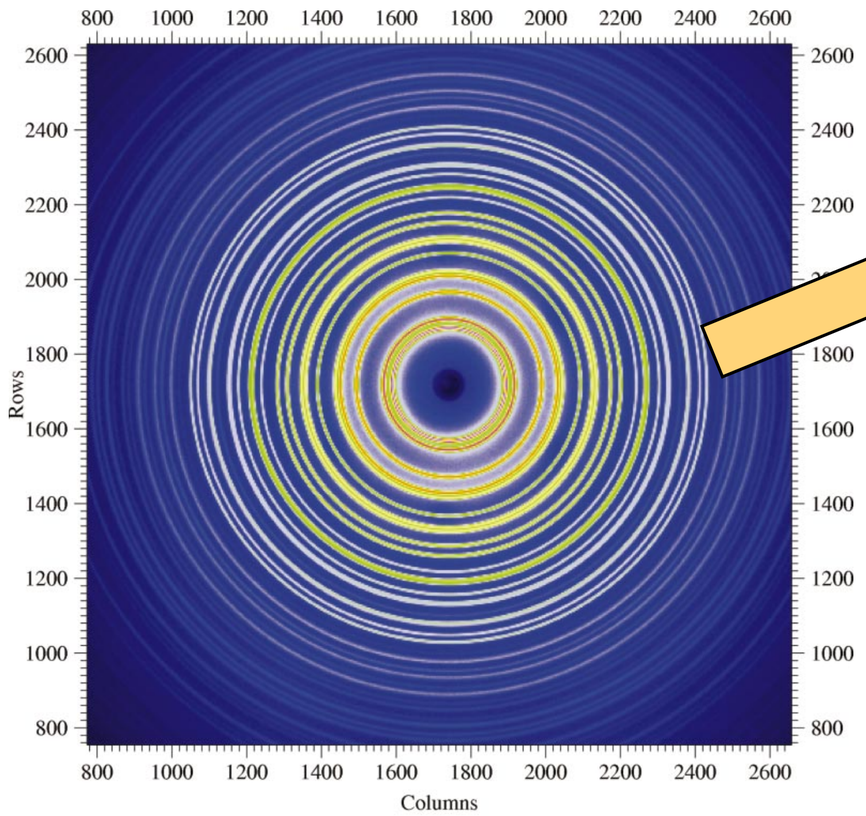
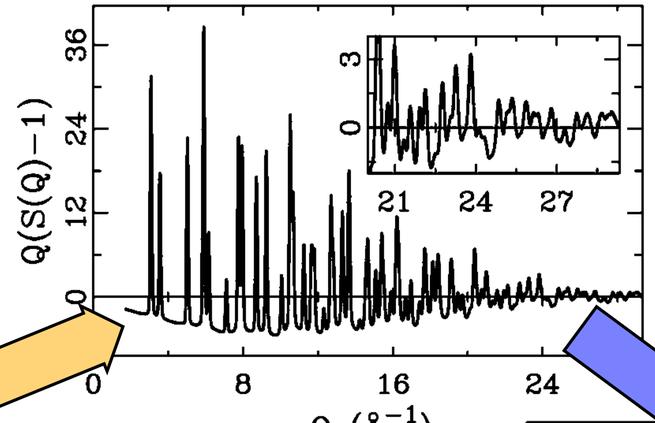
XPDF

