Diamond-II
Proposal for flagship project
NExCUBe & μ15

Science Group: Crystallography

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Outline proposal for a flagship beamline project on Diamond-II

1. Summary/Impact statement

This flagship project will provide two complementary world-class high energy diffraction beamlines to allow the study of natural materials under the extreme physical conditions where they are found and technological materials under the operating conditions in which they function. This will enable, inter alia, study of geochemical materials under planetary core pressures, remarkable new high-pressure high-temperature superconductors, spatiotemporal information on catalysts as they effect chemical transformations and energy devices such as batteries as they operate. We will create beamlines to deliver best-in-class non-routine crystallographic studies that prioritise the needs of both external academic and industry users. The target will be delivered via a 2-for-1 proposition; a new nanofocus undulator beamline operating at 25-30 keV will be built optimised for extreme conditions and *operando* research and this simultaneously allows reconfiguration of I15 as a dedicated microfocussed 35-100 keV high energy scattering/diffraction beamline. In tandem, these will deliver the recommendations made of the CSG in the SAC review of May 2018, views expressed during the Diamond-II crystallography user workshop of September 2018 and facilitate research in areas highlighted in the Diamond-II science case such as:

- Energy research – batteries, fuel cells and photovoltaics
- Materials research – catalysts, porous solids, multiferroics, superconductors
- Earth, environment & planetary science – geochemistry, geophysics and nuclear waste remediation

These beamlines will also strengthen Diamond's position to assist in the delivery of some of the UK government's Industrial Grand Challenges such as *Driving the Electric Revolution*, the *Faraday Battery Challenge*, *Low Cost Nuclear* and *Manufacturing and Future Materials*.

2. Scientific Case

NExCUBe (Nanofocus Extreme Conditions Undulator Beamline). Extreme conditions, in a general sense, refers to *in situ* or *operando* experiments where samples are observed while experiencing stimuli at orders of magnitudes greater or lower than those found at standard conditions. The stimuli that the sample is being subjected to can vary widely; temperature, pressure, light, electric and magnetic fields. The application of multiple stimuli to a sample typically requires a micron-sized sample; using the smallest X-ray beam possible decreases the variation in the applied stimuli within the diffracting volume. The high-brightness Diamond-II design offers a chance to build a world class extreme conditions beamline that is capable of seizing the zeitgeist and enabling cutting edge science to, e.g., the highest pressures. Simply reconfiguring I15 is not a competitive option for the most demanding studies as a wiggler source limits the focussing ability and submicron beams are necessary. NExCUBe will be able to deliver a 300 nm or smaller focussed beam at 30 keV.

One challenge for an extreme conditions beamline is to examine natural and synthetic materials at high pressure conditions and the current landscape is shifting dramatically. Reasons include the development of toroidal anvils that make multi-megabar pressures in a diamond anvil cell (DAC) achievable,[1] Fig 1. Another is advances in detectors that have enabled data collection on minute scale (microgram) and often weakly scattering light element samples surrounded by strongly scattering, background-producing diamonds.

The Diamond-II science case noted that increasingly sophisticated models of the Earth's interior exist but they require experimental data on the chemistry as well as the physical, crystallographic and material properties of the constituents of various regions, ideally at the corresponding temperatures and pressures of the geosphere rather than from samples that have exited the deep Earth. There are many scientific challenges from different depths of the planet to tackle include understanding:

- Chemistry within the earth, including the subduction of light volatile elements to the mantle (C, N, H_2O, noble gases)[2] as well as the lower than expected measured density of the inner core, suspected to be due to the presence of light atoms.[3]
- The structure of other planets, such as whether metallic hydrogen is present within Jupiter's inner atmosphere. Simulating these conditions is an experimental holy grail which is generating huge excitement amongst planetary scientists and solid state physicists alike.[4, 5]

The importance of high pressure studies goes far beyond planetary science; they are also critical for technological developments. Examples include:

