

Chapter 2

Experimental Techniques

2.1 Complementarity of High-Pressure Techniques

High-pressure structural science is a particularly strong example of an area that relies upon the complementarity of various techniques to achieve the final aim of the structural characterisation of novel materials. Furthermore, the advances in this field are intertwined with the evolution of complex sample environments for experiments at elevated temperatures and/or pressures, as well as the development of techniques for the collection and analysis of spectroscopic and diffraction data under extreme conditions. In this work, a combination of X-ray diffraction (both single-crystal and powder), neutron powder diffraction and Raman spectroscopy has been used to identify and structurally characterise numerous phases at a range of pressure/temperature conditions. High pressures have been generated using either the Merrill-Bassett diamond-anvil cell (DAC) [1] or the Paris-Edinburgh Cell [2]. This chapter will therefore feature a detailed description of each of these instruments, with a subsequent discussion of the experimental techniques in which they have been employed.

2.2 The Merrill-Bassett Diamond-Anvil Cell

2.2.1 DAC Components

High-pressure X-ray diffraction and Raman spectroscopic studies were performed using a gasketed diamond-anvil cell (DAC). The premise for this device is relatively simple; the sample is placed between two diamond faces (culets) and is subjected to high pressures when a force pushes the opposed anvils together. The DAC utilised in this work was based on developments by Merrill and Bassett in 1974 [1]. The small size (~ 5 cm diameter) and relative ease of use make these cells extremely versatile and perfectly suited for high-pressure X-ray diffraction studies. Prior to the development of DAC technology, high-pressure experiments

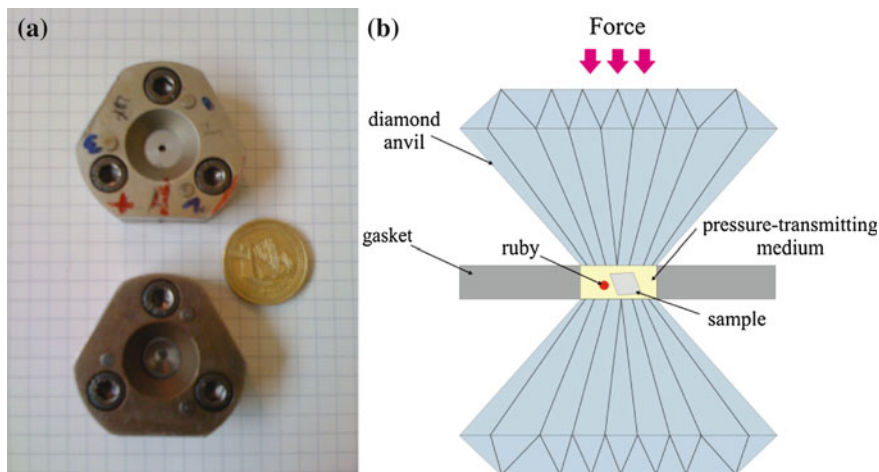


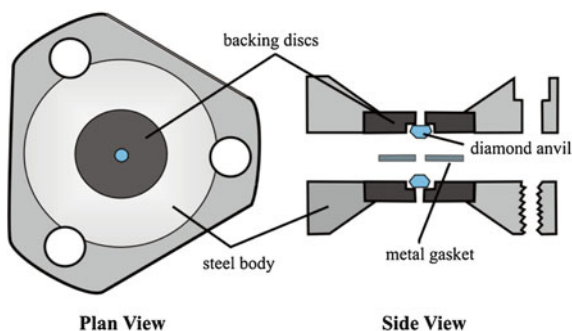
Fig. 2.1 **a** photograph of the Merrill-Bassett DAC highlighting its simplicity and size (the top DAC has Be backing plates, while the diamonds are mounted on WC plates in the bottom cell); and, **b** schematic representation of the principles of the diamond-anvil cell

were limited to using massive Bridgman-type hydraulic or piston-cylinder cells that required specialist laboratories and posed considerable safety hazards in the event of failure [3]. A photograph of the Merrill-Bassett diamond-anvil cell is presented in Fig. 2.1, along with a representation of the principles of such a device.

Although the Merrill-Bassett diamond-anvil cell has garnered widespread recognition in the high-pressure community, the initial inspiration to utilise diamond's compressive strength to generate extreme pressures dates to the late 1940s when Lawson and Tang were able to subject samples to pressures circa 2.0 GPa between two halves of a cleaved diamond [4]. A team of scientists at the National Bureau of Standards (Washington, D.C., USA) meanwhile explored a parallel path by modifying Bridgman's opposed-anvil device using two gem-quality diamonds as anvils, instead of steel or tungsten carbide (WC). They were also in the extremely enviable position of being able to acquire bountiful supplies of diamonds as customs officials at the time were willing to entrust other government bodies with confiscated goods, provided that a convincing case for their use was put forward [5]. Thus Van Valkenburg and colleagues were able to construct an opposed-anvil device, in which two gem-quality diamonds were driven together by the turn of a screw, thus facilitating the visual observation of high-pressure phase transitions in a range of materials (such as KNO_3 and AgI) [6].

The ability to see the sample also brought numerous practical boons, primarily the ability to check anvil alignment and the observation of phase transitions and even sample recrystallisations. Indeed the transparency of diamond to large sections of the electromagnetic spectrum allows optical and spectroscopic analysis of the sample in situ and makes diamond an ideal anvil material for X-ray diffraction studies. The low atomic number (therefore minimal X-ray absorption) and the high

Fig. 2.2 Schematic of the Merrill-Bassett diamond-anvil cell



degree of crystal perfection of gem-quality diamonds mean that it is possible to minimise any interference with the sample diffraction. It is important to note, however, that fluorescence from the significant nitrogen impurity in Type I diamonds make them impractical for spectroscopic studies.

The significant achievement of the Merrill-Bassett DAC was its miniaturisation, allowing it to be mounted on a standard goniometer head [1]. In this cell the diamond anvils are mounted on two backing plates (platens), which are encased in a steel body, as shown in Fig. 2.2. A force is then applied to the outer faces of the diamonds by tightening three screws in the steel body, which is then multiplied many times at the small inner faces (culets). The culet size is the predominant factor in determining the maximum pressure that can be achieved. In the current study, culet sizes of either 600 or 400 μm were used to reach maximum pressures of circa 10.0 and 25.0 GPa, respectively.

In their original design Merrill and Bassett exploited the tensile strength of beryllium and its transparency to X-rays for use as the backing-plates, on which to mount the diamond anvils. A major disadvantage of Be backing discs, however, is the presence of powder rings arising from X-ray scattering from the polycrystalline metal, thus contaminating the diffraction image, as shown in Fig. 2.3. This is exacerbated when high flux and low divergence synchrotron X-ray beams are necessary since the Be lines become more intense and ‘spottier’ in appearance [7]. Moreover, the toxicity of beryllium means that great care must be taken when handling these plates.

In response to the shortcomings of Be-backed diamond-anvil cells, the Merrill-Bassett DAC has been modified to incorporate tungsten carbide or steel backing seats, which do not pose a significant safety risk. However, the opacity of these materials to X-rays means that rather than contaminating the sample diffraction pattern, an equally troublesome dilemma presents itself—the absorption of large sections of the diffracted beam, and thus the severe restriction of the reciprocal space accessible in a high-pressure experiment. In order to overcome this, WC backing plates with wider opening angles have been designed into which a conical Böhler-Almax diamond anvil has been embedded (see Fig. 2.3) [8, 9]. This construction allows the full opening angle of the steel platens (80°) to be utilised, while still ensuring the anvils are adequately supported for applications at very

