International Tables for Crystallography (2018). Vol. H, Section 2.7.3, pp. 157–159.

of an ocean of air') in 1643, Otto von Guericke's experiment pitting the force of six horses against atmospheric pressure acting to squeeze together two hemispheres evacuated using the vacuum pump he had constructed in Magdeburg in 1654, and Blaise Pascal's measurements of pressure differences at different altitudes and his demonstrations of barrels being blown up by the force of water poured in through a tall pipe. The subsequently developed high-pressure devices were mainly of the piston-and-cylinder type.

At the beginning of the 19th century, pressures of about 400 MPa could be obtained, and at the beginning of the 20th century, often referred to as the end of the pre-Bridgman era, pressures up to about 2 GPa could be achieved. Then Percy W. Bridgman's remarkable inventions extended the pressure range greatly, to over 10 GPa (Bridgman, 1964). He devised new techniques for sealing pressure chambers, developed the opposed-anvils apparatus and introduced methods for the controlled measurement of various phenomena. Moreover, he used his new methods to describe a vast number of observations and properties of matter at high-pressure ranges hitherto unexplored. Bridgman's ingenious designs of high-pressure devices, such as the opposed-anvils apparatus, paved the path for future researchers. His scientific achievements won him the Nobel Prize in Physics in 1946.

The Bridgman era in high-pressure research ended in the late 1950s, when the diamond-anvil cell, often abbreviated to DAC, was invented (Weir *et al.*, 1959; Jamieson *et al.*, 1959; Piermarini, 2001). Soon after, the DAC became the main tool of high-pressure researchers; it gradually increased the range of attainable pressure by more than an order of magnitude, and under laboratory conditions it surpassed the pressure level at the centre of the Earth. Most importantly, the DAC allowed many new measuring techniques, particularly X-ray diffraction and optical spectroscopy, to be utilized. Before that, spectroscopic studies were limited to about 0.5 GPa. High-pressure X-ray diffraction, pioneered by Cohen (1933) in Berkeley for powders and by Vereshchagin *et al.* (1958) in Moscow for a single crystal of halite at 0.4 GPa in a beryllium high-pressure vessel, had been expensive, inefficient and inaccurate.

The DAC has become commonly available because of its low cost and easy operation. Today, the DAC continues to be the main and most versatile piece of laboratory pressure equipment and a record-breaking high-pressure apparatus. However, other sample environments provide complementary means of structural studies. For example, the large-volume press can be advantageous for neutron diffraction studies and in experiments where very stable high-pressure/high-temperature conditions are required. Naturally, the success of many high-pressure methods would not be possible without the development of other sciences and technologies, including computers, powerful sources of X-rays and neutrons and their detectors, and lasers.

2.7.3. Main types of high-pressure environments

High-pressure methods can be classified as dynamic or static. In the traditional dynamic methods, the pressure is generated for microseconds, usually at an explosion epicentre or at targets where ultra-fast bullets or gas guns are fired at the sample. The explosions are carried out either in special chambers or in bores underground (Batsanov, 2004; Ahrens, 1980, 1987; Keller *et al.*, 2012).

Even shorter, of a few nanoseconds' duration, the shock compression generated in targets using laser drivers coupled to the powerful X-ray pulses of a free-electron laser, or an otherwise generated X-ray beam, can further extend the attainable pressure limits. While this laser shock generates both high pressure and high temperature in the sample (the so-called Hugoniot compression path), in the ramp compression, also termed the off-Hugoniot path, the signal of the designed profile from an optical laser affords terapascal compression and approximates isothermal conditions (Wicks *et al.*, 2018; Smith *et al.*, 2014; Wang *et al.*, 2016).

The advantage of the gas and laser shock-wave and ramp-compression methods is that the attainable pressure is not limited by the tensile strength of the pressure chamber. Disadvantages include the inhomogeneous pressure, difficulties in controlling the temperature, the requirement for very fast analytical methods and the very high cost. The kinetic products generated during the explosion and in the shock waves can be different from the products recovered after the explosion, and different again from those formed under stable conditions. In most cases the laser-generated shock annihilates the sample.

