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High-pressure X-ray science on the ultimate storage ring

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The advent of the ESRF, APS and SPring-8 third-generation synchrotron sources in the mid-1990s heralded a golden age of high-pressure X-ray science. The high-energy monochromatic micro-focused X-ray beams from these storage rings, combined with the new high-pressure diffraction and spectroscopy techniques developed in the late 1980s, meant that researchers were immediately able to make detailed structural studies at pressures comparable with those at the centre of the Earth, studies that were simply not possible only five years previously. And new techniques, such as X-ray inelastic scattering and X-ray nuclear scattering, became possible at high pressure for the first time, providing wholly-new insight into the behaviour of materials at high densities. The arrival of new diffraction-limited storage rings, with their much greater brightness, and ability to achieve focal-spot diameters for high-energy X-ray beams of below 1 μm, offers the possibility of a new generation of high-pressure science, both extending the scope of what is already possible, and also opening ways to wholly-new areas of investigation.

Keywords: high-pressure diffraction; diffraction-limited storage rings; extreme conditions.

1. Introduction

High-pressure science investigates how materials behave at high density, where the atoms are pushed closer together by external forces. The application of such research to understanding the internal structure of the Earth and other planets, where pressures can reach the TPa (10 Mbar) range, is perhaps immediately obvious. But research at extreme pressures, where complex behaviour emerges in both solid and liquid phases as the core electrons begin to influence material structure and bonding, is also a fruitful route to wholly-new phenomena and novel new materials (McMillan, 2002), and provides rigorous tests of fundamental condensed matter theory and computation (Hemley & Ashcroft, 1998). The construction of a new generation of diffraction-limited storage rings, or the upgrade of existing storage rings, promises a new era of extreme-conditions science as researchers take advantage of the reduced beam size, and much higher brightness, that such machines provide. Before describing the new science that might become possible, a brief history of high-pressure science on synchrotrons over the last 25 years sets the scene.

2. A short history of high-pressure X-ray science on synchrotrons

High-pressure science has always benefited greatly from the use of synchrotron radiation (Paszkowicz, 2002). As pressure is defined as force/area, extremes of pressure can be reached by using only moderate forces if they act on extremely small samples. This is the method employed in the diamond anvil cell (DAC), invented in the late 1950s (Jamieson *et al.*, 1959; Weir *et al.*, 1959), in which samples only tens of micrometres in diameter and a few micrometres thick are compressed between the tips of two gem-quality diamonds (see Fig. 1). The size of the samples used in a DAC requires micro-focused high-intensity X-ray sources in order to obtain high-quality diffraction and scattering data, particularly at pressures above 1 Mbar (100 GPa) (Hausermann & Hanfland, 1996) (see Fig. 2).

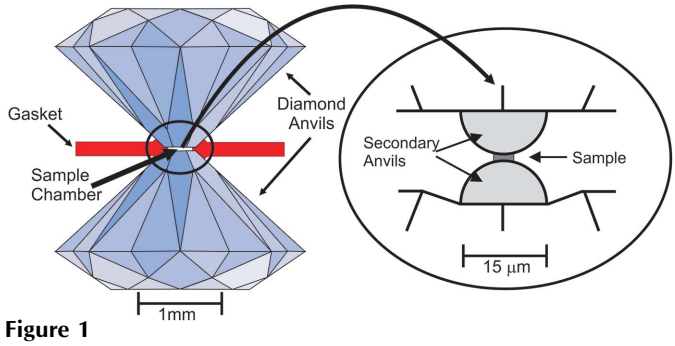

Figure 1
Schematic diagram of a diamond anvil cell (DAC). The sample is contained within the sample chamber in the metallic gasket, which is then compressed between the two diamond anvils. In a two-stage DAC (see main text) the sample chamber contains the secondary set of micro-anvils, between which the sample is compressed (see enlargement). Note the different scales.