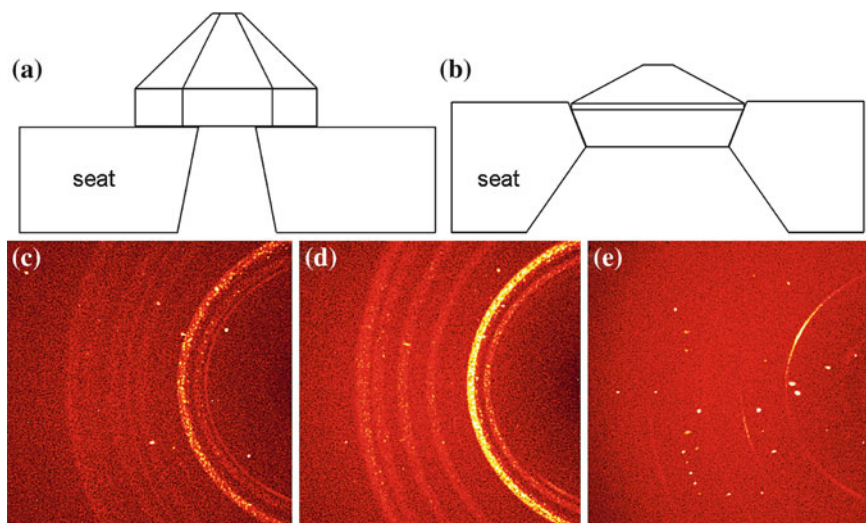


Fig. 2.3 Schematic of the different backing plates and the effects each have on the quality of the diffraction data: **a** Be-backed diamond; **b** WC backing plates, with the specially cut diamonds set into the plate; **c** diffraction image collected on a laboratory source using a Be-backed diamond-anvil cell; **d** an analogous image collected using synchrotron radiation; and, **e** diffraction data collected using DAC equipped with WC backing plates. Images kindly provided by Moggach et al. [7]

high pressures (>20 GPa) [7]. In both cases (Be and WC), the backing plates are held within the steel body by small screws that allow alignment of the diamond anvils normal to the thrust axis [10]; parallelism can only be accounted for while mounting the anvils on the backing plates. It is essential to ensure the anvils are fully aligned and parallel—neglecting to do so risks (unnecessarily) diamond failure, especially at elevated pressures.

The final constituent of the cell is the metal gasket that is sandwiched between the culets of the diamonds. The pressures attained at the diamond culets are sufficient to cause the gasket to extrude around the anvils, thus sealing the sample chamber while also providing support for the diamonds. A variety of metals, for example Re, steel and inconel (an alloy of Ni, Cr and Fe), may be used, but tungsten has high mechanical strength and thus is often the metal of choice for larger sample volumes. The nature and preparation of the gasket are also of considerable importance. For pressure to increase, the volume of the sample chamber must decrease; normally the reduction in the thickness of the sample chamber as the anvil advances is sufficient. If the gasket is too thick however, the outwards force from the sample will exceed the friction between the anvils and the gasket and the hole will expand. Thus, no pressure will be applied to the sample and there is a risk of damage to the diamonds by gasket failure.

A thin gasket will allow higher pressures to be reached and can give better control at low pressure as less force is required to seal the sample chamber

initially [11]. It is therefore preferable to pre-indent the gasket by careful extrusion between the diamond anvils prior to drilling a gasket hole. This approach has the added benefits of imbuing the cell with greater stability due to the massive support from the extruded material and improving the gasket's mechanical stability by hardening. However, pre-indentation must be carried out with perfectly aligned diamonds: diamond failure is more likely to occur during pre-indentation than in the high-pressure experiment itself because the radial extrusion of the gasket material puts maximum tensile stress on the anvil tips [12]. In the majority of the work presented herein a 250 μm thick tungsten gasket was pre-indented to a *thickness* of 100–150 μm , which was sufficient to allow compression studies up to ~ 6.0 GPa. The compression of RDX to very high pressures (circa 25 GPa) necessitated the utilisation of a 150 μm W gasket that was pre-indented to a pressure of 30 GPa, as determined by the ruby fluorescence method (see Sect. 2.2.2).

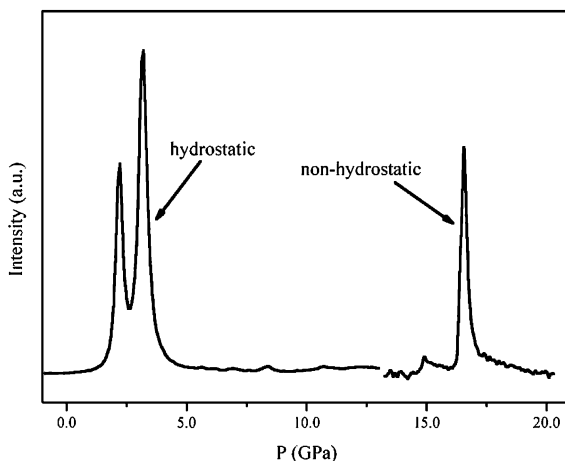
It is normally desirable to ensure that the pressure applied is homogeneous and is free of any deviatoric stresses or strains because pressure, i.e. isotropic stress, is a thermodynamic parameter [5]. Moreover, there are a number of experimental factors which mean that non-hydrostatic conditions should be avoided wherever possible. For example, inhomogeneous strain in the crystal results in broadening of the diffraction peaks; the stresses and strains may promote or suppress phase transitions; irregularities in the relative compression of the unit cell axes may be observed; and, broadening of the ruby fluorescence R_1 line (Sect. 2.2.2) increases uncertainty in the pressure measurement.

In order to achieve completely hydrostatic compression, the sample must be immersed in a medium that displays hydrostatic behaviour throughout the pressure regime of interest. Furthermore the medium should not dissolve or react with the sample being studied. A range of different media have therefore been developed, the hydrostatic limits of which have been investigated by various groups [13–16]. The pressure-transmitting medium used in the majority of the studies presented in this work (a 4:1 mixture of methanol:ethanol) has been shown to remain hydrostatic to ~ 9.8 GPa by Angel et al., who measured the X-ray diffraction maxima from quartz single crystals in a range of media [13]. In cases where MeOH:EtOH (4:1) was found to dissolve the sample, alternatives such as a 5:1 mixture of iso:n-pentane or Fluorinert FC77, a mixture of perfluorinated hydrocarbons, were employed although these have been shown to have lower hydrostatic limits (7.4 GPa [14] and 1.0 GPa [15], respectively).

2.2.2 Pressure Measurement

Direct pressure measurement from the applied force is both inaccurate and impractical. Instead, Piermarini et al. demonstrated that a small chip or sphere of ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$) could serve as a continuous pressure sensor within the DAC by utilising its laser-induced fluorescence [17]. Indeed the simplicity of the ruby fluorescence method for in situ pressure calibration is without question a

Fig. 2.4 Comparison of the hydrostatic and non-hydrostatic ruby fluorescence signals, highlighting the complete reduction of the R_1 – R_2 distance under non-hydrostatic conditions. It should be noted that, in this plot, the non-hydrostatic signal has been scaled to have comparable intensity to the hydrostatic signal and so the significant peak broadening observed under non-hydrostatic conditions is not apparent



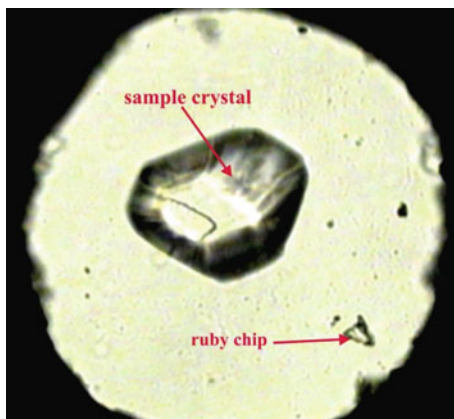
contributing factor to the widespread application of diamond-anvil cell techniques and, as such, was the subject of an extensive review by Syassen in 2008 [18]. The spectral lines of ruby undergo a pronounced red-shift with applied pressure; the R_1 electronic transition shows a linear dependence with pressure up to at least 20 GPa at ambient temperature [17]—this pressure scale will be used throughout the present work. At elevated temperatures, however, the fluorescence signal undergoes significant broadening and it becomes difficult to obtain a reliable measure of sample pressure. In this study, all pressure measurements via ruby fluorescence have been made at ambient temperature. Unless stated otherwise, spectra were collected using the 632.8 nm line from a He–Ne laser and dispersed and detected by a Jobin–Yvon LabRam 300 spectrometer, with typical precision of ± 0.05 GPa.

