

2.7. HIGH-PRESSURE DEVICES

is not determined before collecting the diffraction data. To meet these requirements, a new efficient and semi-automatic method was devised, whereby the diffractometer measures a sequence of shadows of the gasket on the CCD detector and calculates the required corrections to the DAC position along the goniometer-head translations (Budzianowski & Katrusiak, 2004). Precise centring can only be achieved for very stable goniometer heads that do not yield under the weight of the DAC (Katrasiak, 1999).

The mode of data collection for a sample enclosed in a DAC can affect the data quality considerably. Data for a bare crystal on a four-circle diffractometer with a scintillation point detector were measured in the so-called bisecting mode, where the ω angle [diffractometer-axes positioning angles ω , χ , φ and θ of the Eulerian cradle will be used here (Busing & Levy, 1967), unless otherwise noted] was fixed to 0° and not used in the process of crystal positioning. In other words, the shaft φ and circle χ lie in the plane bisecting the angle formed by the incident beam and the reflection actually measured. The bisecting mode was optimal for avoiding collisions between the diffractometer shafts and detector, and also minimized absorption effects for most vertically mounted samples. However, these features are irrelevant for samples enclosed in a DAC. It was shown by Finger & King (1978) that the DAC absorption of the incident and reflected beams is a minimum when the Eulerian goniometer φ axis is not used and is always set to 0° . Hence, this is called the $\varphi = 0^\circ$ mode. The $\varphi = 0^\circ$ mode also minimizes the effect of the sample being shadowed by the gasket edges (Katrasiak, 2008). Moreover, in the $\varphi = 0^\circ$ mode the DAC axis always lies in the diffraction plane of the diffractometer, which gives maximum access to the reciprocal-lattice nodes (Fig. 2.7.6).

The advent of area detectors facilitated high-pressure experiments considerably and extended the range of attainable conditions to simultaneous very high pressure and temperatures of several thousand kelvin. Single-crystal experiments are easier because the diffraction data can be recorded before the orientation matrix UB of the crystal is determined (Busing & Levy, 1967; Finger & King, 1978). The recorded data can thus be analysed after the experiment and all relevant structural models can be tested. The use of area detectors shortens the data-collection times for both single-crystal and powder diffraction measurements, and this is particularly efficient with the extremely intense X-ray beams provided by synchrotrons. In single-crystal experiments, several or even tens of reflections are partly scanned through or fully recorded in one image. Although these reflections are not each recorded at their optimum diffractometer settings, corresponding to the $\varphi = 0^\circ$ mode setting described above, the redundancy of the data is increased and the intensities can be corrected for the absorption coefficients derived from differences between equivalent reflections. It is also advantageous that simultaneous diffraction events in the sample crystal and in one or both of the diamonds, which occur sporadically and weaken the recorded reflections, can be eliminated by comparing the intensities of the same reflection measured at several ψ angle positions as well as the equivalent reflections. Equivalent reflections measured at different positions are particularly useful for eliminating systematic errors in the data collection.

It is important that the so called ‘run list’, defining the diffractometer setting angles and scan directions for the detector exposures, takes into account the $\varphi = 0^\circ$ mode of the DAC orientations, for which access to the DAC is still on average at its widest and the DAC absorption and gasket-shadowing effects are on average the smallest. Most importantly, such an optimum setting can be executed with a four-circle diffractometer, and

cannot be done on simplified diffractometers with the φ shaft fixed at a χ angle of about 50° . Even fewer reflections can be accessed when the DAC is rotated about one axis only, which is still the case for some laboratory and synchrotron diffractometers.

