Diamonds on Diamond: structural studies at extreme conditions on the Diamond Light Source

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Extreme conditions (EC) research investigates how the structures and physical and chemical properties of materials change when subjected to extremes of pressure and temperature. Pressures in excess of one million times atmospheric pressure can be achieved using a diamond anvil cell, and, in combination with high-energy, micro-focused radiation from a third-generation synchrotron such as Diamond, detailed structural information can be obtained using either powder or single-crystal diffraction techniques. Here, I summarize some of the research drivers behind international EC research, and then briefly describe the techniques by which high-quality diffraction data are obtained. I then highlight the breadth of EC research possible on Diamond by summarizing four examples from work conducted on the I15 and I19 beamlines, including a study which resulted in the first research paper from Diamond. Finally, I look to the future, and speculate as to the type of EC research might be conducted at Diamond over the next 10 years.

1. Introduction

The range of pressures found in the Universe varies by some 60 orders of magnitude, from the pressure of approximately $10^{30}$ atmospheres found in the centre of a neutron star to the pressures of approximately $10^{-30}$ atmospheres found in intergalactic space [1]. The pressure at the deepest point of the Pacific Ocean is approximately 1000 times atmospheric pressure, while that at the centre of the Earth is 3.6 million atmospheres,
Figure 1. A schematic diagram of the diamond anvils of a DAC, showing the two diamond anvils and the thin metal gasket between them. The inset shows an enlarged view of the diamond culets, and the sample chamber, which contains the sample, pressure transmitting medium and a pressure marker. Figure courtesy of Dr Simon Macleod. AWE Aldermaston. (Online version in colour.)

or 360 GPa. The pressure at the centre of Jupiter is approximately 4000 GPa, and that at the centre of the sun is $10^{11}$ atmospheres.

An excellent introduction to high-pressure science can be found in Robert Hazen’s book entitled The new alchemists: breaking through the barriers of high pressure [2]. In this book, and its revised edition [3], Hazen describes the history of high-pressure science, and how the desire to use pressure to perform the ‘alchemy’ of converting graphite into diamond has long driven researchers to achieve ever higher pressures in the laboratory. The application of such high pressures to materials provides a profitable route to new physical and chemical phenomena and novel new materials, it provides a rigorous test of fundamental condensed matter theory, computation and simulation, and, increasingly, a knowledge of the behaviour of materials at high pressures is vital to understanding the internal structure of the ever-increasing number of exoplanets [4].

The invention of the diamond anvil cell (DAC) in 1959 [5,6] was perhaps the pivotal development in high-pressure science. By using very small samples compressed within a pressure transmitting medium between the tips of two gem-quality diamonds (figure 1), the DAC allowed very high pressures to be obtained in a device small enough to hold in one’s hand (and mount at a synchrotron!). The optical transparency of diamonds allows visual access to the sample in a DAC and also the use of optical spectroscopy to study materials at high pressures. The DAC celebrated its 50th anniversary in 2009 and, to mark this, Bassett, an early pioneer of high-pressure mineralogy, has recently reviewed its history [7].

By the late 1980s, after three decades of DAC research in which attainable pressures had reached first 1 Mbar (100 GPa) in 1976 [8], then 200 GPa in 1984 [9] and 300 GPa in 1989 [10], there was a generally held view that as materials were compressed they would eventually transform into metals, with simple, nearly close-packed structures. And, indeed, high-pressure studies of simple materials such as sulfur [11], CsI [12], Xe [13] and O$_2$ [14] using DACs did indeed show that they became metals at high pressures. High-pressure X-ray diffraction studies performed in the 1970s and 1980s on such materials were made possible by the availability of greatly increased X-ray flux from synchrotron storage rings. However, these studies typically used polychromatic ‘white’ radiation and energy-dispersive X-ray powder diffraction methods to overcome the weak signal from the very small samples in the DAC, resulting in low-resolution data and inaccurate Bragg intensities. As a result, structural information on many high-pressure phases, even in the elements, remained at the level of simple structure type (cubic, tetragonal, etc.) or ‘distortions’
The major transformation in high-pressure synchrotron studies came in the late 1980s through the pioneering application of image-plate detectors for angle-dispersive X-ray diffraction (ADXRD) at the Photon Factory in Japan [16]. The subsequent development of advanced ADXRD techniques using DACs and an image-plate detector at the SRS synchrotron in the UK [17,18] provided diffraction data of unprecedented sensitivity and resolution and unmatched signal to noise. It was also possible to obtain accurate peak intensities for the first time, allowing the first Rietveld refinements of high-pressure powder diffraction data [19,20]. As a result of these major advantages, the techniques developed at the Photon Factory and SRS are now used routinely on every high-pressure beamline around the world.