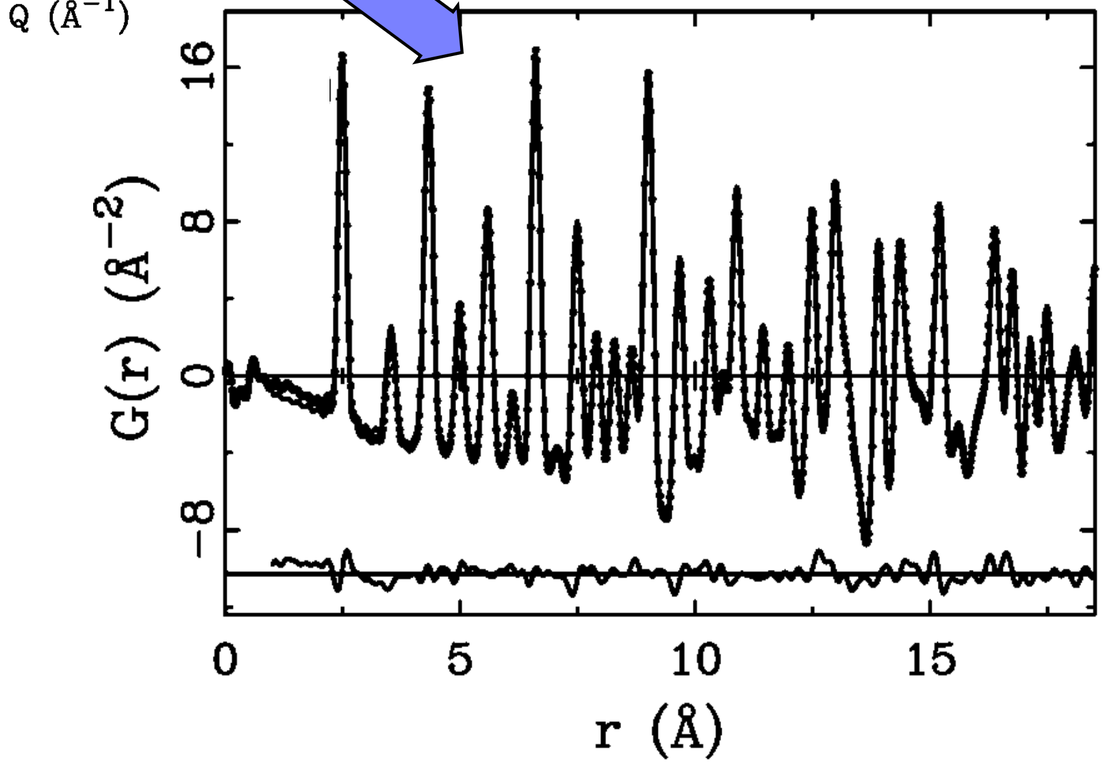
A Dedicated PDF Beamline at Diamond

Phase III Proposal

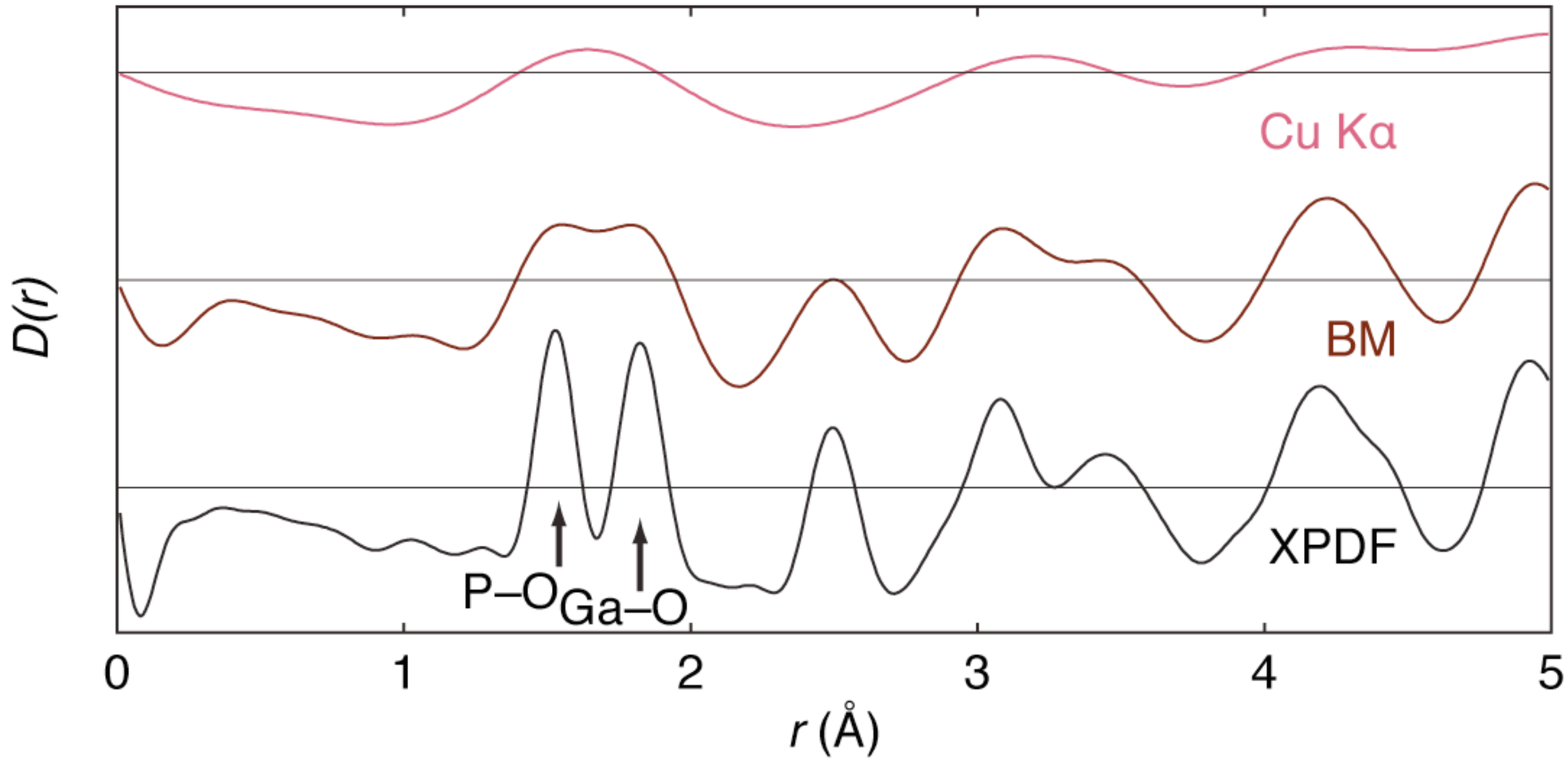
Pair distribution function (PDF)