- Hydride superconductors have been actively explored in recent years, after the observation that H_2S superconducts at 80 K and 160 GPa.[6]
- Novel superhard materials are often made at high pressure or subjected to high pressure in order to characterize their deformation mechanism at extreme uniaxial loadings.[7]
- Functional porous,[8] molecular[9] and framework materials[10,11] are studied at pressure to examine the energetics of intra- and inter-molecular interactions, understand amorphization mechanisms and trigger chemical reactions.
- Producing new polymorphs of molecular systems,[12] such as active pharmaceuticals, by crystallisation at pressure.[13] Pharmaceutical polymorphism can pose a serious industrial risk as physical properties, e.g. solubility, are a function of the polymorph.

Other extreme conditions that will be better examined at NExCUBe include photo-crystallography of metastable and excited states,[14] porous materials within gas environments[15] and samples subjected to electric fields.[16] These techniques are limited by stimuli-permeable volume and would benefit from a brighter, smaller beam matched to a smaller sample.

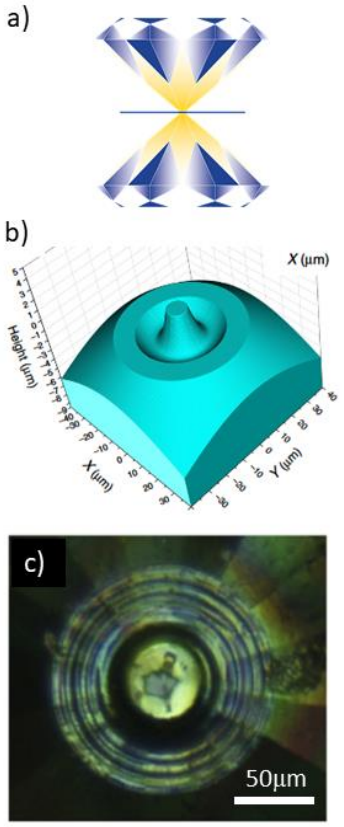

Fig 1. a) A cartoon of a DAC. The surface area of the opposed diamond points, called culets (yellow), are inversely proportional to the achievable pressures. b) A 3-D model of a toroidal diamond anvil manufactured using FIB milling for multi-megabar experiments. c) An image of hydrogen being subjected to 160 GPa for a spectroscopic experiment.

µ15. The move of most of the current I15 science programme to NExCUBe will allow redevelopment of I15 Extreme Conditions into µ15, a dedicated high-energy (35-100 keV) scattering microfocus facility. The combination of the penetration depth of high energy X-rays with microfocus beams opens up new capabilities for *operando* studies and elucidation of structural information across multiple length-scales using both Bragg diffraction for crystalline systems and PDF methods to probe local structure. Mapping and tomographic collections allow a complete structural picture to be built up with spatial resolution to observe inhomogeneities and interfaces in 3D; µ15 will be ideal for collecting data for XRD-CT and PDF-CT. Examples of the information gained from these techniques are show in Fig. 2 for studies of catalysts[17] and batteries[18].

A battery exemplifies a complex multi-length-scale, multi-component and temporal characterisation challenge. Conduction pathways may be governed by the granular microstructure, whilst cycling-induced degradation could be due to atomic scale phase changes, interface effects or nanoscale coarsening. The ability to rapidly scan the 3D structure of a battery at the micron scale and map how crystalline and amorphous components vary in the bulk and at interfaces of real devices *operando* while they cycle will provide key insights, which will inform the next generation of batteries.

