2.7. HIGH-PRESSURE DEVICES

Table 2.7.1
The (pseudo)hydrostatic limits of selected media at 296 K (Holzapfel, 1997; Miletich *et al.*, 2000)

Medium	Freezing point (GPa)	(Pseudo)hydrostatic limit (GPa)	Reference
4:1 Methanol:ethanol	–	9.8	Angel *et al.* (2007)
16:3:1 Methanol:ethanol:water	–	10.5	Angel *et al.* (2007)
Anhydrous propan-2-ol	–	4.2	Angel *et al.* (2007)
Neon	4.7	19	Klotz *et al.* (2009)
Argon	1.2	9/35	Bell & Mao (1981)/You *et al.* (2009)
Helium	11.8	70/150	Bell & Mao (1981)/Dewaele & Loubeyre (2007)
Hydrogen	5.7	177	Mao & Bell (1979)
Nitrogen	2.4	13	LeSar *et al.* (1979)
Glycerol	–	1.4	Angel *et al.* (2007)
Glycerin	–	3.0	Hazen & Finger (1982)
Glycerin		4.0	Tateiwa & Haga (2010)
Fluorinert FC84/87	–	7.0	Klotz *et al.* (2009)
Petroleum ether	–	6.0	Mao & Bell (1979)
Isopropyl alcohol		4.3	Piermarini *et al.* (1973)
1:1 Pentane:isopentane	–	7.4	Piermarini *et al.* (1973)
Silicone oil, viscosity 0.65 cSt	–	0.9	Angel *et al.* (2007)
Silicone oil	–	14	Klotz *et al.* (2009)
Daphne oil 7373		2.3	Murata *et al.* (2008)
Daphne oil 7474		3.7 at 296 K/6.7 at 273 K	Klotz *et al.* (2009)/Tateiwa & Haga (2010)
Vaseline	–	2.0	Tateiwa & Haga (2010)
NaCl	–	0.05/25	Tateiwa & Haga (2010)/You *et al.* (2009)

In situ crystallization at high pressure requires good, though not necessarily very good, solvents. Also, co-crystallizations can be performed in the DAC, and in this case the product that is obtained can depend on the solvents used and their concentration. Pressure effectively modifies intermolecular interactions, and new solvates can be obtained depending on the concentration of the substrates. It can be tricky to avoid co-crystallization of some compounds; in these cases a range of hydrostatic fluids has to be tried. A mixture of petroleum ethers, silicone or Daphne oils can be a good choice. Daphne oil, consisting mainly of alkylsilane (Murata *et al.*, 2008), has the rare feature of negligible thermal expansion, which is particularly useful for low-temperature high-pressure experiments: the DAC can be loaded under normal conditions and then pressurized and cooled to the required temperature, *e.g.* in a cryostat, without significant loss of pressure due to contraction of the medium.

The hydrostatic conditions can be checked by inspecting the width of reflections from the sample (full width at half-maximum, FWHM, is usually plotted), the width of the ruby fluorescence R_1 line and the R_1–R_2 line separation (You *et al.*, 2009). The pressure homogeneity can be checked by measurements for several ruby chips mounted across the DAC chamber. Nonhydrostatic conditions can cause inconsistent results and difficulties in their interpretation, which can prompt the researcher to consider changing the hydrostatic medium.

For hard samples, some departure from hydrostatic conditions is often acceptable. It is assumed that for a hard sample the nonhydrostatic compression component is small in a much softer medium, for example, hard corundum studied in soft NaCl. On the other hand, it may be easier to prepare a sample under normal conditions by uniformly mixing the powder of the specimen with a pseudo-hydrostatic medium, rather than using hydrostatic liquids or gases. The diffraction from the pseudo-hydrostatic medium powder can be used to monitor the pressure and measure non-hydrostaticity effects. Pseudo-hydrostatic solid media are often used for multi-anvil presses, where a solid sample facilitates loading and the uniaxial stress is not as drastic as in the opposed-anvil presses. Also, in high-temperature experiments the process of annealing reduces non-hydrostatic strain.

A relatively low nonhydrostatic effect was reported for argon frozen at 1.9 GPa: its pressure gradient up to 1% only is supported at 9 GPa (Bell & Mao, 1981) and up to 1.5% at 80 GPa (Liu *et al.*, 1990). This illustrates how the pseudo-hydrostaticity limit can be extended depending on the hardness of the specimen, the type of high-pressure device and the acceptance of deviatoric stress in the sample.