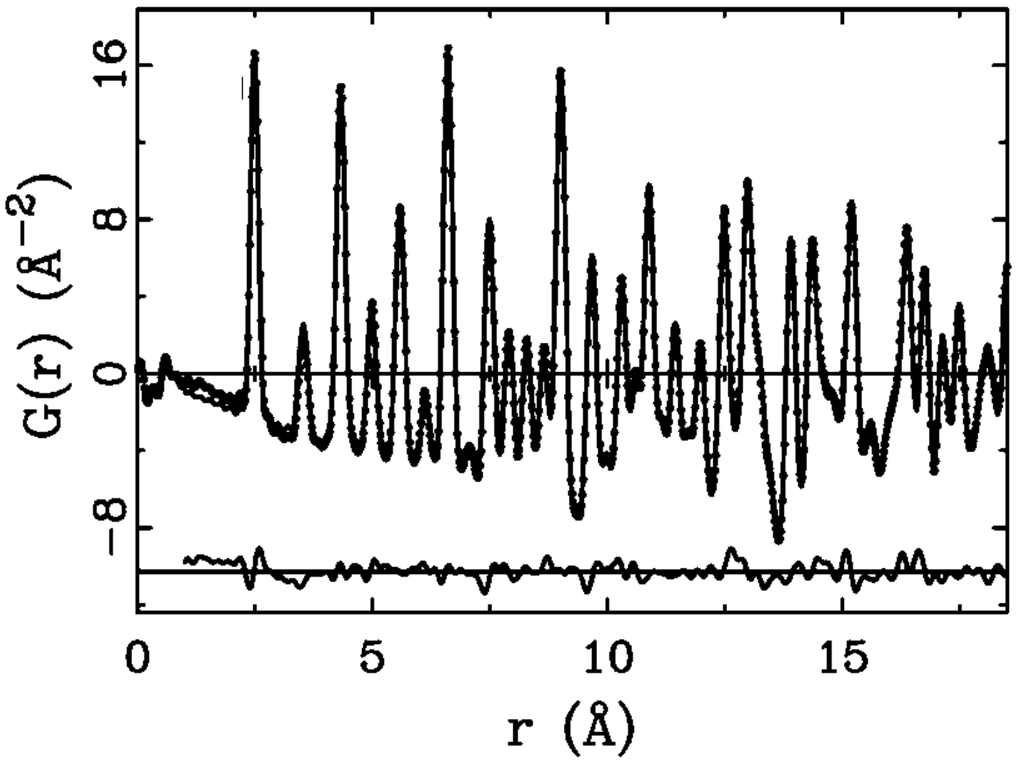


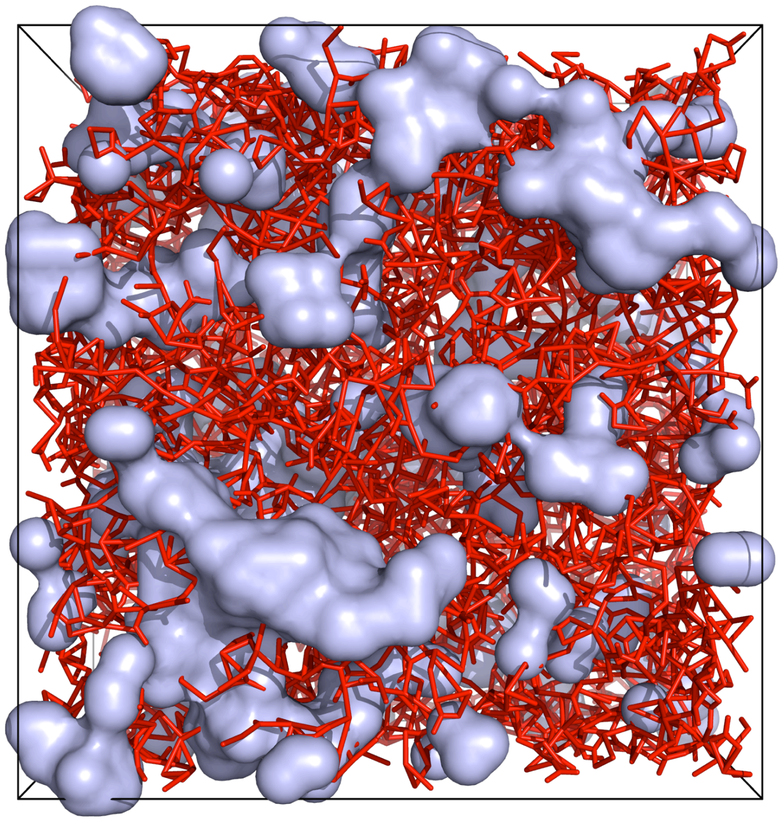


Pair distribution function (PDF)