Static methods are at present more suitable for crystallographic studies. The first variable-temperature sample-environment devices for structural studies of liquids and solids were designed soon after the inception of X-ray diffraction analysis. Structural investigations at high and low temperature at ambient pressure were mainly performed either by blowing a stream of heated or cooled gas onto a small sample (Abrahams *et al.*, 1950) or by placing the sample inside an oven or a cryostat. At present, a variety of attachments for temperature control are commercially available as standard equipment for X-ray and neutron diffractometers. Open-flow coolers using gaseous nitrogen and helium are capable of maintaining temperatures of about 90 K and a few kelvin, respectively, for days and weeks. They are easy to operate and pose no difficulties for centring the sample crystal, because the crystal is mounted, as in routine experiments, on a goniometer head with adjustable x–y–z translations and is visible at all positions through a microscope attached to the diffractometer. Cryostats and furnaces obscure the visibility of the sample and are usually heavy, and hence require strong goniometers; however, they often have the advantage of higher stability, a larger homogeneous area in the sample and a larger range of temperature (see Chapter 2.6).

Devices for static high-pressure generation are more difficult to construct because of the obvious requirement for strong walls capable of withstanding the high pressure applied to the sample. There are several types of high-pressure device and they can be classified in several ways. The piston-and-cylinder (PaC) press is the oldest type of pressure generator. However, the pressure range is limited in most advanced constructions (of multilayer negatively strained cylinders, like one shown in Fig. 2.7.1) to 3.0 GPa (Baranowski & Bujnowski, 1970; Besson, 1997; Dziubek & Katrusiak, 2014). PaC presses are ideal for volumetric measurements on a sample enclosed in the cylinder and for generating pressure in a hydrostatic medium transmitted through a capillary to other external high-pressure chambers containing the sample and optimized for a chosen measurement method, usually optical spectroscopy and diffraction. The external devices include chambers for loading the PaC with gas, which is either the hydrostatic medium or the sample itself (Tkacz, 1995; Rivers *et al.*, 2008; Couzinet *et al.*, 2003; Mills *et al.*, 1980; Yagi *et al.*, 1996; Kenichi *et al.*, 2001). In some pressure generators, a cascade of two or three PaC presses is applied for highly compressible pressure-transmitting media (gases) before the final setup stage.

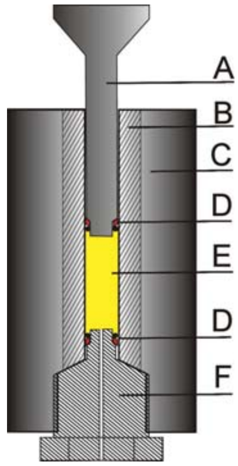

Figure 2.7.1
A cross section through a piston-and-cylinder device with a shrink-fitted double cylinder. In this design, the bottom piston (stopper F) is in the fixed position and only the top piston (A) is pushed into the cylinder by a hydraulic press. The main components of the device are: piston (A), inner cylinder (B), outer supporting shell (C), brass and rubber sealing rings (D), sample (E) and stopper (F).

