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 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).

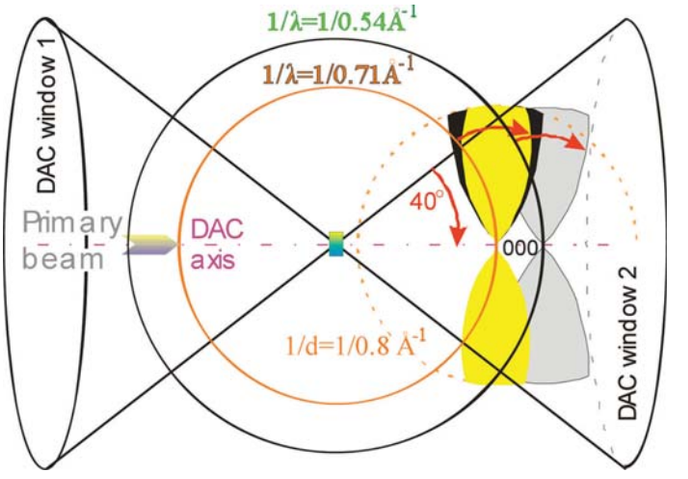

Figure 2.7.6
A diamond-anvil cell, showing the 40° half-angle opening of the conical windows and the reciprocal space accessed for a single-crystal sample and Mo $K\alpha$ or Ag $K\alpha$ radiation. In this schematic drawing, the window cones intersect at the disc-shaped sample (yellow–blue shaded rectangle) 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.

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

as a donut cake by Merrill & Bassett (1974)], as shown in Fig. 2.7.6. In the directions perpendicular to the DAC axis, the maximum coordinate $d^*_{yz} = 2\lambda^{-1} \sin \alpha_M$ of reciprocal vectors is for many crystals larger than the resolution of the data (for a typical DAC, $\alpha_M = 40^\circ$, which for organic crystals or other weakly scattering substances is less than required, as the data measured with Mo $K\alpha$ radiation for molecular crystals often extend up to a maximum θ of only about 25°). However, access to the reciprocal lattice is significantly limited along the DAC axis (perpendicular to the flat cushion). In this direction, only those reflections can be accessed for which

$$d^*_x = 2\lambda^{-1} \sin^2(\alpha_M/2),$$

where d^*_x is the maximum coordinate of accessible reciprocal vectors along the x_L axis running from the sample to the radiation source in the laboratory reference system, λ is the wavelength, and α_M is the opening angle of the window measured from the DAC axis (or the maximum inclination of the DAC axis to the incident beam). For example, a DAC with a full window opening angle of $2\alpha_M = 60^\circ$ limits the laboratory reciprocal x coordinate to 0.1885 Å^{-1} when λ(Mo $K\alpha$) = 0.71073 Å is used; if the crystal x^* axis is aligned along the laboratory x_L axis, and if the crystal a^* = 0.10 Å^{-1}, then the maximum Bragg reflection index $|h|$ is 1. If the wavelength is decreased to λ(Ag $K\alpha$) = 0.56 Å, the maximum d_x increases to 0.2392 Å^{-1} and reflections with index h = 2 can be recorded.

Although the accessible region of the reciprocal lattice depends strongly on the DAC design, the final completeness of the data also depends on several other factors: (i) the symmetry of the sample crystal; (ii) the sample orientation; and (iii) the wavelength of the X-ray radiation. Therefore, the DAC is ideally suited to high-pressure studies of simple and high-symmetry crystals. The Laue-class symmetry of cubic crystals is either $m\bar{3}$ or $m\bar{3}m$, and in most cases the whole of the required resolution falls within the accessible flat-cushion reciprocal region. Thus, the completeness in high-pressure experiments on cubic samples mounted in the chamber at a random orientation is not limited. For hexagonal and tetragonal samples, the crystal orientation is very significant. The maximum completeness can be obtained when the hexagonal or tetragonal axis is perpendicular to the DAC axis. Then the sample reciprocal axis c^* is located along the flat-cushion plane. When two axes of a monoclinic or orthorhombic crystal are at 90° to the DAC axis, a considerable portion of the symmetry-independent part of the reciprocal lattice is not accessible. This reduces the completeness of the data, even though the redundancy of the data is increased. Optimum orientation of the sample can double the completeness compared with experiments measured for the same sample with its axes aligned along the DAC axis and plane.