Another factor affecting the ruby fluorescence signal is the hydrostaticity within the sample chamber. Under hydrostatic compression the R_1 and R_2 lines remain well resolved and pressure measurement is straightforward. The R_1 – R_2 separation has been shown to be strongly dependent on the presence of any deviatoric stresses within the ruby sample (i.e. within the sample chamber). In experiments where non-hydrostatic conditions are being investigated it is therefore common to see these spectral lines overlapping, and the uncertainty in the pressure measurement is significantly increased. A comparison of the ruby fluorescence spectra obtained under hydrostatic and non-hydrostatic conditions can be found in Fig. 2.4.

2.2.3 Sample Loading

The majority of the studies undertaken in this work have been direct compression of either single crystals or polycrystalline powder. In these experiments the sample is initially loaded into the gasket hole along with a small chip or sphere of ruby. Great care must be taken in order to avoid flushing out either the sample or the ruby during the subsequent flooding of the sample chamber with the pressure-

Fig. 2.5 Photograph of a single crystal loaded in the DAC with ruby



transmitting medium. In single-crystal studies it is also desirable to ensure that the gasket impinges on neither the sample crystal nor the ruby. This is to avoid additional stresses being applied to either the sample or the ruby upon gasket extrusion, which would result in crystal destruction and/or greater uncertainty in the pressure calibration. Furthermore careful selection of sample crystals is pivotal for the success of a high-pressure diffraction study. Not only should high-quality single crystals be selected, it is essential to ensure that the crystal be small enough to fit inside the gasket—crystals that bridge the separation between the diamond culets will be crushed upon compression. The successful loading of a single crystal is depicted in Fig. 2.5.

2.3 Experimental Techniques Using the Diamond-Anvil Cell

2.3.1 X-Ray Single-Crystal Diffraction

X-ray single-crystal diffraction is the most definitive method for the determination of atomic positions within a crystalline solid (defined as a three-dimensional array of identical unit cells with long range order and translational symmetry). Diffraction arises from the interference (both constructive and destructive) of scattered photons, which are produced by the elastic scattering of incident electromagnetic radiation by the electron density of atoms within a crystal lattice. The wavelength (or rather range of wavelengths) of X-ray radiation is comparable with interatomic separations, typically of the order of a few Ångströms. This means that the interference of X-rays scattered by different atomic planes within the lattice will result in the observed diffraction pattern, from which it is possible to determine the relative positions of the atoms within the structure.

The condition for the constructive interference of scattered radiation (wavelength, λ) is satisfied only when the path difference is equal to $n\lambda$, where n is an integer. Bragg demonstrated that the path difference of two scattered X-rays may

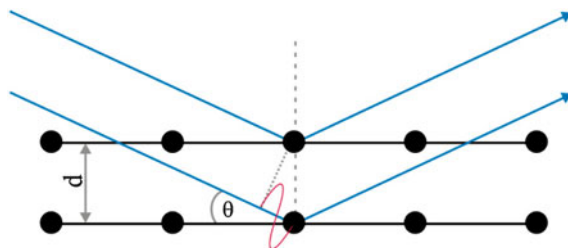


Fig. 2.6 The Bragg construction for diffraction by a three-dimensional crystal lattice. In this scheme the incident X-rays (*blue*) are diffracted by two separate crystal planes (*black*), separated by a distance, d . For constructive interference to occur, the path difference between two diffracted beams should be an integer multiple of their wavelength (*red*, $n\lambda$). This situation arises only at certain scattering angles (θ); at all other angles the beams will interfere destructively

be expressed in terms of the separation of the lattice planes within the crystal (d) and the angle of incidence (θ) [19]. As depicted in Fig. 2.6, constructive interference will occur, and thus diffracted beam intensity will be observed, when $n\lambda = 2d\sin\theta$. At other angles of incidence or interplanar distances, the scattered X-rays will be partly or completely out of phase (destructive interference).

A great deal of information (i.e. the unit cell indexing and space group) can be extracted directly from an observed diffraction pattern. However, while the observed intensities provide information about the amplitudes of the scattered waves, $|F_o|$, any information about the relative phases (φ) is lost. The so-called ‘phase problem’ presents a considerable challenge to crystallographers since both the amplitudes and phases of the scattered X-rays are required for an accurate representation of the electron density within the unit cell:

$$\rho(xyz) = \frac{1}{V} \sum_{hkl} |F(hkl)| \exp[i\varphi(hkl)] \exp[-2\pi i(hx + ky + lz)]$$

In chemical crystallography there are two main techniques for overcoming this phase problem: (i) Patterson methods, and (ii) direct methods. Patterson methods rely on either the presence of a few heavy atoms in the structure (such as in a transition metal complex) or a significant portion of the molecule in question having a well-defined and rigid geometry. In the Patterson synthesis the amplitudes of the scattered waves are replaced by their squares, $|F_o|^2$, and the phases (φ) are omitted, such that:

$$P(uvw) = \frac{1}{V} \sum_{hkl} |F(hkl)|^2 \cos[2\pi(hu + kv + lw)]$$

Peaks in the resultant Patterson maps do not correspond to the electron density but rather the interatomic vectors. As each peak is proportional to the product of the atomic numbers (Z) of the atoms involved, vectors between two heavy atoms are more easily identified. The task then is to deduce the structure directly from knowledge of the distances between the atoms in the unit cell.

In direct methods, no previous knowledge of the structure is employed in structure solution—the phases of the structure factors and therefore the electron density are derived mathematically from a set of observed X-ray intensities. The method imposes constraints that are valid for the (correct) electron density distribution (such as discrete peaks and non-negative values) to the structure factors. Since the amplitudes $|F_o|$ are known, these constraints restrict the possible phases of the structure factors and, in favourable cases, are sufficient to allow phase determination directly.

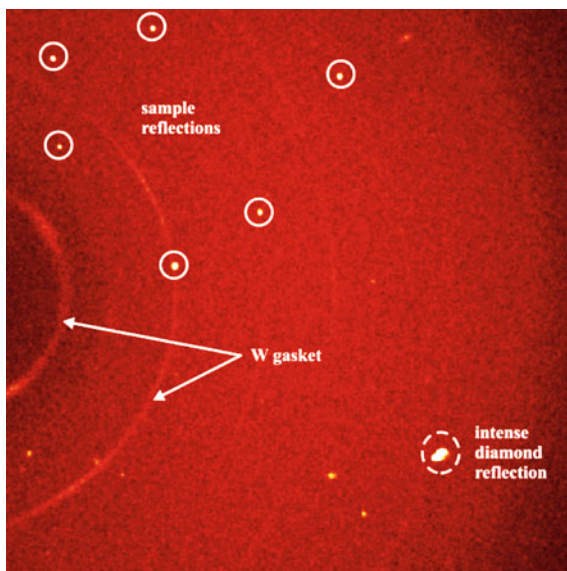
In both cases (Patterson and direct methods) the structure may be refined by calculating the residual electron density ($\Delta\rho$)—the difference between the calculated structure factors, F_c , and the observed structure factors, $|F_o|$. Such Fourier syntheses can be used to determine if any electron density has not been accurately modelled by the proposed structure, and therefore represent an effective test of whether a complete model has been reached. Moreover, it may be possible to determine hydrogen positions in high-quality data-sets.

The success of the above methods for structure solution is dependent upon the accurate determination of reflection intensities. However, this can be complicated greatly by peak overlap in X-ray powder diffraction patterns or missing reflection data, which is often the case in high-pressure experiments. In response to the limitations of these reciprocal-space methods, numerous programs such as DASH [20] and FOX [21] have been developed, which aim to generate calculated patterns based on an accurate unit cell indexing and chemical composition. In these direct-space methods, the agreement between the observed and calculated patterns is optimised using a Monte Carlo approach by varying structural parameters (for example, molecular positions and orientations as well as any torsion angles that may be present). The result of this ‘simulated annealing’ experiment with the lowest goodness-of-fit (χ^2) should therefore correspond to the experimental structure.