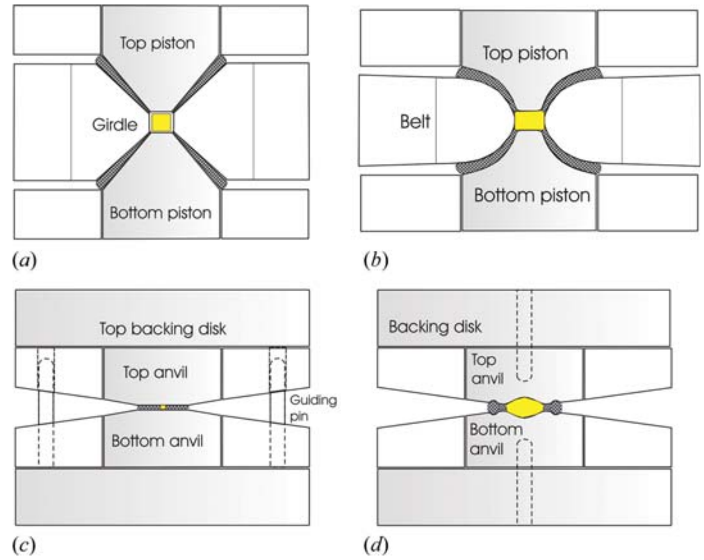

Figure 2.7.2
Cross sections of (*a*) the girdle anvil, (*b*) the belt anvil, (*c*) the Bridgman anvil and (*d*) the toroid anvil. The gaskets are dark grey, the tungsten carbide elements are pale grey and the sample chamber is yellow.

The PaC press can be considered as the prototype of other large-volume presses (LVPs). The PaC press consists of a cylinder closed at both ends with pistons, sealed with gaskets. The attainable pressure depends mainly on the tensile strength of the cylinder and of the gasket. The cylinder can be strengthened by the process of frettage, *i.e.* inducing tensile strain in the outer part and compressive strain inside (Onodera & Amita, 1991). This can be achieved by autofrettage, when a one-block cylinder is purposely overstrained to the point of plastic deformation and the deformation residues result in the required strain. Likewise, the cylinder can be built of shrink-fitted inner and outer tubes (the outer diameter of the inner tube is slightly larger than the inner diameter of the outer tube, which must be heated to assemble the cylinder) or of cone-shaped tubes (with a cone half-angle of *ca* 1°) pushed into one another to generate the frettaging strains. Alternatively, a coil of several layers of strained wire or tape can be wound around the cylinder, or the cylinder can be compressed externally to counteract its tensile strain simultaneously with the load being applied to the pistons (Baranowski & Bujnowski, 1970). The load against the cylinder walls can be reduced by containing the sample in a capsule of soft incompressible material, usually lead (Bridgman, 1964). Cylinder chambers with externally generated pressures up to 0.4 GPa (Blaschko & Ernst, 1974) and PaC cells capable of generating 2 GPa (Bloch *et al.*, 1976; McWhan *et al.*, 1974) have been used for neutron diffraction, and a beryllium cylinder has been used for X-ray diffraction on protein crystals to 100 MPa (Kundrot & Richards, 1986). The range of pressure up to a few hundred megapascals is often described as medium pressure. There are sample-environment chambers with externally generated medium pressure that are designed for in-house powder diffractometers operating in the Bragg–Brentano geometry (Koster van Groos *et al.*, 2003; Whitfield *et al.*, 2008).

If the cylinder length is reduced and the gasket reinforced by compression of the conical pistons, the girdle press is obtained (Fig. 2.7.2*a*). Its optimized modification is the belt apparatus (Fig. 2.7.2*b*). The girdle and belt presses generate pressures of about 10 GPa and can be internally heated to about 1500 K, and hence they have been used widely to synthesise materials. However, the opacity of the girdle/belt and anvils allows no access for X-ray or neutron beams between the anvils. This disadvantage is alleviated in the opposed-anvils press, operating on the massive-support principle, where the beams can pass through the gasket material. After the first record of a simple version of the opposed-anvils experiment in the mid 19th century performed in order to measure the effect of medium pressure on the electric conductibility of wires by Wartmann (1859), the opposed anvils were extensively developed and applied to much higher pressure by Bridgman (1935, 1941, 1952). He also equipped them with a pyrophyllite gasket separating the anvil faces (Bridgman, 1935), and in this form they are commonly known as Bridgman anvils (Fig. 2.7.2*c*). In the 1960s, the flat faces of the Bridgman anvils were modified to so-called toroidal anvils (Fig. 2.7.2*d*), where the sample space is considerably increased by hemispherical depressions at the anvil centre and surrounded by a groove supporting the gasket and preventing its extrusion (Khvostantsev, 1984; Khvostantsev *et al.*, 1977, 2004; Ivanov *et al.*, 1995). Anvils with a spherical sample cavity only, so-called Chechevitsa anvils, preceded the construction of toroidal anvils. Toroidal anvils were optimized for neutron diffraction by adding a small pneumatic press called the Paris–Edinburgh cell (Besson *et al.*, 1992). Toroidal anvils enabled neutron diffraction studies up to 50 GPa and 3000 K (Kunz, 2001; Zhao *et al.*, 1999, 2000; Redfern, 2002). Experiments on magnetic systems in a similar pressure range and at low temperature were performed in a very different design of opposed anvils, the sapphire Kurchatov–LBB cell, shown in Fig. 2.7.3 (Goncharenko & Mirebeau, 1998; Goncharenko, 2004).