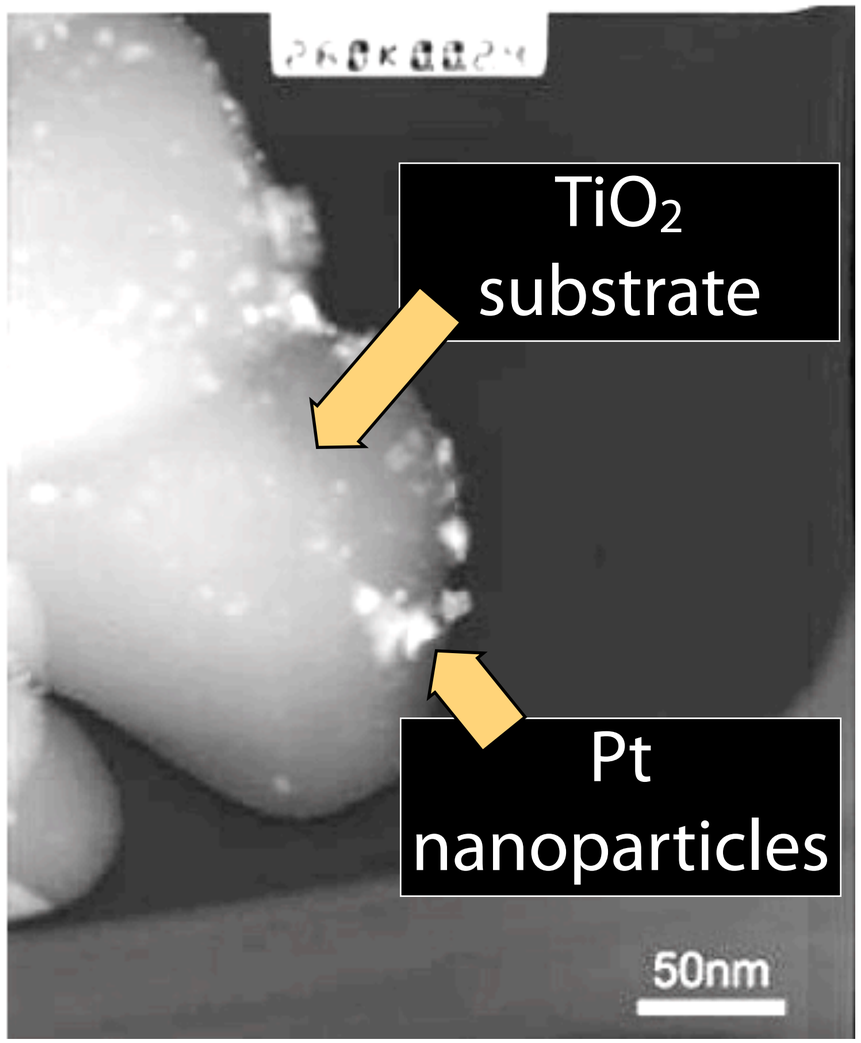


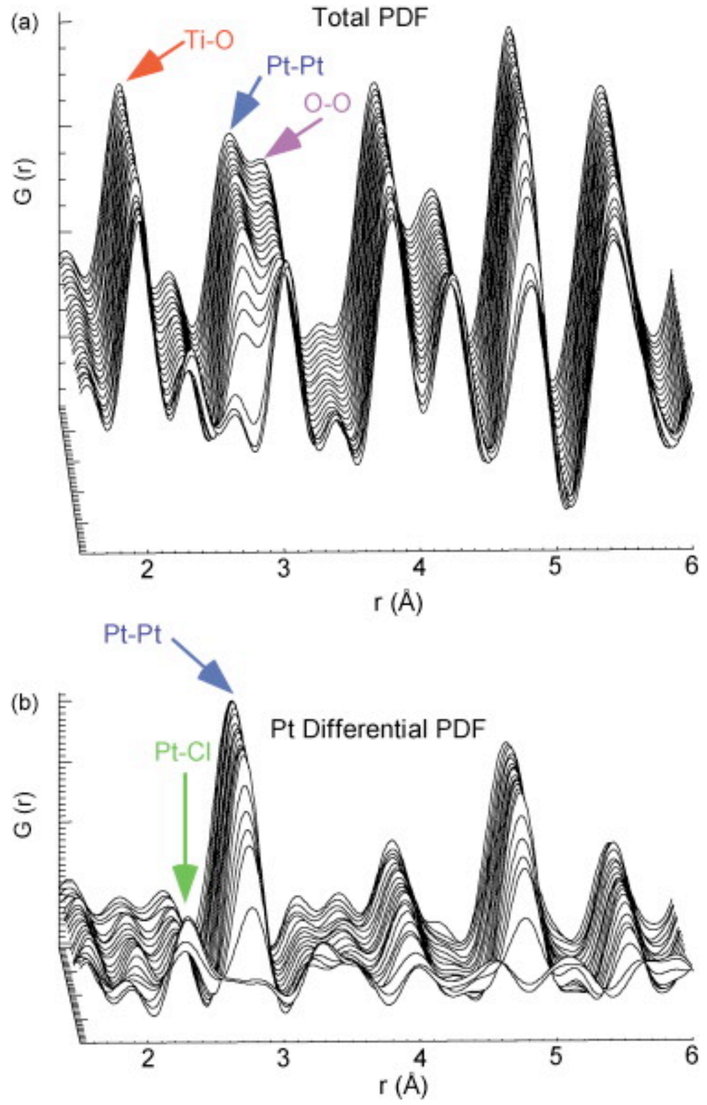
PDF Data analysis





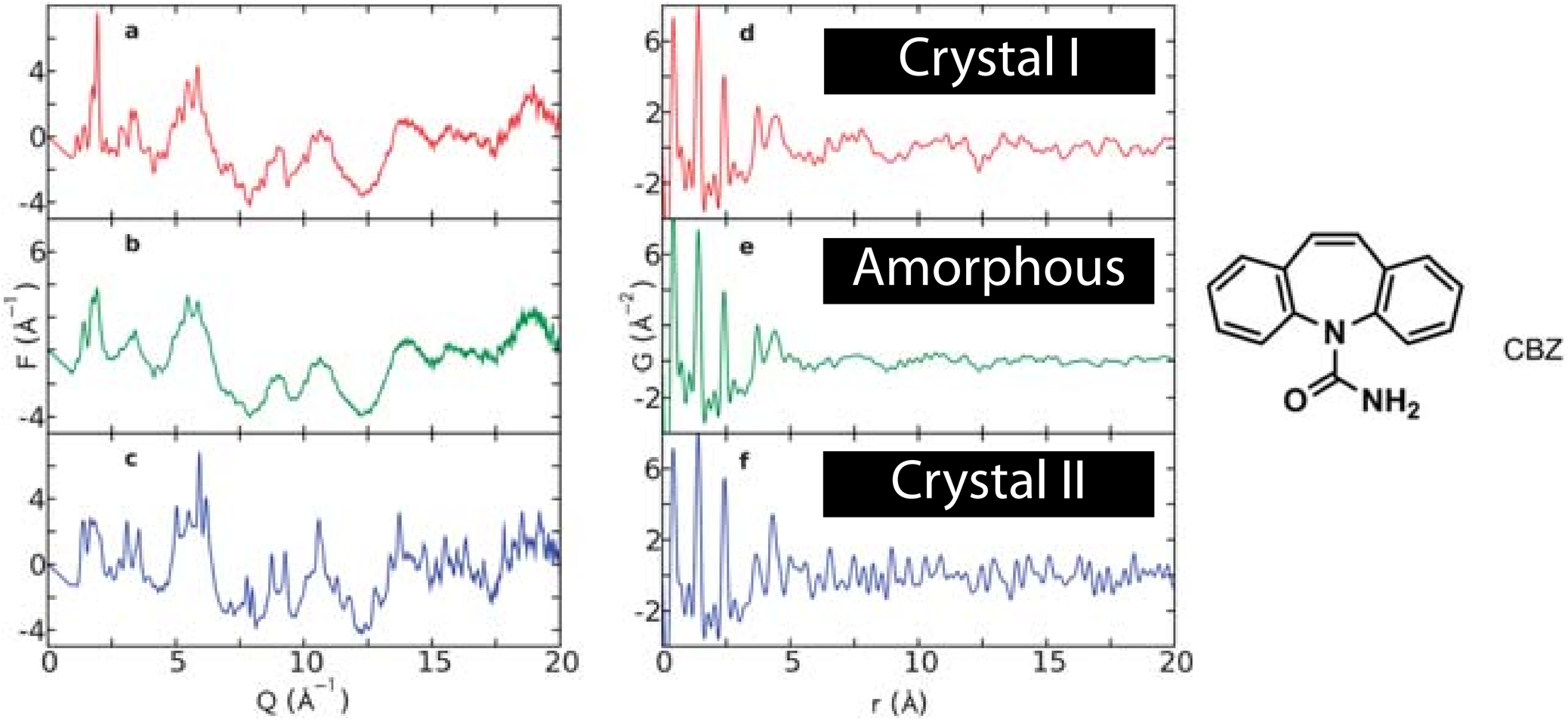
Catalysis





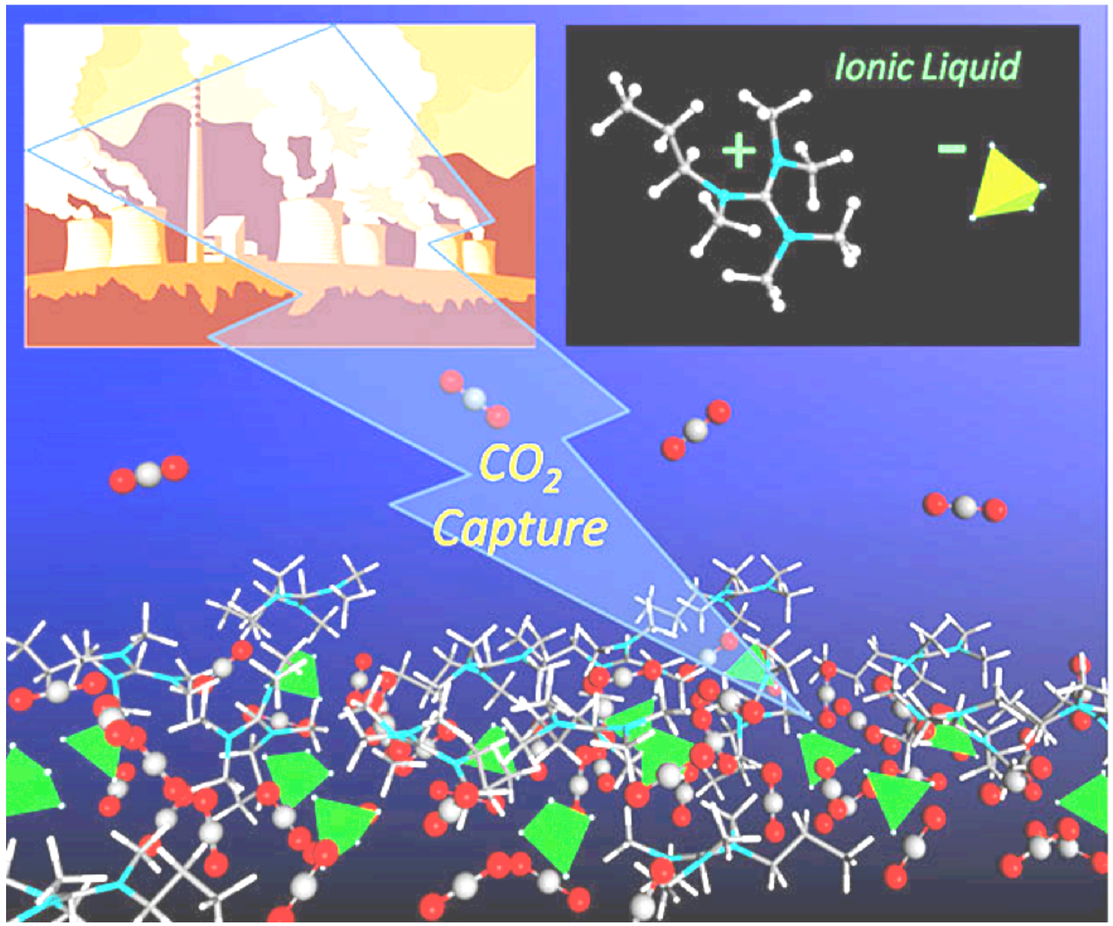
Chupas, Chapman, Chen and Grey, *Catalysis Today* **145**, 13 (2009)

