIC has rapidly developed since it welcomed the first user group in July 2015. A key aim of the centre, enabled by the synchrotron access model, was to provide a state-of-the-art facility for single particle cryo-EM and cryo-ET through cost-effective, peer-reviewed access based on scientific excellence. The rapid provision of high-end microscopes and the embedding within Diamond has allowed this vision to be realised at breakneck speed and the success of the eBIC model has inspired other synchrotron sites worldwide to follow suit.**

**In addition to providing cost-effective access to high-end microscopes for cryo-EM and cryo-ET, eBIC provides a focus for future hardware and software developments and advanced training for the community. The latter has been exemplified by specialised hands-on training workshops in sample preparation for cryo-EM as well as specialised training courses in collaboration with the Collaborative Computational Project for electron cryo-microscopy (CCP-EM, ccpem.ac.uk) which is funded by the MRC and based at the University of York.**

**In collaboration with eBIC, the European cryo-EM facilities have been extremely successful, although are heavily oversubscribed. This is due to sample preparation for cryo-EM remaining a major bottleneck and expertise in the community is lacking which is reflected in the greater than 10-fold oversubscription for the first two practical workshops dedicated to this topic at eBIC in January and October of 2017. Advanced training with support from CCP-EM, and the European funded Horizon 2020 project NEXT (next-em), with which Diamond is a partner, will continue through 2018–19.**

**On the computing front, on-the-fly processing of data has been rolled out and management of data collected and processed at eBIC will be presented in the information system (ISPyB) that is now being developed for use by cryo-EM. The latter project is being coordinated by Diamond through the H2020 NEXT project and will be available for use in the near future at all the European cryo-EM centres. These software developments have been carried out in collaboration with CCP-EM and the developers of the Scipion framework which brings together numerous software packages for EM and presents them to the user in a unified interface for both biologists and developers. This has enabled the accelerated development of these automated workflows at eBIC and ISPyB will provide added value and provides a key tool for users to allow remote access use of eBIC to be realised.**

**The user program at eBIC has continued to grow rapidly in 2017 with two new Titan Krios 300 KeV microscopes (Thermofisher) brought online, taking the total number of high-end microscopes to 4. eBIC is also heavily engaged in developing a user program for cellular studies and during 2017’s cryo focused ion beam scanning electron microscopy (cryo-SIM) has allowed correlative imaging with the B24 X-ray microscope to be developed and workflows are currently being optimised which allow users to take cryo-electron tomography (cryo-ET) at eBIC. The development of the facility is in joint collaboration with the advanced microscopy unit, MRC, at the University of Oxford. B24 is now in the final round of commissioning and optimisation with users and will enter full user operation in the summer of 2018.**

**In summary the new Biological Cryo-Imaging Group at Diamond is at an exhilarating stage of development and we expect research and development to continue at a fast and exciting pace through 2019 as we bring all the instruments in the group fully online.**
How malaria parasites break out of red blood cells during the infection cycle


**Publication keywords:** Malaria; Egress; Electron tomography; Soft X-ray microscopy; Electron energy loss spectroscopy

**Abstract:**

Malaria is a highly infectious disease that is widespread in tropical and sub-tropical regions of the world. It is caused by a group of parasitic single-celled microorganisms, which are carried by mosquitoes. When malaria parasites enter a human via a mosquito bite, they rapidly multiply in red blood cells within a protective casing known as the parasitophorous vacuole. Once the newly mature parasites have matured they can break through this vacuole as well as the membrane of the red blood cell in order to infect other red blood cells.

The exact mechanisms underpinning these crucial, clinical stages of malaria infection were unclear, so 3D images of infected cells were obtained using X-ray tomography at B24 at Diamond. Using special additives to arrest the breakage of the parasites' double enclosures at different steps, the process was explored in detail and compared with live cell video microscopy. 3D electron tomography was also employed to scour tiny slices of the infected cells to examine their structural details.

The work revealed that rather than the parasites causing a gradual breakdown of the red blood cell membrane, the process happened far more abruptly. At a very late stage, the infected host cell underwent a dramatic shape change and then broke to liberate the parasites. Furthermore, the study showed that the membrane of the vacuole became permeable just prior to its rupture. These new insights could help to develop novel antimalarial therapies that target this critical process.

Egress takes place through a highly orchestrated sequence of events triggered by secretion of proteases or other factors from the parasites into their vacuole, leading to a further cascade of protease activation. Two chemical blockers have been discovered that arrest egress at different points. The first block (compound 1 or the closely related compound 2) prevents the parasites from breaking out of their vacuole by blocking secretion of the protease Sub1, so that the infected cell remains full of mature parasites trapped tightly inside their own compartment, with the blood cell retaining a rigid but distorted shape. The second block (the cysteine protease inhibitor E64) arrests egress just before the final escape of the parasites, trapping them inside the remnants of the red blood cell, which has lost its mechanical integrity but still loosely retains the parasites inside a floppy bag-like cell (Fig. 1).

In this study, three-dimensional (3D) reconstructions of these two arrested states were observed by both electron and X-ray tomography. The electron microscopy (EM) images revealed an initial, previously unknown, step in which the vacuole membrane becomes leaky and allows mixing of the cell contents with those of the vacuole. To track the changes in composition of the vacuole and red-cell compartments, we used electron energy loss spectroscopy, which confirmed that the two compartments were initially distinct in composition but then became equalised.

The EM and electron spectroscopy observations were made on the very thin sections needed for transmission EM imaging, so that it was not possible to determine whether the leak arose from tiny holes distributed over the membrane or from a localized broken region that was not captured in the thin sections. A unique feature of soft X-ray beamlines like Diamond’s B24 is that they enable 3D imaging of soft biological samples by X-ray tomography and spectroscopy, to reveal events on the cellular and subcellular scales. These approaches can be extended to the molecular level by using emerging techniques of optical X-ray electron tomography and X-ray energy loss spectroscopy, to reveal events on the subnanometre scale. This workflow will make it possible to computationally extract large macromolecular complexes from cryo tomograms and combine them to get detailed views of the cellular machinery in situ.

**References:**


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Red light photosynthesis


The structure of a photosynthetic protein complex that absorbs infrared light in aquatic bacteria has been determined for the first time, using cryo-electron microscopy (cryo-EM) at eBIC. The work outlined in the journal Nature, showed every component of the photosynthetic complex to an impressive 2.9 Å resolution.

In photosynthesis, light harvesting (LH) complexes funnel absorbed solar energy to reaction centre (RC) complexes, which transiently trap and store the harvested energy in the form of a charge separated state. Thereafter, a series of electron and proton transfers within the RC converts a quinone acceptor to its reduced form, a quinol. Plants and algae usually absorb light energy at wavelengths of up to 700 nm, but one particular photosynthetic bacterium Blastochloris viridis can absorb and utilise wavelengths far greater than these. Remarkably, these bacteria have adapted MCLR complexes with the capacity to absorb energy above 1000 nm – near infrared light that is inaccessible to other photosynthetic organisms.

The central RC component of the Blc. viridis photosynthetic complex was the first ever membrane protein structure to be successfully determined by X-ray crystallography which resulted in the awarding of the Nobel prize in 1985 to Deisenhofer, Huber and Michel. However, the structure of the LH1-RC complex in its entirety had eluded scientists until now. To understand the structural basis of the extraordinary infrared absorption, researchers from the University of Sheffield collaborated with scientists at eBIC and utilised Titan Krios 1 to determine the structure of the LH1-RC complex. The resulting 2.9 Å resolution structure revealed the positions of all bacteriochlorophyll, carotenoid, haem and quinone cofactors, as well as the protein-protein interactions that form the structural basis for infrared light absorption, charge-trapping electron transfers and export of the quinol product.

Plants and algae use chlorophyll a to absorb solar energy at wavelengths up to 700 nm. However, it has been known for decades that some photosynthetic bacteria can make use of other, lower energy regions of the solar spectrum, by absorbing light in the 750–900 nm region. Most of these bacteria use bacteriochlorophyll b, which absorbs at around 770 nm in methanol, and then LH1-RC complexes red-shift the absorption maximum to 870–880 nm. Blc. viridis uses bacteriochlorophyll b (BChl b) which, when solubilised in methanol, absorbs at 795 nm, and remarkably, achieves a red shift of 220 nm from the pigments, enabling photosynthesis to occupy a spectral niche above 1000 nm – near infrared light that is inaccessible to other photosynthetic organisms.

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The team will continue looking at this bacterium and they plan to apply genetic engineering to remove the critical outer ring to see if they can force the complex to absorb light towards higher energy wavelengths. Building on the success of this structural study at eBIC, they will also explore other photosynthetic systems using cryo-EM.

References:


Funding:

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The application of cryo-electron microscopy (cryo-EM) was crucial to understand the whole intact complex and its role in photosynthetic growth as the reaction centre alone cannot harvest sufficient light. The LH1 ring that surrounds the RC and co-ordinates a bacteriochlorophyll array harvests and delivers captured light energy extremely efficiently to the RC special pair. This process is illustrated in fine detail in the published structure.

The cryo-EM structure of the Blc. viridis LH1-RC complex showed that the organism employs a strategy of arrangements to allow its harvesting light at 1000 nm. The presence of BCHL a alone is insufficient to explain the absorption and the high-resolution structure indicated a number of additional contributory factors. As has been demonstrated in related organisms by the specific mutations, the haem quinone interactions that form the structural basis for infrared light absorption, charge-trapping electron transfers and export of the quinol product.

The LH1 complex contains a novel quinone subunit and this enables a triple ring structure that further stabilises the entire array thereby promoting the red shift.

The product of energy trapping is a quinol molecule, which must escape the confines of the LH1 ring that surrounds the RC and move into the quinone pool for subsequent utilisation by the cytochrome bc complex. The Blc. viridis LH1-RC structure illustrates how quinols may traverse the surrounding LH1 ring. A small pore is apparent in the LH1 ring, near a binding pocket, which housed a quinol, designated Qo. This binding pocket provides a binding template that imposes a compact conformation and a suitable orientation on Qo prior to its entry to the pore in the LH1 ring. Thus, the RC-LH1 complex of Blc. viridis reveals a new strategy for fostering quinol/quinone exchange across an LH1 ring.

The structural insights gained from this study could enable near infrared light absorption to be engineered into biosynthetic, bioprocessed or biohybrid photosynthetic systems. In particular, bacteria could be adapted to have a wide impact of solar energy with applications for novel solar cell technologies.

The team will continue looking at this bacterium and they plan to apply genetic engineering to remove the critical outer ring to see if they can force the complex to absorb light towards higher energy wavelengths. Building on the success of this structural study at eBIC, they will also explore other photosynthetic systems using cryo-EM.
Spectroscopy Group
Sofia Díaz-Moreno, Science Group Leader

Following the restructuring of the Diamond Science Division, the Diamond Spectroscopy Group is built around four beamlines: the Microfocus Spectroscopy beamline (I18) the Core X-ray Absorption Spectroscopy (XAS) beamline (B18) and the two independently operating branches of the Versatile X-ray Absorption Spectroscopy beamline, I20-scanning and I20-EDE. These four beamlines are complementary in many aspects, such as the energy range they cover, the size of the focussed beam spot delivered to the sample, and the time resolution they are able to reach.

Nevertheless, each beamline has its unique characteristics and they are optimised for performing different types of experimental studies. Over the last year more than 3,350 peer-reviewed experimental shifts were delivered using the Spectroscopy Group beamlines, covering many different scientific disciplines, from chemistry and catalysis to environmental and life sciences, materials science, hard condensed matter and cultural heritage.

As well as supporting a very robust user programme, many technical developments have also been implemented on the beamlines during the last year. Some of the developments have improved data quality and collection times, while others have added new capabilities to the beamlines.

I18 Update
The Microfocus Spectroscopy beamline (I18) uses a 2x2 µm beam to examine heterogeneous material on the micrometre scale using a variety of techniques, such as X-ray fluorescence (XRF), X-ray absorption near edge structure (XANES) spectroscopy and X-ray diffraction (XRD). During the last year considerable effort has gone into optimising the new mapping perspective used to collect XRF maps, as well as its integration into the Diamond General Data Acquisition program (GDA). This new software, originally installed in November 2016 along with a new motor control platform, has dramatically improved the efficiency of alignment procedures and an increase of the collected solid angle are on-going developments.

The fluorescence capabilities of B18 have been expanded with the development of an X-ray spectrometer with medium energy resolution, working in Von Hamos geometry. This spectrometer has been designed to overcome the limitations of the traditional solid state detectors when the fluorescence detection of an element of interest is affected by the presence of overlapping emission lines and intense backgrounds. The spectrometer has demonstrated very good performance not only for the study of complex samples, but also for very dilute systems. The implementation of streamlined alignment procedures and an increase of the collected solid angle are ongoing developments.

The implementation of a simplified framework has improved the software interface for experiments with a large number of samples. The measurements can be programmed in one go using a spreadsheet-like interface, minimising the chances of errors during the experiment preparation. This functionality has already been used during the Block Allocation Group access mode reducing the time needed for the experiment.

I20 Update
The scanning branch of I20 (I20-scanning) provides high intensity X-rays for the study of very low concentration samples by XAS. It also provides the capabilities to perform X-ray Emission Spectroscopy (RXES) using a Rowland circle spectrometer, enabling the performance of high resolution studies of the electronic structure of samples.

This year the main developments on this branch have been focussed on improving its ability to perform XAS on challenging samples. A new experimental table has been installed to allow the integration of a large rotational stage for the 64-element monolithic germanium solid state detector. With this stage the detector can be located at different angles with respect to the incident X-ray beam which allows the use of sample environments that leave very limited space for the collection of the fluorescence emission. To further improve the beamline performance, new read-out electronics has been developed and integrated with the germanium detector. This new system is the Jupix-4 digital pulse processor that has been developed in-house by the Diamond Detector Group. Jupix-4 is able to deliver a factor of three increase in detector system count rate whilst maintaining the data quality that could be achieved using the previous read-out system. This new read-out system consequently allows the beamline to study samples where the element of interest is surrounded by many other heavy elements that otherwise would saturate the detector signal at high count rates.