More complex LVPs have been based on multi-anvil presses (Liebermann, 2011). These are usually very large devices capable of containing tens of cubic centimetres of sample. The sample is encapsulated and pressurized between anvils sealed with some kind of gasket. The attainable pressure depends on a number of factors, including the applied load and the strength of the anvils, which are made of steel, tungsten carbide, sapphire or sintered diamond; the maximum pressure depends inversely on the sample volume. Multi-anvil presses (Huppertz, 2004; Liebermann, 2011) – tetrahedral, trigonal–bipyramidal, cubic (Akimoto *et al.*, 1987) and octahedral (Onodera, 1987) – are optimized for larger sample volumes and for the high temperatures required for the synthesis of hard materials, especially diamond (Hazen, 1999). The multi-anvil presses are used for diffraction studies.

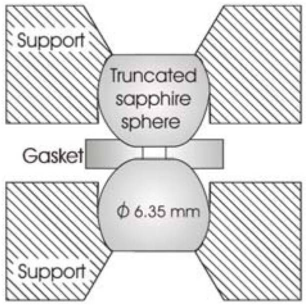

Figure 2.7.3
A schematic view of the opposed-sapphire anvil of the Kurchatov–LBB cell designed for neutron diffraction on magnetic materials (Goncharenko, 2004).

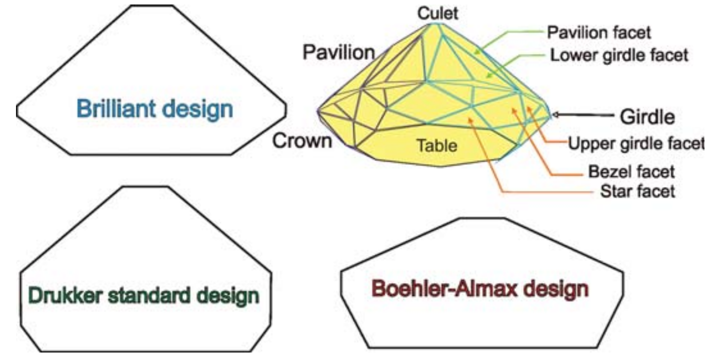

Figure 2.7.4
Cross sections of three types of diamond anvil used in high-pressure cells: the brilliant design (supported either on the table or on the crown rim), the Drukker design (supported on the table and crown) and the Boehler–Almax design (supported on the crown).

The sample can be either contained in a capsule or mixed with a pressure-transmitting pseudo-hydrostatic medium, which is inert and a weak absorber of X-rays. The sample is accessed by the X-ray beam between the anvils through a weakly absorbing sealing material, such as amorphous boron, magnesium oxide, corundum or pyrophyllite. Like the opposed-anvil presses, multi-anvil LVPs can be used effectively for X-ray diffraction at synchrotrons and neutron sources. However, these large installations also require (apart from intense primary beams) powerful translations for their precise centring relative to the primary beam and diffractometer axes. The main advantage of an LVP is stable and homogenous internal heating up to about 2000 K (Besson, 1997). Such stable conditions are particularly valuable for high-pressure synthesis and crystallization, for example of diamonds (Hazen, 1999).

