

2. INSTRUMENTATION AND SAMPLE PREPARATION

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 mm³ 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 (Ti₆₆Zr₃₄) 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 ±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 mm³ 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 $2.4 \times 10^{-5} \text{ GPa}^{-1}$, 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; $\lambda_0 = 694.2 \text{ nm}$) and R_2 (at 0.1 MPa, $\lambda_{R2} = 692.8 \text{ nm}$) lines (Forman *et al.*, 1972; Barnett *et al.*, 1973; Syassen, 2008; Gao & Li, 2012). Synthetic ruby with a Cr³⁺ 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:

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

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:

2.7. HIGH-PRESSURE DEVICES

Table 2.7.2

Luminescence pressure sensors, their electronic transition types (s = singlet, d = doublet) and rates of spectral shifts (after Holzapfel, 1997)

| Sensor | Transition | λ_0 (Å) | $d\lambda/dP$ (Å GPa ⁻¹) | $d\lambda/dT$ ($\times 10^{-2}$ Å K ⁻¹) | $(d\lambda/dP)/\Gamma$ (Å GPa ⁻¹) | $(d\lambda/dT)/(d\lambda/dP)$ ($\times 10^{-2}$ GPa K ⁻¹) |
|---|--|-----------------|---|---|--|---|
| Cr ³⁺ :Al ₂ O ₃ | ² E _g ↓ ⁴ A ₂ /d | 6942 | 3.65 (9) | 6.2 (3) | 4.9 | 17.0 |
| Sm ²⁺ :SrB ₄ O ₇ | ⁵ D ₀ ↓ ⁷ F ₀ /s | 6854 | 2.55 | -0.1 | 17.0 | -0.4 |
| Sm ²⁺ :BaFCl | ⁵ D ₀ ↓ ⁷ F ₀ /s | 6876 | 11.0 | -1.6 | 4.8 | -1.5 |
| Sm ²⁺ :SrFCl | ⁵ D ₀ ↓ ⁷ F ₀ /s | 6903 | 11.2 (3) | -2.36 (3) | 5.8 | -2.1 |
| Eu ³⁺ :LaOCl | ⁵ D ₀ ↓ ⁷ F ₀ /s | 5787 | 2.5 | -0.5 | 1.0 | -2.0 |
| Eu ³⁺ :YAG | ⁵ D ₀ ↓ ⁷ F ₁ /d | 5906 | 1.97 | -0.5 | 0.7 | -2.5 |

Table 2.7.3

Parameters recommended for pressure determination by EOS measurements

Various face-centred cubic (f.c.c.) and body-centred cubic (b.c.c.) metals are used as calibrants, with the EOS given by equation (2.7.1) and the reference temperature $T_R = 300$ K (after Holzapfel, 1997).

| Metal | a_{0R} (pm) | K_{0R} (GPa) | K'_{0R} | α_{0R} ($\times 10^6$ K) | $\delta_{\alpha R}$ |
|-------|------------------|-------------------|-----------|-------------------------------------|---------------------|
| Al | 404.98 (1) | 72.5 (4) | 4.8 (2) | 23.0 (4) | 5.5 (11) |
| Cu | 361.55 (1) | 133.2 (2) | 5.4 (2) | 16.6 (3) | 6.1 (6) |
| Ag | 408.62 (1) | 101.0 (2) | 6.2 (2) | 19.2 (4) | 7.1 (6) |
| Au | 407.84 (1) | 166.7 (2) | 6.3 (2) | 14.2 (2) | 7.2 (6) |
| Pd | 388.99 (1) | 189 (3) | 5.3 (2) | 11.6 (4) | 6.0 (11) |
| Pt | 392.32 (1) | 277 (5) | 5.2 (2) | 8.9 (4) | 5.9 (11) |
| Mo | 314.73 (1) | 261 (5) | 4.5 (5) | 5.0 (4) | 5.2 (14) |
| W | 316.47 (1) | 308 (2) | 4.0 (2) | 4.5 (4) | 4.7 (11) |

Table 2.7.4

Pressure fixed points at ambient temperature (after Holzapfel, 1997; Hall, 1980)

| P (GPa) | Element transition |
|-------------|----------------------|
| 0.7569 (2)† | Hg freezing at 273 K |
| 1.2 (1)† | Hg freezing at 298 K |
| 2.55 (6)† | Bi I–II at 298 K |
| 3.67 (3)† | Tl h.c.p.–f.c.c. |
| 2.40 (10)† | Cs I–II |
| 4.25 (1)† | Cs II–III |
| 4.30 (1)† | Cs III–IV |
| 5.5 (1)‡ | Ba I–II |
| 7.7 (2)‡ | Bi III–IV |
| 9.4 (3)† | Sn I–II |
| 12.3 (5)† | Ba II–III |
| 13.4 (6)† | Pb I–II |

† Onset of forward transition. ‡ Centre of hysteresis.

$$P = 1904[(\lambda/\lambda_0)^B - 1]/B,$$

where $B = 7.665$ for quasi-hydrostatic and 5.0 for non-hydrostatic conditions (Mao *et al.*, 1986, 1978; Bell *et al.*, 1986).