The development project for a new monochromator for the scanning branch of I20 is still ongoing with the aim of delivering a device that is able to provide better use of the high photon flux delivered by the wiggler source, and extend the energy range of the beamline up to 34 keV.

The I20-EDE branch is designed to perform XAS experiments in dispersive configuration, and has been optimised for in situ and operando time resolved studies over time scales ranging from seconds down to milliseconds or even microseconds. The optimisation of this branch has continued during the last year and significant effort has been invested in the development of the software necessary to visualise and analyse the large amount of data that can be collected. In addition, the development and integration into the beamline of a sequential data acquisition mode, turbo XAS, is very well advanced. This mode of data collection is well suited to the investigation of systems in transmission mode when small angle scattering from the samples is significant, or in fluorescence mode when the concentration of the element of interest is low. Two successful user experiments have been performed during the last year that makes use of this new development.

In parallel to supporting the beamlines and the operational science programme, the Spectroscopy Group was also heavily engaged in hosting the International Workshop on Improving Data Quality on XAS Spectroscopy, 26-28 October 2017. At this event, more than 50 participants met to review international standards and protocols, and to revise recommendations for best practice when performing XAS experiments.
Nanocrystallites on micro-catalysts brought into focus


Publication keywords: Catalysis; Tomography; Diffraction; Fluorescence

The Fischer-Tropsch process is used to convert hydrogen and carbon monoxide to hydrocarbons. It relies on the use of catalysts, which make the process more efficient and can control which products are produced, from long hydrocarbon chains to heavy waxes. A team of researchers developed a novel technique to investigate how cobalt catalysts change, at both the micro- and nanoscale, during the Fischer-Tropsch process. They used the Microfocus Spectroscopy beamline (I18) which allowed them to focus X-rays down to the microscopic sizes (5 µm) needed for the study, and to collect all of the different modes of characterisation (absorption, diffraction, fluorescence, mass spectrometry) simultaneously. This was the first simultaneous measurement of all the characterisation techniques on the beamline.

Their work investigated the influence of the deposition sequence on the chemical and physical structure of the catalyst, in 3D, under conditions close to those used in large scale reactors, so the observed structure and activity relationships from the experiment are relevant to the full scale reactors. Their results show that even small modifications in how catalysis is made can significantly affect their performance.

Many active catalysts consist of metal nanoparticles supported on larger grains of refractory oxides, such as silica (SiO₂), titania (TiO₂), alumina (Al₂O₃), or a mixture thereof. This helps optimize the metal nanoparticles dispersion and improve the long-term stability. Recently, additional metals have been added to the catalyst in small amounts to ‘promote’ the activity further (e.g. rhodium, platinum), and help control the long-term stability of the particles. These compounded systems are the catalyst of choice at many plants. However, with the increase in constituents comes an increase in complexity, both in how they can be synthesised, and the resultant chemical and physical structures that are formed. One factor that can affect this is the order in which the catalyst and promoters are added to the support. To that end, two samples were prepared with identical elemental compositions (10 wt% cobalt, 1 wt% rhenium, 5 wt% titanium, supported on silica – Co/Ti.x/SiO₂). The Re is a promoter for the Ceto lower the temperature needed to reduce from an oxide to a metal, the state required to perform FTS, and the Ti is a modifier for the silica support to aid the interaction with Co. The difference between the two samples being whether Ti was added first or last to the support material. Different activity (conversion of CO) and selectivity (formation of desired long chain hydrocarbon products) were observed between the two catalysts, however the reasons for this were not fully understood. Previous studies of similar materials to determine the active state of the catalyst were bulk measurements of an area in a reactor and therefore only revealed the average composition present; supported catalysts possess complex micro- and nano-structures that need to be considered to fully understand the relationship between structure and performance. To this end, the multimodal tomography set up was developed on beamline I18: A microchannel reactor was developed that could be scanned through the highly focussed X-ray beam (200 °C 2H-He at 25°C).

To study the behaviour of these catalysts on the micro and nanoscale, they used two novel approaches: the detection of X-ray diffraction and X-ray absorption. X-ray diffraction measures lattice size and changes in the structure of nanoparticles; X-ray absorption data collected simultaneously. By rotating the reactor in the path of the beam as well as scanning, this data could be collected at different angles (computed tomography, CT), which when reconstructed revealed the location of each grain within the reactor, and the locations of each element and crystalline phase present within each individual grain.

When Ti is added first it is oxidized and partially crystallizes on the large 50 nm, forming the anatase polymorph of titania (TiO₂). Typically, in the precursor material, the Co is present in the form of Co₂O₃, however in regions where anatase is present a small proportion is reduced to Co (Fig. 1). A typical bulk XRD measurement would not have been able to reveal the relationship. Once the cobalt oxide is reduced to metallic cobalt (400 °C), no traces of either oxide phase remains. Once the reduction cycle and into FTS conditions, the catalyst is stable against reduction, with only metallic Co forming.

Furthermore fitting of the diffraction patterns revealed information on the nature of the metallic Co. Typically, metallic Co peaks packed together in two different forms, cubic and hexagonal (Fig. 3). A third, disordered, form of packing known as intergrowth Co was also possible; this is a transformation of cubic and hexagonal packed layers, it results in broader, less intense diffraction peaks, and is harder to quantify. For both catalysts studied here, fitting of the XRD data revealed the degree of intergrowth can be directly correlated with the Ti modification on the silica support. When Ti is deposited before the Co, it increases the strength of the metal-support interaction and results in smaller, strained Co nanoparticles (a result of a higher degree of intergrowth) therefore explaining why they are prone to re-oxidation under FTS conditions (Fig. 2).

The weaker metal-support interaction when Co is deposited first means the Co atoms are more mobile, forming larger crystallites that are less strained, with a lower degree of intergrowth and therefore more stable once under FTS conditions.

In both cases, however, the degree of intergrowth (i.e. disorder) in the Co is linked to the concentration of Ti and not its crystallinity. The Co nanoparticles formed when Ti is deposited first are smaller and more active to Co conversion, whereas when Ti is deposited second, the Co nanoparticles are formed larger and have greater selectivity towards longer chain hydrocarbon products.

The complex relationships between elemental and crystalline phase distributions could only be revealed by the multimodal tomography technique developed and, crucially, correlation of structure with activity and selectivity was possible as the data was recorded whilst the catalyst was operating. The understanding of how the degree of disorder affects catalyst activity and selectivity has not been considered to the same extent as the effect of nanoparticle size has. This opens the way to new means to tune catalyst selectivity for FTS, and in a broader sense, the techniques developed here can pave the way for studying other catalytic reactions.

References:

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Catalysted production process for vinyl chloride, the monomer used in PVC and everything from pipeline to gels and lubricants, relies on a mercury-based catalyst. Mercury is one of the most toxic substances on the planet, and the UK recently ratified the Minamata Convention, meaning that a more environmentally-friendly alternative is required.

It has been shown that gold supported on carbon could be used as an alternative catalyst for this reaction, and although it is currently being commercialised its behaviour under harsh reaction conditions has never been investigated. The reaction is typically carried out at 200°C, using corrosive gas mixtures that can rapidly deactivate catalysts. X-ray absorption spectroscopy (XAS) is the ideal tool for observing the reaction in situ, and the quick acquisition time available on B18 gave a team of researchers the time resolution needed to see activation and deactivation during the reaction.

Their results offer the first example of a single site catalyst remaining atomically dispersed and working under such harsh reaction conditions, and will enable more rational catalyst design to find a replacement for the current mercury catalyst.

The production of vinyl chloride monomer (VCM) as the precursor to polyvinyl chloride (PVC) is a major industrial process. In particular, 42 million tonnes of PVC had been consumed in 2016, constituting 16% of total plastic demand. The production of VCM through acetylene hydrochlorination (the reaction of acetylene with HCl) using a mercuric chloride based catalyst is the dominant method of VCM production in conical rich areas such as China. However, the catalyst loses significant amounts of mercury, posing a great risk to the environment. The recently united Minamata convention has outlined that VCM production must move to mercury-free production by 2022, necessitating the development of a new commercial catalyst for VCM production.

This need had been recognised previously and led, in 1985, to the prediction of gold-based catalysts as effective for this reaction. This prediction was based on correlation of activity with the standard electrode potential of metal chlorides supported on carbon and has been subsequently proven experimentally, leading to the exponential growth in the field of gold catalysts. With the legislative pressure to replace the current catalyst体系 system Au/C has become a viable alternative due to its stability, limited metal toxicity via loss to the environment and high selectivity to the desired product.

To date effective catalysts have been studied which were prepared by impregnation of a gold precursor (HAuCl₄) with an acidic solution of aqua regia (a mixture of nitric and hydrochloric acid). This impregnation method prevents the agglomeration of large metallic Au nanoparticles which are readily seen when exposing the precursor in aqueous solution and have been shown to be inactive. Despite these observations, there remained in the literature confusion about the active form of the catalyst with many active catalysts appearing to contain metal nanoparticles. Multiple examples of active catalysts showed the prevalent species present to be metallic Au characterised by transmission electron microscopy (TEM) examination of the fresh catalyst material and by X-ray absorption spectroscopy. Previous studies claimed that active species were Au nanoparticles, while carrying out an acetylene hydrochlorination reaction at realistic reaction conditions with product analysis by mass spectrometry (Figure 1). This allowed the decomposition of the AuCl₄⁻ type species into AuCl₃ type species corresponding to Au on AuCl₄⁻ decomposition temperature of AuCl₃ to AuCl₄⁻ at around 160°C. On the introduction of the reagent gases to the reactor evolution, initially through re-oxidation to a AuCl₃ type species before equilibration to a stable AuCl₄⁻ (40%) AuCl₃ (50%) ratio with the Au – Au scattering distances present throughout this equilibrium phase. Analysis of the VCM productivity achieved at the same time as the reaction, revealed an induction period where the catalyst is becoming more active over time until equilibration at steady state. This induction period was able to be correlated with the AuCl₃ to AuCl₄⁻ ration of the catalyst material (Fig. 2). At all points, no metallic Au was detected. A subsequent high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) analysis, optimised to reduce beam damage, confirms the observation of isolated Au species in the fresh catalyst material (Fig. 3).

This study provided the evidence that the isolated catalytic Au species present in the catalyst were in fact the active species and damage and photodecomposition of the catalytic materials through ex situ characterization measurand and confirmed the interpretation of the active form of the catalyst in previous studies. By characterising the catalyst during the reaction, the research team was able to conclusively show that the active catalyst for this reaction is isolated catalytic Au sites able to homogenous catalysis. This provides an opportunity to design the ligand environments around the Au centre to improve catalyst activity and stability which could result in Au becoming the replacement for the mercury based catalysts for VCM manufacture. In fact Au catalysts have been successfully operated at a commercial scale and look set to lead the demand in mercury usage in this large scale industrial process.

References:

**Image 1:** Experimental setup to carry out acetylene hydrochlorination with simultaneous acquisition of X-ray absorption spectra

**Image 2:** (a) Weight loss; (b) BET Surface areas of a macroporous Au/C Catalyst and Au foil standard. (c) Normalised white line intensity, with XCP productivity over the course of the reaction induction period

**Image 3:** Representative STEM-EDX image showing several dispersed single site isolated Au species.
Phosphorylation Enhances Cytochrome c Dynamics to Modulate its Function


Publication keywords: Cytochrome c; Mitochondrial dysfunction; Nuclear magnetic resonance; Phosphorylation; Respiratory supercomplexes

Some diseases, including cancer and ischemia (an inadequate blood supply to an organ or part of the body), involve reversible phosphorylation at a given site on the cytochrome c protein. Cytochrome c is essential for human metabolism and contains a heme iron, which allows it to function as an electron carrier. To understand the molecular basis underlying the effects of phosphorylation, an international team of researchers has used several methods to analyse the structure, dynamics and functional features of an engineered, stable variant of cytochrome c.

The aim of the work was to understand how a change in the protein affects its function within the cell, and the team used X-ray Absorption Spectroscopy (XAS) to determine the protein’s structural features. They chose the Versatile X-ray Spectroscopy beamline (I20), in particular the I20 Scanning branchline for its ability to measure highly diluted biological samples. Nuclear Magnetic Resonance (NMR) showed that cytochrome c phosphorylation only induces local structure changes, hardly affecting the overall protein conformation. Both XAS and NMR experiments showed an increase in the mobility of the protein region surrounding the heme group, explaining the observed functional changes.

The response of cells to physiological changes and oxidative stress involves the modulation of mitochondrial respiration. This affects the intensive activities of the electron transport chain components and their assembly within the mitochondrial inner membrane. In fact, hypertrophy induces the grouping of these proteins into the so-called supercomplexes, which facilitates the transfer of electrons between the distinct components of the electron transport chain, while decreasing the generation of reactive oxygen species (ROS). The best known supercomplex is called the respirasome, and comprises the membrane complexes I, II and IV. Alterations in the formation of the supercomplexes lead to the development of hyperdiabetic pathologies, such as cancer or ischemia. A key modulator of the mitochondrial activity is cytochrome c (Cc). Cc is a small heme-protein which acts as an electron carrier between complexes III and IV, and is highly conserved throughout evolution. Cc also plays a critical role in cell life and death decisions in mammalian and plant cells. This pleiotropic role of Cc makes post-translational modifications an essential mechanism to regulate its functions tightly. Phosphorylation and nitration of tyrosine residues stand out among these modifications. Indeed, they affect the conformational equilibria of the protein along with its ability to bind physiological partners.

Specifically, post-translational Cc phosphorylation at tyrosine 48 is key in modulating mitochondrial signalling. Nevertheless, the mechanism by which it alters the conformation and function of the protein is barely understood. To address this subject requires solving the 3D structure of the phosphorylated species. However, cell extracts phosphorytase reverse Cc phosphorylation, hampering the isolation of the modified protein from tissues. This makes any structural analysis a highly challenging task. Here, we solved the 3D structure of a Cc phosphorylated by replacing tyrosine 48 with the synthetic amino acid (4-chloro-3-phenylalanine) (pCMF). The targeted residue is also shown. Bonds are represented by sticks. Heavy atoms are in CPK colors, except for Y48 pCMF carbons (in green).