2.7.4. The diamond-anvil cell (DAC)

The invention of the DAC revolutionized high-pressure studies, diversified their scope, greatly simplified the experimental procedures, increased the range of pressure and temperature, and initiated constant growth in the number of high-pressure structural studies, starting in the 1960s and continuing up to today. The DAC is built from a pair of opposing diamond anvils and a vice to generate their thrust. The sample is compressed between the culets of the anvils. Since its inception, the DAC has been modified and redesigned frequently, in order to adapt it to new experimental techniques or to take advantage of the parallel progress in scientific equipment. The original DAC built at the National Bureau of Standards (Maryland, USA) was used for infrared spectroscopy. Another DAC designed for powder diffraction experiments was made of beryllium, a relatively strong metal which weakly absorbs short-wavelength X-rays (Weir *et al.*, 1959; Bassett, 2009). The DAC, with steel frames and beryllium discs supporting the anvils, is still in use today.

The original and most efficient concept applied in the operation of the DAC was that the incident beam enters the pressure chamber through one diamond anvil and the reflections leave through the other anvil; this mode of operation is often referred to as transmission geometry. Together with the diamond anvils, Be discs constitute windows for the X-rays. However, beryllium has several disadvantages. It is the softest and weakest of the materials used in DAC construction, it softens at about 470 K, beryllium oxide is poisonous, and machining beryllium is difficult and expensive. Therefore, except for the pioneering DAC design by Weir *et al.* (1959), Be parts were initially limited to disc supports for the anvils. Moreover, polycrystalline Be discs produce broad reflection rings and a strong background, and the small central hole in the disc obscured optical observation of the sample. In many modern DACs the beryllium discs have been completely eliminated, and the diamond anvils are directly supported by steel or tungsten carbide platelets (Konno *et al.*, 1989; Ahsbahs, 2004; Boehler & De Hantsetters, 2004; Katrusiak, 2008). For this purpose new diamond anvils, exemplified in Fig. 2.7.4, were designed. Anvils of different sizes, culet dimensions, height-to-diameter ratios and other dimensions can be adjusted for the experimental requirements, such as the planned pressure range and the opening angles of the access windows.

Another DAC was independently designed for X-ray powder diffraction by Jamieson *et al.* (1959). In their DAC, the incident beam was perpendicular to the axis through the opposed anvils, and the primary beam passed along the sample contained and squeezed directly (no gasket was used) between the culets. The reflections were recorded on photographic film located on the other side of the DAC, perpendicular to the incident beam. This geometry was described as either panoramic, perpendicular or transverse. The transverse geometry is also used with beryllium or other weakly absorbing gaskets (Mao *et al.*, 1998). Other DACs, for example where both the incident beam and the reflections pass through one diamond anvil, were also designed (Denner *et al.*, 1978; Malinowski, 1987); however, the transmission geometry is most common owing to its advantages. In the transmission geometry the uniaxial support of the anvils leaves a window for optical observation of the sample, as well as for spectroscopic and diffractometric experiments along the cylindrical pressure chamber. Therefore, at present most DAC designs operate in transmission geometry.

The DAC construction can generally be described as a small vice generating thrust between opposed anvils. In the first DACs designed in the late 1950s, no gasket nor hydrostatic fluids were used and the sample was exposed to strong anisotropic stresses. Van Valkenburg (1962) enclosed the sample in a hole in a metal gasket, filled the hole with hydrostatic fluid and sealed it between the culets of the anvils. This most significant development of the miniature high-pressure chamber opened new possibilities for all sorts of studies under hydrostatic conditions, in particular powder and single-crystal diffraction studies. Since then, the gaskets have become an intrinsic part of the DAC. The hydrostatic conditions in the DAC have been used to grow *in situ* single crystals from the melts of neat compounds (Fourme, 1968; Piermarini *et al.*, 1969) and from solutions (Van Valkenburg *et al.*, 1971*a*,*b*). Now it is a common method for *in situ* crystallization under isothermal and isochoric conditions (Dziubek & Katrusiak, 2004; Bujak *et al.*,