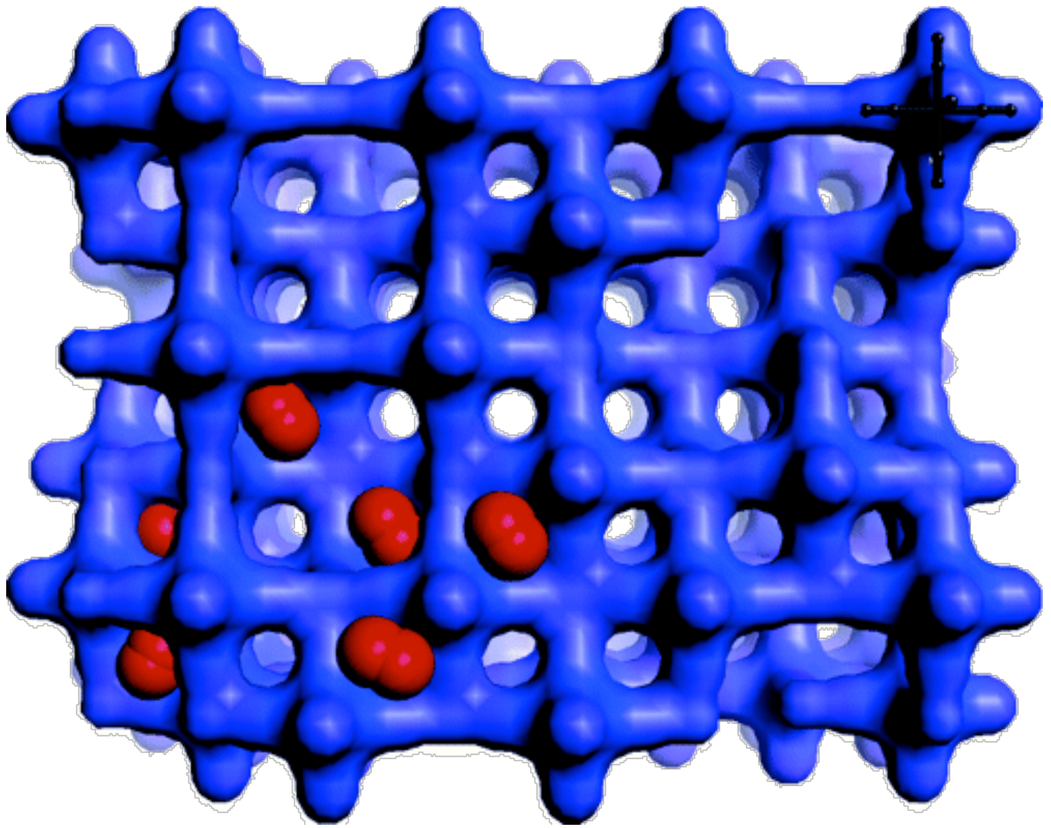
Health and Pharmaceuticals



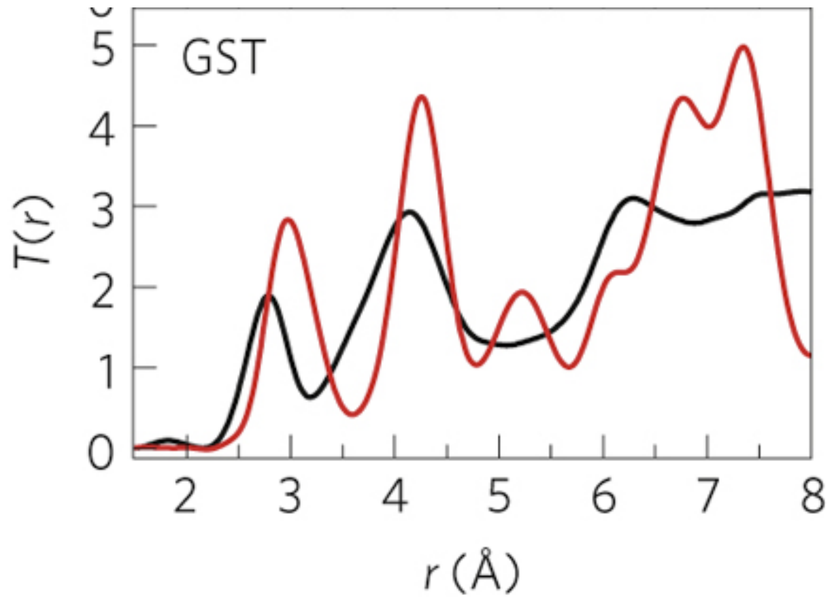
Billinge, Dykhne, Juhas, Bozin, Taylor, Florence and Shankland, *CrystEngComm* **12**, 1366 (2010)