To test this hypothesis, yeast mitochondria preparations were prepared under conditions, either avoiding or eliciting supercomplex formation. The performance of WT and mutant Cc species was tested. No difference was found between the two species when supercomplex formation was inhibited. However, when supercomplex assembly was favoured, the activity of Cc as an electron carrier for complex IV increased – according to oxygen evolution measurements – but the activity of the phosphorymic species was substantially lowered when compared to the WT species.

High complexity of the activity has been related to ROS generation. Hence, the inhibition of the electron shuttling from complex III by phosphorylation of Cc may downregulate such a harmful side-reaction. In addition, phosphorylated Cc shows an enhanced peroxidase activity – probably due to higher heme accessibility – which makes it a better ROS scavenger. These findings will eventually aid the development of a robust therapeutic approach, either to foster or silence, as required, the pro-survival action of phosphorylated Cc reported here.

which determined the lowest squared deviations in distances for the distinct scattering paths selected. Interestingly, there was no significant difference in metal-to-ligand distances in between the two species. Nevertheless, Debye–Waller factors indicated an increase of the disorder in the eruptational ligands – those belonging to the phosophor ring – in agreement with the broadening of the 713 eV feature in the XANES region and the decrease of intensity of the first peak of the Fourier transform.

The solution structure of the phosphorymic mutant revealed small, but significant conformational changes in loops containing the phosphorylation site and adjacent residues providing axial ligands for the heme iron (Fig. 2). Furthermore, NMR relaxation data and the presence of signals undergoing slow chemical exchange indicated that phosphorylation enhanced the dynamics of the above-mentioned loops – which surround the heme group. Notably, this facilitates the access of water molecules into the heme pocket. To summarise, the NMR and XAS data indicated that the mutant showed both similar overall 3D structure and iron coordination geometry to the WT protein, but exhibited enhanced dynamics.

Phosphorylation may affect the interaction between Cc and its partners by several means. The addition of a phosphate results in Cc carrying a negative charge, with a significant impact. Additionally, enhanced dynamics in the unfolded species increases the conformational entropy penalty. In fact, NMR and Isothermal Titration Calorimetry (ITC) data indicate that one of the two reported docking sites for Cc at its electron donor (complex III) is lost. In the context of the respirasome supercomplex, the docking site where the modified Cc no longer binds lies on the pathway towards its electron acceptor (complex IV). This site was proposed to be involved in restraining the diffusion path of Cc across the respirasome surface (Fig. 3).

To test this hypothesis, yeast mitochondria preparations were prepared under conditions, either avoiding or eliciting supercomplex formation. The performance of WT and mutant Cc species was tested. No difference was found between the two species when supercomplex formation was inhibited. However, when supercomplex assembly was favoured, the activity of Cc as an electron carrier for complex IV increased – according to oxygen evolution measurements – but the activity of the phosphorymic species was substantially lowered when compared to the WT species.

High complexity of the activity has been related to ROS generation. Hence, the inhibition of the electron shuttling from complex III by phosphorylation of Cc may downregulate such a harmful side-reaction. In addition, phosphorylated Cc shows an enhanced peroxidase activity – probably due to higher heme accessibility – which makes it a better ROS scavenger. These findings will eventually aid the development of a robust therapeutic approach, either to foster or silence, as required, the pro-survival action of phosphorylated Cc reported here.

Spectroscopy Group Beamline I20

Figure 1: 3D x-ray absorption spectra of WT (a) and mutant (pCMF) Cc species at cryogenic temperatures, recorded at the I20-Scanning beamline. Notably, the absorption spectra of the two proteins are very alike. Both structure the pre-edge feature at ca. 7131 eV, indicative of the optimal geometry for the first iron coordination sphere. Overall, the X-ray Absorption Near Edge Structure (XANES) region of the spectra for the two species are almost identical, as can be seen in the figure. The absorption edge appears at 7126 eV in both cases, indicating that the oxidation state of the metal ion is not affected by the mutation. However, some spectral features are broadened for the pCMF Cc species, as compared to the WT Cc species at the first peak of the Fourier transform.

Figure 2: Structural changes in cytochrome c upon phosphorylation. (a) Richardson’s ribbons representation of the XAS structures of WT (pale yellow) and pCMF (green) cytochrome c species. The positions of the heme and – when present – the docking site for the WT and mutant Cc species at the electron donor (complex III) is lost. In the context of the respirasome supercomplex (b), the docking site where the modified Cc no longer binds lies on the pathway towards its electron acceptor (complex IV). This site was proposed to be involved in restraining the diffusion path of Cc across the respirasome surface (Fig. 3).

Figure 3: Two-dimensional X-ray absorption spectra of WT (a) and mutant (pCMF) Cc species at cryogenic temperatures, recorded at the I20-Scanning beamline. In panels (a) and (b), continuous lines correspond to experimental data and dotted lines to theoretical fits.
The Soft Condensed Matter Group provides the infrared (IR) and Circular Dichroism (CD) spectroscopy and, both Small and Wide Angle X-ray Scattering (SAXS and WAXS) imaging capabilities of Diamond. The Soft Condensed Matter Group comprises of four beamlines B21, B22, I22 and B23. This unique portfolio of beamlines can analyse a range of samples that include two-dimensional thin films (photovoltaics), living mammalian cells, three-dimensional matrices (metal-organic frameworks) and nanoparticles in non-crystalline states.

The Soft Condensed Matter Group maintains a dedicated laboratory space for our visiting users. The laboratory houses vital equipment for sample preparation and analysis such as a centrifuges, a small tissue-culture facility, spectroscopy equipment (including CD, standalone IR and UV spectroscopy, multi-angle and quasi-elastic light scattering) and the ability to work with different gases. Laboratory and offline instrumentation usage can be reserved through the User Administration System at any time throughout the operational year of Diamond. Since the start of 2017, both B21 and B23 now offer mail-in services for solution-state SAXS and CD measurements.

B23 Update

Operational since 2009, the Circular Dichroism beamline (B23) uses circularly polarized light to characterise the structure of complex materials in thin films, quantification of the spatial distribution of a sample at the highest, optically-achievable resolution. B23 features a unique extreme-environment high pressure cell (HPC). The high pressure sample cell can withstand 2500 times atmospheric pressure while allowing researchers to measure the sample CD spectra. In the hard sciences, this sample cell allows researchers to investigate the stability of proteins and enzymes in the solution state under extreme conditions.

B22 Update

The Multimode Infrared Imaging and Microspectroscopy (MIRIAM) beamline (B22) is dedicated to the study of non-crystalline, randomly oriented particles. SAXS measurements can be made on any type of sample and in any physical state. For the life sciences community, solution state SAXS measurements allow for the opportunity to study biological machines in conditions that are comparable to their liquid, hydrated environment. This ability complements the many solid-state studies performed at Diamond using X-ray crystallography and cryo-electron microscopy. B22 end-station can be configured for low-throughput, syringe-pump based experiments and high-throughput batch mode experiments using either the bioSAXS sample delivery robot or high-performance liquid chromatography (HPLC) instrument for inline size-exclusion chromatography (SEC) coupled SAXS.

In the continued quest to lower the instrumentation background, B21 relocated the sample and detector downstream by nearly five metres (Fig. 2). The move, coupled with the recent optics upgrade, increased the operational flux at the sample position by nearly 21-fold with a comparable decrease in instrumentation background in the highest resolution region of the detector. This optimised sample position enabled further improvements in the SEC-SAXS sample cell reducing the exposed sample volume from 24 to 10 µL. The new configuration will be complemented by in-line multi-angle light scattering that will not only inform on the sample’s molecular mass but also, enable measurements at smaller scattering angles.
**Complex Self-assembly Inside Atmospheric Aerosol Droplets?**


**Publication keywords:** Atmospheric aerosols; Small-angle X-ray scattering (SAXS); Raman spectroscopy; Acoustic levitation; Lyotropic liquid crystalline phases

Aerosols are significant to the Earth’s climate, with nearly all atmospheric aerosols containing organic compounds that often contain lipophilic molecules. However, the nature of how these compounds are arranged within atmospheric aerosol droplets remains unknown. It was recently demonstrated that fatty acids in proxies for atmospheric aerosol self-assemble into highly ordered three-dimensional nanostructures known as lyotropic liquid crystalline phases. This finding may have implications for environmentally important processes. In this research, acoustically trapped droplets of oleic acid/sodium oleate mixtures in a sodium chloride solution were analysed by simultaneous synchrotron small-angle X-ray scattering (SAXS) and Raman spectroscopy in a controlled gas-phase environment. It was demonstrated that the droplets contained crystal-like lyotropic phases including hexagonal and cubic close-packed arrangements of spherical and cylindrical micelles, and stacks of bilayers, whose structures responded to atmospheric relative humidity changes and chemical reactions. Further experiments showed that self-assembly reduces the rate of reactions with atmospheric oxidants. These experiments at the High Throughput SAXS beamline (B21) demonstrated that lyotropic-phase formation also occurs in more complex mixtures more closely resembling compositions of atmospheric aerosols. This suggests that lyotropic-phase formation likely occurs in the atmosphere, with potential implications for cloud formation and properties of molecules in the atmosphere, and other important aerosol characteristics.

In these experiments single droplets were held in levitation and followed changes in these droplets at the same time using X-rays to track the movement and arrangement of the molecules in the droplet. The droplets were exposed to conditions that could be met in the atmosphere: changes in humidity and presence of the atmospheric oxidant ozone. In all humidities, the droplets exhibited highly complex self-assembled three-dimensional structures. Exposure to ozone eventually broke down the molecules and destroyed the complex molecular arrangement. However, the molecules survived much longer in these arrangements than expected. This could explain longer lifetimes of such molecules found in the atmosphere compared to laboratory experiments where the complex arrangements that may be encountered in atmospheric conditions is not taken into account.

It was demonstrated that complex 3D self-assembly occurs in proxies for atmospheric aerosols. Many of these 3D structures are strongly anisotropic and are known to significantly affect optical properties, diffusion, viscosity, surface tension and water uptake, and therefore, in an atmospheric context, may have a dramatic impact on aerosol behaviour (Fig. 1).

- Fatty acids represent a significant proportion of marine (up to 15 ng m⁻³) and urban aerosol, ranking organic aerosol emissions was recently estimated to be surprisingly high at 7400 tons per year; this corresponds to nearly 10% of the total man-made small particle (PM₂.₅) load in the United Kingdom based on measurements in London. Nevertheless, atmospheric aerosol composition is far more complex. Thus further studies were carried out utilizing acoustically levitated droplets (Fig. 2) more complicated organic mixtures, specifically mimicking aerosol compositions found in urban environments by adding additional components to our aerosol proxy.

**During the experiments on more complex mixtures on B21, two further atmospheric aerosol components were introduced: first, sucrose (fructose) and then hydrocarbon (hexadecane). Two mixtures were prepared fatty acid/sugar and fatty acid/sucrose/hydrocarbon. The fatty acid/sucrose/hydrocarbon ratios were chosen according to ratios found by Wang et al. in field studies of real atmospheric aerosols in the Chinese city of Chongqing in winter, where the three main classes of organic compounds were fatty acids, sugars and alkanes (3244, 2799 and 948 cm⁻¹, respectively). For experimental ease, the mixtures were analysed not as levitated droplets but as dry coatings on the inside of X-ray capillary tubes, which were exposed to high and low relative humidities. As demonstrated in Figure 2, both the sodium oleate/oleic acid fructose and the sodium oleate/oleic acid/hexadecane systems showed complex 3D self-assembly. SAXS patterns from the sodium oleate/oleic acid/sucrose on humidification clearly show three Bragg peaks from the inverse hexagonal (H₂) phase, with further peaks indicating additional coexisting phases. On drying, the structure changes, but different Bragg peaks are nonreversibly observed, inferring that this is the changes to be reversible, suggesting that they represent thermodynamic phases in equilibrium with water vapor in the surrounding environment. The sodium oleate/oleic acid/sucrose/hexadecane mixture showed a different self-assembly here, while it was not possible to get the peaks to a particular symmetry phase—indeed, more than one phase may be present—the presence of multiple peaks shows the existence of periodic ordering on the nanometre-length scale, while the reversible responses to humidity changes again show lyotropic formation.

While it is clear that further studies are urgently needed to test the impact of this complex self-assembly on the atmosphere, this work demonstrates the potential of these arrangements to explain substantially extended atmospheric lifetimes found for reactive organic molecules. Further investigations combining laboratory and field studies are required to establish the influence of complex three-dimensional self-assembly on a wider range of properties such as light scattering, hygroscopicity, viscosity and diffusion in aerosol particles. These properties potentially affect cloud nucleation and albedo, and atmospheric reaction rates, and so are key to understanding the impact of aerosols on the environment and climate.

**Figure 3:** The capillary holder used on B21, with the atmospheric aerosol coating inside.

**Figure 2:** SAXS of more complex atmospheric aerosol proxies collected on B21. a) Fatty acid/sucrose (sodium oleate/oleic acid/sucrose ratio 1:1:1.8) b) Fatty acid/sucrose/hydrocarbon (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8) c) Fatty acid/sucrose/hexadecane (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8 to mimic aerosol compositions in Chongqing) d) Fatty acid/sucrose/hexadecane (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8 to mimic aerosol compositions in Chongqing) e) Fatty acid/sucrose/hexadecane (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8 to mimic aerosol compositions in Chongqing).

**Figure 1:** Complex 3D self-assembly of surfactant molecules in proxies for atmospheric aerosol. Lyotropic phases formed; impact on key properties of atmospheric aerosols (highlighted in red); and examples of complex self-assembly from other fields.

