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XPDF

A Dedicated X-ray PDF Beamline at Diamond
Phase III Outline Proposal
Based on "Ideas" 09 and 10

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Summary

Our vision for XPDF is straightforward: to build an instrument that measures X-ray pair distribution function (PDF) data of the highest quality possible at DLS, servicing the very large number of UK research groups whose work relies on understanding local structure in materials.

Never has the importance of understanding local structure been so clear in so many disciplines. The ability to measure PDF data at Diamond is crucially needed because the technique is the *only* truly quantitative probe of local structure correlations in materials. The accuracy with which newer-generation instruments at spallation neutron sources and X-ray synchrotrons can measure the PDF, together with an increasing sophistication in the analysis methods, has seen a step-change in the significance of the scientific questions addressed using the technique. The success of neutron PDF measurements at ISIS has developed a rapidly-growing UK community using PDF in their research. As this user base continues to grow and diversify, so too does the range of scientific questions addressed using the technique. There is an increasing desire for high-throughput measurements, a more diverse range of materials to be studied, and varied sample environments and measurement timescales. Many of these studies are fundamentally better suited to X-ray PDF measurements than neutron PDF; many more will benefit enormously from exploiting the two techniques in tandem.

Diamond is the right place for an X-ray PDF instrument, not only because the UK community needs such a facility, but because (i) it offers the right X-ray energy profile, (ii) there is the right expertise to make the facility successful, and (iii) having X-ray *and* neutron PDF facilities on the same campus offers a synergistic relationship that increases value both at DLS and at ISIS. PDF studies require very careful measurement; it is no accident that many more beamlines would claim to be capable of measuring PDF data than produce high-profile PDF work. Our focus on a *dedicated* PDF beamline is to ensure a design and mode of operation that will produce world-class PDF data of genuine use to the research community. XPDF will ensure that the UK remains at the forefront of this emerging field, and that the Harwell campus becomes the world centre for PDF analysis.

Our preferred option is for a dedicated insertion device that delivers a beam profile optimised for PDF measurements. Mindful of the current economic pressures, however, we present also a second, cheaper, option that would exploit an existing insertion device to feed a smaller PDF side-station. For both options, our design focus is on ensuring the highest quality PDF measurements possible.

Scientific Case

Of all the experimental probes of local structure, PDF techniques benefit from the unique advantage that the PDF is a directly-measurable histogram of interatomic distances. Because it is quantitative, it can be used for *local* structure refinement in much the same way as Bragg diffraction patterns are used for *average* structure refinement. The immense scientific insight this can provide is rapidly gaining notice: it means PDF methods can be used to produce realistic atomic-scale models of the local structure in materials — crystalline, nanocrystalline, amorphous or fluid. Indeed, for glasses and fluids, the PDF has always been the primary approach to understanding atomic structure, but increasingly PDF methods are being used to provide unique insight into the properties of crystalline materials. There is a growing realisation that for many important classes of crystalline material the instantaneous local structure is significantly different from the average. Surprisingly often it is this difference that is so crucial to the physical and chemical properties of these materials.

Examples of the science achievable using PDF methods include:

- Characterising host-guest interactions in porous materials, notably clathrates, zeolites and metal-organic frameworks, where structural cavities are filled by atomic clusters or molecules.
- Understanding mechanisms of ionic conduction, including conduction in materials where the mobile ions are part of the chemical compound or introduced as defects.
- Developing a coherent picture of dynamics in materials with large thermal motion, particularly network materials such as zeolites and metal-organic frameworks, where the actual framework shows a high degree of flexibility.
- Establishing local structure/property relationships in materials with mixed valence states, such as the colossal magnetoresistance (CMR) manganites.
- Understanding the actual processes and structural consequences of radiation damage in nuclear waste containment materials and reactor moderators.
- Solving the structures of nanocrystalline materials — including naturally-occurring minerals and synthetic nanoparticles — and using these results to understand differences in bulk and nanocrystalline material properties.
- Establishing protocols for fingerprinting poorly crystalline organic materials, including many active pharmaceutical ingredients (APIs) which are thought to be poly-amorphic.
- Developing bioactive glasses and amorphous bone replacement candidates, and monitoring leaching processes in bioimplanted materials.
- Characterising local structure in ionic liquids, and understanding the role of solvation in non-traditional solvents used in advanced catalysis.
- Direct observation of the mechanism of local strain coupling to processes such as magnetic and charge order in multiferroics and superconductors.
- Understanding the role of different forms of atomic site disorder in mechanical, acoustic and electronic properties of metallic alloys, electroceramics and relaxor ferroelectrics.
- More generally, watching the atomic-scale rearrangements associated with phase transitions and other structural transformations in a broad range of crystalline and non-crystalline materials: nucleation, growth, deposition, (de)sorption, (de-)intercalation, and amorphisation.