The completeness of the data can be increased by collecting several data sets for samples oriented differently in the DAC and merging these data (Patyk *et al.*, 2012). This purpose can also be achieved by placing several crystal grains at different orientations in the high-pressure chamber, and then separating their reflections, indexing them and merging.

When the powder diffraction method is used, this problem of completeness is irrelevant. As shown in Fig. 2.7.7, for an ideal powder with randomly oriented grains all reciprocal-lattice nodes can be represented as spheres and they all satisfy the Bragg diffraction condition. The main problem occurring for samples with low symmetry and long lattice constants is overlapping reflections. The intensity of the powder reflection rings is low,

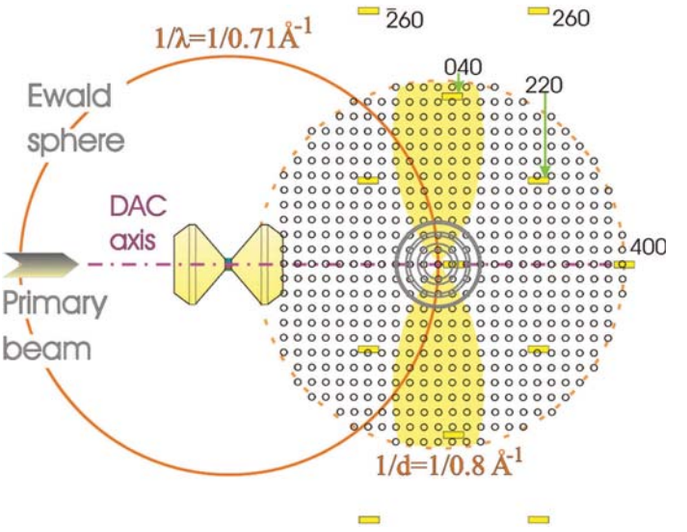

Figure 2.7.7
A schematic illustration of the reciprocal space associated with a sample enclosed in a diamond-anvil cell (DAC). For clarity, the sizes of the sample and diamond anvils have been increased. The Ewald sphere is drawn for the sample only and cubic symmetry with an a parameter of 10 Å has been assumed. Of the reciprocal lattice of the sample, only the layer of $hk0$ nodes is shown as small circles within the resolution limit of $1/d_{hkl}$ = 1/0.8 Å^{-1}. The Ewald spheres of the diamond anvils have been omitted, and only the layer of nodes $hk0$ of the detector anvil is shown as yellow rectangles. Owing to its short unit-cell parameter of 3.57 Å and $Fd\bar{3}m$ symmetry, there are few diamond reflections in the pattern. Note the displaced origins of the reciprocal lattices of the sample and of the detector anvil (the anvil on the detector side) as a result of the off-centre positions of the anvil. For a powdered sample, each node is distributed on a sphere. In this drawing, the spheres are represented by circles only for nodes 100, 110, 200, 210, 220 and 300. The other node spheres contained within the chosen resolution limit have been omitted for clarity; for a triclinic sample, the $hk0$ layer would include 266 powder reflections.

because only a small fraction of the sample volume, less than one part per million, contributes to the intensity at a specific point on the reflection ring. Furthermore, the sample volume in the DAC is very small. For these reasons, powder X-ray diffraction in the laboratory usually provides only qualitative information. After the introduction of synchrotron radiation and area detectors, powder diffraction became one of most efficient methods of high-pressure structural studies.

2.7.8. Single-crystal data collection

It is essential that a crystal sample is centred precisely on the diffractometer. Optical centring of a crystal is hampered by the limited view of the sample through the DAC windows in one direction only and by the strong refractive index of diamonds. Consequently, diffractometric methods of crystal centring are more precise for DAC centring. Hamilton's method comparing the diffractometer setting angles of reflections at equivalent positions (Hamilton, 1974) was modified for the purpose of the DAC by King & Finger (1979) and then generalized for any reflections, not necessarily at equivalent positions (Dera & Katrusiak, 1999). These methods are very precise, but they require the approximate orientation matrix (UB matrix) of the sample crystal (Busing & Levy, 1967) to be known and the reflections to be indexed. This information was determined at the beginning of an experiment when traditional diffractometers with a point detector were used. However, nowadays diffractometers with area detectors are used, and generally the crystal orientation