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2004; Fabbiani *et al.*, 2004; Fabbiani & Pulham, 2006; Budzianowski & Katrusiak, 2006*a*,*b*; Dziubek *et al.*, 2007; Paliwoda *et al.*, 2012; Sikora & Katrusiak, 2013).

The original designs of the DAC (Weir *et al.*, 1959; Jamieson *et al.*, 1959) were later adapted to various purposes. Significant modifications take advantage of new designs of diamond anvils and their supports. Initially, the brilliant-cut diamonds of traditional design, but with the culet ground off to form a flat thrust surface parallel to the table, were used (Fig. 2.7.4). Culets of 0.8 mm in size can be used to about 10 GPa, 0.4 mm culets to about 50 GPa, 0.1 mm culets to about 100 GPa and 0.02 mm (20 μm in diameter) or even smaller (Akahama *et al.*, 2014; Akahama & Kawamura, 2010; Dalladay-Simpson *et al.*, 2016) culets can be used for the megabar 200–400 GPa range. The megabar range requires bevels on the culets to protect their edges from very high strain and damage. The bevels are about 6–7° off the culet plane and the ratio of bevel-to-culet diameters is between 10 and 20. Also, the gasket material, the hole diameter and its height, being a fraction of the hole diameter, are of primary importance. Double bevels can be used to release the strain further, but it appears that a value of about 400 GPa is the maximum pressure attainable in the conventional DAC (c-DAC).

The pressure limits of the c-DAC are surpassed in a double-stage DAC (ds-DAC), in a toroidal DAC (t-DAC) or by shock compression. In the ds-DAC a pair of small anvils, constituting a microscopic DAC (m-DAC, also described as second-stage anvils), is contained inside the c-DAC. The micro-anvils are prepared from diamond or amorphous diamond using the focused ion-beam technique (Sakai *et al.*, 2015, 2018). For another type of ds-DAC, employing microscopic diamond hemispheres (Dubrovinsky *et al.*, 2012; Dubrovinskaia *et al.*, 2016), pressures exceeding 1 TPa have been reported. In the t-DAC, each diamond culet is modified in such a way that an ion-beam-eroded groove surrounds the central micro culet (Dewaele *et al.*, 2018; Jenei *et al.*, 2018; Mao *et al.*, 2018).

At present, the DAC most commonly applied in laboratories is a miniature Merrill–Bassett DAC, where the anvils are installed on two triangular frames driven by three screws along three sliding pins (Merrill & Bassett, 1974). Analogous designs with two or four thrust-generating screws are also in use. The original Merrill–Bassett DAC was equipped with a pair of brilliant-cut 0.2 carat diamonds with polished culets (Fig. 2.7.4) and the anvils were supported on Be discs. The Merrill–Bassett DAC is optimized for use with automatic diffractometers. It contains no rocking blocks but allows translation of one of the anvils. The light weight and small size allow the Merrill–Bassett cell to be routinely used on single-crystal diffractometers. This simple DAC design is suitable for experiments up to about 10 GPa. Dedicated DACs for higher pressure have rocking supports for the diamonds, in the form of either hemispheres or half-cylinders (Fig. 2.7.5).

A very fine adjustment of the anvils and fine and remote pressure control can be obtained in a membrane DAC, where the thrust is generated by a metal membrane operated with gaseous helium or nitrogen (Letoullec *et al.*, 1988; Chervin *et al.*, 1995). Owing to the ideally coaxial thrust generation by the membrane and the stable supports of the anvils, usually in the form of a piston and cylinder, the membrane DAC is suitable for generating pressures of hundreds of gigapascals. The membrane DAC can be operated remotely through a flexible metal capillary, which is advantageous for spectroscopy and both powder and single-crystal diffraction experiments at synchrotrons.