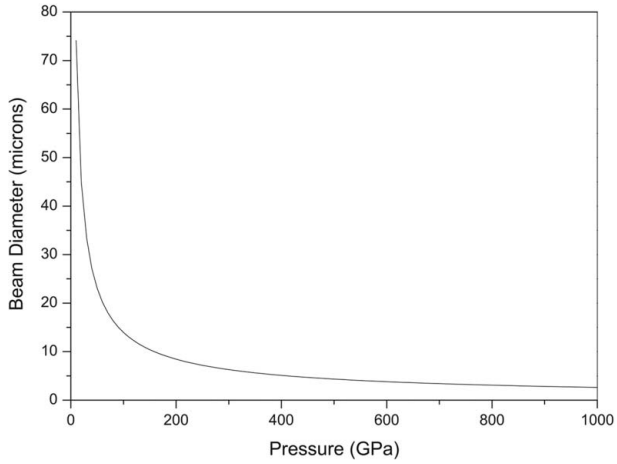

Figure 2
Typical X-ray beam diameters used as a function of sample pressure in order to obtain clean diffraction patterns free from scatter from the metallic gasket. The curve is taken from the equation developed by Hausermann & Hanfland (1996).

High-pressure researchers utilized DACs for X-ray diffraction studies on second-generation synchrotron storage rings from the late 1970s at DESY (Buras *et al.*, 1977), and also at CHESS (Baublitz *et al.*, 1981) and SSRL (Skelton *et al.*, 1983), typically using energy-dispersive (ED) diffraction techniques, which utilized the full white beam from the synchrotron in order to overcome the problems of a weak signal from the very small sample. The 1980s also saw the development of high-pressure X-ray spectroscopy techniques (principally EXAFS) to probe the local environment of atoms in the crystalline, amorphous and liquid phases at high pressure (Shimomura *et al.*, 1978; Ingalls *et al.*, 1980; Itie *et al.*, 1989; Polian *et al.*, 1989), although the limited intensity from second-generation sources restricted the maximum pressure at which data could be attained, while the limited range of accessible X-ray energies narrowed the number of absorption edges that could be studied. Other synchrotron X-ray techniques developed in this period for samples at *ambient* pressure, such as inelastic X-ray scattering (Burkel *et al.*, 1987; Dorner *et al.*, 1987), nuclear scattering (Gerdau *et al.*, 1985) and other X-ray spectroscopy techniques (Tohji & Udagawa, 1987, 1989), could not be utilized at high pressure due to the unfeasibly weak signal from the small samples, or the limited flux at the X-ray energies required to penetrate the pressure-generating apparatus.

Despite these limitations, however, the equations of state and phase transitions of a wide range of systems fundamental to physics, chemistry and earth science were mapped out to pressures well in excess of 100 GPa. An excellent summary of the state of knowledge of the phase diagrams of the elements and mineralogical materials at this time can be found in the excellent books of Liu & Bassett (Liu & Bassett, 1986) and Young (Young, 1991). However, the limitation of ED methods, *i.e.* the poor inherent resolution and inaccurate peak intensities, meant that the level of knowledge of the structural behaviour of many systems at this time remained at the level of structure type [face-centred cubic (f.c.c.), body-centred cubic (b.c.c.) *etc.*] and 'distortions' thereof; more complex structures simply could not be determined. But a full understanding of the mechanisms of metallization, and other high-pressure phenomena, requires a detailed knowledge of the structures of the relevant high-pressure phases.

The fixed scattering geometry of the ED technique also meant that little angular access was required to the pressure cells, and, as a result, high-strength cells could be used that enabled multi-megabar pressures. The fixed diffraction geometry was also well suited to 'large volume' studies, where millimetre-sized samples are compressed with hydraulic rams, and where angular access to the sample must be obtained between the highly absorbing anvils (see Wang, 2010, and references therein), and in combined diffraction/laser-heating studies, in which infrared (IR) lasers are used to obtain the high-pressure high-temperature states of great interest to earth scientists (see Bassett, 2001, and references therein).