Using ADXRD techniques, two things became immediately apparent: (i) many of the high-pressure structures reported previously in many materials were incorrect (compare, for example, the phase diagrams of the elements published in 1991 [15] with those published in 2005 [21]) and (ii) the true structural behaviour of even the simplest elemental and binary systems at high pressures was often extremely complex, and far more interesting than believed previously [22,23]. Subsequent computational studies have shown that rather than becoming more free-electron like at high densities, with nuclei sitting in a sea of pressure-ionized electrons, wave function orthogonality, the exclusion principle, and the increasing percentage of the sample volume occupied by the atomic core, can lead to electrons becoming localized between the ion cores, and the formation of complex, electride-like phases [24]. In sodium, perhaps the archetypical free-electron metal at ambient conditions, this results in a phase transition to a remarkable transparent, insulating state above 180 GPa [25].

The developments at the Photon Factory and SRS were perfectly timed with regards to the start-up of the first third-generation synchrotrons in Europe (the ESRF), the USA (the APS) and Japan (SPring-8). Such sources are ideal for high-pressure diffraction studies, by providing extremely high-intensity, high-energy, micro-focused, monochromatic X-ray beams [26]. Diamond Light Source, as a modern third-generation light source, is also perfectly matched to performing highly detailed diffraction studies of materials at high pressure, and the I15 and I19 beamlines have been used extensively for high-pressure powder and single-crystal studies, respectively.

**Figure 2.** The Debye–Scherrer diffraction geometry used in high-pressure powder diffraction experiments. After the two-dimensional diffraction image is collected on the area detector (an image plate in this example), the pattern is integrated azimuthally to give a standard one-dimensional diffraction profile suitable for analysis. Figure courtesy of Dr Simon Macleod, AWE Aldermaston. (Online version in colour.)
The experimental set-up needed for ambient-temperature high-pressure diffraction studies is relatively straightforward [18] and is shown in figure 2. EC beamlines normally have high-energy radiation (typically wavelengths of 0.41 Å or shorter) in order to penetrate the diamond anvils; beams that can be focused to 30 µm or less; and large area detectors, such as CCDs, image plates, amorphous-Se detectors such as the Mar555, or a Perkin-Elmer flat panel detector, to collect data in a classical Debye–Scherrer geometry. In addition, the goniometry on a high-pressure beamline should be able to accommodate and accurately align pressure cells and their high/low temperature environment, which might have a mass of 5–20 kg. All of these criteria are met by the large goniometers in both I15 and I19 at Diamond.

In order to highlight the extreme conditions (EC) science that has been conducted at Diamond over the last 6 years, I have picked four examples of published work from the I15 and I19 beamlines, as follows.

2. Example 1: first single-crystal diffraction above 100 GPa

I was fortunate to be one of the first users to perform a high-pressure experiment on I15 at Diamond in late July 2007, and this resulted in the first user publication from the synchrotron [27], the manuscript of which was submitted two weeks after the beamtime. In the paper, we reported the first ever structural study using a single-crystal sample (of sodium) at a pressure above a megabar (100 GPa). Obtaining such a crystal was made possible by sodium’s unique behaviour at high pressures, where the melting temperature ($T_m$), which is 371 K at ambient conditions, first increases rapidly, reaching a maximum of approximately 1000 K at 30 GPa, before decreasing rapidly to a $T_m$ of only approximately 300 K at 118 GPa [28]. Above 100 GPa, therefore, it is relatively easy to grow high-quality single crystals of Na directly from the melt. The typical melting temperature of elements at such pressures is more than 1000 K [15,21].

At ambient conditions, Na adopts the bcc crystal structure, and on compression there is a phase transition to the fcc structure at 65 GPa [29]. On further compression, there is a transition to a body-centred cubic structure with 16 atoms per unit cell (cI16) at 103 GPa [30], followed by transitions to a number of very complex phases above that pressure [31,32]. The cI16 structure had already been determined in lithium, where it exists above 40 GPa at 180 K [33] and is shown in figure 3. It has space group I4 3d with 16 atoms on a 16c site, $(x, x, x)$, and refinements of powder diffraction data for Li gave a value of 0.055(1) for $x$ at 46 GPa and 180 K. The cI16 crystal of Na was prepared by compressing a powdered sample of Na to 108 GPa, followed by careful annealing just below the melting curve at 313 K. The diffraction data were collected on an image-plate detector in a sequence of contiguous $\pm 0.25^\circ$ oscillations over a total scan range of 14$^\circ$ around the vertical axis using an X-ray wavelength of 0.3444 Å. A total of 31 reflections were observed, which were then averaged to give 15 unique reflections, six of which were observed as zero intensity. The final refined value of $x$ is 0.044(1).