2.7.9. Powder diffraction with the DAC

The DAC is often described as the workhorse of high-pressure research, owing to its versatile applications, low cost, easy operation and unrivalled attainable static pressure. However, the small size of the DAC chamber, containing sample volumes between 0.025 mm^3 for pressure to about 5 GPa, 0.005 mm^3 to about 10 GPa and less than $3 \times 10^{-6} \text{ mm}^3$ for the megabar range, can be disadvantageous for powder diffraction studies. The disadvantages include the inhomogeneous distribution of temperature within the sample (particularly as it remains in contact with a diamond, which is the best known thermal conductor) and nonhydrostatic strain (often due to the technique of generating pressure by uniaxial compression of the chamber). In some samples close to the melting curve some grains increase in size at the expense of others, partly or fully dissolving, so the number of grains may be insufficient for obtaining good-quality powder diffraction patterns. This difficulty can be partly circumvented by rocking the DAC during the experiment about the ω axis. On the other hand, for a sample consisting of tens of grains it is possible to perform multi-grain analysis by merging the diffraction patterns to give the equivalent of single-crystal data. High-pressure powder diffraction patterns can also be affected by a low signal-to-noise ratio, too few crystal grains, and their preferential orientation in the DAC uniaxially compressed chamber. The preferential orientation is particularly significant when the grains are elongated and their compressibility is anisotropic; these effects can be further aggravated by the non-hydrostatic environment. Powder reflections are much weaker in intensity than the equivalent single-crystal reflections from the same sample volume. Small sample volumes are compensated for by the powerful beams available at synchrotrons. At present, high-pressure powder diffraction experiments are mainly carried out at synchrotrons by energy-dispersive (Buras *et al.*, 1997*a,b*; Baublitz *et al.*, 1981; Brister *et al.*, 1986; Xia *et al.*, 1990; Oehzelt *et al.*, 2002) and angle-dispersive methods (Jephcoat *et al.*, 1992; Nemes & McMahon, 1994; Fiquet & Andrault, 1999; Crichton & Mezouar, 2005; Mezouar *et al.*, 2005; Hammersley *et al.*, 1996). Angle-dispersive methods are currently preferred to the energy-dispersive method owing to their higher resolution and simpler data processing. However, the energy-dispersive method requires less access for the X-ray beams probing the sample, and hence it is often preferred for studies in the megabar range (hundreds of gigapascals). For high-pressure powder diffraction studies in the laboratory, energy-dispersive methods are still preferred (Tkacz, 1998; Palasyuk & Tkacz, 2007; Palasyuk *et al.*, 2004). The main advantages of experiments at synchrotrons are:

- (i) They have a very intense beam compared with traditional sealed X-ray tubes and modern micro-focus sources;
- (ii) They offer the possibility of very narrow collimation of the beam, to a diameter of one or a few micrometres;
- (iii) Very quick collection of high-quality diffraction data is possible, which is most useful for high-pressure and very high temperature data collections;
- (iv) It is possible to measure diffraction data from very small samples, to reduce the dimensions of the DAC chamber and

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hence to increase the attainable pressure, which is inversely proportional to the chamber diameter;

- (v) The microbeam can illuminate a small selected portion of the sample chosen for the investigation, which can be used to perform single-crystal diffraction on a selected grain or for X-ray tomography of the sample and its inclusions;
- (vi) The beam diameter is smaller than the diameter of the chamber, which minimizes or even eliminates the effects of beam shadowing;
- (vii) The X-ray wavelength is tuneable down to about 0.3 Å. This considerably increases the data completeness and reduces absorption effects in the sample and DAC.

Owing to these features, synchrotron beams are ideally suited for high-pressure diffraction experiments and some researchers have completely stopped using in-house laboratory equipment with sealed X-ray tubes. Historically, the first use of synchrotron radiation for high-pressure studies was reported by Buras, Olsen & Gerward (1977) and Buras, Olsen, Gerward *et al.* (1977). Conventional diffractometers with sealed X-ray tubes can be effectively used for preliminary powder diffraction experiments. For example, a new high-pressure phase of (+)-sucrose was found in this way (Patyk *et al.*, 2012), although the data were insufficient for any structural refinements.

Diffraction data are collected in single and multiple exposures, and the pressure is controlled remotely by inflating a membrane through a gas system. Currently assembled high-pressure powder diffraction synchrotron beamlines incorporate on-line pressure calibration using ruby fluorescence and, often, Raman spectroscopy.

2.7.10. Sample preparation

Several basic techniques can be used to prepare a sample for a high-pressure experiment, for example:

- (i) A solid sample can be mounted under ambient conditions in the high-pressure chamber together with the hydrostatic fluid, then sealed and pressurized;
- (ii) A solid sample can be mounted under ambient conditions in the high-pressure chamber, condensed gas loaded at elevated pressure (Tkacz, 1995; Rivers *et al.*, 2008; Couzinet *et al.*, 2003; Mills *et al.*, 1980; Yagi *et al.*, 1996; Kenichi *et al.*, 2001) or under cryogenic conditions, and the sample sealed and further pressurized by gasket compression;
- (iii) A liquid sample can fill the whole chamber volume under ambient conditions, or condensed gases or their mixtures can be loaded at elevated pressure, and after sealing the DAC the sample is frozen under isothermal conditions;
- (iv) A crystal of the pure compound or of a solvate can precipitate from the mixture (solution) when compressed isothermally – the crystal can be in the form of a single crystal or a powder, fully or partly filling the DAC chamber;
- (v) Samples completely filling the DAC chamber can be compressed isothermally or undergo isochoric treatment, but strains can be generated in a single crystal or in the grains of a compressed powder conglomerate by anisotropic thermal contraction/expansion; this strain can be avoided by having an excess of the hydrostatic component of the mixture;
- (vi) A solid powdered sample can be mixed with a powder of another compound, which is much softer than the sample and is used as a pseudo-hydrostatic medium (halite and MgO are often used for this purpose) – this technique is mainly used for cubic or isotropic samples in large-volume

presses, where (pseudo)isotropic strain and pseudo-spherical compression minimize the effect of preferential orientation in the sample.

Preferential orientation can significantly hamper the quality of powder diffraction data, and corrections for this effect should be applied in the Rietveld refinement. All Rietveld refinement programs include preferential orientation models, which fit the data with satisfactory results (McMahon, 2004, 2005; Filinchuk, 2010).

2.7.11. Hydrostatic conditions

Hydrostatic conditions in the sample chamber are essential for good-quality high-pressure diffraction data. They are equally important for single-crystal and powder diffraction experiments. To secure hydrostaticity, the sample is submerged in a hydrostatic medium. The pressure and temperature ranges of the planned experiment depend on the hydrostatic properties of the applied medium. Eventually all substances solidify because of crystallization or vitrification (Piermarini *et al.*, 1973; Eggert *et al.*, 1992; Grocholski & Jeanloz, 2005), which can lead to damage of single crystals, anisotropic strain in powder grains and inhomogeneity of pressure across the sample. It is also important to protect a solid sample from dissolution in the hydrostatic fluid. The dissolved sample can lose its required features (such as shape, polymorphic form or chemical composition) and recrystallize at higher pressure in an undesired form. For example, a fine powder may recrystallize into a few large and preferentially oriented grains. Another potential problem can arise from reactions between the sample and the hydrostatic medium. For example, a pure compound can form solvates incorporating molecules of the hydrostatic fluid (Olejniczak & Katrusiak, 2010, 2011; Andrzejewski *et al.*, 2011; Tomkowiak *et al.*, 2013; Boldyreva *et al.*, 2002; Fabbiani & Pulham, 2006). This has also been observed for helium and argon penetrating into the structures of the fullerenes C₆₀ and C₇₀ (Samara *et al.*, 1993) and into arsenolite As₄O₆ (Guńka *et al.*, 2015). High-pressure crystallization of water in the presence of helium leads to an inclusion compound interpreted as ice XII. Therefore, the hydrostatic medium should be carefully chosen for a specific experiment, depending on the sample solubility, the pressure range and the type of investigation, whether a mounted-sample study, or *in situ* crystallization or reaction (Sobczak *et al.*, 2018; Pórolniczak *et al.*, 2018).

Many minerals and inorganic samples hardly dissolve at all and a commonly applied pressure-transmitting medium is a mixture of methanol, ethanol and water (16:3:1 by volume), hydrostatic to over 10 GPa at 296 K (see Table 2.7.1); separately, pure methanol crystallizes at 3.5 GPa, ethanol at 1.8 GPa and water at 1.0 GPa. If a sample dissolves well in methanol, ethanol and water, other fluids can be selected (Piermarini *et al.*, 1973; Angel *et al.*, 2007). Liquids like glycerine (hydrostatic to 3 GPa) and special inert fluids, such as silicone oil (Shen *et al.*, 2004; Ragan *et al.*, 1996), Daphne oil (Yokogawa *et al.*, 2007; Murata *et al.*, 2008; Klotz *et al.*, 2009), or condensed gases, like helium, argon and hydrogen (Tkacz, 1995; Dewaele & Loubeyre, 2007), can be used. Alternatively, a saturated solution of the sample compound, for example in a methanol–ethanol–water mixture, can prevent sample dissolution, but on increasing the pressure the compound can precipitate in the form of a powder or single crystals. One can choose to load an excess of the sample into the chamber before filling it up with the hydrostatic fluid, which would dissolve only some of the sample.