Finally, in contrast to the aforementioned methods, the most recent approach to solving the phase problem, the charge flipping algorithm, requires no information on either symmetry or chemical composition and is therefore an extremely powerful tool in structure solution. Although more details may be found in the original manuscript by Oszlányi and Sütő [22], the algorithm may be treated as a subtle adaptation to the simple Fourier cycle between the real-space electron density (ρ) and the reciprocal-space structure factors, F_o . Charge flipping exploits volumes of low electron density in the unit cell by introducing a threshold (δ) into a pixelated electron-density map. Any pixels whose electron density is below this threshold have their signs reversed, such that $\rho(r)$ becomes $-\rho(r)$, where $\rho(r) < \delta$. Temporary structure factors G_c are then calculated based on this modified electron-density map and it is the phases of these temporary structure factors that are subsequently combined with the observed amplitudes F_o to generate the new electron density. This iterative cycle is then repeated several hundred times to obtain an accurate representation of the experimental electron density.

The particular strengths of this method are its simplicity and its truly *ab initio* character. Since the electron density is represented on a grid, no atomicity is

Fig. 2.7 Diffraction image collected for an orthorhombic crystal ($Pca2_1$) at 5.5 GPa, showing the juxtaposition of sample reflections, tungsten powder rings and intense diamond reflections



acknowledged during structure solution and therefore no prior knowledge of the chemical composition is required. Furthermore, all structures may be solved in the space group $P1$, requiring no knowledge of the crystal symmetry—this can be determined afterwards. Charge flipping therefore represents an attractive alternative to direct-space and reciprocal-space methods, particularly in problematic cases, such as unknown composition, ambiguous space group assignment and the presence of disorder.

For a full discussion of these methodologies, the reader is invited to consult comprehensive texts on X-ray diffraction, such as those of Massa [23] and Giacovazzo et al [24].

2.3.2 High-Pressure Single-Crystal X-Ray Diffraction

Although diamond is transparent to X-ray radiation and every effort is made to minimise X-ray diffraction from the atomic planes within the diamonds themselves, it is inevitable that reflections due to the anvils are observed in the course of a high-pressure data collection. Furthermore depending of the orientation of the sample chamber (i.e. the DAC) with respect to the incident beam, one can observe powder diffraction rings due to the W gasket and Be backing discs (where used). This is exemplified in Fig. 2.7, which clearly shows that in one diffraction image one can observe sample peaks, diamond reflections and W rings, and in Fig. 2.8a.

Another complexity in high-pressure data collections is imposed by shading from the steel body of the cell. While ambient pressure diffraction studies of a

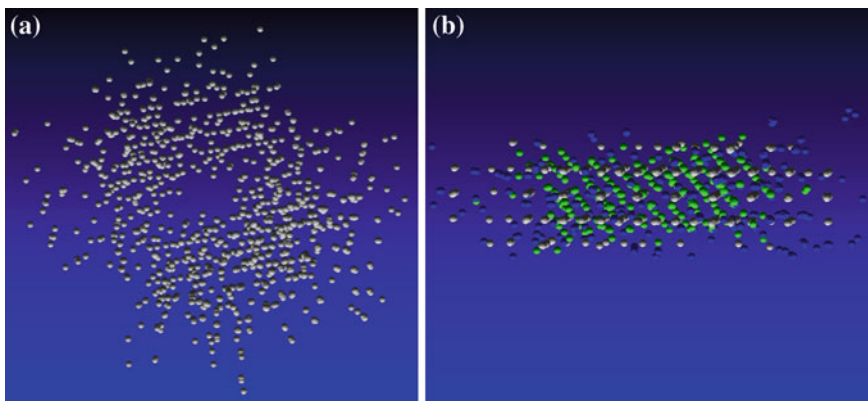


Fig. 2.8 Three dimensional renderings of reciprocal lattices, created in RLATT (BrukerNonius) [26]: **a** all of the observed diffraction intensities—indexing of the sample is hampered by scattering from all the other cell components; **b** by judicious selection of the observed reflections, it is possible to separate diffraction from sample crystals (*grey and green*) from intensities arising from the diamond anvils, ruby and gasket (*blue*)

crystal mounted on a fibre allow the whole of reciprocal space to be sampled, this is severely restricted in high-pressure studies. A data-collection strategy to optimise completeness of high-pressure diffraction data on a CCD diffractometer was developed by Dawson et al [25]. This strategy has been applied in all of the high-pressure single-crystal X-ray diffraction studies presented here. Despite this optimisation, however, one can easily appreciate the severe restriction of the diffraction data accessible in high-pressure studies by comparison of the observed intensities for a high-pressure study, using the strategy outlined in [25], and an ambient-pressure study of a comparable crystal system, in Fig. 2.9. In order to increase completeness further, it may be possible to load two single crystals of the same sample into DAC in different orientations (Fig. 2.8b), although this adds further intricacy to data processing. Finally, another popular method to improve completeness of the data is to follow the same data-collection strategy with the DAC in a different orientation, normally by rotation of the triangular cell by 120° .

In a similar way to the development of data-collection strategies, methods for harvesting the diffraction intensities from CCD images have had to be optimised. Sample reflections were harvested using a threshold algorithm applied within the APEX-II program; orientation matrices and indexing of unit cells were determined using the same program [26]. In order to address the shading of large sections of the detector during data collection, it was necessary to apply a set of dynamic masks (written by Dawson et al. [25]) during integration. Integration and global-cell refinement were carried out in SAINT [27]. The avoidance of harvesting data overlapped with reflections from the diamond anvils has also been shown to improve data quality [28]. Other strategies to enhance data-quality include the application of an analytical absorption correction in SHADE [29] (that rejects reflections that lie within 2° of the DAC opening angle (40°) and have

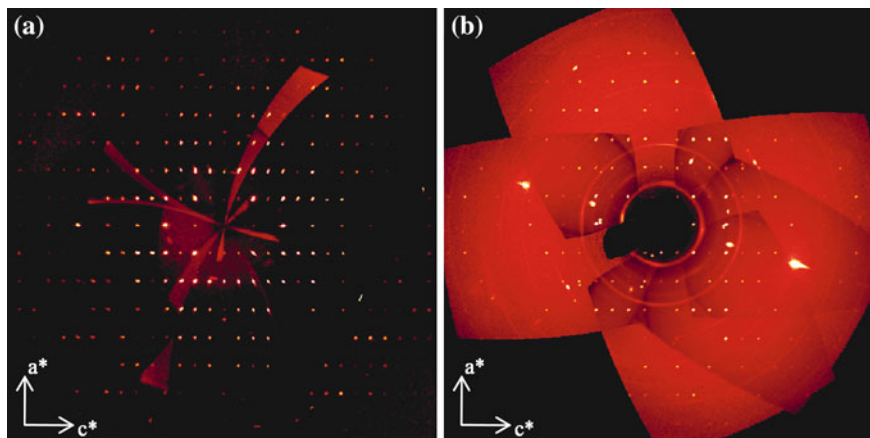


Fig. 2.9 Comparison of the completeness of high-pressure data-sets with that of ambient pressure data collections: **a** calculated precession image of the $h0l$ zone calculated for an ambient pressure data collection for a crystal on a fibre (space group $Pca2_1$); **b** the same image calculated for a high-pressure data-set on an analogous crystal system ($Pca2_1$ at circa 5.0 GPa). Precession images were calculated in the APEX-II program [26]

poorly-resolved peak profiles); and a multi-scan absorption correction in SADABS [30], which corrects for differences in the X-ray path length arising from the different orientations of the crystal during data-collection. Finally data were merged in SORTAV in the WinGX suite of programs [31].

In this work, structure solution from single-crystal X-ray diffraction data was carried out using either reciprocal-space methods (Sir92 [32]) or direct-space methods (FOX [21]). Once determined, structures were refined using CRYSTALS [33]. The details for each structure solution and refinement will be expanded upon in the relevant sections. It should be noted, however, that in some cases it was not possible to solve the crystal structure on the basis of the single-crystal data alone due to the low completeness of the high-pressure data-sets. In such cases complementary data provided from X-ray powder diffraction and neutron powder diffraction proved invaluable.