At very high pressure, exceeding 60 GPa, no compounds persisting as liquids are known (*cf.* Table 2.7.1). Diffraction data must then be corrected for a deviatoric stress component, causing the broadening of reflection rings and affecting their $2\theta_{\mathrm{Bragg}}$ positions, when the uniaxial stress is not collinear with the incident beam (Singh, 1993; Singh & Balasingh, 1994; Singh *et al.*, 1998; Mao *et al.*, 1998). The effect of uniaxial stress can be reduced or eliminated by sample annealing, which is often applied to improve the hydrostaticity of the sample.

2.7.12. High-pressure chamber and gasket in the DAC

A high-pressure device should be adjusted to the experiments planned, and in particular to the chemical activity of the sample. Gaseous hydrogen penetrates and dissolves in most metals, and therefore special alloys, such as beryllium bronze, have to be used for hydrogen setups. For some experiments non-metallic gaskets can be used, for example amorphous boron, corundum or diamond powders mixed with a resin. Owing to the insulating properties of such a gasket, the pressure dependence of the electric, dielectric and magnetic properties of the sample can be measured. Chemically aggressive samples can interact with the gasket material of the DAC chamber, and even with the diamond anvils, and this effect usually intensifies at high temperature and pressure. Consequently, both the sample and the high-pressure device can be affected. The erosion caused by an aggressive liquid can be considerably slowed down by its crystallization, which freezes the diffusion of molecules into the gasket. For example, *in situ* crystallization of halogen derivatives of acetic acid could only be performed in a DAC chamber with tungsten gaskets (Gajda & Katrusiak, 2009). In these experiments, the gasket was gradually eroded by the acid, but after its crystal-

lization the measurements could be performed over several days. In order fully to prevent erosion of the gasket, it can be coated with a layer of inert material, for example gold or platinum. Alternatively, a composite chamber can be prepared: after pre-indenting the gasket and drilling a hole at the centre of the indentation, a piece of gold wire can be fitted to the hole, and after pressing into a hole in the DAC again, a smaller hole can be drilled through this inset. A DAC chamber formed in this way has a gold lining and can be resistant to aggressive compounds.

2.7.13. High-pressure neutron diffraction

Neutron scattering is an indispensable and complementary technique in materials research (see Chapter 2.3), particularly for compounds containing heavy elements that strongly absorb X-rays, or light-atom weak X-ray scatterers (*e.g.* see Goncharenko & Loubeyre, 2005). However, the flux of neutron sources, both reactors and spallation targets, is several orders of magnitude lower than that of X-rays, even from traditional sealed X-ray tubes. Moreover, the scattering cross sections of neutrons are on average two orders of magnitude smaller than for X-rays (Bacon, 1975). These two considerations conflict with the requirement of small sample volume preferred for high-pressure devices. Consequently, a prohibitively long measurement time would be required to obtain meaningful neutron diffraction data from the DAC in its original form and size-optimized for X-ray studies. Therefore, initially, the designs of high-pressure devices for neutron scattering studies were based on typical large-volume presses: gas bombs with external multi-stage pressure generators, and piston-and-cylinder, multi-anvil and belt presses (Worlton & Decker, 1968; Bloch *et al.*, 1976; McWhan *et al.*, 1974; Srinivasa *et al.*, 1977; Besson, 1997; Klotz, 2012). The sample volume in the Bridgman-type opposed-anvil press, with flat anvils separated by a gasket of pipestone, was increased severalfold by making a recess at the centre of the pressure chamber of the so-called Chechevitsa anvils (Stishov & Popova, 1961*a,b*). The sample volume was further increased in toroid anvils by grooves supporting the gasket around the central recess (Khvostantsev *et al.*, 1977). This made them ideal for powder diffraction neutron measurements on samples of about 100 mm^3 to above 10 GPa in a Paris–Edinburgh hydraulic press (Besson *et al.*, 1992; Besson, 1997). The application of sintered diamond anvils increased this pressure range. High-pressure cells in a form optimized for neutron diffraction can contain between several cubic millimetres and a few cubic centimetres of sample volume. Such a large sample volume naturally limits the pressure range of cells used for neutron diffraction, compared with the DAC used for X-rays. However, the pressure range has increased considerably for neutron diffraction experiments during recent decades, to over 20 GPa in a moissanite anvil cell (Xu *et al.*, 2004; Dinga *et al.*, 2005), and to 40 GPa in a high-pressure cell capable of operating in helium cryostats at 0.1 K and in magnetic fields up to 7.5 T (Goncharenko, 2006; Goncharenko *et al.*, 1995). High-pressure high-temperature cells for neutron diffraction are usually equipped with internal heaters capable of exceeding 1500 K (Zhao *et al.*, 1999, 2000; Le Godec *et al.*, 2001, 2002).