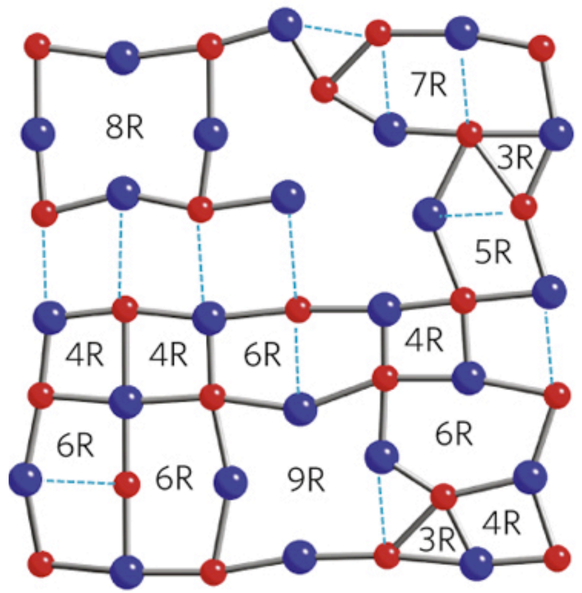
Energy

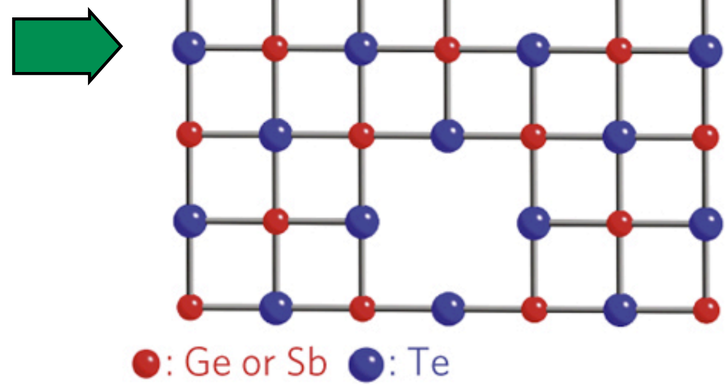




Digital Economy







Mastunaga *et al*, *Nature Materials* **10**, 129 (2011)