The advent of angle-dispersive diffraction techniques in the late 1980s at the Photon Factory in Japan (Shimomura *et al.*, 1992), and their subsequent development at the SRS in the UK (Nelmes *et al.*, 1992; Nelmes & McMahon, 1994), led to a revolution in high-pressure structural science. By utilizing the newly available image-plate area detectors, and then azimuthally integrating the two-dimensional Debye–Scherrer images, accurate Bragg intensities could be obtained from polycrystalline samples. Combined with diffraction patterns that had a significantly higher resolution than those obtained with ED techniques, structural studies could be made with powder-diffraction techniques for the first time. These revealed that rather than retaining simple high-symmetry structures at high pressure, or adopting close-packed structures, almost all materials become more structurally complex at higher densities (McMahon & Nelmes, 2006), sometimes very much more complex (Nelmes *et al.*, 1999; Takemura *et al.*, 2003; Hejny & McMahon, 2003; Degtyareva *et al.*, 2004; Loa *et al.*, 2012).

These developments were perfectly timed with regard to the start-up of the third-generation light sources (ESRF, APS and SPring-8) from the mid-1990s, and high-pressure structural science was ready to take immediate advantage of the micro-focused high-energy X-rays that were available (Hausermann & Hanfland, 1996; Nelmes *et al.*, 1996), thereby ushering in two decades of unparalleled opportunities in high-pressure X-ray science. Structural studies of even the lowest-Z materials have been made, to pressures well in excess of 100 GPa (Loubeyre *et al.*, 1996; Guillaume *et al.*, 2011). Both liquid and solid phases have been studied (Monaco *et al.*, 2003), and, combined with developments in X-ray spectroscopy techniques (Pascarelli & Mathon, 2010), new insight has been obtained into phase transitions, structures and bonding in both liquid and amorphous phases (Santoro *et al.*, 2006).

By combining micro-focused high-energy X-ray beams with focused IR lasers, diffraction studies have been made at the P–T conditions existing deep within the Earth and other planets (Tateno *et al.*, 2010; Anzellini *et al.*, 2013; Sanloup *et al.*, 2013). And wholly-new types of experiments, such as inelastic X-ray scattering studies of phonons (Fiquet *et al.*, 2001; Loa

et al., 2007) and nuclear scattering (Lubbers *et al.*, 2000), have been performed at high pressure on an almost routine basis.

3. Diffraction-limited storage rings

Now, a new generation of storage rings is under development, that utilize multi-bend achromat (MBA) magnet lattices to overcome some of the limitations imposed by more 'traditional' magnetic lattice designs, opening the way to designing and building storage rings that approach the diffraction limit in the hard X-ray region. These new storage rings will place considerable challenges on a wide range of technologies used in the storage rings, such as the accelerator system, vacuum system, heat absorbers *etc.* The small beam spots generated by diffraction-limited storage rings (DLSRs) will present significant advantages to a wide range of scientific disciplines, such as to protein crystallography as well as to X-ray spectroscopies such as RIXS and ARPES.

But as micro-focused high-energy X-ray beams are absolutely *vital* for all high-pressure X-ray techniques, research at extreme conditions stands to benefit enormously from the construction of DLSRs, such as MAX IV in Sweden and Sirius in Brazil, or the installation of MBA lattices in existing current storage rings such as ESRF and Soleil in France, the SLS in Switzerland, the Diamond Light Source in the UK, SPring-8 in Japan, and the ALS and APS in the USA. At the ESRF, '*Science under Extreme Conditions*' has been identified as a key science driver behind the case for upgrading the ESRF to an MBA lattice, and the new science that would be enabled by an upgraded machine was discussed at a recent (February 2014) workshop held at the ESRF. In the remainder of this review, the new avenues of research that would be opened in international high-pressure science by DLSRs, and which would usher in a second golden age of X-ray extreme-conditions science, are described.