3. Example 2: synthesis of a new complex form of CaB$_6$

An example of how high-pressure experiments at DLS can lead to the development of new materials is provided by the work of Kolmogorov et al. [34] on the synthesis and structural study of a new CaB$_6$ compound. CaB$_6$ is a member of a large MB$_6$ family of materials known to have a range of properties and applications [35]. The ambient pressure structure of CaB$_6$ can be described as having B$_6$ octahedra and metal ions arranged in a CsCl-like arrangement (the so-called cP7 structure, see figure 4). Ab initio calculations suggested that this structure would become unstable at pressures above approximately 25 GPa, but compressing samples at room temperature to approximately 30 GPa did not show the transition reported previously in this strongly covalently bonded material [36]. However, laser-heating samples at pressures of 30–44 GPa, resulted in very complex diffraction patterns that gave the first conclusive evidence of a significant structural transformation for any metal hexaboride (figure 4).
Figure 3. The cI16 crystal structure, which can be regarded as a distorted \(2 \times 2 \times 2\) superstructure of the bcc structure. A distorted-bcc sub-unit is highlighted.

Figure 4. The competing high-pressure structures of CaB\(_6\): the B and Ca atoms are shown as small black and large silver spheres, respectively. The known cubic structure (cP7 in Pearson notation, spacegroup \(Pm\bar{3}m\)) is made out of boron octahedra. The oS56 structure (spacegroup \(Cmmm\)) has the lowest calculated enthalpy for pressures between 13 and 32 GPa, and half of its boron octahedra are opened up to form zig-zag strips. The tI56 structure (spacegroup \(I4/mmm\)), comprises large 24-atom boron units, is the new ground state candidate structure above 32 GPa and is supported by the X-ray data. (Reprinted figure with permission from A. N. Kolmogorov et al. [34]. Copyright © 2012, by the American Physics Society.) (Online version in colour.)

Attempts to index the complex diffraction patterns were unsuccessful, and it was also observed that the patterns did not match those expected from a 14-atom structure predicted as a possible high-pressure phase. Indeed, the diffraction data suggested that the true unit cell was larger still. \textit{Ab initio} structure searching for structures containing 2, 3 and 4 CaB\(_6\) formula units per primitive cell suggested that two larger structures—oS56 and tI56—were energetically favourable in the 13–32 GPa, and above 32 GPa pressure ranges, respectively (see figure 4). The diffraction patterns obtained from the laser-heated samples at pressures above 30 GPa matched those expected from the tI56 structure, confirming its stability above that pressure. No evidence of the oS56 structure was found below 30 GPa, and indeed the tI56 phase was found to be quenchable back to ambient pressure.
The discovery of the first non-cP7-type MB₆ compound quenched down to ambient pressure may help in the design of boron-based intermetallics with new electronic, magnetic and superconducting properties through a careful choice of the metal and the synthesis conditions. The complexity of the high-pressure tI₅₆ structure is such that it could only have been determined through the use of powerful \textit{ab initio} structure-searching algorithms. While such structure-searching is easiest performed when one has additional experimental information, such as lattice parameters and spacegroup, the correct identification of the complex tI₅₆ structure as the stable form of CaB₆ above 30 GPa shows that it is now also possible to deal with increasingly large systems and unfamiliar structural motifs without any input whatsoever from experiment.

4. Example 3: high-pressure single-crystal studies of metal–organic frameworks

The current interest in gas-storage materials has led to increasing interest in the properties of metal–organic framework (MOF) materials [37,38]. Previous studies of these materials under pressure had shown that the pressure transmitting medium could enter the pores of the framework (figure 5a), affecting its behaviour at high pressures [39]. Graham et al. [37] have recently studied the prototypical MOF, MOF-5 [Zn₄O(BDC)₃, BDC = 1,4-benzenedicarboxylate] to 3.2 GPa on beamline I19 at DLS.

In their study, the authors used diethyl formamide (DEF) as the pressure transmitting medium as more volatile media, such as alcohols, caused the single crystal to become polycrystalline (figure 5b). A key aim of the experiment was to determine the volume of the pores in the structure, and their solvent content. At the lowest pressure studied, 0.33(8) GPa, the diffraction data showed that the 7.6 Å diameter pores contained on average 119 DEF molecules per unit cell. Somewhat counterintuitively, increasing the pressure to 0.78(5) GPa, increased the volume of the unit cell, as a result of the incorporation of a further nine DEF molecules into the pores. Thus, the application of pressure resulted in solvent being forced into the pores, making the framework resilient to compression.