Importantly, these research areas span all the key priority themes of materials development: energy (battery materials, carbon capture via gas sorption, hydrogen storage, catalysts); health (pharmaceuticals, biomaterials); digital economy (digital storage media, electronics materials and semiconductor components, display materials, plastic electronics).

Experimentally, the PDF is measured as the Fourier transform of the X-ray or neutron scattering function taken to large maximum values of the scattering vector Q. These measurements present a number of challenges. Unlike traditional crystallography, where the focus is on extraction of Bragg peaks, it is critical to be able to minimise and measure accurately the background scattering. This directly impacts on the design of the instrument, including the way in which sample environment control is incorporated into the design. It is essential to measure to maximum values of Q that far exceed those traditionally used in crystallography, because the maximum value directly determines the best resolution possible in determination of interatomic distances. The situation is made more difficult for X-ray PDF measurements by the unavoidable loss of scattering intensity at high-Q arising from the X-ray form factors, compounded further by the increasingly dominant contribution of Compton scattering that degrades the signal to background ratio in the same region of the scattering pattern. The DLS offers the combination of high X-ray energies (hence wide Q range) and high flux (hence accurate measurements at high-Q) that is crucial for measuring accurate PDF

data. But it is equally important that the experimental requirements necessary for low backgrounds and robust data normalisation are not underestimated; the community experience is that this is only practicable at dedicated PDF facilities, and hence the imperative behind our XPDF bid.

X-ray PDF techniques are complementary to neutrons rather than being competitive. The differences in atomic scattering factors between X-ray and neutrons mean that the different radiation sources will provide different degrees of sensitivity for different atoms. As the complexity of systems being studied using the PDF method increases, the use of both types of radiation becomes increasingly important. While PDF analysis is not inherently element-specific, the combined use of X-ray and neutron PDF techniques ameliorates the lack of element-specificity to a reasonable extent. And while XAFS and NMR can provide element-specific information, typically this is for first and second atomic coordination shells only; moreover it is often difficult to resolve the information XAFS and NMR give in the context of the long-range structure obtained using diffraction. PDF methods offer a self-consistent approach to studying structure on local, medium and long-range scales from a single experiment. Consequently, without dedicated PDF instruments at radiation beam facilities, the scientific community is left with a large gap in our understanding of a huge range of important materials.

The current international situation is that neutron and X-ray PDF instruments are only found in separate and geographically widely distributed institutes. However, there are significant advantages in having PDF instruments for both X-ray and neutron beams located at the same site under a common umbrella research council. This will enable researchers to submit applications for both radiation beams at the same time. Moreover, the strength of PDF instrumentation at the ISIS neutron facility has led to the development of international leadership in this area within the UK research community, including the development of flagship computer codes for PDF analysis (RMC, EPSR). This leadership will be significantly enhanced by the provision of a PDF instrument at Diamond. At the present time, UK PDF work with X-ray beams is being exported to overseas facilities, such as SPring-8 and the APS.

Outline Specification

The optimal performance of X-ray total scattering and PDF experiments requires the use of short wavelength (high energy) radiation with high flux (10^{12} photons.s^{-1}) and high spectral purity ($\Delta E/E = 10^{-3}$ to 10^{-4}). As discussed above, the short wavelengths and high flux are required to facilitate the measurement of the structure factor to large values of momentum transfer, Q, with sufficient counting statistics to compensate for the X-ray form factor driven decrease in scattering intensity. The high spectral purity will help resolve closely spaced Bragg features in the signals of crystalline or partially crystalline systems. A PDF beamline should also be capable of operating at a range of different photon energies in order to facilitate its application to the widest range of samples and to avoid problems associated with unfavourable X-ray absorption edges. These three basic requirements allow us to specify the key instrumental characteristics that XPDF must deliver:

Operating X-ray photon energy/wavelength range:	40 to 80 keV	0.31 to 0.15 Å
Optimal photon flux at sample:	10^{11} to 10^{13} photons.s^{-1}	
Optimal energy resolution:	$\approx 10^{-4}$ $\Delta E/E$	

To obtain these characteristics on the 3 GeV DLS we require a superconducting multipole wiggler as the optimal radiation source, with a cryogenically cooled double crystal monochromator as the

key element in the beamline optics train. Given the existing suite of diamond instruments and the availability of free insertion device straights, two options emerge for the construction of XPDF:

Option 1 is the construction of a fully independent beamline with a dedicated insertion device, and a comprehensive optics train that would allow fully tuneable operation over the whole energy range specified above.

Option 2 is the construction of a short side-station on an existing superconducting wiggler source (*e.g.* I-15), that would operate with a limited selection of wavelengths in a fixed monochromator geometry. The use of Si(111), Si(220) and Si(311) crystal pairs could deliver beams of ≈ 40, 65 and 80 keV, respectively. Counting against this option is the lack of tuneability in X-ray energies (otherwise exploitable for anomalous scattering) and space restrictions imposed on hutch design that will influence the variety of sample environments possible.

In either instance, we anticipate the use of a range of detector options for XPDF. For time resolved studies and measurements that do not require access to the highest Q-values, flat panel amorphous silicon detectors matched with CsI scintillators are ideal; *e.g.* the Pixium 4700 (Thales Electron Devices, France) or the XRD1621 N ES (PerkinElmer, Canada). Such detectors will measure to a scattering angle (2θ) of 60º, giving Q_{max} values of approximately 20, 25 and 30 Å^{-1} for the three energy settings, with a frame rate of up to 30 fps. This detector configuration would be ideal for challenging sample environments such as pressure cells and furnaces. Alternatively, for measurements that require access to the highest Q-values, a standard two circle scanning diffractometer would make the optimum detector option. By scanning to 120º, a point scanning detector would allow measurement of the structure factors to a Q_{max} of 35, 50 and 70 Å^{-1} (40, 65 and 80 keV, respectively). We are also aware of the likely development of 1D "strip" detectors capable of operating at these X-ray energies (similar to the Mythen2 system currently used at I11). Such detectors offer the attractive combination of fast acquisition times with a large 2θ range.

A further very important characteristic of a total scattering/PDF experimental station is the delivery of low background contributions to the scattering signals, in order to facilitate quantitatively accurate measurement of the scattering intensities. To achieve this capability, care will be taken to maximise the use of evacuated flight paths for the incident and scattered X-rays.

Community

The strong community support expressed for XPDF (80 Expressions of Interest representing 34 Institutions) is all the more significant for the fact that PDF techniques are still a relatively new experimental approach. Many of the expressions of interest received in the lead-up to this proposal come from groups yet to use PDF in their research, and it is this sense of the XPDF beamline being key to driving *future* scientific discovery in the UK — beyond the state of the art — that is particularly exciting. To quote one response, which is typical of many:

> *"Establishment of a dedicated beamline at Diamond would provide a UK focus for developments that would enable new materials science and support a large number of researchers including non-experts (in PDF) such as myself who are now recognising the impact that this technique can have on their future research."*

But perhaps the most striking aspect of the expressions of interest is the breadth of research disciplines they span — Chemistry, Physics, Materials, Engineering, Geology, Pharmacology, and Biological Sciences — a key indicator of the scope of impact that XPDF will have on UK research.