2.3.3 X-Ray Powder Diffraction

X-ray powder diffraction may simply be considered an extension of the single-crystal regime discussed in Sect. 2.3.1, but rather than one crystal being examined, powder samples contain many crystallites oriented at random. This situation results in concentric cones of diffracted intensity emanating from the sample position. These would then appear as a series of concentric rings on an area detector (such as a Mar345 Image Plate) placed normal to the X-ray beam. The development of powder diffraction rings from single-crystal diffraction spots is

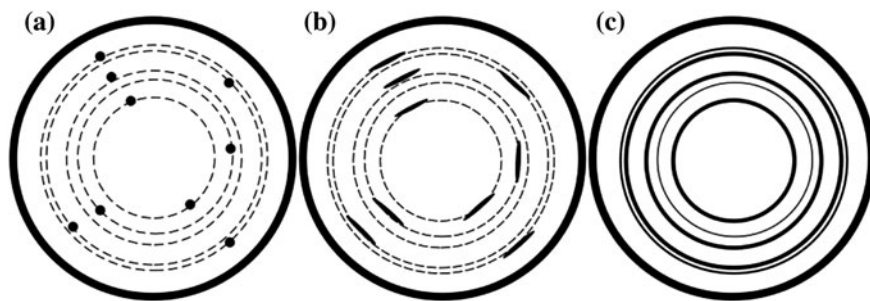


Fig. 2.10 Schematic representing the development of a powder diffraction pattern, arising from the spatial averaging of numerous single crystals: **a** diffraction from a single crystal resulting in discrete spots on the image plate detector; **b** poor-quality single-crystal diffraction pattern, in which the diffracted intensities are smeared out along the Debye-Scherrer rings; and **c** 'ideal' powder pattern, in which the rings are well-resolved and each is of uniform intensity (H.E. Maynard-Casely, personal communication, 2010)

represented in Fig. 2.10. The diffraction images may then be integrated (using calibration values individual to each instrument, such as wavelength and sample-to-detector distance) to produce a 1-dimensional plot of intensity against diffraction angle (2θ).

In addition to image plate detectors, ambient-pressure X-ray powder diffraction data in this work were collected using position-sensitive devices (PSD) which measure diffracted intensity at variable angle, thus negating the need for integrating the diffraction image. Diffraction may also be carried out in either of two modes: transmission or reflection. In powder samples of sufficient volume to allow complete powder-averaging, the diffraction patterns observed in these modes should be identical. Reflection mode is often preferred for samples containing heavy atoms as this minimises the effect of X-ray absorption. This may be accounted for by the inclusion of an absorption parameter during refinement or by using thin sample capillaries. One should therefore not be discouraged from attempting to conduct a diffraction study on these materials in transmission mode.

Irrespective of the collection procedure, X-ray powder diffraction presents a quick yet definitive representation of the scattering arising from the atomic planes within the sample of interest. It is therefore an invaluable tool for assessing sample purity and for the detection of polymorphism, without the need for the sometimes arduous task of growing single crystals. Furthermore, as long as the correct structural model is used it is possible to carry out full-profile refinements of the powder diffraction patterns, thus providing important crystallographic information on the bulk sample rather than a solitary crystal. Most commonly this refinement is carried out using the Rietveld method, which facilitates the refinement of the structural model against the diffraction data directly [34].

A powder diffraction pattern may be described as a plot of diffraction intensity (I_{obs}) against scattering angle (2θ). The Rietveld method progresses by a least-squares refinement of the structural parameters so as to minimise the difference

between the calculated and observed intensities (I_{obs} vs I_{calc}). These structural parameters comprise: the structural model, a model to describe the variation in peak-widths over the observed 2θ -range, and a background model. The quality of the diffraction fit is usually quantified by two parameters: wR_p and χ^2 . The weighted R-factor (wR_p) represents the minimisation of the difference between the calculated and observed patterns, while χ^2 is a comparison of wR_p to the statistically expected value R_{exp} . Throughout the course of a powder refinement, however, these values may yield erroneously low values, especially with data suffering from a high background or broadened diffraction peaks. It is often the case that visual inspection of the diffraction profile and difference curve is the best assessment for the quality of the refinement.

A secondary refinement method that does not necessitate prior knowledge of the structural model is Le Bail refinement [35]. In this method the calculated diffraction intensities (I_{calc}) are set to be equal to the observed intensities (I_{obs}), while the unit cell, background and peak profiles may be refined. Any peaks which cannot be modelled by a given Le Bail refinement routine are clear evidence that either the unit cell indexing or space group assignment (or both) is wrong. This therefore provides an extremely useful test, particularly in the initial forays into structure solution from powder diffraction. In this work, Rietveld and Le Bail refinements of the various powder diffraction patterns were carried out using GSAS [36]. Any special considerations during refinement will be highlighted in the appropriate chapters.

2.3.4 High-Pressure X-Ray Powder Diffraction

Compared to high-pressure single-crystal X-ray diffraction, powder diffraction using the diamond-anvil cell does not present quite such a practical or theoretical obstacle, although for reasons discussed below (Sect. 2.3.5) these experiments have been carried out using synchrotron radiation. The data presented herein were collected at the Extreme Conditions Beamline (I15) and the High-Resolution Powder Diffraction Beamline (I11) at Diamond Light Source, UK. The experimental set-up for a high-pressure X-ray powder diffraction experiment is represented in Fig. 2.11. Data are collected on an image plate detector (Mar345) and are processed according to the procedure outlined for ambient pressure powder diffraction, with one exception. In some cases it may be necessary to mask out intense single-crystal reflections arising from the diamond anvils to ensure no anomalies occur in the I_{obs} vs 2θ profile. The image can then be integrated to provide the one-dimensional powder diffraction pattern using programs such as Fit2D [37]. It is also possible to mask intense powder diffraction rings due to the W gasket although should this interfere with sample peaks it is also possible to carry out Rietveld refinements, in which the tungsten diffraction pattern is incorporated. This process is represented in Fig. 2.11b–d.

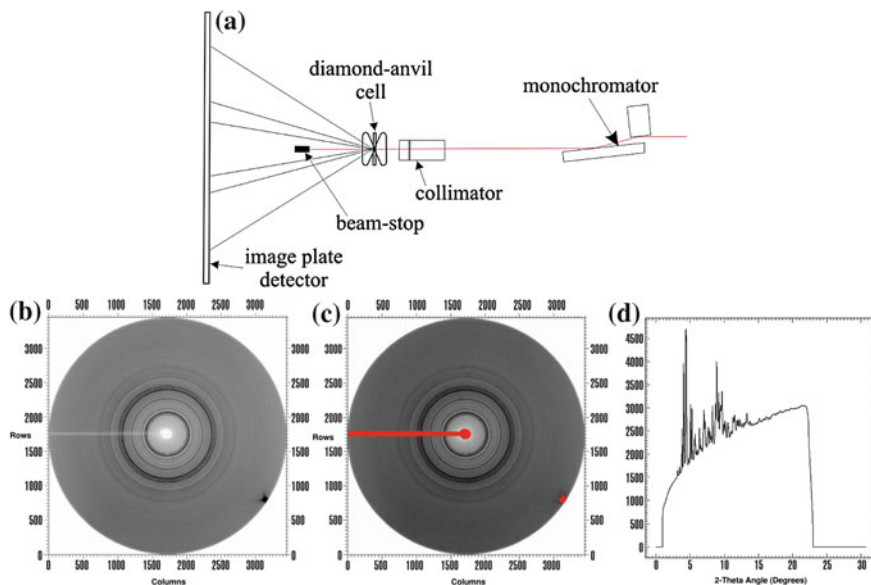


Fig. 2.11 **a** schematic illustrating the key components of a high-pressure X-ray powder diffraction experiment; and **b–d** the stages of data reduction. The raw image collected on the Mar345 detector is shown in **(b)**. The concentric rings correspond to the diffracted intensities from the sample; the dark spot at the edge of the image is an intense diamond reflection from the DAC. This can be masked to avoid contamination of the sample diffraction pattern—the masking process is shown in **(c)**. It is also necessary to mask the lighter areas of the image that arise due to shading from the beam-stop. Finally the data can be integrated, in programs such as Fit2D [37], thus reducing it to a plot of diffraction intensity against scattering angle **(d)**. The large background common to such data collections is due to Compton (inelastic) scattering from the diamonds and can be subtracted prior to data refinement

2.3.5 X-Ray Sources: Laboratory Versus Synchrotron

The ambient pressure X-ray diffraction experiments detailed in this work (both single-crystal and powder) were performed using monochromatic laboratory X-ray sources at the School of Chemistry, University of Edinburgh: both Mo $K\alpha$ and Cu $K\alpha_1$ radiation sources have been utilised ($\lambda = 0.71073$ and 1.54056 Å, respectively). High-pressure single-crystal data were collected at ambient temperature using Mo $K\alpha$ radiation on a modified Bruker SMART APEX-II CCD diffractometer at the Centre for Science at Extreme Conditions (CSEC), University of Edinburgh. In order to allow rotation of the DAC during data collections, a shortened collimator must be used in high-pressure experiments and there was no facility to carry out these studies at sub-ambient temperatures. Details of the data collection procedures will be reserved for discussion in the relevant chapters.