3.1. Terapascal research

As said, pressure is defined as force/area, and higher pressures can be generated on samples using the same force if the area over which it is applied is made smaller. Pressures of 50 GPa (0.5 Mbar) can be generated routinely using DACs with diamond culets with a diameter of 300 μm. Pressures above 100 GPa require culets of 100 μm, with the diamond tips bevelled to overcome the distortions they undergo at the highest pressures (Mao & Bell, 1978), and pressure of more than 300 GPa can be generated using diamond culets of 30–50 μm (Akahama *et al.*, 2005). In all cases the sample diameter is approximately one-third of the culet diameter, and has a thickness approximately one-tenth of the diameter. Thus, above 300 GPa, the sample is 10 μm in diameter and 1 μm thick. High-quality diffraction data can be obtained from such samples, and complex crystal structures determined (Akahama *et al.*, 2005; Fujihisa *et al.*, 2013).

Pressures of 300 GPa were first generated in 1989 (Mao *et al.*, 1989), but the maximum pressure of just above 400 GPa attainable with traditional DAC designs had not, until 2012, increased significantly in more than a decade. The key breakthrough in achieving pressures well above the long-standing 400 GPa limit was made by Leonid Dubrovinsky and colleagues (Dubrovinsky *et al.*, 2012). By utilizing a conventional DAC equipped with a second-stage set of micro-semi-ball anvils (10–50 μm in diameter) made of super-hard nanocrystalline diamond (see inset to Fig. 2), they extended the upper pressure range of the DAC firstly to 640 GPa (Dubrovinsky *et al.*, 2012) and, more recently, to ∼800 GPa. The quality of the diffraction data obtained at these pressures using a ∼2 μm-diameter synchrotron X-ray beam is remarkable (Fig. 3), and this technical breakthrough is perfectly timed with regards the availability of sub-micrometre diameter hard X-ray beams from DLSRs.

The utilization of the two-stage DAC to achieve pressures that edge ever closer to 1 TPa (10 Mbar) opens the way to studying *all* materials at pressures where the energy of compression is sufficient to break all chemical bonds, leading to wholly-new structural forms in such fundamental materials as H_2O (Hermann *et al.*, 2012) and O_2 (Zhu *et al.*, 2012). And in metallic systems, the Pauli exclusion principle, and the required orthogonality of the electron wavefunctions, means that at very high densities, where the ionic cores occupy an ever-increasing volume of the crystal, the electrons in metals are forces to localize in interstitial regions (Neaton & Ashcroft, 1999), leading to electride structures in simple metallic systems such as Li, Mg and Al (Ma *et al.*, 2008; Li *et al.*, 2010; Pickard & Needs, 2009, 2010). And, using the two-stage DAC, such studies can be conducted at room temperature and below, *P–T* conditions that cannot be accessed *via* dynamic laser-compression pathways.