**Figure 3:** The capillary holder used on B21, with the atmospheric aerosol coating inside. **Figure 2:** SAXS of more complex atmospheric aerosol proxies collected on B21. a) Fatty acid/sucrose (sodium oleate/oleic acid/sucrose ratio 1:1:1.8) b) Fatty acid/sucrose/hydrocarbon (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8) c) Fatty acid/sucrose/hexadecane (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8 to mimic aerosol compositions in Chongqing) d) Fatty acid/sucrose/hexadecane (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8 to mimic aerosol compositions in Chongqing) e) Fatty acid/sucrose/hexadecane (sodium oleate/oleic acid/hexadecane ratio 1:1:1.8 to mimic aerosol compositions in Chongqing).
Building 3D nanomaterials with sticky DNA bricks

Over the last two decades, the ever-expanding research field of DNA nanotechnology has demonstrated how synthetic nucleic acid molecules can be used to create nanoscale motifs of near arbitrary shape. DNA is indeed an ideal nanoscale construction material, mostly owing to the exquisite selectivity of the Watson-Crick base pairing interactions; responsible for holding together double-helical DNA and enabling most of DNA’s biological functionalities. By carefully designing the base-sequence of DNA strands, it is possible to exploit base pairing to create complex shapes. Furthermore, synthetic DNA can be commercially produced at relatively low cost, is robust against degradation, highly biocompatible, and can be connected to a plethora of other molecules that can impact advanced technologies.

A long-term goal of structural DNA Nanotechnology has been the creation of morphologies that can support long-range order in three dimensions, forming macroscopic crystalline materials. Until recently, however, only very few examples of DNA nanostructures have proven capable of achieving this result, substantially limiting our opportunity of tailoring the characteristics of the DNA crystals to specific technological needs.

Most of the available routes for creating ordered nanomaterials involve self-assembly, from small clusters, to filaments, to 2D membranes, to 3D crystals. These include loop, soup molecules and specifically designed synthetic polymers, and features on, each of which have been important in the design and prototyping of different shapes, the easy functionalisation as assembling through the robust frustrated phase separation mechanism. At the same time, C-Stars retain all of the advantages of DNA-based materials, including the facile design and prototyping of different shapes, the easy functionalisation, and the biocompatibility.

A recent contribution, the team featuring Mr R. Brady, Prof P. Cicuta, Dr L. Di Michele (University of Cambridge), and Dr N. Brooks (Imperial College London), combined the best of both worlds: introducing a new type of amphiphilic DNA nanostructures, dubbed C-Stars, capable of effectively forming macroscopic 3D crystalline aggregates. C-Stars are simple branched motifs self-assembled from a small number of synthetic single-stranded (ss)DNA molecules (Fig. 1a). Some of these strands are modified with a hydrophobic cholesterol molecule, ultimately positioned at the tip of each DNA arm. Since DNA itself is very hydrophilic, cholesterol modifications make C-Stars amphiphilic, and capable of self-assembling through the robust frustrated phase separation mechanism. At the same time, C-Stars retain all of the advantages of DNA-based materials, including the facile design and prototyping of different shapes, the easy functionalisation and the biocompatibility.

Figure 1 demonstrates the self-assembly principle of C-Stars. The ssDNA components are dispensed in buffered aqueous solution, and heated up to 90°C. At this high temperature, the DNA double helices (duplexes) cannot form, but the hydrophobic forces are still active, causing the cholesterol-bearing ssDNA strands to cluster into micelles (Fig. 1b). As the temperature is slowly decreased, the duplexes forming the C-Star junctions start to self-assemble, linking together the micelles and forming a network whose structure is determined by the shape of the C-Star, and thus in the chosen sequence of DNA bases. The resulting aggregates grow over time and coalesce (Fig. 1e), eventually forming macroscopic networks exceeding 40 μm in size, equivalent to billions of individual C-Stars. When inspected with light microscopy, the aggregates display a polyhedral shape, strongly hinting at an underlying crystalline structure (Fig. 1c).

Small-Angle X-ray Scattering (SAXS), performed at Diamond beamline I22, was used for the macroscopic structural characterisation of aggregates self-assembled from 4-arm C-Stars. Powder diffraction experiments were performed at small-angle length scales by illuminating dense, millimetre-size pellets prepared by concentrating a large number of DNA crystals. The generated diffraction patterns are the result of several crystals being exposed to the Bragg ray once, and show well-defined rings (Fig. 2b), which when averaged remarkably highlight Bragg peaks indicative of an ordered network. Using the microlens end-station available at I22, which can reduce the cross-section of the X-ray beam down to 10 μm, we could illuminate individual C-Star crystallites and obtain single crystal diffraction patterns (Fig. 2b).

The positions of the peaks in the powder diffraction and the spots of the single-crystal diffraction patterns are compared with body-centred cubic (BCC) lattice. Combining this information with the size of the individual C-Stars (imposed by design), and the coordination of cholesterol DNA micelles, we could identify the likely arrangement of the DNA building blocks in the BCC network (Fig. 2c). In our model, the unit cell, the elementary cube periodically filling the 3D space, has a size (lattice parameter) of 23 Å, and contains 6 C-Stars. Interestingly, C-Star networks are extremely empty, with DNA and cholesterol occupying only about 5% of the volume of the crystal. In other words, C-Star aggregates have a very high porosity (~85%), which makes them ideal to encapsulate molecules within the DNA.

Powder diffraction experiments were also performed on C-Stars featuring different numbers of arms. Remarkably, 3- and 6-arm building blocks are also capable of effectively supporting long-range order (3D). This design flexibility makes it possible to incorporate functional molecules within the DNA network, which can make the crystalline materials responsive to external stimuli. With the support of the I22 Diamond team, we are planning to demonstrate this possibility in an upcoming SAXS session.

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Shockling protein crystals into action: combining electrochemistry and infrared microscopy provides insight into [NiFe] hydrogenase mechanism


Publication keywords: Protein crystallography; Infrared microspectroscopy; Infrared spectroscopy; Redox protein; Metalloprotein; Electrochemistry

P roteins are the nanoscale ‘machines’ that control almost all processes in cells, and revealing their structures is paramount to understanding how they work. X-ray crystallography is a valuable tool for providing ‘snapshot’ images of working proteins at an atomic level; however, some proteins are very tricky to freeze at particular moments in time. [NiFe] hydrogenases are enzymes that allow microbes to survive using hydrogen gas as their only energy source. These enzymes have drawn much attention because of their potential applications in future green energy technologies, but to fully determine how they work, it is imperative to image them at specific stages of their reactions.

Fortunately, [NiFe] hydrogenases naturally contain markers that are easily studied using infrared light, which made them ideal subjects for the Infrared Microspectroscopy beamline (B22, MIRIAM). Crystal forms of the enzymes were analysed at B22 within a custom-built electrochemical cell which allowed their reactions to be slowed down. This setup provided the opportunity to study an otherwise extremely fast reaction in unprecedented detail.

The demonstration that hydrogenase protein crystals could be controlled using electrochemistry is an important finding as many other proteins can be studied in the same way, including proteins that convert carbon dioxide into useful chemicals.

Understanding the structures of individual proteins at the atomic level has been key in building up our understanding of how they contribute to the function of cells. In particular, X-ray crystallography has been extremely valuable in providing ‘snapshot’ images of many different proteins at the level of individual atoms. It is often difficult to trap proteins in specific states relevant to their function, however. This is particularly true for redox proteins, which catalyse chemical reactions involving the transfer of electrons, where crystallographic structures can represent structural averages from mixtures of states at similar redox levels. The benefits of using complementary spectroscopic techniques alongside protein crystallography, at the single-crystal level, are becoming more widely acknowledged in order to gain a more complete understanding of biocatalytic structure and function. However, methods which offer direct control over the oxidation state of a redox protein crystal and simultaneous microspectroscopic measurement are lacking. It is timely that new tools are developed for studying redox proteins because they catalyse many chemical reactions which are relevant to solving big global challenges, including how to use hydrogen as a sustainable fuel, how to capture the greenhouse gas carbon dioxide and turn it into useful chemicals, and how efficiently produce the fertilisers needed to sustain the world’s growing population.

Nickel-iron ([NiFe]) hydrogenases are an important class of redox proteins, which allow bacteria such as E. coli to live using hydrogen gas as their sole energy source. Hydrogenases are essential catalysts as they catalyse the reversible oxidation of H₂ at active sites bound around cheap, abundant metals, and at high turnover frequencies (>9,000 s⁻¹). The active site of [NiFe] hydrogenases incorporates biologically unusual ligands, G and CN⁻, bound to iron (Fig. 1a). Vibrational stretching bands of these ligands can be probed using infrared (IR) light, and the precise wave number positions of the bands (in particular of the CN⁻ chromophore) are diagnostic of specific redox states of the [NiFe]-active site (Fig. 1b). Electrochemistry has proved critical to understanding the catalytic activity of [NiFe]-hydrogenases and has been used in conjunction with spectroscopic methods to navigate between the equilibrium redox states of the active site, or to study the distribution of active site states during steady-state catalytic turnover. Here, unprecedented electrochemical control over the redox state of single crystals of hydrogenase is combined with in situ synchrotron IR microspectroscopy to tease out chemical reactivity that is too fast to see in solution studies but is slowed in the crystal state.

This study exploited the synchrotron IR source of the Multimode IR Imaging and Microspectroscopy (MIRIAM) beamline, Diamond Light Source, to monitor the active site of [NiFe] hydrogenase 1 from E. coli in the crystalline state as a case study. Hydrogenase 1 yields large, well-diffracting crystals with a typical cross-section of 50 × 50 µm² and a length of 1000 – 2000 µm. An electrochemical cell was custom-built to allow precise potential control, with a cocktail of redox mediators in solution employed to facilitate electron transfer between the crystal and working electrode. Spectra recorded following alternating reductive and oxidative potential steps confirmed that electrochemical control of the hydrogenase 1 active site was fully reversible over multiple reduction-oxidation sequences. The brightness of the X-ray source enabled collection of high signal-to-noise spectra at discrete 15 × 15 µm² sub-sections along the length of single hydrogenase 1 crystals, and electrochemical control was shown to extend over the whole crystal length. Spectral changes were complete within 30 minutes of application of a potential step.

The [NiFe] hydrogenase catalytic cycle (Fig. 1b) consists of both electrochemical steps and chemical steps involving protein transfer. The most reduced equilibrium state of the [NiFe]-hydrogenase active site, Ni₅R₄, actually consists of three sub-states at the same redox level. The precise nature of the Ni₅R₄ sub-states is unknown but they are thought to represent different protonated forms of the [NiFe]-active site, possibly indicative of different proton transfer events following initial activation of H₂. In solution and steady-state turnover studies the different Ni₅R₄ sub-states are observed at constant ratio, regardless of the potential, presumably interchanging on a timescale faster than the spectroscopic measurement. Interestingly in the crystalline state the interconversion of individual Ni₅R₄ sub-states can be temporally resolved, providing the first evidence that these sub-states might be sequential intermediates in the catalytic cycle (Fig. 2).

The results of this study have two important implications. Firstly, the ability to control, electrochemically, the redox state of a metalloprotein in a single protein crystal offers possibilities for obtaining ‘snapshots’ of complex redox states in well-defined states that have not been accessible previously. When combined with imaging of crystals using IR microspectroscopy, the state of the protein in the crystal can be checked before X-ray crystallography is used to obtain a structural ‘snapshot’, and afterwards to check whether there has been any damage to the crystal during the structural measurement. Secondly, our observations that chemistry is slowed down inside the hydrogenase crystal offers possibilities of trapping out specific states that must too fast to be detected in alternative solution studies. Thus, this work of represents an important advance in understanding the interplay between structure and function in some of the complex metal-containing proteins that are critical to life.

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Acute myeloid leukemia (AML) is a type of blood cancer that originates from white blood cells in the bone marrow. It is often fatal and is considered one of the most common cancers of children and the elderly. The high mortality rate associated with this cancer can partly be ascribed to ineffective current treatments, which consist of aggressive chemotherapy and stem cell transplantation. There is a great need to find alternative treatments for AML patients to improve their outcomes. By understanding the molecular mechanisms employed by AML cells to proliferate and avoid detection by the immune system, it is hoped this unmet need could be fulfilled.

Synchrotron Radiation Circular Dichroism (SRCD) spectroscopy at beamline B23 was used to probe the interactions of proteins involved in a molecular pathway responsible for AML immune escape. It was found that the pathway did not exist in healthy cells and was unique only to AML. The pathway results from a malignant transformation that involves the secretion of an immunoprotective protein, galectin-9, and the expression of a neuronal receptor, latrophilin 1, which triggers exocytosis upon interaction with other cells or soluble factors. The proteins help to impair parts of our immune system that try to destroy the cancer cells. Therefore, targeting this pathway could significantly enhance the patients’ immune defences and thus might be considered as a fundamentally new strategy for anti-AML therapy.

A fundamental biochemical pathway has been discovered, which includes ligand-dependent activation of latrophilin 1, a neuronal receptor that facilitates exocytosis and is expressed in malignant but not healthy human myeloid cells. This results in increased translation and secretion of the immune receptor Tim-3, and its ligand galectin-9. The process depends on activities of protein kinase C and mammalian target of rapamycin (mTOR). Tim-3 was found to have a dual role in the whole process by participating in galectin-9 secretion and by being released in a free soluble form. Galectin-9 impairs the anti-cancer activity of NK cells while free soluble Tim-3 attenuates secretion of interleukin-2 (IL-2) required for development of NK cell cytotoxic activity. These results were validated in vivo experiments using primary samples obtained from AML patients. Tim-3/galectin-9-dependent impairing of anticancer activity of cytotoxic lymphocytes is summarised in Figure 1.

Synchrotron radiation circular dichroism (SRCD) spectroscopy at beamline B23 was used to characterize the secondary structure of Tim-3, galectin-9 and the complex made by these two proteins presented in Figure 2a. Structural organisation of both Tim-3 and galectin-9 are presented in the Figure 2a. It was found in earlier studies that galectin-9 interacts with non-glycosylated Tim-3 with high affinity (Kd = 2 × 10⁻⁸ M). However, this binding is further strengthened by interaction of galectin-9 with sugars of glycosylated Tim-3. In AML cells Tim-3 undergoes glycosylation which means that its affinity to galectin-9 is very high in AML cells; this assumption was confirmed by the fact that the complex is detectable by Western blot analysis, which suggests a strong high affinity binding between the two proteins. SRCD spectroscopy was also applied to galectin-9 and Tim-3 and revealed a stoichiometry of 1:1 molar ratio (Fig. 2b). When mixed together with Tim-3, galectin-9 showed a CD spectrum which was clearly different from the simulated spectrum. This suggested that the interaction of Tim-3 with galectin-9 caused a conformational change of both proteins. An obvious increase in β-strand component was observed. Based on these findings, one may suggest that Tim-3 binding possibly alters the conformation of galectin-9. This results in increased capability of galectin-9 to interact with receptors on target cells. Galectin-9 is a protein, which contains two sugar-binding domains. Therefore, one domain could bind Tim-3 (or other proteins/receptor/traffickers) and leave the other domain open for interaction with a receptor molecule (for example Tim-3) associated with the plasma membrane of a target cell (for example NK cell or cytotoxic T cell).