It is particularly advantageous for the construction of large presses for neutron studies that most of the materials used have very low absorption of neutrons. There are also metals (vanadium, aluminium) with very low scattering lengths, and it is possible to obtain alloys ($Ti_{66}Zr_{34}$) with the scattering length scaled to zero. This allows access of the neutron beam to the sample and exit of reflections. In a Paris–Edinburgh cell operating in the time-of-flight mode, the incident beam enters the pressure chamber through the tungsten carbide anvil, along its axis, and the reflections leave the chamber through the gasket along the slit between the anvils with approximately $\pm 6°$ opening (Besson *et al.*, 1992; Takahashi *et al.*, 1996). In this operation mode, highly neutron-absorbing anvils made of sintered cubic boron nitride (cBN) can also be used (Klotz, 2012). Alternatively, the monochromatic angle-dispersive mode of operation, with the incident and diffracted beams passing through the slit between the anvils, is possible but it is less efficient with regard to the use of the full spectrum of neutrons. The application of a focused neutron beam and the time-of-flight technique allow the use of small sample volumes of a fraction of a cubic millimetre in compact opposed-anvil high-pressure cells (Okuchi *et al.*, 2012). Two DACs were recently optimized for neutron diffraction on single crystals. Owing to the application of a white neutron beam, the structure of a crystal 0.005 mm^3 in volume was determined. All reflections could be recorded because of the smaller Merrill & Bassett (1974) design made of neutron-transparent beryllium–copper alloy (Binns *et al.*, 2016). Another design with a wide access to the sample for the primary and diffracted beams has been successfully used at a hot-neutron source (Grzechnik *et al.*, 2018).

2.7.14. Pressure determination

Pressure determination inside a high-pressure sample chamber is most straightforward in piston-and-cylinder devices, where the force applied to the piston and its surface area are known. Pressure is the force per unit area, with corrections for the friction between the cylinder wall and the piston (particularly significant above 1 GPa) and for the buoyancy of the piston, marginally important for all high pressures. Several types of mechanical pressure gauge are available. In the Bourdon gauge, a spiral metal tube that is pressurized inside unwinds and moves a pointer around a precise scale. Electrical resistance gauges are most often based on a manganin alloy sensor. The resistance of manganin changes at the rate of $2.4 \times 10^{-5} \, GPa^{-1}$, although precise calibration depends on the alloy composition and it changes with the age of the sensor. The resistance of manganin depends only very weakly on temperature.

The most common pressure calibration method used for the DAC is the fluorescence pressure scale of the ruby R_1 (λ_{R1} at 0.1 MPa is the reference; $\lambda_0 = 694.2$ nm) and R_2 (at 0.1 MPa, $\lambda_{R2} = 692.8$ nm) lines (Forman *et al.*, 1972; Barnett *et al.*, 1973; Syassen, 2008; Gao & Li, 2012). Synthetic ruby with a Cr^{3+} concentration of 3000–5500 p.p.m., illuminated with green laser light, is commonly used. Inclusions of spinels make natural ruby unsuitable as a pressure gauge. A piece of ruby is usually crushed into small pieces and one or several small chips are placed in the DAC chamber close to the sample (Hazen & Finger, 1982). Alternatively, small ruby spheres can be used for this purpose (Chervin *et al.*, 2001).

The linear pressure dependence of the ruby R_1 fluorescence line was established according to the equation of state (EOS) of NaCl to 19.5 GPa:

$$P \, (GPa) = 2.74 \Delta \lambda \, (nm),$$

where $\Delta \lambda = \lambda_{R1} - \lambda_0$ (Piermarini *et al.*, 1975). The extension of the pressure range to 180 GPa, according to the equations of state of copper, gold and other metals, showed that $P(\Delta \lambda)$ is quasi-linear:

references