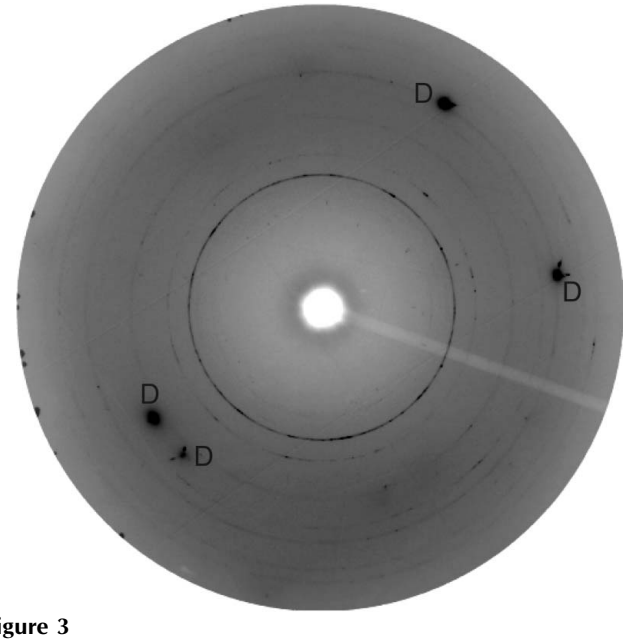

Figure 3
Two-dimensional diffraction pattern collected from a sample of Pt at 731 GPa. The data were collected at the Advanced Photon Source using an X-ray beam diameter of 2 μm (but with tails extending to 4–5 μm) and an exposure time of 120 s. The features marked with 'D' are scattering from the diamond anvils. Image courtesy of L. Dubrovinsky.

Studies using two-stage DACs will require extremely intense X-ray beams focused to sub-micrometre diameters, criteria that will be amply met by DLSRs. However, advances in X-ray focusing technologies will be required if such beams are to be 'clean', that is, without any tails that would lead to intense parasitic scattering from the high-Z metallic gasket surrounding the sample, or scattering from areas of the sample that are at very different pressures to that sampled by the main beam.

What type of diffraction experiments might be performed using two-stage DACs on a DLSR? An example of the kind of complexity expected at high pressures in simple metals is demonstrated by the high-pressure behaviour of Mg which *ab initio* calculations have predicted undergo a series of phase transitions above the 400 GPa limit of standard DACs: from b.c.c. to f.c.c. at 450 GPa, from f.c.c. to the simple hexagonal (s.h.) structure at 750 GPa, from s.h. to simple cubic at 1 TPa, and from simple cubic to orthorhombic at 30 TPa (Li *et al.*, 2010; Pickard & Needs, 2010). The f.c.c. and s.h. phases are predicted to have electride structures, with non-nuclear maxima, or 'blobs', of interstitial electron density that act as almost massless pseudo-anions, thereby making the f.c.c. and s.h. structures reminiscent of the binary NaCl and MgB_2 structures, respectively, with the ion cores as the cations. There is currently no direct experimental evidence of the reality of electride structures at high pressure, even in the most extreme example of transparent insulating Na above 200 GPa (Ma *et al.*, 2009). The observation of the predicted phase transitions in Mg *via* X-ray diffraction, and the experimental determination of the detailed electron density of the high-pressure phases *via* accurate intensity measurements, would present a significant experimental challenge, and one that DLSRs place within our grasp.

3.2. Liquids

With a DAC it is as easy to study a liquid sample at high pressure as a solid, and the use of third-generation synchrotrons has led to the discovery of a number of pressure-induced phenomena in liquids, such as strongly first-order liquid–liquid phase transitions in elements such as phosphorous (Monaco *et al.*, 2003), and unusual melting behaviour in a number of elements, most notably Na (Gregoryanz *et al.*, 2005), which has a melting temperature of only 300 K at 120 GPa, and Li (Guillaume *et al.*, 2011), where the melting temperature drops to only 200 K at 50 GPa. However, the presence of two large single-crystal diamonds on either side of the liquid sample produces a large amount of Compton scattering in the diffraction patterns from liquids, which makes the extraction of the sample-only signal a difficult proposition (Eggert *et al.*, 2002). In addition, the limited angular access afforded by DACs means that the angular scattering range of the data is reduced compared with non-high-pressure experiments, limiting the resolution of the data, and thereby the quality of the information that can be obtained. This can be improved by using higher-energy radiation, but there is then an increase in the Compton scattering.

There have been a number of recent improvements in the experimental methods to increase the quality of the data obtainable. In the first, the diamond culets have shallow pits drilled into them using a laser, thereby increasing the sample volume and the scattered signal (Boehler & De Hantsetters, 2004). The same laser-drilling technology can also be used to partially drill through the backs of the diamonds, reducing the path length of diamond that the direct beam passes through, and, as a result, the Compton scattering from the diamonds is reduced (Dadashev *et al.*, 2001; Soignard *et al.*, 2010). The same perforated diamonds can also be used to reduce the absorption of lower-energy X-rays, of particular importance for X-ray absorption studies where the range of accessible absorption edges can be extended to lower-Z elements (Dadashev *et al.*, 2001). A very recent improvement in high-pressure liquid techniques has been the use of a Soller slit system at the ESRF to greatly reduce the amount of diamond scattering that reaches the detector (Weck *et al.*, 2013) (see Fig. 4). With this slit system, and the micro-focused radiation available from a DLSR, what liquid system might one study?