On increasing the sample pressure further to 1.35(7) GPa, however, the unit cell volume finally began to decrease, accompanied by a marked and sudden decrease of 42% in the solvent content as the DEF molecules were squeezed out of the pores. Further increases in the pressure resulted in a sharper drop in unit cell volume, compression of the framework and an approximately constant number of DEF molecules per unit cell. The quality of the diffraction data decreased as the sample became amorphous, and at pressures above 3.24(1) GPa the sample became completely amorphous, ending the diffraction study.

Comparison with a previous high-pressure study of MOF5 [40] suggests that hydrostatic compression delays the onset of amorphization and indicates that pressure-induced solvent inclusion into the framework of the MOF makes it more resilient to pressure. Analysis of the compressibility of the framework showed that it is mediated through Zn–O bonds, but with different Zn–O bonds showing very different compressibilities. Computational studies of the evacuated framework structure also showed strong compressibilities of the Zn–O bonds, although, interestingly, the relative compressibilities were different to those observed experimentally. How the presence of solvent within the framework pores affects the compressibility of Zn–O bonds thus still requires investigation.

5. Example 4: europium—the first incommensurate lanthanide element

As a final example of the quality of data that can now be collected on I15, I use a recent example from my own research group on trying to determine the structures adopted by the divalent lanthanide element europium above 20 GPa [41]. If one looks at the high-pressure behaviour of all of the stable elements, none has as few studies as europium [15,21]. Two diffraction studies in 1985 and 1990 [42,43] agreed that there was a phase transition from the ambient pressure bcc phase to
Figure 5. (a) The packing arrangement in MOF-5. The large sphere represents the largest van der Waals’ sphere that can be fitted into the cavity in the structure. (b) Microphotograph of a single crystal of MOF-5 in the gasket hole of the diamond anvil cell. The gasket hole is 300 µm in diameter. (A. J. Graham et al. [37]. Copyright © Wiley-VCH Verlag GmbH & Co. KGaA. Adapted with permission.)

an hcp phase at 12.5 GPa, followed by a second phase transition to an unidentified structure at 18 GPa. The next reported study was in 2010, when Bi et al. [44] reported that the phase above 18 GPa was monoclinic, and that there was a further phase transition to an orthorhombic phase at approximately 35 GPa.

However, we had high-quality diffraction data collected at the SRS in 2008, just before it was shut down, which showed that the Bi et al. structure assignments were almost certainly incorrect, and that the true behaviour of Eu above 18 GPa was considerably more complex than previously reported. Using high-pressure diffraction data from I15, and also data collected at the ESRF, we have now unravelled the complexities of Eu, which are unlike anything seen previously in any other element.

The changes in the diffraction pattern at 18 GPa do not arise from a phase transition in the Eu itself, which remains in the hcp structure to well above that pressure, but rather they mark
the appearance of a rhombohedral contaminant phase of which there is no evidence below 18 GPa [45]. While the diffraction pattern from this rhombohedral phase can be well fitted using 18 europium atoms alone, the volume per Eu atom is then less than that from pure hcp-Eu at the same pressure, showing that the phase cannot contain Eu atoms alone. The volume difference and the quality of the fit, though, suggest that the non-Eu atoms must be (i) small and (ii) weakly scattering. Our current best guess is that the peaks appearing above 18 GPa arise from a Eu subhydride, EuH$_x$ with $x \sim 0.3$ [46].

At 34.8 GPa, this contaminant phase undergoes a phase transition to a cubic phase, accompanied by a change in stochiometry of the (possible) hydride [45]. The simplicity of the cubic diffraction pattern enabled us to determine that hcp-Eu itself undergoes a structural

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**Figure 6.** (a) Rietveld refinement of incommensurate Eu at 33.9 GPa. The upper and lower tick marks show the calculated positions of the main and satellite peaks, respectively. Inset (c) illustrates the excellent fit to the large number of weak satellite peaks. Peaks are indexed using four-dimensional (hklm) indices. Inset (b) illustrates the unusual movement of the (002) satellite reflection to lower angles (larger $d$-spacing) with increasing pressure, a behaviour fully explained by the incommensurate structure. (Figure adapted from R. J. Husband et al. [41]. Copyright © 2012, by the American Physics Society.)
transition at 31.5 GPa, and, more importantly, to identify those peaks that came from the Eu alone [46]. Determining the structure of this high-pressure phase was greatly aided by our finally being able to load samples of Eu that remained contaminant free above 18 GPa. Indexing of a profile of Eu at 33.9 GPa showed that the main peaks could be explained as arising from a monoclinic distortion of the hcp phase. Attempts to index the many weaker peaks were unsuccessful, however, until we tried to index them as incommensurate satellites of the monoclinic structure. This was successful, and revealed Eu to be the first lanthanide element to have an incommensurate structure at high pressure, and the first with a two-dimensional incommensurate wavevector. The final Rietveld fit to the diffraction profile collected at 33.9 GPa is shown in figure 6 [41].