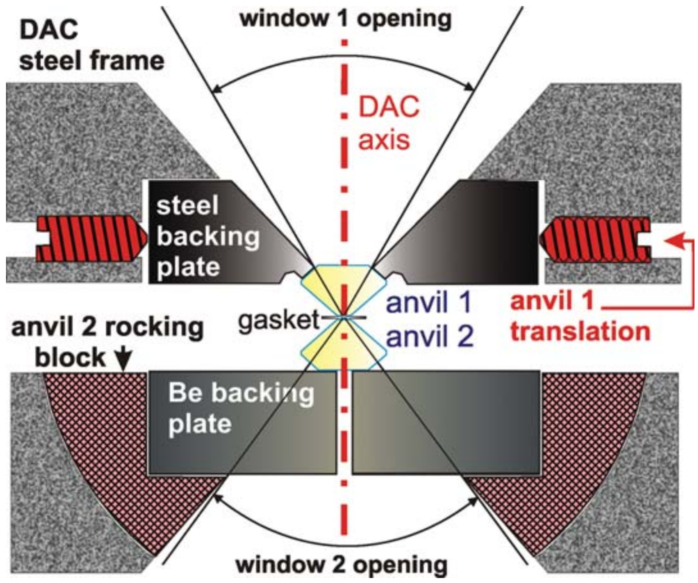

Figure 2.7.5
A cross section through the central part of a diamond-anvil cell, schematically showing the main elements applied in various designs. Usually, either beryllium backing plates or steel/tungsten carbide backing plates with conical windows are used. One of the plates can be translated and the other rocked in all directions (the hemispherical rocking mechanism). In other designs, one of the anvils can be rocked around and translated along one axis, and the other anvil rocked and translated in the perpendicular direction (two perpendicular hemi-cylindrical mechanisms). The usual thickness of the beryllium plate is 3 mm or more, and most constructions allow a window opening of about 40° to the DAC axis. The thickness of the diamond window (the table-to-culet distance) is usually about 1.5 mm.

2.7.5. Variable-temperature high-pressure devices

One of the most common interests in extreme conditions combines high pressure and high temperature. Several techniques for simultaneously controlling both pressure and temperature have been developed (Fei & Wang, 2000). The DAC can be heated externally (with respect to the sample chamber between the anvils' culets) when the entire DAC is placed in an oven or in a hot stream of air from an electrical heater (Fourme, 1968; Allan & Clark, 1999; Podsiadło & Katrusiak, 2008; Bujak *et al.*, 2008). External resistance-wire heaters placed immediately around the diamond anvils and the gasket are often used (Bassett & Takahashi, 1965; Takahashi *et al.*, 1982; Adams & Christy, 1992; Eremets, 1996; Moore *et al.*, 1970; Hazen & Finger, 1982; Besson, 1997; Dubrovinskaia & Dubrovinsky, 2003; Fei & Wang, 2000). External heating can routinely operate up to about 673 K. Its main advantages are stability, reliable measurement of temperature and high homogeneity of temperature in the chamber. The disadvantages include the relatively low temperature range and the large mass of the DAC mechanical parts that are heated. Their thermal expansion can cause loss of pressure. This does not apply to the membrane DAC, where a constant thrust from the membrane is transmitted to the anvils. A sophisticated externally heated DAC in an atmosphere of inert gases is capable of operating between 83 and 1473 K (Bassett *et al.*, 1993).

A very small turnbuckle DAC, about 6 mm in diameter, was originally constructed of plastic and hardened beryllium–copper alloy (BERYLCO 25) in order to perform magnetic measurements at low temperature in the small bore of a superconductive quantum interference device (SQUID) (Graf *et al.*, 2011; Giriat *et al.*, 2010). These are at present the smallest designs that can be used for X-ray diffraction studies, with the whole DAC cooled by commercial low-temperature gas-stream attachments. Alireza & Lonzarich (2009) built another miniature DAC for high-pressure magnetic measurements in a SQUID.

Temperatures of several thousand kelvin can be achieved by internal heating, where the sample absorbs the focused light beam of a laser (Bassett, 2001; Ming & Bassett, 1974; Shen *et al.*, 1996) or is heated by a thin wire passing through the chamber or its immediate surroundings, either in the gasket walls (Boehler *et al.*, 1986; Mao *et al.*, 1987; Zha & Bassett, 2003; Dubrovinsky *et al.*, 1998) or in the culets of intelligent diamond anvils (Bureau *et al.*, 2006). Composite resistance gaskets, with a platinum chamber wall acting as a 35 W resistance heater, can increase the temperature to over 2273 K (Miletich *et al.*, 2000, 2009). Laser beam(s) focused through the DAC anvil(s) onto the sample (Boehler *et al.*, 2001) can heat it to over 3273 K. This requires that the laser beam, or several beams, or a fraction of their energy, be absorbed in the sample. In order to increase the absorption, the sample can be mixed with another compound, for example gold powder. The main disadvantage of laser heating is inhomogeneous distribution of the temperature within the sample.

Much smaller temperature gradients, of a few kelvin at 2773 K, can be obtained in large-volume presses (LVPs). The multi-anvil LVP has traditionally been applied for the synthesis of diamond, which requires stable conditions of both high pressure and high temperature (Hazen, 1999; Liebermann, 2011). In the LVP, a resistance heater installed inside the chamber can provide stable control of the temperature for days, while the pressure is controlled by a hydraulic press. Owing to the large sample volume, the diffraction pattern can be quickly recorded. Most often, energy-dispersive diffraction is applied for the beams entering and leaving the pressure chamber through the gasket material between the anvils. LVPs are generally very large and heavy, which contrasts with the compact construction of the Paris–Edinburgh and Kurchatov–LLB pressure cells (Besson *et al.*, 1992; Goncharenko, 2004, 2006). Both these opposed-anvil cells can be placed in cryostats, and they can be used for either energy- or angle-dispersive diffraction of neutrons or X-rays. The Kurchatov–LLB cell has been optimized for neutron diffraction studies of magnetic structures at high pressure and low temperature (Goncharenko & Mirebeau, 1998; Goncharenko *et al.*, 1995).