The alkali metals K, Na and Li offer systems where the complex melting curves, and striking melting minima, have been interpreted in terms of phase transitions in the liquid phases that mirror those in the solid phases (Tamblyn *et al.*, 2008; Narygina *et al.*, 2011). There is as yet no experimental data to back up these ideas, however. By utilizing the extreme brightness of a DLSR, coupled with high-energy X-rays to increase the q-range of the data, pits to increase the sample volume, and advanced collimation on the detector, ideally coupled with some form of energy-discriminating detector to further help remove the inelastically scattered background from the elastically scattered diffraction pattern, data of

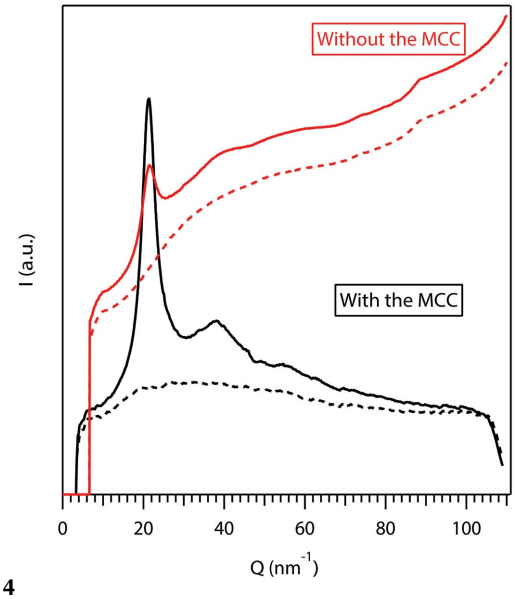

Figure 4
Azimuthally integrated X-ray diffraction profiles collected from liquid argon in a DAC at 0.9 GPa, recorded with (lower) and without (upper) a multi-channel collimator (MCC). In each spectrum the dotted lines show the background, which is predominantly Compton scattering from the diamond anvils. Reprinted with permission from Weck *et al.* (2013). Copyright 2013, AIP Publishing LLC.

sufficient quality can be obtained to follow the structures of the liquids in K, Na and (most challenging) Li just above their melting curves. Should such measurements prove possible, then the same techniques might be applied to the study of liquid H_2 at extreme pressures (Weck *et al.*, 2013), where the investigation of the fluid–plasma transition (Landau & Zeidovich, 1943) at ∼150 GPa and ∼1500 K forms one of the most highly sought transitions in extreme-conditions science (Dzyabura *et al.*, 2013).

3.3. Still more extreme *P–T* conditions

Combined high-pressure high-temperature conditions can be achieved using resistive heating of either the whole DAC or just the immediate environment of the diamonds and sample, or by using IR lasers to heat a small region of the sample. For metallic samples, the IR lasers typically have a wavelength of ∼1 μm, and, because of their limited penetration depth, the sample is typically heated from both sides simultaneously to ensure as uniform axial temperatures as possible. However, extreme temperature gradients still exist within the sample, with gradients of 100 K μm^{-1} being typical. It is then important to have the two IR beams aligned perfectly with respect to each other, on either side of the sample, and for the X-ray probe beam to be much smaller than the heated spot, so that the sample region being probed has as uniform a temperature as possible. To thermally insulate the sample from the high-conductivity diamond anvils, the sample must be separated from them by a thin (5–10 μm) barrier layer of a transparent low-thermal-conductivity material. Commonly used materials include NaCl, MgO and solid argon. The temperature of the sample is determined from an analysis of its thermal emission spectrum, which is fitted with a Planck or Wien function to yield temperatures with a precision of a few Kelvin and an accuracy of 50–100 K. Such experimental arrangements are utilized at almost all modern third-generation synchrotron sources, and have enabled the phase transition behaviour and melting temperatures of a wide range of materials to be measured to well above 100 GPa and 5000 K. Determining the phase behaviour and melting of iron at extreme *P–T* conditions continues to provide a strong driving force in developing novel laser-heating techniques (Tateno *et al.*, 2010; Anzellini *et al.*, 2013).