Examples of other studies envisioned at µ15 are:

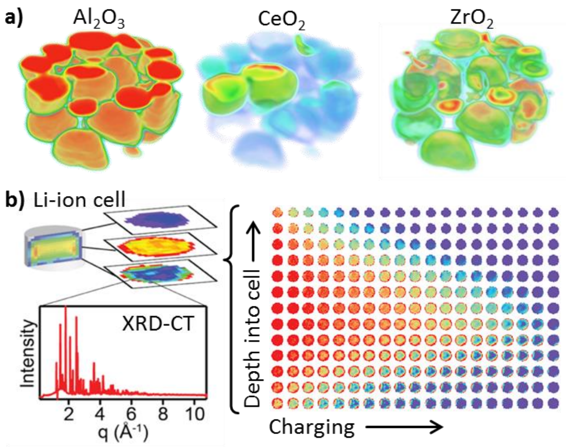

Fig 2. a) Crystallographic composition maps from a 5D *operando* XRD-CT experiment on an active catalyst bed. 5D comprises 3-spatial dimensions, 1-scattering axis (allowing crystallographic differentiation) and 1-time/environmental axis. b) Operando XRD-CT study on a Li-ion battery revealing spatial distribution of Li-rich species (in red) as a function of depth within the cathode during charging.

- Interfaces in solid oxide fuel cells where the electrochemically active regions near the ceramic electrolyte are a few µm thick, it is a significant challenge to probe this buried interface but key to developing a mechanistic understanding. XRD- and PDF-CT mapping will allow the fuel/electrolyte/air electrode interfaces to be studied in operational devices, providing correlative information on structure, electrochemistry processes and microstructure, all with high spatial resolution and depth penetration, in a single measurement.
- Structural studies on single crystal multiferroics using high energy X-rays to provide charge density and 3D-ΔPDF data will reveal local structural correlations and compliment magnetic measurements, leading to improved materials for magnetic read heads, magnetoelectric memory and logic devices.
- Anomalous XRD and PDF measurements at the K-edge of critical elements to the electronics industry, such as the rare earths Nd, Tb and Dy, will be key to understanding structure-properties relationships of these materials and designing the next generation of devices.
- Nuclear waste storage materials will be directly probed in their encapsulated, functional form. High energies penetrate metal containers and XRD- and PDF-CT can be used to study the complex matrix of a grouted waste or glass-ceramic composite, revealing both crystalline and amorphous components.
- Thin film coatings of down to a few nanometers thick will be studied using grazing-incidence PDF as they are being deposited, revealing how synthesis conditions can affect optoelectronic devices and coatings at an atomic level.

World-leading software for highly-automated, real-time processing and analysis of the large, multivariate datasets µ15 collects will allow for dynamic operando experiments where experimenters can respond to events as they unfold. Monte Carlo modelling of the full experiment will allow unprecedented quality of PDF processing from even the most challenging operando setups. Flexible processing and analysis workflows combined with reconstruction and visualisation tools will allow data to be routinely explored in upwards of 6-dimensions, covering spatial, temporal and environmental domains.

3. Benefit to the Diamond research community

NExCUBe and µ15 will be high energy beamlines that offer the community complementarity in energy ranges, beam size and sample stages/techniques. NExCUBe operating at 30 keV with a 300 nm or smaller beam will allow X-ray nanocrystallography. It will have the capability to bridge the gap between conventional X-ray single crystal work and 3D electron diffraction for structural studies, but with the benefits of high energy X-ray penetration for *operando* studies and analysis using kinematical rather than dynamical diffraction theory. It will make Diamond competitive in the most demanding high-pressure science and especially attractive to users in combination with the developments in laser heating, gas cell loading and the new cryostat. This beamline would attract greater demand from the UK extreme conditions community as well as its significant and growing international user base; high pressure scientists travel the world to visit the best facilities and NExCUBe aims to be the top choice. The new capabilities offered by µ15 will support academic researchers in structural studies from pure phases and small test systems all of the way up to full-scale devices. The combination of a highly-competitive beamline with world-leading software for highly-automated processing and analysis of the large, multivariate datasets it creates will particularly attract users from the fields of nuclear, catalysis, energy, materials and engineering. Industrial partners will be able to study the interfaces within their products while they are operating to feed into further product development. As an example, in the field of batteries µ15 would benefit the UK's aim to become a world leader in battery technology for the automotive sector and support major investments such as the Faraday Challenge. The capabilities of µ15 also align well with the "Atoms to Devices" theme of the Henry Royce Institute and their combination would likely lead to breakthroughs in storage capacity, longevity and safe operation of batteries.