In some cases, however, the restrictions applied to data completeness by the diamond-anvil cell means that it is has been necessary to use X-ray radiation of

shorter wavelengths (i.e. $\lambda \leq 0.5 \text{ \AA}$) at synchrotron sources. This improves data completeness relative to laboratory experiments by compressing the characteristic diffraction pattern into a smaller volume of reciprocal space, thus allowing a larger portion to be accessed through the 40° opening angle. Synchrotron radiation has the added benefit of increasing the incident flux that counteracts the weak diffraction from organic samples with restricted volumes and in complex sample environments, i.e. the DAC, in which absorption from the diamonds and backing plates reduces the intensity of measured reflections [36]. The results of high-pressure single-crystal diffraction studies conducted at synchrotron sources are not within the scope of this thesis, but the productivity of beamlines with high-pressure capabilities (such as Station 9.8 at the Daresbury Laboratory [38], Beamline I19 at Diamond Light Source [39] and ID09 and ID27 at the European Synchrotron Radiation Facility [40]) is a strong indication of the thriving research in this field.

In the current work synchrotron radiation has been essential in obtaining high-resolution powder diffraction data using the diamond-anvil cell, which is impossible using typical laboratory diffractometers. As outlined above, the short wavelengths and high flux of the synchrotron beam improve data quality significantly. Moreover, it is relatively straightforward to change parameters such as the sample-to-detector distance to suit the requirements of the experiment at hand. A further experimental parameter that may be changed (although not so easily) is the wavelength selected for the experiment, thus allowing the optimisation of the data-collection strategy. Finally an important factor in diffraction studies at very high pressures ($>10 \text{ GPa}$) is the high degree of collimation possible, allowing the analysis of very small sample diameters without contamination from the DAC components. In such studies, however, great care must be taken to ensure effective powder averaging of such a small sample volume.

2.3.6 Raman Spectroscopy

Scattering of light by a molecule occurs by the promotion of the molecule from its ground state to a virtual energy state and the subsequent relaxation, which results in emission of a photon (i.e. the scattered light). The vast majority of the scattered light is of the same frequency as the incident radiation (elastic; Rayleigh scattering). Raman spectroscopy, however, relies on inelastic scattering of intense monochromatic light ($<5\%$ of cases). In such cases the molecule relaxes to a different vibrational ground state, resulting in an energy difference between the incident and scattered photons. This is perhaps best explained pictorially. In Fig. 2.12 it can be seen that if the molecule relaxes to a vibrational state of lower energy than the starting level, the scattered photon will have a higher energy than the incident radiation (anti-Stokes radiation); if the $E_{\text{virtual}} - E_{\text{final}}$ difference is less than the initial transition, the scattered photon will instead undergo a red-shift (Stokes).

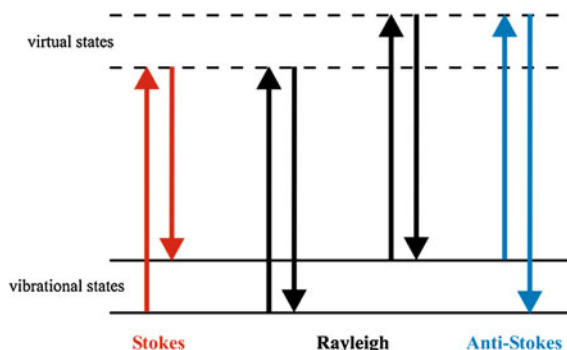


Fig. 2.12 A representation of the transitions involved in Raman spectroscopy. Incident photons excite the molecule into a virtual state and the relaxation of the molecule results in emission of a ‘scattered’ photon. Rayleigh scattering occurs when the incident and emitted photons are of the same frequency. When the molecule relaxes to a vibrational energy level higher than the starting level, the emitted photon will be shifted to a lower frequency (Stokes). Conversely, anti-Stokes radiation has higher frequency than the incident radiation

Generally, Raman spectra are plotted such that the Rayleigh band lies at 0 cm^{-1} . On this scale, the band positions will lie at frequencies that correspond to the energy levels of different functional group vibrations, facilitating comparison with similar (but complementary) results from IR spectroscopy. The selection rule that must be satisfied for a vibrational mode to be Raman active is that there must be change in the polarisability tensor of the vibration. This is best imagined as the ease with which the electron cloud is distorted (i.e. polarised) and explains the complementarity between Raman and IR spectroscopy, which relies on changes in dipole moments.

An advantage of Raman spectroscopy, particularly in high-pressure studies, is that since monochromatic light is used, any material that is transparent to visible light may be used as a sample chamber (e.g. glass capillaries and diamond-anvil cells). Furthermore Raman spectroscopy is sensitive to changes in the molecular symmetry and changes in the inter- and intramolecular interactions and is therefore an extremely powerful tool in the identification and characterisation of new polymorphs and the observation of phase transitions. Although not conducted in this study, it may also be appropriate to plot the general increase in frequency of a selected vibrational mode with increasing pressure. If the sample remains in the same phase, a linear shift in wavenumber is generally observed but in the event of a new spectral bands may be observed and there may be an abrupt change in the gradient of $\bar{\nu}$ versus P plots.

Raman spectra were collected using a LabRam instrument equipped with a 50 mW He-Ne laser ($\lambda = 632.8\text{ nm}$); typically, objectives of 10x and 20x magnifications were used.

2.4 The Paris-Edinburgh Cell

2.4.1 Construction of the Paris-Edinburgh Cell

Neutron diffraction experiments (see Sect. 2.5.1) require sample volumes circa 10^6 times larger than those required for X-ray powder diffraction, thus precluding the use of diamond-anvil cells. High-pressure neutron diffraction experiments were therefore severely limited until the advent of the Paris-Edinburgh cell (PEC), developed in 1992, which extended the pressure range of 10–20 GPa [2]. The popularity of the PEC arose from its (relatively) light-weight design and its portability—the Paris-Edinburgh cell weighs ~ 50 kg, in contrast to other commercial devices of the time with comparable sample volume that weighed close to 1 tonne. This portability, coupled with the fact that load can be applied to the cell by a hydraulic ram while it remains in situ on the beamline, greatly simplified high-pressure experiments.

The PEC is also an opposed-anvil device, like the diamond-anvil cell and the Bridgman cell. In this construction, however, the sample is compressed between anvils made of either tungsten carbide (WC) or sintered diamond, see Fig. 2.13a. Early designs utilised null-scattering TiZr toroidal gaskets located into corresponding grooves machined into the anvil faces to confine the sample and, generally, a solid pressure-transmitting medium. Compression studies using the preferred fluid pressure-transmitting media (methanol:ethanol and iso:n-pentane) were limited to circa 2.0 GPa before anvil failure. It was realised that complete encapsulation of the sample and pressure-transmitting medium in two flanged hemispherical caps (TiZr) would prevent the fluid media coming into direct contact with the anvil surface [41]. In this way the anvils were shown to be protected and the available pressure range for hydrostatic studies were extended up to the freezing pressure of methanol:ethanol (i.e. >9.0 GPa). The encapsulated gasket is compared to the ‘standard’ TiZr toroidal gasket in Fig. 2.13b.