This discovery opens new avenues for development of anti-leukaemia immunotherapy. Targeting this pathway might crucially enhance the patients’ immune defences helping them to eliminate leukaemia cells and could fundamentally change existing approaches to leukaemia diagnostics and anti-leukaemia therapy (and possibly the treatment of other cancers).

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**Figure 1:** Tim-3-dependent secretion of galectin-9 in human AML cells impacts the anti-leukaemic activity of NK cells and cytotoxic T cells (based on Goncalves Silva, I. et al. [2016]).

**Figure 2:** Tim-3/galectin-9 interaction leads to significant conformational changes possibly increasing solubility of the protein complex. (A) The schematic structural model of galectin-9 (on the right) and extracellular domain of the Tim-3 (on the left). In the structural model of the Tim-3, amino acids involved in galectin-9-independent binding are highlighted using open colour. Amino acid residues of the Tim-3, which are potential targets for glycosylation, are highlighted using red colour. (B) The SRCD spectrum of galectin-9, Tim-3, and the complex made by both proteins. (Adapted from Goncalves Silva, I. et al. [2016]).
Phase III Overview

At the end of the 2016/17 Financial Year, there were 31 operational beamlines at Diamond. The remaining five beamlines to join are either in commissioning phases or under construction. By 2020, all Phase III beamlines will be operational with user experiments underway. An overview of their activities and progress is outlined below.

I05 - Angle-Resolved Photoemission Spectroscopy (ARPES)

I05 is a facility dedicated to the study of electronic structures by Angle-Resolved Photoemission Spectroscopy (ARPES). This technique is applied to materials with exotic electronic ground states such as unconventional superconductors, solids exhibiting charge and spin density waves, electronic insulators and non-fermi liquids. The first branch, which is for X-ray (high resolution) ARPES experiments, has been successfully operating since 2013. The second branch is dedicated to nano-ARPES measurements and welcomed its first users in spring 2016. Together these two branches support users studying materials such as oxide superconductors, topological matter and transition metal chalcogenides.

B21 - High Throughput SAXS

Small-Angle X-ray Scattering (SAXS) is used to study particle in solution on I01. SAXS provides a limited-resolution, structural snapshot of the sample and can be used to study slow processes, such as fibre formation. In early 2017, B21 upgraded its X-ray optics with an eighty-fold increase in X-ray intensity and up to a two-hundred-fold increase in the signal-to-noise ratio. This upgrade involved replacing the monochromator with a double multilayer monochromator. Coupled with the exceptionally low background scatter, the increased intensity has pushed the sample concentration requirements substantially lower and enabled sub-nanosecond measurements. As a result of these enhancements, B21 is now one of the most sensitive beamlines internationally.

I08 - Scanning X-ray Microscopy (SXM)

I08 is the Scanning X-ray Microscopy (SXM) beamline for morphological, elemental and chemical speciation on a broad range of organic and inorganic interactions in a 250-4000 eV photon energy range and sample investigations under ambient or cryogenic conditions, which is unique for an SXM facility. The beamline extended its portfolio of specimen environments to functional cells allowing in situ nano-fluorides and electromagnetic biasing. In early 2017, I08 faced its first major upgrade in the frame of Scanning and Mapping projects, which offer optimised and improved data collection and analysis. The design and construction of a dedicated soft X-ray spectroscopy and tomography beamline branch has begun. This branch is expected to be available to the user community in 2019.

B24 - Full Field Cryo-Transmission X-ray Microscope (Cryo-TXM)

B24 is a full-field transmission microscope designed specifically to meet the rising demand for tomographic imaging of biological specimens under near physiological conditions. The technique bridges the resolution gap that exists between electron microscopy and conventional light microscopy and allows acquisition of tomographic data from both native and fluorescent-labelled samples. The operational energy range for B24 is 200 eV-2.6 keV, which allows imaging via absorption contrast within the water window as well as phase contrast at higher energies. The beamline is presently operating in optimisation mode. In the future, B24 will be upgraded to allow for the study of samples requiring Contrast Adjustment Level 5.

I23 - Long-Wavelength Macromolecular Crystallography

The Long-Wavelength Macromolecular Crystallography (ML) beamline (I23) is a unique facility dedicated to directly solving the crystallographic phase problem from native proteins. It is the first ML beamline internationally optimised for the long-wavelength region which allows for identification and measurement of light elements like hydrogen, deuterium and lithium. The beamline has the facility to store thousands of user crystallisation experiments and features an automated transfer between sample storage and the beamline, as well as highly automated data collection and analysis. VMX welcomed its first users in late 2016 and is currently under optimisation and is fully open to users. Once fully operational, this beamline will enable users to monitor their crystallisation experiments remotely, and request X-ray analysis without the need for their direct participation in the X-ray experiment. Equipped with an intense X-ray beam, very rapid detector and operating in a fully automated manner, VMXi will accelerate new discoveries in structural biology. The whole approach will allow for the study of crystals as they emerge and for the collection of data from all crystals, including those that are too fragile to handle and those that cannot be cryo-cooled.

B07 - Versatile Soft X-rays (VERS0D)

B07 offers Key Photoelectron Spectroscopy (KPS) and X-ray Absorption Spectroscopy (XAS) at ambient pressure. The beamline gives users the ability to carry out studies of catalysts under gas phase reaction conditions or investigations in atmospheric science and biology with samples under native conditions such as liquid environments. The ambient pressure beamline under construction is now operational. The first users were welcomed in summer 2017. A second branch line with moderate vacuum restrictions and automated sample manipulation for high throughput experiments and XAS is currently under construction and is expected to open for users in 2019.

I14 - Hard X-ray Nanoprobe

Currently, the end-station is being installed and the first users are expected in summer 2018.

B21 - Inelastic Soft X-ray Scattering

B21 is a dedicated Inelastic Soft X-ray Scattering (IXS) facility that will produce highly monochromatised, focused and tunable (250-1000 eV) X-ray beams. It is suited to investigate the electronic, magnetic and lattice dynamics of samples particularly those with magnetic and electronic interactions. The beamline is 81.6 m long with its end station and 15 m long IXS spectrometer accommodated in an external building adjacent to the Diamond ring. First light in the internal and external beamline was achieved in December 2015 and September 2016 respectively. The beamline construction has been completed and the X-ray commissioning occurred during summer 2017.

I02 - Versatile MX micro (VMXi)

VMXi will perform atomic structure determination for structures where large crystals are difficult to produce or suffer from weak diffraction. This is a common challenge for protein complexes and other flexible biological macromolecules. The smallest X-ray beam size on VMXi will be 0.5 µm and will uniquely combine scanning electron microscopy with X-ray diffraction, to allow the smallest protein crystals to be aligned into the X-ray beam and small wedges of rotation data to be recorded. VMXi can be thought of as a hybrid of X-ray and cryo-electron microscopy techniques, making use of methods for sample preparation from cryo-electron microscopy, imaging scanning electron microscopy and diffraction data collection methods from X-ray crystallography. In 2017, the X-ray optics were installed and successfully commissioned. Currently, the end-station is being installed and the first users are expected in summer 2018.

DIAD: Dual Imaging and Diffraction

DIAD is based on an innovative X-ray optical concept allowing the study of in situ processes with both imaging and diffraction simultaneously, enabling the use to take measurements of a live process as it evolves. Obtaining monochromatic resolution, the instrument will provide the spatial and time-resolved microstructural properties of samples that undergo a range of treatments including mechanical, chemical or thermal. As a result of the unique dual beam design, DIAD is able to simultaneously obtain data from the 3D microstructure, phase composition and stress state of the material. This means that a whole range of research can be carried out within a wide variety of fields including biomedical, material science, chemistry, geological science, biology and energy. DIAD is in the final construction stages.
The annual operating statistics are shown in Figure 1. The Mean Time Between Failures (MTBF) for the year was 79.9 hours, a little disappointing when compared with the previous two years but nevertheless still exceeding the target minimum of 72 hours. The reduction in MTBF this year is mainly attributed to an elevated number of trips due to power outages, BPM (Beam Position Monitor) electronics faults and front-end vacuum interlocks. The latter two are problems that have been known for some time, and for which solutions have been devised and are in the process of being implemented. Despite these issues the overall uptime (beam delivered as a percentage of scheduled hours) remained high at 98.2%.

Normal conducting cavities

In response to the risk of extended downtime in the event of further superconducting radiofrequency (RF) cavity failures, it was decided that the first NCL cavity should be deployed on the second normal conducting cavity and later also on the two superconducting cavities. Further systems are in construction and will be deployed on the second normal conducting cavity and later also on the two superconducting cavities.

Longitudinal Multi-Bunch Feedback system

A Longitudinal Multi-Bunch Feedback (LMBF) system has recently been implemented, in order to combat potential longitudinal instabilities of the electron bunches due to higher order modes in the normal conducting cavities, as well as to provide valuable additional diagnostic features.

To implement the LMBF a new kicker cavity was needed to be designed, manufactured and installed. The fabricated structure was installed in April 2017 in straight 22 just upstream of the insertion device and is only recognisable by the eight feedthroughs connecting power from the amplifier to the complex structure on the inside (Fig. 3a).

The feedback processor is based on commercial MicroTCA hardware, while FPGA and EPLS components were developed in-house. During this project the opportunity was taken to update the TMBF to the new hardware, which now allows synchronised measurements of the horizontal, transverse and longitudinal position of each individual bunch, a formidable new diagnostic tool.

'Missing sextupole' scheme

The Dual Imaging and Diffraction (DIAD) beamline (X11) is the last new beamline to be funded and is currently under construction. Originally envisaged to be installed on a ‘Superbeta’ (a bending magnet with higher magnetic field than the standard bending magnets in the ring) it was later proposed to be installed on an insertion device, using a second Double-Double Bend Achromat (DDBA) cell (as described in last year’s Annual Review). Calculations however indicated that a second DDBA cell posed a significant risk to the operation of the ring, and so another scheme was investigated, the ‘missing sextupole’ scheme (Fig. 4). This involves removing a sextupole magnet from one of the achromats and using the space created to install a short 10-pole wiggler magnet as the source for the DIAD beamline. Having confirmed its feasibility in simulations, this mode of operation has now been thoroughly tested during machine development periods by switching off the relevant magnet and returning the machine. Meanwhile the new vacuum vessels have been designed and constructed, and the modified grilles are being prepared (Fig. 5). These are due to be installed in the June 2018 shutdown.

Digital low-level RF systems

A digital low-level RF system (for stabilisation of cavity RF voltage and phase) is being developed in collaboration with ALBA. The first system is in operation on the first normal conducting cavity and has already demonstrated superior stability compared to the analogue system currently in use on the superconducting cavities. Further systems are in construction and will be deployed on the second normal conducting cavity and later also on the two superconducting cavities.

The feedback controller is continuously calculating 500 million control values per second, which it sends through an amplifier to a kicker to influence each bunch. The whole feedback process takes only a few microseconds and relies on the predictability of the motion of a bunch over such short periods.

Conceptually, the system is similar to the Transverse Multi-Bunch Feedback (TMBF) already in use since 2008 (Fig. 3a). A pickup registers the arrival time of each bunch, which is then processed in a digital feedback controller. This feedback controller is continuously calculating 500 million control values per second, which it sends through an amplifier to a kicker to influence each bunch. The whole feedback process takes only a few microseconds and relies on the predictability of the motion of a bunch over such short periods.

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Optics and Metrology Group
Kawal Sawhney, Optics and Metrology Group Leader

A

93

92

73 to 526x392

Figure 1: Photograph of a Cu-like horizontal mirror focussing on a X-ray beam.

Optics and Metrology Group continue to provide expert support in the design, testing, and optimisation of X-ray optics for new and upgraded beamlines. Looking to the future, the Optics and Metrology Group is also heavily involved in planning for Diamond II. Ray-tracing and wavefront propagation simulations are being used to predict the likely performance of current beamlines, and how they might be upgraded to optimally use the proposed brighter X-ray source.

Ultra-high accuracy characterisation of state-of-the-art X-ray optics continues to be an essential procedure, both for quality control and the development of novel optics. Continuous improvement of metrology instrumentation and techniques has led to ever more accurate at-wavelength (using X-rays) and ex situ (using visible light) characterisation of X-ray optics. We have also increased the technical capabilities of many existing and future beamlines by pursuing a broad range of optical research projects.

With our strong reputation for optical metrology expertise, we have also begun offering a paid commercial service to manufacturers to characterise and optimise beamline optical systems of other synchrotrons. Diamond’s enhanced metrology capabilities provide manufacturers with a two-fold advantage: helping to improve the quality of their products, and to provide an independent verification of high-quality fabrication.

Rapidly varying the size and shape of X-ray beams using high speed, bimorph deformable mirrors.

Piezo-electric, deformable ‘tangential’ mirrors are used to focus X-rays on many beamlines at Diamond and at other facilities around the world. The tangential curvature of bimorph mirrors is typically only changed every few hours or days. This operation can take tens of minutes and often requires expert guidance. Following a large change in curvature, bimorph mirrors are known to take more than 15 minutes to stabilise on the nanometre scale. Historically, the dynamic performance of active X-ray optics has therefore not been exploited at synchrotrons. This is in stark contrast to ultra-fast adjustments made to adaptive optics in other scientific fields such as Astronomy. However, many synchrotron beamlines, especially those dedicated to macromolecular crystallography, now analyse hundreds of samples per day. Such beamlines would greatly benefit from the ability to rapidly modify the X-ray beam profile in only a few seconds to match the size of small samples, or to vary the illuminated region of larger samples. The time-dependent behaviour of a series of micro-focus, bimorph mirrors was investigated using Fizeau interferometry in the Optical Metrology Lab. A novel ‘speedy’ bimorph Fig. 1) was developed by making several hardware and software improvements. Utilising a new high-voltage power supply, the magnitude of the mirror’s curvature drift after applying a large voltage shift to the piezo actuators was significantly reduced (Fig. 2a). The residual drift, attributed to piezo creep, was shown to be repeatable and could readily be compensated. Once installed on the Microfocus Macromolecular Crystallography beamline (I04) at Diamond, the Kirkpatrick-Baez (KB) pair of bimorphs focussed the X-ray beam in less than 10 seconds. Of equal importance, compensating piezo creep ensured that the X-ray beam remained stable for more than one hour after making a major change (Fig. 2b). This enables continuous ‘adaptive’ shaping of the X-ray beam in almost real time. Such innovations could lead to significant scientific improvements in how active X-ray optics are utilised at synchrotron and free-electron laser (FEL) sources.