The complexity of this problem was greatly increased by the phenomenon of a pressure-induced contaminant which is not present at lower pressures, a phase transition in this contaminant at a very similar pressure to the europium, and a high-pressure phase with a previously unseen complexity. However, the collection of ever-better diffraction profiles at SRS, ESRF and Diamond has finally resolved the behaviour of Eu to 40 GPa. However, our most recent data collected on I15 [45] suggests there is a further transition above this pressure—which will form the basis of further studies in the near future.

6. Conclusion and the future

The I15 and I19 beamlines at Diamond are now fully functional and are able to provide users with diffraction data of the highest quality. I15 is currently developing a second experimental table which will use Kirkpatrick–Baez (KB) mirrors to provide a smaller beam and which will have optics to enable in situ laser heating of samples. Higher pressure studies, and studies to more extreme P-T conditions, will thus soon become possible. On I19, recent developments for high-pressure studies in the second experimental hutch have involved the development of a close-in pinhole system to decrease the beamsize to below 20 µm, and to reduce the ‘tails’ on the focused beam.

In addition, I15 is about to extend its capabilities by using the relatively wide fan of radiation from its superconducting wiggler magnet to develop a side station for PDF (pair distribution function) studies of liquid and amorphous samples, including those at high pressures. It may also be possible to develop a further smaller side station that would enable larger experimental set-ups, such as a Paris–Edinburgh press, or DACs inside large cryostats, to be used.

What further developments might we see on Diamond and other synchrotrons in the future? The ESRF is currently undergoing a major multi-year upgrade, with ‘Science at extreme conditions’ as one of the five core areas of applied and fundamental research that form the focus of the upgrade. The upgraded ESRF will have significantly lower horizontal emittance and a much higher brilliance—improvements which are ideal for high-pressure studies. Sub-micrometre X-ray beams would be ideal to exploit the double-anvil DAC design of Dubronvinsky et al. [47], where the sample is compressed between two approximately 10–15 µm secondary micro-anvils located within the traditional gasket hole. Such DACs can access pressures well above 500 GPa, and look set to reach 1000 GPa (or 1 TPa) in the not too distant future. Samples in such cells might also be heated to temperatures above 5000 K using pulsed or flash laser-heating methods, where rather than heating in a CW or quasi-CW mode, samples are heated with a single heating pulse and data collected during only that very short time interval when the samples is very hot [48,49]. The collection of many such exposures enables a high-quality diffraction pattern to be obtained. Such methods not only allow data to be collected at very high temperatures, but also greatly reduce the chances of the sample reacting with the pressure medium or indeed the diamond anvils, both of which may occur if the sample is heated for long periods of time. All of these developments will also be possible at Diamond, particularly after further upgrades.

And finally, the availability of the state-of-the-art research facilities contained within the Research Complex at Harwell (www.rc-harwell.ac.uk/) will also be greatly beneficial to the ability of researchers to conduct highly difficult EC experiments on Diamond. For many of the most
complex experiments, it is no longer possible to prepare pressure cells in advance and then simply make a number of pre-planned measurements at the synchrotron. Many samples are so small and so weakly scattering that it is only by studying them on the synchrotron that you can determine whether they are what they should be. And more complex sample environments—cryostats or high-temperature vessels—require careful and lengthy assembly and pre-testing. Highly reactive samples must be loaded (or reloaded) away from home laboratories, and this requires access to high-quality glove boxes. Spectroscopic studies of exactly the same samples studied on Diamond—at the same P-T conditions—require state-of-the-art optical spectroscopy set-ups close to the beamlines. And post-experiment analysis of samples requires access to a suit of high-quality microscopy and microanalysis techniques. All such facilities are available in the RCaH, and their use promises to make a new level of complex EC experiments possible for the first time.

In conclusion, EC research at Diamond is moving forward rapidly on I15 and I19. Planned upgrades to both beamlines, and the availability of the facilities within the RCaH, promise to makes Diamond’s second decade a highly productive one for researchers.

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