4. Outline Specification

NExCUBe will be built on the principles of preserving the Diamond-II brightness and maximizing the flux at 30 keV utilising a short period undulator (CPMU or SCU) on a mid-straight section of the new lattice. Calculations show that the brightness would increase by at least a factor of 250 over what the U22 undulator of I19 can currently deliver at the same energy. A schematic of the proposed optics and experimental hutches is shown in Fig. 4. The double crystal monochromator will be equipped with both Si(111) and multilayer crystals, to enable low and high bandpass modes. Use of the multilayer monochromator give an additional factor of 100 in brightness. To minimize X-ray loss on optics and preserve brightness, the number of optical elements would be kept to a minimum.

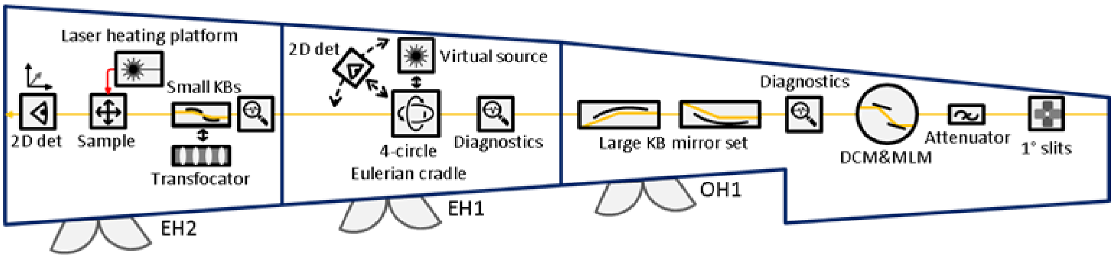

Fig 4. Schematic layout of NExCUBe.

EH1 will house a 4-circle Eulerian cradle diffractometer designed to support 1kg DACs on a sphere of confusion less than 10 µm, with absolute encoded sample positioning. The X-ray focus in this hutch would be ~30 µm, with an adjustable collimator system to allow the user to further slit the beam down. This system would be coupled to a fast 2-D pixel detector, either photon counting or integrating. This hutch would also be home to the virtual source for the second experimental hutch. EH2 will be home to the microfocus (300 nm or less) endstation, equipped with a laser heating system. The smallest achievable focus would be provided by a transfocator but due to these systems being achromatic, a pair of KB mirrors would be present for microfocus at other energies; the ability to have both present and choose based on the experiment would be similar to other world class beamlines. This endstation would be designed for high speed, high repeatability sample alignment and mapping and would also be equipped with a large 2-D pixel detector capable of > 250 Hz readout, to allow pulsed laser heating experiments and diffraction mapping.

µ15, Fig 5, will be developed with a new monochromator with variable bandwidth and energy scanning capabilities, new primary focussing and micro-focussing optics and two refurbished in-line experiment hutches with high-speed mapping and tomography stages. Diamond-II's higher ring energy will allow µ15 to optimise for a higher energy range of 35-100 keV for greater penetration depth and to facilitate more complex experimental setups with limited exit scattering angles. EH1 will perform microfocus diffraction mapping (including XRD-CT and PDF-CT) of operando set-ups. A small 3-circle diffractometer will be available for high energy single crystal diffraction (e.g. for charge density analysis and 3D-ΔPDF measurements). EH2 will be dedicated to diffraction mapping of larger components with larger beams and high throughput experiments. The hutch arrangement will allow complex experiments in EH2 to be prepared while experiments are running in EH1. The primary detector for each endstation will be a fast, high-Z large area detector for Bragg and PDF studies. A secondary multi-analyser crystal array equipped with 2-D high-Z detectors will facilitate high resolution and rapid depth-profile studies.