A portable device for in situ characterisation of X-ray mirrors.

The push towards imaging samples with higher spatial resolution requires diffraction-limited and coherence-preserved X-ray beams. This demands accurate metrology of X-ray mirrors, ideally under working conditions. The Optics and Metrology Group have developed a portable device for in situ characterisation and optimisation of X-ray mirrors using X-ray speckle-based techniques. A schematic of the mechanical layout and a photograph of the device are shown in Fig. 3. The entire setup has been purposefully designed for ease of portability. The diffuser is mounted on a piezo stage for precision scanning, and a pair of crossed gold wires is also attached to the piezo stage to permit measurement of the X-ray beam size. Further downstream, a CCD detector and a photodiode detector are used to record the speckle pattern and determine X-ray beam size. The device is capable of measuring either horizontal or vertical X-ray mirror which, is especially useful if there is a need to characterise composite optics, such as Kirkpatrick-Baez (KB) mirror systems. Trial experiments were conducted at the Test beamline (B16) and Hard X-ray Nanoprobe beamline (I14). Ultra-high angular sensitivity is achieved by scanning the speckle generator in the X-ray beam. In addition to the compact setup and ease of implementation, a user-friendly graphical user interface has been developed to ensure that characterisation and alignment of X-ray mirrors is simple and fast. This fast, compact and accurate X-ray speckle-based device can be easily implemented on a variety of beamlines and is expected to find wide application in in situ characterisation or optimisation of X-ray mirrors at Diamond and other synchrotron radiation facilities.

Publications:

1-6

57x63

42

301x424

100

100

361

100
Detector Group
Nicola Tartoni, Detector Group Leader

During the past 12 months the Detector Group at Diamond has been working on two major development projects. The first project is the completion of the Xpress4 digital pulse processor, and the second the development of the large area detector for time resolved experiments, now called Tristan. The latter is still ongoing but has made substantial progress towards the delivery of the first prototype.

In January 2018 the Detector Group successfully completed the final installation and commissioning of the Xpress4 digital pulse processor (DPP) on a branch line of the Versatile X-ray Spectroscopy beamline, I20-Scanning (Fig. 1). Xpress4 is Diamond’s new spectroscopy DPP and has been designed to significantly improve the spectral and rate performance that can be measured using the existing 64-element monolithic high-purity germanium (HPGe) detector – the workhorse for fluorescence X-ray Absorption Spectroscopy on I20-Scanning.

Analysis of the HPGe detector signals had shown that a major barrier to high rate, high resolution performance was the presence of element to element crosstalk within the HPGe detector. A digital domain based signal processing algorithm was developed (and patented) to effectively remove crosstalk, allowing further downstream processing to more accurately measure fluorescence X-rays. Xpress4 is the physical and firmware realisation of this algorithm. It is a channel count scalable, custom designed, rack mounted hardware architecture whose salient features include a new high performance front-end digitiser, the latest high capacity high performance digital processing FPGA hardware and high speed serial links to cross-connect all channels in the digital domain. New firmware implements the crosstalk correction algorithm, enhances X-ray energy measurement precision, and reliably manages the inherently high data flows within the system in real-time.

The Xpress4 DPP manages to considerably enhance the energy resolution of spectra at high counting rates (Fig. 2). For a polychromatic sample (K-alpha fluorescence at 17.47 keV) the maximum input count rate (ICRmax) increases six-fold from 210 kcps per pixel to 1250 kcps per pixel for the same usable FWHM resolution (< 600 eV at an peak). At lower energies where crosstalk has less impact, ICRmax increases four-fold (e.g. manganese K-alpha (5.9 keV)) ICRmax increases from 200 kcps to 800 kcps for a usable FWHM resolution < 300 eV.

With challenging user samples it is sometimes not possible to operate at very high count rates simply due to the diluteness of the sample under study. In such cases, using Xpress4 still improves measurement accuracy by enhancing the resolution of the small fluorescence peak of interest whilst suppressing the impact of the inevitably large close-by elastic peak in an XAS scan. Comparative tests with ultra-dilute nickel nitrate solutions shows a two-fold improvement in dilution for a given performance using Xpress4 compared with previous results. Finally the characteristics of the spectra delivered by Xpress4 do not depend heavily as before on the counting rate, which helps in improving the data quality of absorption spectroscopy beam lines when the beam intensity changes during a scan.

In parallel to the development of the Xpress4 DPP some work has been carried out to characterise a demonstrator of a 19-channel monolithic segmented HPGe detector with a pad size smaller than the pad size currently in use at Diamond. The pads of the demonstrator have hexagonal shape with 1 mm apothem as opposed to the current ones that have square shape with 5 mm side. The demonstrator has been equipped with Lube preamplifiers and it was tested twice at Diamond’s Test beamline (B16). The results of the first beam test have been published at the IEEE 2017 Nuclear Science Symposium. During the second beam test the demonstrator was read-out with Xpress4, a very preliminary analysis shows that the detector can operate at about 1 million counts per second per channel with a count less than 15% that is still in the usable range of X-ray Absorption Fine Structure (XAFS) experiments. The energy resolution is still sub-optimal because in order to keep the cost within the budget the optimisation of all the parts was not pursued; however the tests done give a clear indication that this is a possible path to enhance the throughput of the fluorescence systems for XAFS by increasing the segmentation of the detector and by enhancing the counting rate of the individual channels.

The Tristan project aims at building a detector for time resolved experiments based on the Timepix3 chip. Sixteen Timepix3 chips are bonded to a monolithic planar silicon sensor with more than a million pads. The Tristan project is being carried out in two phases: the first phase is the development of a prototype with a single sensor (Tristan 1M), which serves as pilot detector and the second phase delivers a detector with ten sensors (Tristan 10M), which will then be installed on the Small Molecule Single-Crystal Diffraction beamline (I19).

Most of the parts of Tristan 1M have been developed and assembled. The detector is undergoing tests with a single chip connected to the rest of the electronics through an adapter board (Fig. 3). The front end printed circuit board to which the Timepix3 chips are wired and routes the signals to the back end electronics is currently under manufacturing. When this printed circuit board is delivered the Tristan 1M will be able to be tested in full. In parallel the mechanics of the Tristan 10M has been designed and the parts are currently being manufactured. The timescale for the completion of the project is to deliver a working Tristan 1M during the summer 2018 and then to assemble the Tristan 10M in autumn 2018 with the target to install it on the I19 during the winter of 2018/19.

References

Figure 1: The Xpress4 digital pulse processor installed in I20.

Figure 2: Molybdenum fluorescence spectrum acquired from channel 10 at 760 kilocounts per second by using algorithms with no crosstalk correction (blue line) and with crosstalk correction (red line). The energy resolution is greatly enhanced as it goes from 2138 eV FWHM down to 500 eV FWHM.

Figure 3: chassis of the Tristan 1M with all the electronics installed. The system currently drives a single Timepix3 chip connected to the rest of the electronics through an adapter board and a cable as shown in the picture.
**DAWN Steering Committee and Data Visualisation**

This year saw the formation of the DAWN Steering Committee, a collection of Diamond scientists selected to help guide the fundamental data visualisation features and general usability of the DAWN package. Under the supervision of the committee, a completely new 3D visualisation library has been integrated, greatly adding to DAWN’s existing tools.

The DataVis perspective developed in collaboration with the committee also integrates with the latest version of GDA, and is being used for live visualisation of raw and processed data on the XPDF beamline (I15-1).

**Small Angle Scattering**

Building on one of last year’s key successes whereby DAWN gained functionality in automatically process data following data acquisition, this year’s focus has moved to harnessing this capability, extending the visualisation of raw and processed data on the XPDF beamline (I15-1).

**Edo Science and IoT**

This year at Diamond, we hosted one of the Eclipse Science group and Internet of Things (IoT) workshops, which involved several invited talks and an IoT playground. Participants from Diamond, around the Harwell campus, and the wider business community all enjoyed the excellent presentations and demos which showcased the state of the art in software for science.

**DAWN**

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**Savu**

2017 saw the release of Savu version 2.0, which features an improved user interface and significant performance increases. The roll-out of Savu onto Diamond’s mapping tomography beamlines has reduced multi-modal processing from eight hours to ten minutes, and Savu is now able to replicate the standard full-field tomography processing of its predecessor in less computational time.

**Zooniverse**

Building on last year’s success with the SuRVoS software for analysing data from the Full Field Cryo-Transmission X-ray Microscope beamline (B24), SuRVoS has gone on to analyse biological data from other imaging beamlines as well, such as the Imaging branchline (I13-2). In addition to this, the scope has been extended further by making use of the Zooniverse platform (www.zooniverse.org) to host some work on protein misfolding disorders, specifically Huntington’s disease initially, but with the aim to extend to other problems where humans are better than machines at identifying information in complex image data.

**ISPyB**

The ISPyB database and SynchWeb software services store and present experimental meta-data, generate beamline performance statistics and provide remote access to users and beamline scientists. To reflect its growing importance, the team supporting the ISPyB and SynchWeb software services is increasing. A full time project lead was appointed in September 2017 and will be followed by a full time SynchWeb developer joining the team in early 2018. Additional support has also been contracted to re-establish support for mobile devices.

New features added to SynchWeb in the past year have included the integration of automated sample shipping to the facility. This includes support for users across the EU. Work has also been underway to add support to new and emerging techniques including XFEL beamline (I15-1) and continued refinement of the in situ beamline HIMI. Diamond and the Scientific Software team continue to support the international ISPyB collaboration through developer, scientific and steering committees. Diamond co-hosted the most recent joint ISPyB-MOGAGE meeting in January 2018. One of the key areas for discussion in the collaboration is the growing field of cryo-electron microscopy. The team at Diamond established the integration of electron microscopy experimental data with ISPyB through the development of Spino workflow. The development activities continue to enhance ISPyB as it evolves from a bespoke solution for a single technique to a general purpose Laboratory Information Management System (LIMS) for Diamond.

**Acknowledgements**

We wish to thank all our collaborators, Diamond beamline staff and users for their continued support and input.
Data Acquisition Group

Keith Ralphs, Interim Data Acquisition Group Leader

In recent years Diamond has invested a lot of software engineering effort across the Data Acquisition, Data Analysis and Beamline Controls groups in an attempt to standardise and advance the frameworks that support the science carried out here. Under the auspices of the Mapping Project, this has delivered a platform, initially proven on a few beamlines, which can now start to be rolled out across the organisation as a whole to deliver enhanced capabilities in terms of the definition, orchestration and visualisation of experimental scans. Building on this, during the last year we have begun to see these benefits feeding into areas of usability and beamline development as well as facilitating the development of more advanced approaches such as ptychography. Going forward, this should allow us to better support the needs of Diamond’s scientists and users as these new tools are adopted across the organisation.

The Data Acquisition Group develops, supports and maintains the software that controls experiments carried out on the majority of beamlines at Diamond. All aspects of the experimental process are covered, but initial setup of the sample environment is always crucially important in obtaining accurate and meaningful results further down the line. It is here that software usability can be very significant in enabling quick, easy, repeatable instillation of the experimental environment to guarantee consistency between groups of measurements.

Focus on Usability

Focus scans, which are made to ensure the hardware holding an experimental sample is correctly positioned with respect to the incoming beam, are a particular example where usability becomes a key factor in making progress, as the ability to re-establish the best focus point with a few clicks of the mouse can save a lot of time. Automating the data gathering part of this operation as much as possible, leaving the user to just select the focus point itself, can become especially important during long, perhaps overnight runs, offering users the ability to re-establish the best focus point with a few clicks of the mouse can save a lot of time. Automating the data gathering part of this operation as much as possible, leaving the user to just select the focus point itself, can become especially important during long, perhaps overnight runs.

Try before you buy

In producing Data Acquisition support software for new and upgraded beamlines, the ability to prototype, evaluate and hone the tools we develop as early as possible in the beamline build and commissioning process is key to ensuring successful delivery of new experimental capabilities at Diamond. It allows us to debug and address problems up front and to work closely with beamline scientists to collaboratively design the user experience that will eventually be delivered, long before the finished beamline exists. During the last year, the opportunity to do this has been improved substantially by the installation of the P99 test beamline as part of the ongoing ptychography Data Acquisition project being carried out by the data analysis group. Use of this small scale laser based analogue of a full beamline setup enables Data Acquisition engineers to exercise the software tools and processes that are developing, whilst connected to actual representative hardware of the sort that will eventually be used on the real installation. This approach has come to the fore in recent months on the project to develop Data Acquisition support of the new DIAD (Dual Imaging And Diffraction) beamline, currently under construction next to I12. DIAD will produce two separate beams to enable the use of two different X-ray measurement techniques; diffraction and imaging. To allow each technique to capture the desired results a novel Beam Selector device (a prototype of which exists) is placed in the path of the main beam at the end of the optics hutch. This selector will need to be controlled by our data acquisition software via the hardware triggering layer developed by the Controls Group to ensure the high speed switching required for the planned experiments. The availability of the P99 test beamline has allowed both our teams to start actively developing the processes that will drive this selector on the real beamline by temporarily installing the prototype on P99 and working together to design and debug scans on a setup that closely resembles the real installation. Working in this way ensures that we maximise the chance of discovering and addressing any issues that arise long before the functionality is needed and also allows us to engage DIAD’s beamline scientists in this process to get their feedback and ensure that our approaches are valid.