The ruby fluorescence depends strongly on temperature (Barnett *et al.*, 1973; Vos & Schouten, 1991; Yamaoka *et al.*, 2012) and a temperature change of about 6 K causes R_1 line shifts equivalent to 0.1 GPa. The fluorescence-line dependence on temperature is much weaker for Sm²⁺:SrB₄O₇ (Lacam & Chateau, 1989; Lacam, 1990; Datchi *et al.*, 1997) and the other rare-earth-doped sensors listed in Table 2.7.2. These sensors can be more sensitive to pressure than ruby, and together with ruby can be used simultaneously for both temperature and pressure calibration.

The calibration of most pressure gauges is based on comparisons of theoretical and shock-wave data (Holzapfel, 1997), so the derived equations of state are used with an accuracy of about 5% up to 1 TPa. The EOS recommended by Holzapfel (1997) is

$$P = [3K_0(1-x)/x^5] \exp[c_0(1-x)], \quad (2.7.1)$$

where $x = a/a_0 = (V/V_0)^{1/3}$, $c_0 = 3(K_0' - 3)/2$, a is the unit-cell dimension, V is the unit-cell volume, a_{0R} and V_{0R} are the reference parameters under ambient conditions (Table 2.7.3), α_{0R} is the thermal expansion coefficient, K_{0R} is the bulk modulus, and $K_0' = dK_0/dP$. $dK_0/dT = -3\alpha_{0R}K_0\delta_{\alpha R}$, where $\delta_{\alpha R} = \partial(\ln\alpha)/\partial(\ln V)_{TR}$. Pressure can be computed by assuming constant K_0' and linear temperature relations for T close to or higher than $T_R = 300$ K:

$$a_0(T) = a_{0R}[1 + \alpha_{0R}(T - T_R)],$$

$$V_0(T) = V_{0R}[1 + 3\alpha_{0R}(T - T_R)],$$

$$K_0(T) = K_{0R}[1 - \alpha_{0R}\delta_{\alpha R}(T - T_R)].$$

The details of the parameterization are explained by Holzapfel (1991, 1994) and listed for the simple face-centred (f.c.c.) and body-centred (b.c.c.) cubic metals in Table 2.7.3 (Holzapfel, 1997). Powders of these metals can be mixed with the sample and its pressure can be calibrated according to the unit-cell dimension of the standard. The well known compressibilities of NaCl, CaF₂ and MgO, in the form of either powders or single crystals, are also often used as internal pressure standards (Dorfman *et al.*, 2010, 2012; Dorogokupets & Dewaele, 2007).

An independent pressure assessment can be obtained from standard materials undergoing pressure-induced phase transitions (Table 2.7.4). This method is limited to just a few pressure points (Holzapfel, 1997), but they can provide a useful verification of other pressure gauges.

Other methods of pressure calibration are still being developed. For example, it has been shown that very high pressure can be determined from the Raman shift of strained diamond-anvil culets (Akahama & Kawamura, 2004). The strong piezochromic effect of visible colour changes in soft coordination polymers allows pressure calibration without spectrometers. These changes can proceed gradually (Andrzejewski & Katrusiak, 2017a) and abruptly at phase transitions (Andrzejewski & Katrusiak, 2017b). Another method of pressure calibration is based on the luminescence lifetime of lanthanide nanocrystals (Runowski *et al.*, 2017).

2.7.15. High-pressure diffraction data corrections

Apart from the Lorentz and polarization (Lp) corrections routinely applied to reflection intensities measured for bare crystals (*i.e.* crystals not enclosed in environment devices), as well as other corrections like extinction and absorption in the sample, the effects of the high-pressure cell should additionally be accounted for. These effects mainly include absorption in the pressure-vessel walls, shadowing of the sample by the pressure-cell opaque elements and elimination of the reflections of the diamond anvils for measurements in a DAC. The set of corrections is usually described for the specific pressure vessel. For a