UK Priority Research Areas

>> Digital Economy

>> Energy

>> Nanoscience through engineering to application

>> Towards next-generation healthcare

>> Ageing – lifelong health & wellbeing

>> Global uncertainties

>> Living with environmental change

XPDF Industrial Supporters

AstraZeneca

gsk GlaxoSmithKline

Pfizer

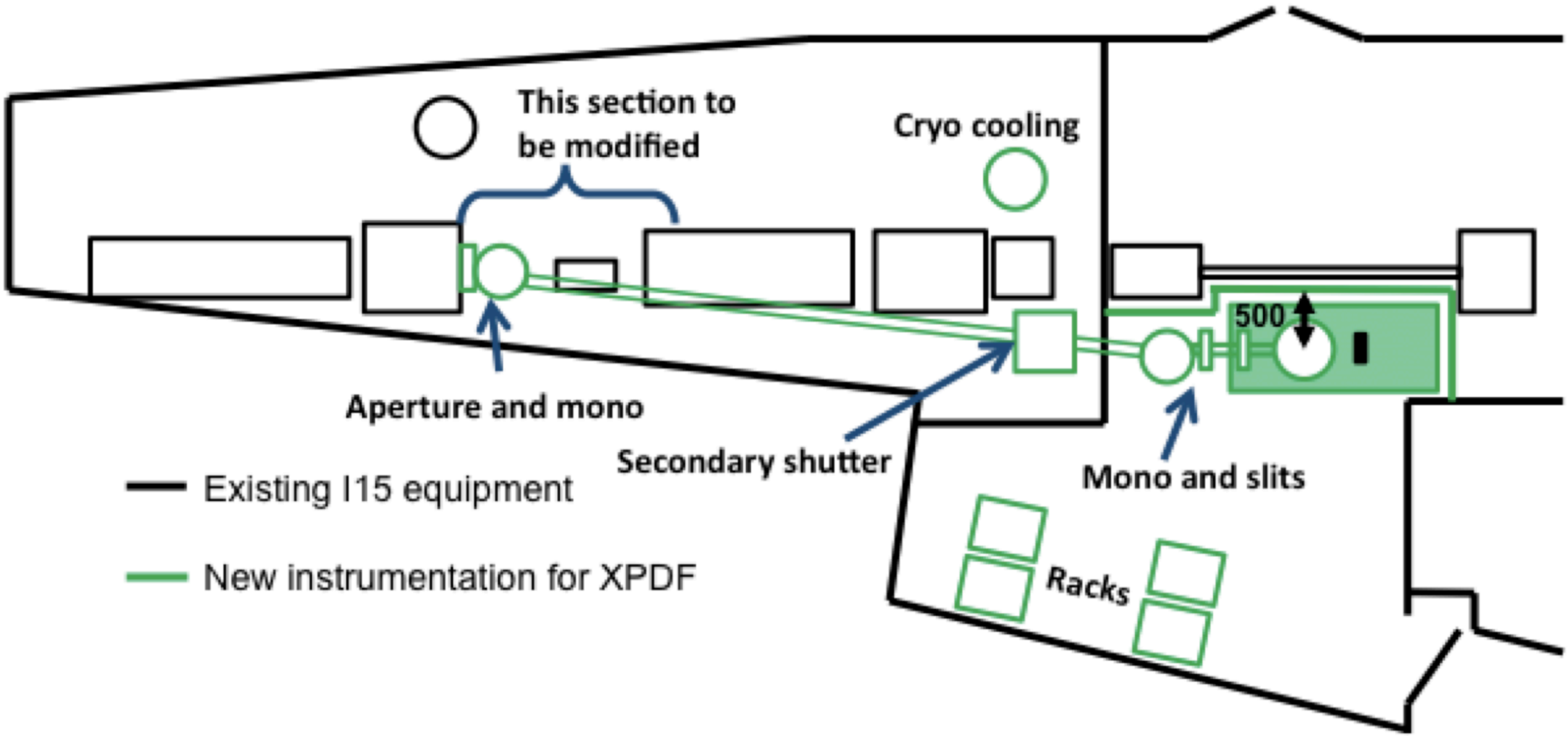
Bristol-Myers Squibb Company

JM Johnson Matthey

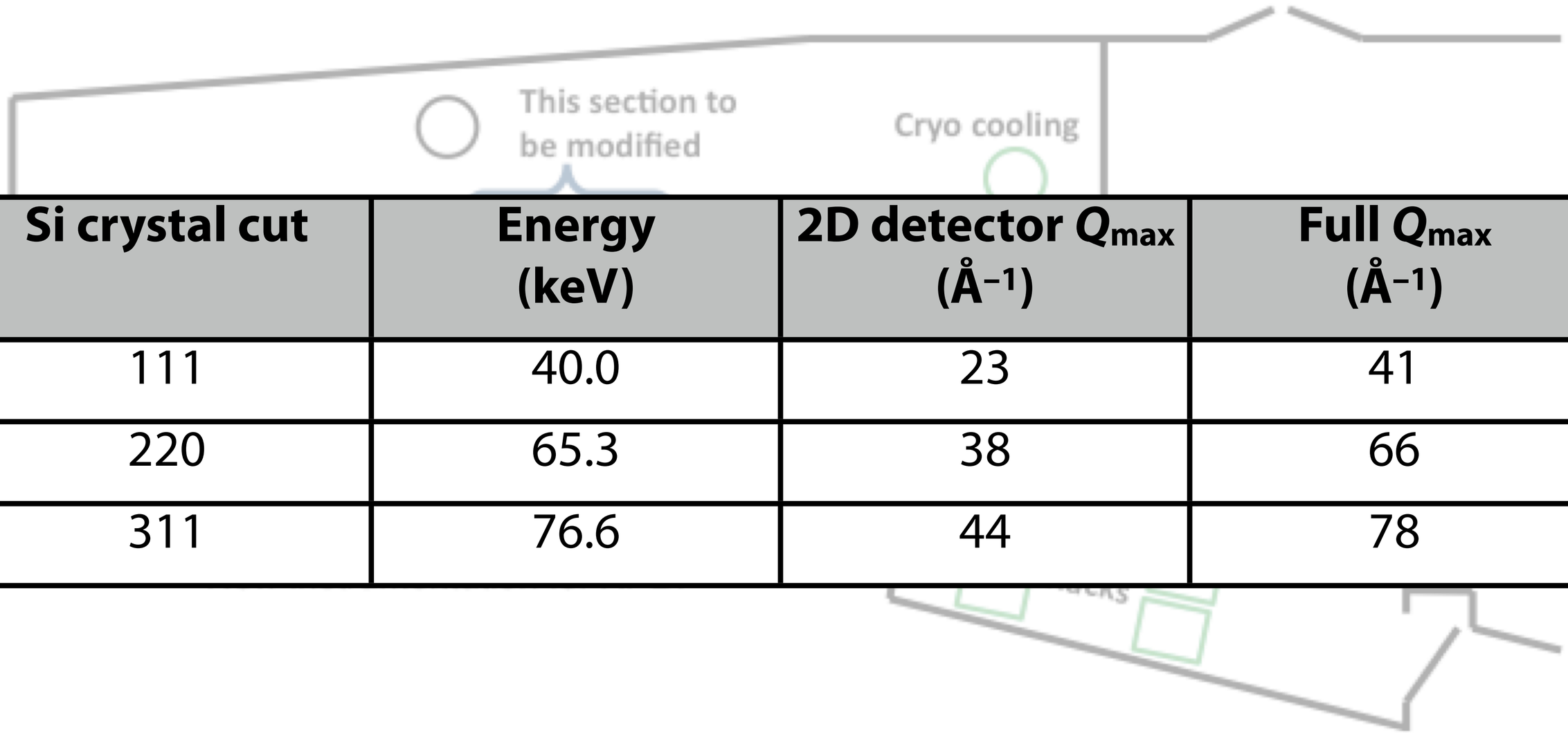
MERCK

PILKINGTON

XPDF Beamline design



XPDF Beamline design



Si crystal cut	Energy (keV)	2D detector Q_{max} (Å^{-1})	Full Q_{max} (Å^{-1})
111	40.0	23	41
220	65.3	38	66
311	76.6	44	78

XPDF Referees: Points for discussion

>> **Monochromators:** Number and type (Laue/Bragg)

>> **Background:** Minimising fluorescence and sample background

>> **Detectors:** Scanning *vs* 1D *vs* 2D

>> **Focussing:** Compound refractive lenses

>> **Wiggler:** Opportunity for I-15 upgrade?

>> **Beam stop and low-Q component**

XPDF Referees: Dedicated PDF?

The XPDF proposal delivers a compelling scientific case that is clearly internationally competitive. A dedicated beamline will certainly go a long way in delivering the science that is proposed.

The decision to optimize the beamline purely for PDF studies rather than making technical compromises in order to carry out diverse experiments is clearly the right one.

The push for a simple to operate and stable beamline will ensure that the focus of the XPDF is scientific output.

Dedicated PDF

Bozin *et al*, *Science* (Dec 2010)

Entropically Stabilized Local Dipole Formation in Lead Chalcogenides

Emil S. Božin,[1] Christos D. Malliakas,[2] Petros Souvatzis,[3] Thomas Proffen,[4] Nicola A. Spaldin,[5] Mercouri G. Kanatzidis,[2,6] Simon J. L. Billinge[2,7]*

We report the observation of local structural dipoles that emerge from an undistorted ground state on warming, in contrast to conventional structural phase transitions in which distortions emerge on cooling. Using experimental and theoretical probes of the local structure, we demonstrate this behavior in binary lead chalcogenides, which were believed to adopt the ideal, undistorted rock-salt structure at all temperatures. The behavior is consistent with a simple thermodynamic model in which the emerging dipoles are stabilized in the disordered state at high temperature due to the extra configurational entropy despite the fact that the undistorted structure has lower internal energy. Our findings shed light on the anomalous electronic and thermoelectric properties of the lead chalcogenides. Similar searches may show that the phenomenon is more widespread.

Ferroelectric materials are characterized by a spontaneous alignment of static local dipole moments leading to a net electric polarization that can be switched by an applied electric field (*1*). Above their critical Curie temperature, T_c, they undergo a phase transition to a higher symmetry, nonpolar state, which by analogy with ferromagnets is called paraelectric. Although the question of whether the paraelectric phase consists of fluctuating local dipole moments or entirely centrosymmetric arrangements of atoms remains open (and likely depends on material, temperature, and length scale), the transition from paraelectric to ferroelectric on cooling always involves a lowering in symmetry that is well described within the traditional Landau picture of phase transitions, for example, in $BaTiO_3$ (*2*). In PbTe and PbS, we have observed the existence at high temperature of such a paraelectric phase of disordered, fluctuating dipoles, but the ground state rather than being the ferroelectric state is a dielectric with no local dipoles. There is no macroscopic symmetry change associated with the spontaneous local dipole formation, so the behavior is invisible to conventional crystallographic techniques. We detect the local atomic off-centering at high temperature using recently developed local structural probes.