The way forward

In the coming years the upgraded Data Acquisition and Controls platform now available to us will allow us to start to roll out similar targeted functionality across all of Diamond’s beamlines using this collaborative approach. This should allow us to deliver functionality that enables new techniques and optimises existing ones, allowing our scientists and users to concentrate on the specifics of their experiments and the insights they yield. In addition, the hardware level control now supported will help develop other recent automated beamline installations such as VMI allowing them to optimise the control of their experiments to maximise their efficiency.
Key Facts and Figures

Facility usage

In our eleventh year of operations (1st July 2017 to 31st March 2018), we received 1,515 proposals for experiments on our instruments via peer reviewed access routes, requesting a total of 19,507 shifts. After peer review, 1,095 proposals were awarded beamtime. This resulted in 11,667 experimental shifts being awarded across 28 operational beamlines, one commissioning beamline and eight electron microscopes. We welcomed 5,668 onsite user visits from academia across all instruments, with an additional 3,656 remote user visits.

In the last 12 months, Diamond started to review its reporting method on facility usage. A new reporting tool is currently being developed and allows us to report more precisely and more consistently. As a result, some of the reporting criteria in this review have evolved compared to previous years. Further efforts on reporting are being carried out and should continue in the next 12 months.

User shifts requested, awarded and delivered by group, beamline and electron microscope 2017/18

Cumulative number of items in Diamond Publications Database by our scientists and users and cumulative number of protein structures solved

Proposals by discipline and research theme

Experimental shifts scheduled by Diamond by main subject area for 2017/18

Machine performance

Total no. operational beamlines by end FY

Scheduled hours of machine operation

Scheduled hours of user operation

Machine uptime %

Mean time between failures (hours)
Collaborations

Diamond Manchester Collaboration

The collaboration between the University of Manchester and Diamond Light Source was established to construct and operate an imaging facility at Diamond’s X-ray Imaging and Coherence beamline (I13). Complementary to the Coherence branchline (I13-1), the Diamond Manchester Imaging branchline (I13-2) performs real-space imaging and tomography on a length or timescale not achievable in home laboratories. Thanks to the high flux from Diamond, images of high signal-to-noise ratios can be recorded very quickly on I13-2. This enables the study of dynamic processes such as electrochemical degradation for explaining battery failure, bubble dynamics in molten metals for understanding how metals solidify and therefore fail, and the dynamics of the closed cochlea, the part of the ear that converts sound waves to electrical signals.

Manchester assisted financially to the building of the I13-2 branchline and continues to contribute to its beamtime staff, operations and development. Diamond owns and has overall responsibility for the branchline, and provides all other funding necessary to ensure I13 conducts world-leading science. I13 has its own beamline team which is led by Principal Beamline Scientist Professor Christoph Rau and director of the collaboration is Professor Neil Bourne.

In return for its investment, Manchester has guaranteed access to beamtime at Diamond. The majority of this is carried out on I13-2, but substantial amounts of beamtime are available on other beamlines as well. Manchester uses I13-2 for research that spans materials science, biomeedicine, geology and engineering, as well as methods to develop the fields of X-ray imaging and tomography. To complement the work undertaken at Diamond, Manchester has set up a chapter of the Manchester X-ray Imaging Facility at the Research Complex at Harwell (RCaH) situated next to Diamond. To date the collaboration has produced 78 publications.

The partnership formally began in May 2010 and will continue until at least 2020. Both partners view the collaboration as a long-term, ongoing relationship, working together as key national players in X-ray imaging and tomography as well as providing access to the forefront of new technology. With this vision in mind there are significant plans on the horizon for the collaboration. These plans include technical and instrument upgrades as well as increasing the extent of the collaboration to involve many stakeholders. The partnership continues to contribute to its beamline staff, operations and development.

The Diamond Manchester collaboration has been involved in many other collaborations

The UK Catalysis Hub

Catalysis is a core area of contemporary science, engineering and technology that has substantial economic and societal impact. Although rooted in chemistry and chemical engineering, catalytic science is now largely multidisciplinary, drawing strongly from materials and bio-sciences.

The UK Catalysis Hub

The UK catalysis effort and expertise on a global stage. The Hub has strong links with industry which are coordinated by an Industrial Advisory Panel comprising of several UK and international industrial members.

One of the main benefits of the Catalysis Hub is sustained access to a synchrotron radiation source. Members of the Hub may apply for access to Diamond through a Beamtime Access Group (BAG), which provides the team with access to the Core EXAFS beamline (B18) per allocation period. This access route increases the efficiency of data acquisition by coordinating projects to reduce the dead time of experimental setup, and by allocating small amounts of time for proof of concept investigations before a full study starts. Applications are judged by a panel of expert academics and beamline scientists, who consider (i) the quality of the underpinning science, (ii) the likely success of the experiments, (iii) bringing in new users of synchrotron radiation, and (iv) coordinating time effectively to maximise efficiency.

This opportunity is open to every academic working in catalysis in the UK. The model of access brings together complementary expertise to ensure that experimental time is maximised, and provides opportunity for researchers that have not used a synchrotron before. The Catalysis Hub team have worked with a variety of catalysis samples, and the B18 beamline team know exactly how to get the best out of the samples they are working on.

The UK catalysis Hub also presents a training experience; a number of PhD students and postdocs have had the opportunity to work on beamlines at Diamond.

The Hub provides a platform for researchers to work collectively and gain frequent access to the Diamond synchrotron, as well as other facilities at Harwell. A whole system approach to the study of catalysis combined with high throughput allows optimal experiments to be carried out which shorten the path to development of commercially useful products, and promote the UK catalysis effort and expertise on a global stage.
Industrial Liaison at Diamond

Elizabeth Shotton, Head of Industrial Liaison

The past year has once again been a year of growth for the industrial user programme at Diamond. From across the globe 50 companies are making regular use of the beamlines, and increasingly the cryo-electron microscopy (cryo-EM) facilities. The Industrial Liaison team are supporting around 250 different experimental sessions with industrial users each year, with the majority of users coming from the life science sector.

The growth in industrial usage by life science companies has been supported by the expansion of Diamond’s capabilities in this area and we are now able to offer a wider range of structural biology services than ever before. Recent developments in detection and the latest generation of microscopes has meant that previously unattainable resolutions are now routinely possible through cryo-EM at Diamond’s Electron Bio-Imaging Centre (eBIC). This has resulted in an increased demand for the technology across both academia and industry. To support this growth, Jason Van Rooyen joined the team in May 2017 from the University of Cape Town as the Industrial Liaison Scientist for cryo-EM.

The XChem facility for X-ray structure-advanced, synthesis-aligned fragment medicinal chemistry which has been established at Diamond in partnership with the Structural Genomics Consortium is also proving an attractive service for our industrial users. Several campaigns have been conducted through the service; with demand outstripping supply, a parallel facility has been funded for industrial users. This will allow us to provide more timely access to our clients to allow for quicker feedback into their drug discovery programmes.

We are working to enable industrial access to the full wealth of technology and knowledge available at Diamond by extending our services to the technical expertise of our Optics and Metrology Group in addition to our beamlines and microscopes.

At synchrotron radiation sources and free-electron lasers (FELs), the quality of X-ray optics is often a major limitation to beamline performance. Recent advances in deterministic polishing techniques have greatly improved the quality of optical surfaces but have revealed a new challenge for X-ray optics; minimising additional slope errors introduced by mounting the substrate into its holder, adding cooling manifolds, and bending it.

High quality metrology instruments and ultra-stable environments are essential to avoid optimisation of damping and bending to guarantee the best possible X-ray performance for beamline optics. Ex situ optimisation and fault-finding investigations of such systems prior to beamline installation have saved significant amounts of valuable X-ray commissioning time, and it is here where the testing capabilities of the Optics and Metrology Group at Diamond come into play (Fig 3). Commercial suppliers of synchrotron optical systems have been able to benefit from Diamond’s state-of-the-art metrology instruments and facilities that enable testing to unprecedented levels.

A successful industrial consultancy between Diamond and FMB Oxford Ltd, an established leader in the supply of beamlines and beamline components, has developed mechanical systems that can accurately bend long X-ray mirrors to a range of useful slithers. On several occasions, FMB Oxford have successfully exploited this metrology service, including the recent tests of their newly developed two-moment actuator systems for elliptical bending of long X-ray mirrors which have been published in Journal of Synchrotron Radiation.

In an effort to reduce barriers to innovation, the Industrial Liaison team have been working with colleagues across STFC in two funding schemes which aim to help companies overcome intractable product, manufacturing or process performance problems through advanced measurement and analytical technologies.

The first scheme was funded through Innovate UK and STFC plus other external partners such as the National Physical Laboratory. Analysis for Innovators (A4I) opened to applications in January 2017, allowing companies to apply for a share of £4.5 million to work with facilities such as Diamond on solutions for analysis and measurement problems. Two projects were funded to use Diamond, including one with a micro-SME, Lewtas Science & Technologies, studying “phase change control by very low power ultrasound”.

Low power (<10 W m⁻¹) ultrasound spectroscopy has been used for many years for the characterisation of materials, particularly in the food industry, with respect to particle size distribution, adiabatic compressibility, particle solution and dissolution, crystal nucleation and solid content. High power (>1 kW m⁻¹) ultrasound methods are applied for material modification and processing, ultimately speeding up processing times, improving product quality and reducing costs. However, high power ultrasound methods are well known to impact on crystallisation and structure so can have many drawbacks. In the case of food products, they can cause off-flavours through product oxidation. Furthermore, the success of process development with power ultrasound is hit and miss, mainly due to the complex and poorly understood detailed physics involved, but also issues such as the generation of free radicals (which can promote oxidation of fats) and shock-wave related wear of the sonotrode and processing equipment, ultimately leading to contamination of the product.

Recent experiments have shown that well-controlled crystal nucleation can be obtained using low power ultrasound but fundamental studies in this area are lacking and this is where the project aimed to gain deeper understanding (Fig 2). In order to measure and understand the nature of this effect the team used simultaneous Small Angle and Wide Angle X-ray Scattering (SAXS and WAXS) on the Small Angle Scattering and Diffraction beamline (S22) to test many different types of candidate molecules such as waxes, fats, fuels and oils, model pharmaceutical and agrochemical molecules in a specially created acoustic cell. Schemes such as A4I are invaluable to micro-SMEs such as Lewtas Science & Technologies as they give small companies the opportunity to better protect their IP and get to the market much quicker.

As well as growing the industrial programme here at Diamond, the Industrial Liaison team has been active in a number of international collaborations. Within the EU, the team participates in CALIPSOplus, a project funded through the European Union's Horizon 2020 Research and Innovation programme. The grant provides funding for marketing activities where the light sources can join forces to have a greater impact on the European industrial science community and also for SME access to the facilities.

Further afield, the team have been awarded funding via the Newton Fund. The Newton Fund’s aim is to develop science and innovation partnerships that promote the economic development and welfare of collaborating countries. The grants awarded to the Industrial Liaison team are for projects in Thailand and Indonesia. For the Thai project, the aim is to support the Thai synchrotron facility, SART, in the development of their industrial user engagement through a four-year programme. In December 2017, the first activity under this grant took place in Thailand where a three-day workshop was held to demonstrate the importance of large-scale scientific facilities to business (Fig 1). We were supported in this workshop by the British Embassy in Bangkok and by the participation of Peter Dowding from Infineon and Paul Caffin from Johnson Matthey who both spoke about the importance of Diamond and access to large science facilities to their research.

As the facilities and knowledge available at Diamond continue to expand and develop, the industrial programme continues to flourish. Our range of services has now extended to include a broader range of instrumentation and expertise and the demand from our clients has enabled us in turn to add capacity to some of Diamond’s facilities. Through participation in a range of funding schemes, we have additional resources to help us spread the message of the great value of synchrotron science to both the UK industry base and the European industrial science community as well as to support regional development with our global synchrotron partners. We look forward to sharing the results of our new initiatives in due course. If you would like to learn more about any of these recent developments, please do contact us on industry@diamond.ac.uk.

Figure 1: Participants in the Newton Fund workshop held in Bangkok in December 2017.

Figure 2: Two identical samples, 30% Titanium Oxide. The cell on the right is associated with specific four power ultrasound while the cell on the left is not. The sample on the left crystallises as needle shape nucleation is completely suppressed in the controlled sample.

Building on the success of A4I, Diamond has joined STFC to further support UK business productivity and growth as part of the government funded bridging for Innovators (B4I) programme. The four-year programme run by STFC will provide access to the world leading large-scale science facilities at Harwell, Daresbury and the Royal Observatory in Edinburgh covering a wide range of analytical techniques and exploiting their expertise and capabilities. The aim is to increase growth and productivity throughout the UK by helping organisations overcome product, manufacturing or process performance challenges. The Industrial Liaison team has participated in a number of briefing sessions across the country to enable organisations to explore the potential of the programme and discuss their requirements. We look forward to welcoming participants of the programme in the coming months.

Figure 3: Two identical samples, 30% Titanium Oxide. The cell on the right is associated with specific four power ultrasound while the cell on the left is not. The sample on the left crystallises as needle shape nucleation is completely suppressed in the controlled sample.
Engaging with Diamond Light Source
Communications and Engagement Team

Diamond has continued to commit to its engagement programme throughout 2017-18, linking the facilities world leading science and engineering professionals with a diverse range of audiences. The year has seen us deliver a wide range events and engagement opportunities, reflecting the needs of our staff and users as well as the interest of a range of communities in the public.

In total our events welcomed 5,615 visitors to the facility, comprising; 1,413 for scientific and technical events, 668 undergraduate and postgraduate visitors, 3,211 school students and members of the general public, and 433 VIPs and stakeholders.

The majority of our visitors come for Diamond’s core program of events, including our regular Inside Diamond open day, which continues to be extremely popular and gives members of the public a chance to visit the facility in small groups, to see inside the synchrotron and visit a beamline.

“From start to finish the atmosphere was great with many people on hand to chat … The tour around the facilities was also most informative with some aspects and numbers producing jaw dropping reactions from members of the group.”
- visitor to an Inside Diamond open day, 2018

In July we hosted a new family focused event ‘Meet the Scientist’, where over 20 Diamond staff and members of our user groups came with a suit of interactive exhibits to showcase their work to a younger audience. Over 600 visitors attended over the day to participate in activities that included levitating trains, lifting weights with vacuum and building rollers while as taking tours inside the synchrotron building.