Expressions of Interest Received

Prof Neville Greaves FRS	Mathematics and Physics	Aberystwyth
Dr Martin Wilding	Mathematics and Physics	Aberystwyth
Dr Richard Martin	Life and Health Sciences	Aston
Dr Anne Kavanagh		AstraZeneca
Dr Andrew Burrows	Chemistry	Bath
Prof Philip Salmon	Physics	Bath
Dr Adrian Barnes	Physics	Bristol
Dr Jacqui Cole	Physics	Cambridge
Prof Martin Dove	Earth Sciences	Cambridge
Prof Stephen Elliott	Chemistry	Cambridge
Prof Lindsay Greer	Materials Science	Cambridge
Prof Clare Grey	Chemistry	Cambridge
Prof Simon Redfern	Earth Sciences	Cambridge
Prof Kenneth Harris	Chemistry	Cardiff
Dr Kirsten Christensen		DLS
Prof John Evans	Chemistry	Durham
Dr Ivana Radosavljevic Evans	Chemistry	Durham
Dr Christoph Salzmann	Chemistry	Durham
Dr Stephen Moggach	Chemistry	Edinburgh
Prof Simon Parsons	Chemistry	Edinburgh
Prof Duncan Gregory	Chemistry	Glasgow
Dr Ian MacLaren	Physics and Astronomy	Glasgow
Prof Chick Wilson	Chemistry	Glasgow
Dr Matthew Johnson		GSK
Dr Stephen Skinner	Materials	Imperial
Dr Emma Barney	Disordered Materials	ISIS
Dr Daniel Bowron	Disordered Materials	ISIS
Dr Samantha Callear	Crystallography	ISIS
Prof Felix Fernandez-Alonso	Molecular Spectroscopy	ISIS
Prof Alex Hannon	Disordered Materials	ISIS
Prof David Keen	Crystallography	ISIS
Prof Robert McGreevy	Diffraction & Muon Division	ISIS
Prof Alan Soper	Disordered Materials	ISIS
Dr Matthew Tucker	Crystallography	ISIS
Dr Tim Hyde		Johnson Matthey
Dr Serena Corr	Physical Sciences	Kent
Dr Gavin Mountjoy	Physical Sciences	Kent
Prof Bob Newport	Physical Sciences	Kent
Dr Fiona Meldrum	Chemistry	Leeds

Dr John Claridge	Chemistry	Liverpool
Dr Yaroslav Khimyak	Chemistry	Liverpool
Prof Matthew Rosseinsky FRS	Chemistry	Liverpool
Dr Sandie Dann	Chemistry	Loughborough
Dr Jeppe Christensen	MAX-lab	Lund
Prof Paul O'Brien	Chemistry	Manchester
Dr Brett Cooper		Merck
Prof Robert Jones	Chemistry	Nottingham
Dr Simon Clarke	Chemistry	Oxford
Prof Peter Edwards FRS	Chemistry	Oxford
Dr Andrew Goodwin	Chemistry	Oxford
Dr Michael Hayward	Chemistry	Oxford
Prof Dermot O'Hare	Chemistry	Oxford
Dr Cheryl Doherty		Pfizer
Prof Chris Hardacre	Chemistry & Chemical Engineering	Queen's University Belfast
Dr Ann Chippindale	Chemistry	Reading
Dr Simon Hibble	Chemistry	Reading
Dr Kenneth Shankland	Pharmacy	Reading
Prof Keith Ross	Engineering & Physical Sciences	Salford
Prof Lee Brammer	Chemistry	Sheffield
Prof Mike Gibbs	Materials Science & Engineering	Sheffield
Dr Russell Hand	Materials Science & Engineering	Sheffield
Prof Neil Hyatt	Materials Science & Engineering	Sheffield
Dr Michael Ojovan	Materials Science & Engineering	Sheffield
Prof Ian Reaney	Materials Science & Engineering	Sheffield
Dr Nik Reeves-McLaren	Materials Science & Engineering	Sheffield
Prof Derek Sinclair	Materials Science & Engineering	Sheffield
Prof Panos Tsakiropoulos	Materials Science & Engineering	Sheffield
Prof Anthony West	Materials Science & Engineering	Sheffield
Prof Philip Lightfoot	Chemistry	St Andrews
Prof Russell Morris	Chemistry	St Andrews
Dr Alastair Florence	Pharmacy & Biomedical Sciences	Strathclyde
Dr John Turner	Chemistry	Sussex
Prof Richard Catlow FRS	Chemistry	UCL
Prof Gopinathan Sankar	Chemistry	UCL
Prof Neal Skipper	Physics	UCL
Dr Diane Holland	Physics	Warwick
Prof Tim Jones	Chemistry	Warwick
Dr Dean Keeble	Chemistry	Warwick
Prof Pam Thomas	Chemistry	Warwick
Dr Richard Walton	Chemistry	Warwick