2.4.2 Variable-Temperature Insert for the Paris-Edinburgh Cell

The capabilities of the Paris-Edinburgh cell have recently been enhanced by the development of a variable-temperature (v-T) insert, which has been shown to vary sample temperature between 110 and 500 K with excellent control (Marshall WG, Francis DJ, Barry CJ, Kirichek O, Pulham CR, Tucker MG, manuscript in preparation, 2010). A liquid nitrogen circuit is used to cool just the sample and the WC anvils, while temperature is increased and controlled by the incorporation of 240 W resistive heaters into the latter, see Fig. 2.14. This was in an effort to reduce the volume that is heated or cooled, in order to minimise temperature response times. Cooling to 120 K from room temperature previously required 4–5 h, when the whole of the PE-cell had to be cooled with liquid nitrogen. Commissioning

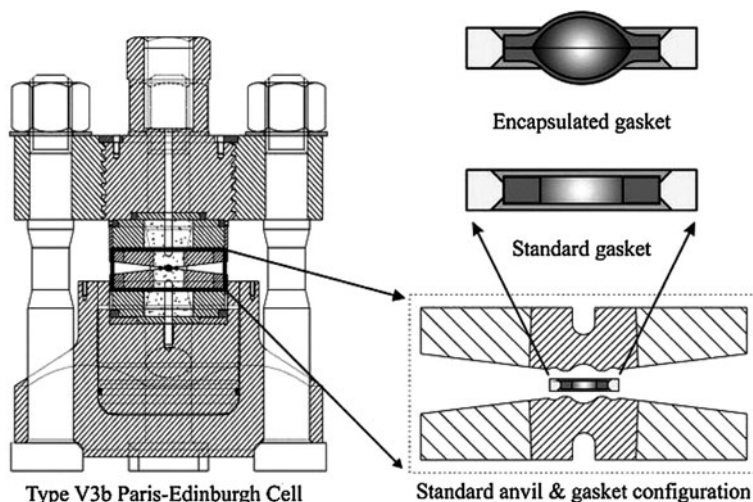


Fig. 2.13 a Cross-section of the Paris-Edinburgh cell (V3b) and a comparison of the standard and encapsulated gaskets [41]

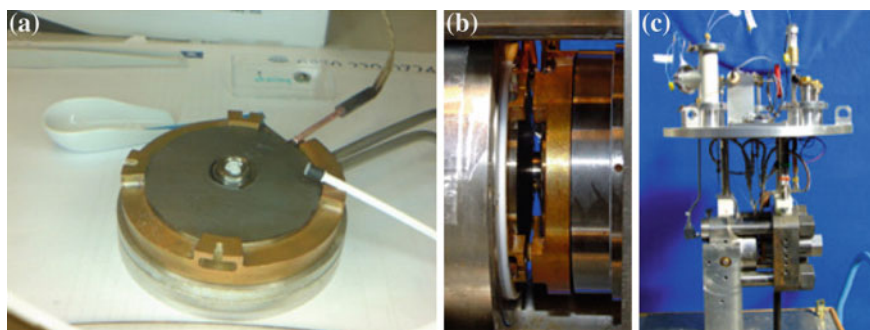


Fig. 2.14 The variable-temperature insert for the Paris-Edinburgh cell: **a** the WC anvils, into which both a liquid nitrogen feed and resistive wires have been incorporated to allow rapid heating and cooling; **b** a close-up of the modified anvil within the cell; and, **c** the complete construction of a PE-cell equipped with the vT-insert, underscoring the complexity of such experiments

tests on the v-T insert demonstrated its ability to cool to 100 K or warm to 473 K from ambient temperature within 45 min (Marshall WG, Francis DJ, Barry CJ, Kirichek O, Pulham CR, Tucker MG, manuscript in preparation, 2010). This development has therefore not only opened up the possibility of conducting variable temperature neutron powder diffraction experiments at pressure but also presents a route for rapidly quenching high-pressure or high-pressure/high-temperature polymorphs for their recovery to ambient pressure.

2.4.3 Pressure Measurement

Unlike the diamond-anvil cell, the Paris-Edinburgh cell does not allow optical access to the sample chamber and therefore a method for pressure calibration other than the ruby fluorescence method had to be developed. Instead, small quantities of internal pressure calibrants are used, typically either NaCl(s) or Pb(s). Both materials have clearly defined equations of state [42, 43], which means that the unit cell volume of the chosen calibrant (as determined by Rietveld refinement of the powder diffraction patterns) is directly related to the pressure within the gasket.

2.5 Experimental Techniques Using the Paris-Edinburgh Cell

2.5.1 Neutron Powder Diffraction

While X-ray diffraction is the most widespread technique applied in the determination of crystal structures, a complementary technique using exactly the same principles is neutron diffraction. Neutrons display wave-particle duality and may therefore also be diffracted by a three-dimensional grating. The momentum of a free particle, p , is related to its wavelength, λ , by the de Broglie equation:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

where h is Planck's constant, m = mass and v = velocity of the particle. Thus thermal neutrons with average velocities of circa 2500 ms^{-1} will have suitable wavelengths for diffraction from atomic planes within a crystal lattice.

In contrast to X-rays, neutrons do not interact significantly with the electron density within a crystal lattice and instead are diffracted by the nuclei of atoms. Since both nuclei and neutrons are small, significant scattering occurs only when a neutron passes close to a nucleus, and thus the total intensity of diffraction of neutrons by a crystal is low compared to that of X-rays—larger sample volumes are required to give comparable diffraction intensities. The point scattering from nuclei imbues this technique with a significant advantage however; the scattering factor does not fall off at higher angles, in stark contrast to X-ray diffraction (see Fig. 2.15). This highly penetrating nature of neutrons (in contrast to X-rays) also allows the construction of rather complex sample environments, such as the Paris-Edinburgh cell. Furthermore neutron diffraction locates the atomic nuclei and not the electron density, which may be distorted due to bonding effects, and thus is far more accurate for the determination of atomic positions.

While the scattering power of an atom with respect to X-ray radiation is directly proportional to its atomic number (Z), there is no direct relationship in neutron diffraction. Indeed neighbouring elements, and even isotopes of the same element, may have considerably different neutron scattering cross-sections—represented in

Fig. 2.15 Scattering factor of X-rays and neutrons w.r.t. angle of incident

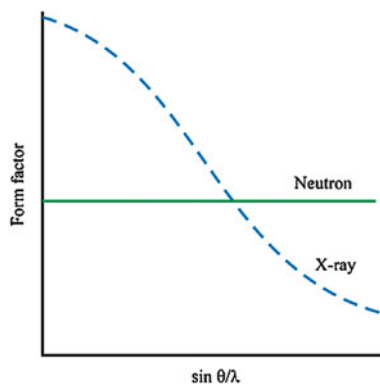


Fig. 2.16. This random variation has practical benefits since it is possible to select elements or alloys which display null or very little neutron scattering to construct sample environments. Vanadium (neutron scattering-length, $b = -0.4$) is regularly used as a sample container for ambient pressure studies; TiZr (null scatterer) is used for sample encapsulation in the Paris-Edinburgh cell. This dramatic effect also means that neutron diffraction is an extremely powerful technique for the structure solution of compounds containing a mixture of light and heavy elements, such as the inorganic azides AgN_3 and $\text{Pb}(\text{N}_3)_2$ reported in Chaps. 5 and 6.

The complementarity of X-ray and neutron diffraction is further underlined by studies aimed at the accurate determination of hydrogen positions in a range of molecular and co-ordination solids [44]. X-ray diffraction from hydrogen atoms, having just one electron, is extremely weak. This is not the case, however, in neutron diffraction, although the incoherent scattering from hydrogen normally necessitates sample deuteration.

Finally a significant advantage neutron diffraction displays over X-ray diffraction, although not explored in the present context, is the determination of magnetic structures by the interaction of the magnetic moments of the neutrons with magnetic ions within the crystal lattice. For a detailed account of neutron diffraction of magnetic materials, the reader is directed to Harrison's review [45].