“A good way of engaging children and adults in science. My children loved it.”

“Enthusiastic and passionate staff were great at engaging with children and gave a real positive impression about working in a science, in a way my daughters perhaps don’t see anywhere else.”
- visitors to Diamond’s ‘Meet the Scientist’ event, July 2017

We have offered regular schools open days, giving A-level students a general overview of the facility and highlighting career opportunities available to them. There are also dedicated activities for students to experience specialist areas within the facility including biology, computing, engineering and science applications. The Diamond schools work experience program continues to develop taking its third cohort in 2017, offering 26 students an immersive week of project based work in areas across the organisation.

Away from site, Diamond has also been active promoting our work. In September we partnered with Harwell Campus and the Medical Research Council to host a stand at the New Scientist Exhibition at the ExCeL Centre in London, with over 30,000 people attending the four day event. The Bluedot music festival at Jodrell Bank Observatory, where music is combined with a programme of live science and expert talks, provided the opportunity to engage with a different audience. Thousands of festival goers were able to visit our exhibition stand and talk to some of Diamond’s summer placement students.

Diamond continues to work closely with the engagement team at STFC, jointly delivering a series of activities, including the school’s Particle Physics Masterclasses and public events which among them welcomed over 1,200 visitors to site every year.

Over the past 15 years of operation, Diamond’s staff numbers have continued to grow and as the past year has seen a targeted increase in internal engagement activities. As well as talks and training, an internal science open day took place in November, where 20 beamlines opened their doors and welcomed 168 staff from across the facility to learn more about the operations and science delivered within.

The demand for visits from the university student community continues to increase and Diamond met this by hosting 26 postgraduate and undergraduate groups from across the country in 2017.

Scientific Workshops and Conferences
Diamond hosted a range targeted events to meet the interests and development needs of our staff and user community. A summary of these events is outlined herein, which includes workshops, conferences and training schools relating to specialist fields, techniques and software that can further research and discoveries in Synchrotron Science.

During the summer months, Diamond hosted three international conferences, each from an established conference series. The 20th International Magnetic Measurement Workshop (IWM20) was held onsite in June 2017 with a whole week of presentations and open discussions on the equipment and techniques used to measure and characterise magnetic fields on accelerator magnets and insertion devices. In August, we welcomed experts in the field of X-ray Absorption Spectroscopy to discuss aspects of the technique that affect data quality in XAS experiments at Q2XAFS, a satellite workshop the IUCS Congress meeting. We ended the summer with the ninth International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources (WIRMS 2017) at Worcester College in Oxford, a key meeting for staff and users of IR/THz facilities at Synchrotrons (SLS), Energy Recovery Linac (ERL) and Free Electron Laser (FEL) facilities around the globe.

“...a great way of engaging children and adults in science. My children loved it.”
“Enthusiastic and passionate staff were great at engaging with children and gave a real positive impression about working in a science, in a way my daughters perhaps don’t see anywhere else.”
- visitor to Diamond’s ‘Meet the Scientist’ event, July 2017

…It was so good, I wondered why we had not done it before. Thanks to everyone involved!”

“Seeing Principal Beamline Scientists interact with staff they wouldn’t normally even see was very rewarding.”
- Diamond staff attending the internal open day, November 2018

Engaging with Higher Education
Our work placement schemes for undergraduates continued to provide students with in-depth research projects whilst also developing life-long skills in communication, engagement and project management. In June 2017, six Year in Industry and 14 summer placement students arrived at Diamond to begin their projects. Whilst based at Diamond, the students also had opportunities to visit other research teams and facilities on-site and to present their research to the wider Diamond organisation.

Diamond welcomed 25 new PhD students in 2017, bringing the total number of co-funded PhD studentships to over 90 active students. We proudly collaborate with research organisations around the UK and beyond, hosting co-funded PhD students and training the synchrotron scientists of the future. Continuing from the successful introduction of a centralised call for collaborative PhD proposals in 2016, the 2017 scheme received 59 proposals. Following an internal review process, 16 studentships were funded and we look forward to welcoming our new students starting in October 2018.

The demand for visits from the university student community continues to increase and Diamond met this by hosting 26 postgraduate and undergraduate groups from across the country in 2017.

<table>
<thead>
<tr>
<th>Date</th>
<th>Event</th>
<th>Participants</th>
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<tr>
<td>4 April 2017</td>
<td>Advanced Characterisation for Functional Materials</td>
<td>58</td>
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<tr>
<td>12 April 2017</td>
<td>Spectre XAS conference, Poster session and Tours</td>
<td>26</td>
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<tr>
<td>26 - 24 April 2017</td>
<td>WBC Openings and EPS-DMSP SPRing Symposia</td>
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<td>1 - 2 June 2017</td>
<td>Beam Training for Small Angle Scatter Workshop</td>
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<tr>
<td>4 - 9 June 2017</td>
<td>9th International Magnetic Measurement Workshop (IWM20)</td>
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<tr>
<td>6 June 2017</td>
<td>2017 WorldCNC Group Meeting</td>
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<tr>
<td>13 June 2017</td>
<td>Advances in X-ray Imaging: Expanding the Frontiers of Knowledge</td>
<td>70</td>
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<tr>
<td>23 June 2017</td>
<td>Microscopy, Tomography, Photochemistry Data Analysis, Diamond, Future Planing Workshop</td>
<td>50</td>
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<tr>
<td>4 July 2017</td>
<td>BDS Warwick school organised by MMT in Lead (CO2) framework</td>
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<tr>
<td>5 - 6 July 2017</td>
<td>MPG Beam Training Workshop</td>
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<tr>
<td>18 - 19 July 2017</td>
<td>Electron Structure of 2D Materials (area department)</td>
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<tr>
<td>24 - 25 July 2017</td>
<td>International Workshop on Improving Data Quality in XAS Spectroscopy (Q2XAFS)</td>
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<tr>
<td>1 September 2017</td>
<td>Early Career Scientist Symposium</td>
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<td>26 - 20 September 2017</td>
<td>MRI International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources (WIRMS 2017)</td>
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<td>2 - 4 October 2017</td>
<td>Synchrotron Sample Preparation Workshop</td>
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<td>24 - 26 October 2017</td>
<td>Novas International Advisory Committee Annual Fall Camp</td>
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<tr>
<td>26 - 31 October 2017</td>
<td>Beam Training for Small Angle Scatter Workshop</td>
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<td>17 November 2017</td>
<td>Microscopy of Catalysts Workshop</td>
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<td>29 November - 7 December 2017</td>
<td>Diamond CCP4 Data Collection and Analysis Workshop</td>
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<tr>
<td>8 - 9 January 2018</td>
<td>EPSL – diamond meeting</td>
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<tr>
<td>31 – 2 January 2018</td>
<td>Joint CCP4 and MRCoder Collaboration Meetings</td>
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<td>5 - 9 February 2018</td>
<td>SBC User Training Workshop</td>
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<td>8 February 2018</td>
<td>EPSL Science User Meeting</td>
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<td>21 - 22 February 2018</td>
<td>MPG Beam Training Workshop</td>
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<td>23 February 2018</td>
<td>Eclipse Science and EMB Workshop</td>
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<td>18 - 21 March 2018</td>
<td>Key X-ray Absorption Spectroscopy Training Workshop</td>
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<td>26 - 27 March 2018</td>
<td>EPSL Hyperge Training Workshop</td>
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<td><strong>Total</strong></td>
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<td><strong>1,222</strong></td>
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Governance and Management

Diamond Light Source Ltd was established in 2002 as a joint venture limited company funded by the UK Government via the Science and Technology Facilities Council (STFC) and by the Wellcome Trust, owning 86% and 14% of the shares respectively. Diamond now employs over 630 scientists, engineers, technicians and support staff from over 40 countries worldwide. The Chief Executive and Directors are advised by committees representing key stakeholder groups, including the Science Advisory Committee (SAC), Diamond User Committee (DUC), and Diamond Industrial Science Committee (DISCo).

Diamond is free at the point of access for researchers accessing Diamond via peer review, and provided the results are published in the public domain for everyone’s benefit. Allocation of beam time is via a peer-review process to select proposals on the basis of scientific merit and technical feasibility. Eight peer-review panels meet twice a year to assess the proposals submitted for each six-month allocation period. Diamond also welcomes industrial researchers through a range of access modes including proprietary research.

Board of Directors

- Prof Sir Adrian Smith (Chairman)
  Vice-Chancellor, University of London
- Prof Andrew Harrison
  Chief Executive Officer, Diamond Light Source
- Marshall Davies
  Business Advisor, Science and Technology Facilities Council
- Prof Mark Thomson
  Executive Chair, Science and Technology Facilities Council
- Prof Michael Fitzpatrick
  Pro-Vice-Chancellor, Coventry University
- Tim Livett
  Chief Financial Officer, The Wellcome Trust
- Jane Tirard
  Director of Finance & Corporate Services, Diamond Light Source
- Company Secretary
  Andrew Richards, Diamond Light Source
- As at April 2018

Executive

- Prof Andrew Harrison: took the helm as CEO of Diamond Light Source in January 2014. He was previously Director General of the Institut Laue-Langevin neutron source in Grenoble, France, where he had worked since 2006. With a background as an inorganic chemist and Professor of Solid State Chemistry at the University of Edinburgh, Prof Harrison brings a wealth of experience of scientific leadership to the organisation.

- Prof Laurent Chapon: joined Diamond as Director of Physical Sciences in 2016 from the Institut Laue-Langevin in Grenoble, France. Whilst there, Prof Chapon was Senior Fellow and Leader of the Diffraction Group for over five years. He is an expert in materials science as well as X-ray and neutron diffraction techniques. His principal interests include transmission metal oxides, frustrated oxides, and multifilms.

- Prof David Stuart: is MRC Professor of Structural Biology at the University of Oxford, and Head of the Division of Structural Biology at the Department of Clinical Medicine. He was appointed Director of Life Sciences at Diamond in 2008. His principal research interests include the structure of viruses and viral proteins as well as cellular proteases, especially those that interact with viruses.

- Prof Richard Walker: joined Diamond Light Source as Technical Director in January 2002. He was previously Director of the Light Sources Division at Sincrotrone Trieste in Italy, and prior to that he was a key member of the Daresbury Laboratory SRS team. He is a visiting Professor of Physics at the University of Oxford.

- Jane Tirard: joined Diamond as Director of Finance and Corporate Services in 2015. With over 30 years of regional and global experience in business and financial management, she was most recently Finance Director at Queen Mary University of London, and previously held the post of Executive Director of Finance at STFC. Prior to joining the public sector, Jane held several positions at Pfizer.

Staffing and Financial Information

Summary of Financial Data

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<td>30.5</td>
<td>33.5</td>
<td>36.5</td>
<td>39.9</td>
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<td>Total Staff (Year End)</td>
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<td>419</td>
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<td>Capital Expenditure – Operations £m</td>
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<td>5.7</td>
<td>8.6</td>
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<td>6.2</td>
<td>8.0</td>
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<td>Phase II £m</td>
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<td>Phase III £m</td>
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<td>10.3</td>
<td>14.2</td>
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<td>23.7</td>
<td>20.6</td>
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<td>Other capital projects £m</td>
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<td>7.3</td>
<td>4.3</td>
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Figures up to and including 2014/15 include VAT, thereafter figures include VAT.
The Scientific Advisory Committee (SAC) advises the CEO and the Science Directors on the scientific and technical questions impacting the specification, design, commissioning and operation of the facility, experimental and user support facilities, and opportunities for scientific exploitation.

Dr Andrew Thompson (Chair) SOLEIL (France)
Dr Tom Hase (Vice-Chair) University of Warwick (UK)
Dr John Barker Evotec (DISCo Representative)
Dr Bridget Carragher New York Center for Structural Biology (USA)
Dr Nick Brooks Imperial College (UK – Chair of the DUC)
Prof John So Evans University of Durham (UK)
Dr Paul Fuss SLAC (USA)
Prof Philip Hofmann Aarhus University (Denmark)
Prof Peter Hatton University of Durham (UK)
Prof Tim Lodge University of Minnesota (USA)
Dr Lisa Miller Brookhaven National Lab/NLS-II
Prof Arwen Pearson The Hamburg Center of Ultrafast Imaging (Germany)
Dr Ilme Schlichting Max Planck Institute for Medical Research (Germany)
Prof Christian Schroer DESY (Germany)
Prof Sam Shaw University of Manchester (UK)
Prof Moniek Tromp University of Amsterdam (Netherlands)

The Diamond Industrial Science Committee (DISCo) advises the CEO and Directors on opportunities for industry to be engaged in research at Diamond, industrial research priorities that will help shape operational strategy, including the best way to exploit the current suite of beamlines and to develop the case for investment in future beamlines, and to develop best practice for industrial engagement.

Dr Malcolm Skingle (Chair) GlaxoSmithKline
Dr John Barker Evotec
Dr Andrew Barrow Ribo-Biogene
Prof. David Brown Charles River Laboratories
Dr Paul Collier Johnson Matthey
Dr Rob Cooke Heptares Therapeutics
Dr Cheryl Doherty Pfizer
Prof. Peter Dowding Infinx
Prof. Jonathan Hyde NNLS
Prof. Ken Lewtas Lewtas Science & Technologies
Dr Jonathan Mitchener Innovate UK
Dr John Pollard Vertex Pharmaceuticals (Europe) Ltd
Dr Richard Storey AstraZeneca
Dr Ian Tucker Unilever

Membership as at April 2018

The Diamond User Committee (DUC) has been set as a platform for discussion between Diamond and the user community of matters relating to the operation and strategy of Diamond.

Dr Nick Brooks (Chair) Imperial College London
Dr Arnaud Baule University of Newcastle
Dr Yvonne Grunder University of Liverpool
Dr Tim Knowles University of Birmingham
Dr Garrett Law University of Manchester
Dr Ed Lowe University of Oxford
Prof Colin Pullen University of Edinburgh
Dr Neil Telling Keele University
Dr Andrew Thomas The University of Manchester
Dr Amber Thompson University of Oxford
Dr Laura Spagnolo University of Glasgow

Membership as at April 2018