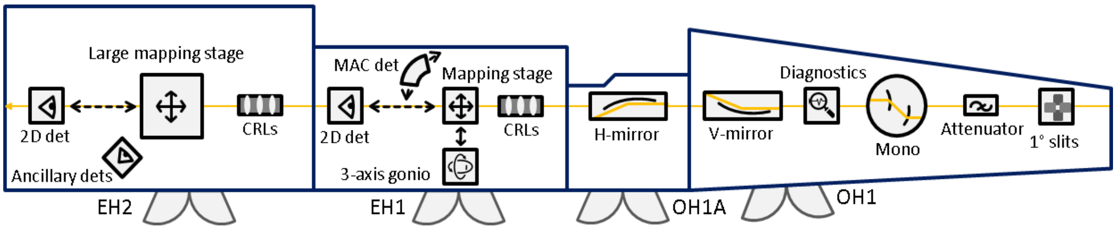

Fig 5. Schematic layout of µ15.

5. State of the art benchmark

The NExCUBe beamline, as simulated in the table below, would be highly competitive with extreme conditions beamlines at the APS and ESRF. Flux at ID27 and GSE-CARS were simulated using SPECTRA to give direct comparisons at the same energy, using the available accelerator and source parameters. The brightness is calculated to be over two orders of magnitude improved on current Diamond undulator beamlines, with 1.9 x 10^{20} and 9 x 10^{19} ph/s/mm^2/mr^2/0.1%BW at 25.5 keV and 31.15keV, respectively. All simulations were calculated using the CPMU15.6 specifications and mid-straight beam parameters.

Criteria	**GSE-CARS, 13-ID-D, APS**	**ID27, ESRF (pre-EBS)**	**NExCUBe, Diamond-II**
Energy range[keV]	10-42	20-80	15-40
Typical energy[keV]	37	33	30
H, V Divergence [µrad]	15,6	208,12	15,12
Flux at 30keV [ph/s]	7 x 10^{13}	7 x 10^{14}	2 x 10^{14}
Focussed h×v [µm]	2 x 2	1.7 x 2.7	0.3 x 0.3

µ15 will rival other leading high energy materials science/engineering beamlines at the ESRF, DESY and APS as set out in the table below. It would complement the unfocussed and lower energy capabilities on I12 and DIAD, respectively. The energy range of 35–100 keV is similar to comparable facilities as is the predicted flux and beam size: 5×$\cdot 10^{12}$ ph/s @ 80 keV for 1$\cdot 10^{-3}$ bandwidth delivered into 5 µm (h) × 5 µm (v).

Criteria	**1-ID, APS†**	**ID15A, ESRF(EBS)‡**	**µ15, Diamond-II**
Energy [keV]	41–136 [45–116]	20–69 [40–250]	35–100
Bandwidth	1.3×10^{-3} [1×10^{-4}]	3.7×10^{-3} [1×10^{-4} – 1×10^{-2}]	1.0×10^{-3}
Flux [ph/s]	6×10^{12} [2×10^{11}] @80 keV	4.5×10^{13} @ 50 keV	5×10^{12} @ 80 keV
Focussed h×v [µm]	13 × 1.4	300 × 300 [0.3 × 0.3]	5 × 5
Unfocussed h×v [mm]	1.5 × 1	6.4 × 1.2	6 × 4

†Values with bent double-Laue mono. [] indicates with high resolution monochromator.
‡Initial values are with standard KB focussing. [] indicates range available with other optics.

6. Community engagement

This proposal grew out of discussions at the CSG SAC review of May 2018 and from the Diamond-II Crystallography User Workshop of September 2018; the proposed 2-for-1 approach is the best way to meet the needs of the evolving crystallographic community including those specialising in high pressure and materials science. Experts in their fields have already been identified who will act as champions to guide the development of both beamlines in parallel via two UWGs that interact with each other. NExCUBe will draw from leaders in extreme conditions and nanocrystallography, it will be important to have good representation from leaders in Earth and Planetary science as well as others with an interest in DAC research. The µ15 development group will draw from leaders in materials science and operando measurements to ensure that the hardware and software delivered meet the needs of a diverse community. For both, industrial as well as academic scientists will be recruited.

7. References

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