2.5.2 Neutron Sources

The nature of neutron diffraction experiments is dependent on the source of neutrons. They may be generated by fission (at nuclear reactor sources) or spallation, where short pulses of energetic protons bombard a heavy metal target causing a cascade of high-energy neutrons. At reactor sources the neutron beam is continuous and the wavelength is fixed by means of a crystal monochromator—during the diffraction experiment the detector angle is varied (angle dispersive). In contrast, at spallation sources the energetic neutrons produced must be slowed down

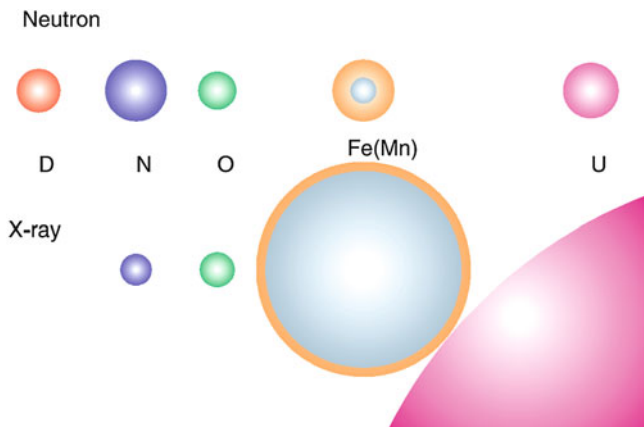


Fig. 2.16 Comparison of the scattering powers of different elements with respect to neutrons and X-rays (H.E. Maynard-Casely, personal communication, 2010)

(moderated) by collisions with atoms of comparable mass, usually H or D in water or methane, resulting in a distribution of energies impinging on the sample. The pulse of moderated neutrons is very short but stretches out in space as it moves down the flight path, with the higher energy neutrons travelling more quickly. The neutrons travel a known distance, L , from the source to the sample and subsequently the detector, which is positioned at a fixed angle. The diffraction pattern is then obtained as a function of the time of flight (ToF) of the arriving neutrons (energy dispersive). Substituting the de Broglie wavelength into Bragg's law then allows the diffraction condition to be expressed in terms of ToF:

$$2d \sin \theta = \lambda = \frac{h}{p} = \frac{h}{m_n v} = \frac{ht}{m_n L}$$

$$t = \frac{2m_n L}{h} d \sin \theta$$

where t is time, m_n is the mass of the neutron, L is the length of the flight path from source to detector, h is Planck's constant, d is the spacing between the atomic planes in the crystal (d -spacing), θ is the scattering angle (fixed) and p is momentum.

It is therefore possible to collect a complete diffraction pattern using a single detector although typical ToF diffractometers utilise banks of detectors to minimise counting times. Outputs from each detector may be summed, provided each diffraction pattern is initially converted into d -spacings.

The high-pressure neutron diffraction experiments conducted in this body of work were carried out at ISIS spallation neutron and muon source, STFC Rutherford Appleton Laboratory, UK. The high-flux, medium-resolution instrument PEARL-HiPr is specifically designed for data collections using the Paris-Edinburgh cell, as shown in Fig. 2.17. ToF diffraction data were collected



Fig. 2.17 PEARL-HiPr instrument with the Paris-Edinburgh cell, in which the Paris-Edinburgh cell is mounted onto a Tomkinson flange and lowered into a vacuum tank (Marshall WG, personal communication, 2010). The *red arrow* indicates the path of the neutrons through the instrument. Diffracted intensities can be collected by two banks of detectors; transverse geometry was used in this study. Longitudinal mode (detectors situated at $20^\circ < 2\theta < 40^\circ$ and $100^\circ < 2\theta < 120^\circ$) can also be employed to access a wider section of reciprocal space, although resolution is compromised

in transverse geometry. This arrangement, in which the detectors are fixed at $83^\circ < 2\theta < 97^\circ$, allows access to a range of 0.5–4.1 Å in d -spacing, with a resolution ($\Delta d/d$) of $\sim 0.8\%$. The individual detector element spectra are electronically summed and normalised to the incident beam monitor and the scattering from a standard vanadium calibration sample. Lastly, the diffraction pattern intensity scale was corrected for the wavelength and scattering-angle dependence of the neutron attenuation by the anvil (WC) and gasket (TiZr) materials. Full-profile Rietveld refinements were carried out using GSAS [36], while any special considerations are highlighted in the pertinent sections.

2.6 Equations of State

By the structural characterisation of a material throughout its compression, it is possible to obtain a measurement of the variation of the material's density (or volume) with pressure, and sometimes temperature. Generally, static compression studies are conducted at constant temperature, thus the resulting variation of volume with pressure is termed the isothermal 'Equation of State' (EoS). Measured equations of state are usually parameterised in terms of the bulk modulus, $B_0 = -V\partial P/\partial V$, and its pressure derivatives: $B' = \partial B/\partial P$ and $B'' = \partial^2 B/\partial P^2$, which are evaluated at zero pressure. Despite actually being under finite pressure, it is generally accepted that the unit cell volume under ambient conditions may be

employed as an approximation to V_0 , the zero-pressure volume (which is not measurable).

There is no fundamental thermodynamic derivation of equations of state and therefore a number of approaches have been developed based on a number of assumptions about the behaviour of dense solids, which are addressed in more detail in Anderson's review [46]. The validity of such assumptions may only be assessed on whether the derived EoS accurately reproduces the experimental compression behaviour. The most commonly used formulations, and the only ones used in this study, are the Murnaghan [47], Birch-Murnaghan [48] and Vinet [49] equations.

The Murnaghan EoS is popular due to its simplicity since it can be derived from the assumption that the bulk modulus varies linearly with pressure, such that:

$$P = \frac{B_0}{B'} \left[\left(\frac{V_0}{V} \right)^{B'} - 1 \right]$$

The Murnaghan EoS has been found to reproduce both PV data and B_0 for compressions up to about 10% (i.e. $V/V_0 = 0.9$) but is not recommended for use beyond this regime [50].

Other isothermal equations of state, such as the Birch-Murnaghan, employ an assumption that the strain energy applied during compression can be expressed as a Taylor series in the finite strain, f . The 3rd order Birch-Murnaghan EoS is based on the Eulerian strain, $f_E = [(V/V_0)^{2/3} - 1]/2$, such that:

$$P = 3B_0 f_E (1 + 2f_E)^{5/2} \left[1 + \frac{3}{2} (B' - 4) f_E + \frac{3}{2} \left(B_0 B'' + (B' - 4)(B' - 3) + \frac{35}{9} \right) f_E^2 \right]$$

It may also be appropriate to truncate this expression at second order in the energy term, resulting in the 2nd order Birch-Murnaghan EoS. In this case, the coefficient of f_E must equal zero, thus requiring that B' be fixed at a value of 4.

Finally, the Vinet formalism is often applied for solids under very high compression (i.e. $V/V_0 = 0.6$), since it has been observed that finite strain equations of state do not accurately reproduce PV observations in this region [49]. The Vinet EoS is based on a general inter-atomic potential and has been particularly useful in the representation of the compression of simple solids at very high pressures [50]. The Vinet EoS can be calculated according to the following, where $f_V = (V/V_0)^{1/3}$:

$$P = 3B_0 \frac{(1 - f_V)}{f_V^2} \exp \left[\frac{3}{2} (B' - 1)(1 - f_V) \right]$$

In this work, the parameters for the equations of state have been determined by a least-squares fit of the PV data using the program EoSFit v5.2 [51]. In this routine it is simpler to consider pressure as the dependent variable [$P_{calc} = EoS(V_{obs})$] and the sum of the squares of the differences between the calculated and observed pressures are minimised during the least-squares solution.

It is therefore critical to the success of the fitting procedure that the experimental uncertainties in both the pressure and volume are determined.

The quality of the EoS fitting procedure is also largely dependent upon the number of data points that have been obtained for a particular phase. For example, large errors in B_0 and V_0 may arise in cases where there are very few measurements made close to atmospheric pressure. This is exacerbated in the calculation of these parameters for high-pressure polymorphs, for which it is impossible to determine the unit cell volume at ambient pressure. It is may therefore be more appropriate to fix V_0 to be the volume determined at the lowest pressure for which structural data have been obtained. It is then necessary to offset all succeeding pressures by this value.

In all of the compression studies reported herein, equations of state have been calculated using all four of the formalisms above. The most appropriate EoS was selected by comparison of the relative uncertainties in the parameters (namely, V_0 , B_0 and B') as well as the 'goodness-of-fit' of the least-squares refinement, χ^2 . However, the most critical assessment of the quality of the fit is often visual inspection. Where previous EoS data have been published, the same function has been adopted to facilitate comparison between studies, except where this resulted in a considerable reduction in the quality of the fit. A summary of the equations of state derived in this work can be found alongside an assessment of the quality of the fit in each case (by means of R and χ^2) in Appendix A.2.

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