2.7.6. Soft and biomaterials under pressure

Interest in the effects of pressure on biological materials is connected to the processing of food and the search for methods of modifying the structure of living tissue and its functions. Soft biological compounds, including proteins, membranes, surfactants, lipids, polymer mesophases and other macromolecular assemblies present in living tissue, are susceptible to pressure, which can affect the molecular conformation and arrangement with relatively low energies of transformation (Royer, 2002). Medium pressure suffices for protein coagulation, as observed for egg white at 0.5 GPa by Bridgman (1914). However, single crystals of egg-white lysozyme survived a pressure of several gigapascals (Katrusiak & Dauter, 1996; Fourme *et al.*, 2004), which was connected to the concentration of the mother liquor used as the hydrostatic fluid. Cells with externally generated pressures up to about 200 MPa for diffraction measurements on single crystals in a beryllium capsule (Kundrot & Richards, 1986) and on powders contained between beryllium windows (So *et al.*, 1992) have been built. Powder diffraction studies have also been

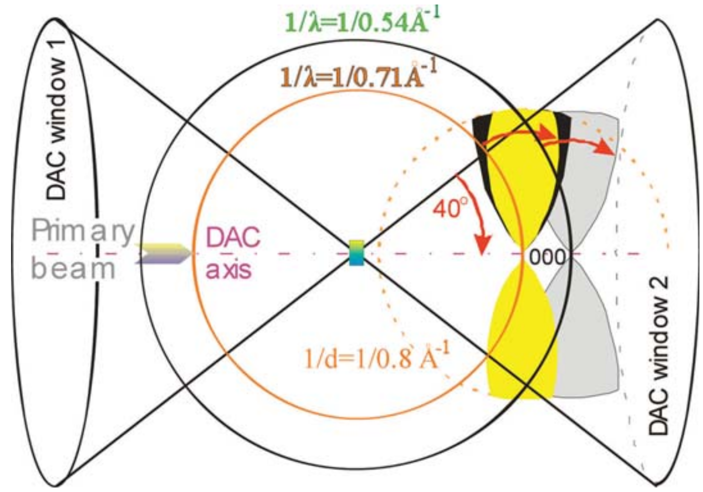

Figure 2.7.6
A diamond-anvil cell, showing the 40° half-angle opening of the conical windows and the reciprocal space accessed for a single-crystal sample and Mo $K\alpha$ or Ag $K\alpha$ radiation. In this schematic drawing, the window cones intersect at the disc-shaped sample (yellow–blue shaded rectangle) and around it the Ewald spheres of reciprocal radii corresponding to Mo $K\alpha$ and Ag $K\alpha$ wavelengths are drawn. The shape of the two yellow profiles meeting at the reciprocal 000 node is the cross section through the torus-like accessible volume of reciprocal space for Mo $K\alpha$ radiation; this torus is circularly symmetric about the DAC axis. The grey shape is likewise the accessible space for Ag $K\alpha$ radiation. Both are at the same resolution of $1/d_{hkl} = 1/0.8$ Å^{-1} (corresponding to θ angles of 26.4° for Mo $K\alpha$ radiation and 19.7° for Ag $K\alpha$). For a powdered sample, all reciprocal-space nodes contained within the resolution sphere (dotted circle) can be recorded. The DAC windows and the sample are shown at the initial 'zero' position, when the DAC axis coincides with the primary beam; the red arrows indicate the rotation of the DAC, sample and Ewald sphere to the limiting 40° angle.

performed on samples frozen under high pressure and recovered to ambient pressure (Gruner, 2004). High-pressure studies can be conveniently performed in the DAC, but because of the usually weak scattering of macromolecular samples, synchrotron radiation is preferred for such experiments (Fourme *et al.*, 2004; Katrusiak & Dauter, 1996).

2.7.7. Completeness of data

The steel parts of the DAC can restrict access of the incident beam to the sample and can obscure the exit of reflections. For a typical DAC working in transmission mode, the incident beam can be inclined to the DAC axis by up to about 25–40°, for the full opening of the window of 50–80°, respectively. In most DACs the collimator and detector sides are symmetric, so the opposing conical windows have the same opening angle. This limited access to the sample can affect the completeness of diffraction data for low-symmetry crystals, which can then pose considerable difficulties in solving and refining crystal structures from single-crystal measurements.

The restricted access of the primary and diffracted beams to the sample can conveniently be described by the concept of the reciprocal lattice (Fig. 2.7.6). The initial orientation of the crystal in the DAC defines the accessible region of the reciprocal lattice in such a way that the Ewald sphere can be inclined to the initial direction of the incident beam by up to the maximum window opening angle, denoted α_M. The sample can be accessed from both sides of the DAC (by rotating the DAC by 180°) and thus the accessible region of reciprocal space has the form of a round flat cushion, with surfaces touching at the cushion centre [described