However, the upper *P–T* limit accessible with laser heating had remained relatively static for some time, and there has been a move, therefore, to dynamic laser-heating methods to overcome the limit of the more classical 'continuous' method (Rekhi *et al.*, 2003; Deemyad *et al.*, 2005; Goncharov *et al.*, 2008, 2009, 2010). In dynamic laser heating, the sample is heated by short pulses of IR light at kHz frequencies. The optimal pulse duration is still the subject of investigation, but is typically 10–100 ns for spectroscopic studies (Rekhi *et al.*, 2003; Deemyad *et al.*, 2005; Goncharov *et al.*, 2008, 2009), and tens of microseconds for *in situ* X-ray diffraction studies (Goncharov *et al.*, 2010). The temperature of the hot spot in the sample rises rapidly, with a peak temperature that can be far higher than that obtained in steady-state laser-heating experiments. In order to collect diffraction data at these high-*T* conditions, short X-ray exposures must be made when the sample reaches its peak temperature (Goncharov *et al.*, 2010). If the source is bright enough, the data can either be collected with a single ∼100 ps bunch of photons or in a 'strobed' fashion, with many short diffraction images, each timed to occur at the same point on the heating pulse, and therefore at the same temperature. In the latter case a high-quality diffraction image is thus built up over a total integrated acquisition time of 10 s (Goncharov *et al.*, 2010). Very similar experiments can be conducted using X-ray absorption spectroscopies such as EXAFS, where high-quality spectra can be assembled from the collection of data from single bunches of photons (Pascarelli & Mathon, 2010).

These techniques are still in their infancy, and their use will benefit enormously from the use of a DLSR. Data collection times will be reduced considerably, and the use of shorter laser-heating pulses, combined with the thinner samples required to give a suitable diffraction signal, thereby increasing the thickness of thermal insulation that can be used, will increase the maximum temperature accessible. A key goal will be to combine pulsed-heating technology with the two-stage DAC, thereby opening the possibility of extending *in situ* laser-heating studies towards 1 TPa (10 Mbar) and 10000 K. A key scientific goal will be the determination of the structures and melting curve of Fe to beyond earth-core pressures of 360 GPa, thereby extending such studies into the realm of exoplanet interiors, where the *P–T* behaviour of relevant geoplanetary materials is almost entirely unknown and is currently estimated from extrapolation of lower-pressure data (Swift *et al.*, 2012).

3.4. Warm dense matter

Warm dense matter (WDM) exists between the solid and plasma states (see Fig. 5), where the interaction potential energy between the electrons and nuclei, and the kinetic