Lead chalcogenides such as PbTe and the mineral galena (PbS) have been known and exploited since ancient times (*3*). They are particularly important today, with PbTe currently the leading thermoelectric material in applications just above room temperature (*4*). Despite their long history, their nanoscale structure has only recently been studied in detail (*5–7*), motivated by the realization that intrinsic nanoscale structural modulations are helpful in producing low thermal conductivity and, therefore, high thermoelectric figures of merit (*4*, *8*). Such studies of the nanostructure have been enabled by powerful synchrotron-based local structure probes, such as atomic pair distribution function (PDF) analysis (*9*, *10*). The PDF is obtained by Fourier transforming appropriately collected and corrected x-ray or neutron powder diffraction data (*9*) and has peaks at positions corresponding to interatomic distances in the solid. We show in Fig. 1B the PDF of the simple rock-salt structure (Fig. 1A) that the lead chalcogenides were previously believed to adopt at all temperatures. Because both Bragg and diffuse scattering signals are used, the PDF yields local structural information rather than just the average crystallographic structure.

Our main results, obtained from temperature-dependent neutron diffraction studies, are summarized in Fig. 1, C to I. Because PbTe and PbS behave qualitatively similarly, we present only the PbTe results in the figure; data for PbS are contained in figs. S1 and S2 in the supporting online material (*11*). The dramatic effect of temperature on the structure of PbTe is evident in the powder diffraction pattern, shown in the form of the corrected and normalized diffraction intensity function $F(Q)$ (*11*) in Fig. 1C. This figure also serves to illustrate the high quality and good statistics of the neutron powder diffraction data collected over a wide range of momentum transfer, Q ($Q = 4\pi\sin\theta/\lambda$, where θ is the Bragg angle and λ the wavelength of the x-rays or neutrons). The dramatic loss of intensity in the Bragg peaks at high Q in the 500 K data (red) compared with the 15 K data (blue) is clear. The attenuation is due in part to the usual Debye-Waller effects (*12*) from increased thermal motion; however, the extent of the changes is extraordinarily large. In Fig. 1, D and E, we show the PDFs at 15 K and 500 K, respectively; the effect of temperature on the PDFs is anomalous, with notable broadening evident at 500 K compared with 15 K. (The scale in Fig. 1E is one-fifth that in Fig. 1D.)

To study the temperature-induced local structural effects in more detail, we next analyze the temperature dependence of the low-r region, where r is the interatomic pair separation distance, of the PDF (Fig. 1F), where measured PDFs are shown every 50 K from 15 K to 500 K. The PDF peak broadening is reflected in the drop in the maxima of the peaks. Particularly striking is the drop in the nearest-neighbor peak, which occurs as rapidly as those in the higher-neighbor peaks. This strong broadening of the nearest-neighbor PDF peak does not occur in conventional materials. This is because of the highly correlated dynamics of nearest-neighbor atoms (*13*), which results in the relative motion of directly bonded atom pairs having a much smaller temperature dependence than the higher-neighbor pairs.

In Fig. 1, G and H, we show the Pb-Te nearest-

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Matsunaga *et al*, *Nat Mater* (Jan 2010)

nature materials
ARTICLES
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From local structure to nanosecond recrystallization dynamics in AgInSbTe phase-change materials

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Phase-change optical memories are based on the astonishingly rapid nanosecond-scale crystallization of nanosized amorphous 'marks' in a polycrystalline layer. Models of crystallization exist for the commercially used phase-change alloy $Ge_2Sb_2Te_5$ (GST), but not for the equally important class of Sb–Te-based alloys. We have combined X-ray diffraction, extended X-ray absorption fine structure and hard X-ray photoelectron spectroscopy experiments with density functional simulations to determine the crystalline and amorphous structures of $Ag_{3.5}In_{3.5}Sb_{75.0}Te_{17.0}$ (AIST) and how they differ from GST. The structure of amorphous (a-) AIST shows a range of atomic ring sizes, whereas a-GST shows mainly small rings and cavities. The local environment of Sb in both forms of AIST is a distorted 3 + 3 octahedron. These structures suggest a bond-interchange model, where a sequence of small displacements of Sb atoms accompanied by interchanges of short and long bonds is the origin of the rapid crystallization of a-AIST. It differs profoundly from crystallization in a-GST.

Phase-change (PC) recording is used extensively in rewritable high-density storage media, particularly in optical recording discs, for example digital versatile disc—random access memory (DVD-RAM), digital versatile disc re-recordable (DVD-RW) and Blu-ray disc—rewritable (BD-RE), and non-volatile computer memory such as PC random access memory (PC-RAM). Information is stored as a row of nanosized amorphous marks in a polycrystalline layer or cell arrays and accessed by means of the difference between optical or electrical properties in the amorphous (a-) and crystalline (c-) phases[1]. The most common materials are GeTe–Sb_2Te_3 pseudobinary compounds[2] (group 1 in Fig. 1a) and Sb–Te binary compounds with small amounts of In, Ag and/or Ge, for example $Ag_{3.5}In_{3.5}Sb_{75.0}Te_{17.0}$ (AIST), shown as group 2 in Fig. 1a (ref. 3). It is well known that recrystallization in the two groups is strikingly different: in group 1 it proceeds mainly by way of nucleation inside the marks (Fig. 1b), in group 2 by way of crystal growth from the rim (Fig. 1c; ref. 1).

Materials in both groups have superior rewrite speeds and their amorphous phases are stable at room temperature (RT) for long periods, indispensable characteristics of PC memories. Elements in groups v and vi (including As, Sb, S, Se and Te) readily form disordered structures[4] that are often short lived at RT (a supported a-Sb film crystallizes in a few minutes), but compounds containing other elements, including Ag and In or Ge, can remain amorphous at RT for several decades. Pronounced stability implies a low tendency to crystallize, but this process can be accelerated greatly by laser irradiation or electric heating. A rapid transformation to the crystalline phase can occur within tens of nanoseconds in amorphous $Ge_2Sb_2Te_5$ (GST) and AIST materials[5,6], which then have both the long-term stability and the rapid switching needed for effective PC memories. Crystallization is the rate-limiting process in all PC materials, and an atomistic understanding of it is essential.

There have been many studies of crystalline GST (rock salt) and AIST (A7) materials[7–9]. The average number of p electrons is

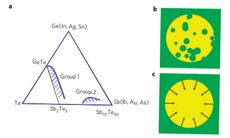

Figure 1 | Phase diagram of PC materials and crystallization patterns. **a**, The most commonly used materials for optical recording are in groups 1 and 2. **b**, Nucleation-dominated recrystallization (as in GST). **c**, Growth-dominated recrystallization (AIST).

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XPDF Referees: Impact

Not building XPDF would have a long-term negative impact on science and technology in a number of important and emerging fields.

I am in complete agreement as to the growing importance and power of PDF methods. These methods find ever-increasing application in problems high on the scientific agenda.

I believe that the XPDF beamline will allow the UK community to maintain the leading role in many scientific fields using PDF methods.