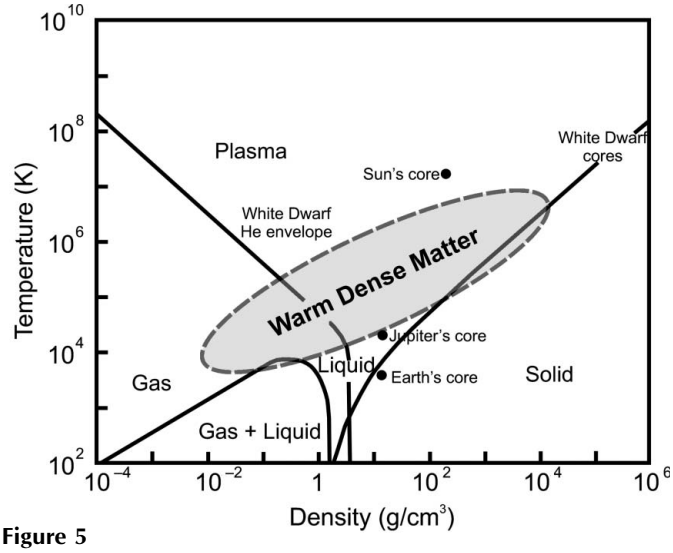

Figure 5
Density–temperature phase diagram showing the location of the warm dense matter region at the boundary of the plasma, gas, liquid and solid. Based on a figure by M. Desjarlais.

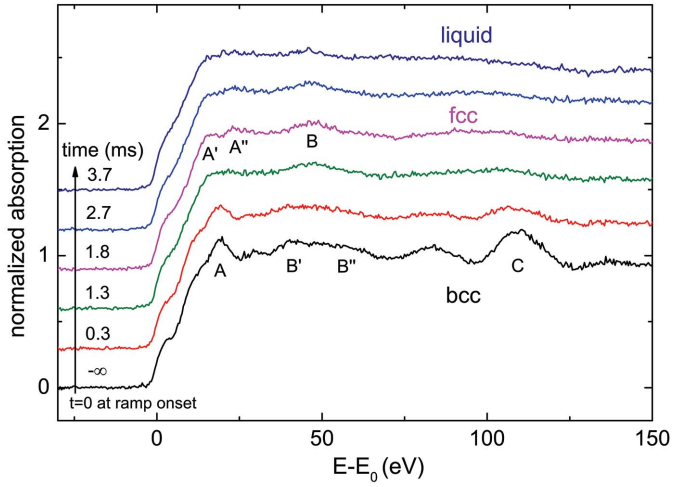

Figure 6
XANES spectra from Fe undergoing rapid heating along a quasi-isochoric path. The sample is initially in the b.c.c. phase at 1 GPa and 300 K, and then transforms into the f.c.c. phase at 6 GPa and 1500 K, before transforming into the liquid phase at 26 GPa and 3000 K. The acquisition time was 25 µs per spectrum, and the total acquisition time was 3.7 ms. The labels A, B, C *etc.* are explained in the original manuscript. Reprinted with permission from Marini *et al.* (2014). Copyright 2014, AIP Publishing LLC.

energy of the electrons, are of the same magnitude. As a result, WDM is not well described by either plasma or condensed matter physics. WDM states can be created by compact high-powered lasers for nanosecond timescales, and DLSRs will produce enough photons from each 100 ps duration electron bunch to enable detailed EXAFS and XANES studies of WDM states. Preliminary measurements on existing storage rings have shown the potential of ultra-fast X-ray spectroscopy to probe the liquid (Marini *et al.*, 2014) (see Fig. 6) and WDM state (Cho *et al.*, 2011), and the large energy spectrum that will be accessible from DLSRs, compared with that available from free-electron X-rays lasers, will enable a wide range of different absorption edges to be probed, allowing the study of a wide range of elemental, binary and multi-element systems in the WDM state. This entire area of research is relatively unexplored, and the scope for transformative research is high.

4. Conclusions

High-pressure X-ray science has always benefited enormously from the use of synchrotron radiation. The ideal X-ray source would deliver the maximum number of photons possible in a micrometre-sized focal spot, and provide the widest possible range of X-ray energies. These criteria will be amply met by the new generation of diffraction-limited storage rings currently being planned around the world. The last 20 years have seen extreme-conditions X-ray science advance to the extent that measurements that were once impossible can now be conducted with a precision and accuracy that are comparable with those obtained at ambient conditions. The future use of DSLRs will provide the means of pushing such studies to still more extreme pressures and temperatures, utilizing dynamic techniques in order to make measurements on sub-nanosecond timescales. The future of high-pressure X-ray science looks very bright indeed.

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