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,

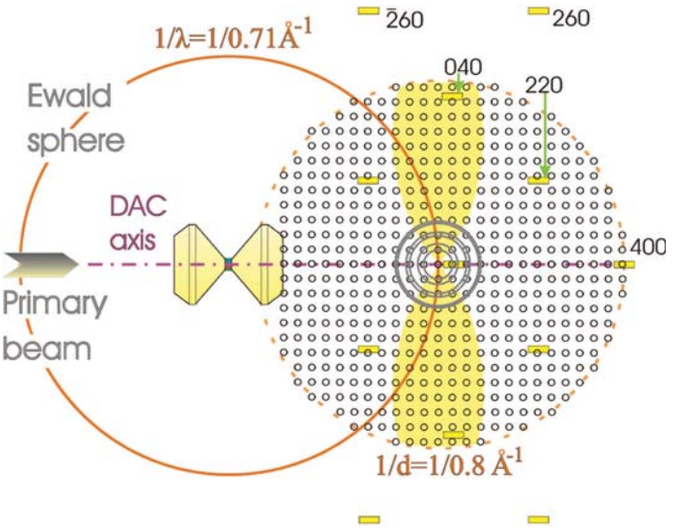

Figure 2.7.7
A schematic illustration of the reciprocal space associated with a sample enclosed in a diamond-anvil cell (DAC). For clarity, the sizes of the sample and diamond anvils have been increased. The Ewald sphere is drawn for the sample only and cubic symmetry with an a parameter of 10 Å has 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

is not determined before collecting the diffraction data. To meet these requirements, a new efficient and semi-automatic method was devised, whereby the diffractometer measures a sequence of shadows of the gasket on the CCD detector and calculates the required corrections to the DAC position along the goniometer-head translations (Budzianowski & Katrusiak, 2004). Precise centring can only be achieved for very stable goniometer heads that do not yield under the weight of the DAC (Katrusiak, 1999).

The mode of data collection for a sample enclosed in a DAC can affect the data quality considerably. Data for a bare crystal on a four-circle diffractometer with a scintillation point detector were measured in the so-called bisecting mode, where the ω angle [diffractometer-axes positioning angles ω, χ, φ and θ of the Eulerian cradle will be used here (Busing & Levy, 1967), unless otherwise noted] was fixed to 0° and not used in the process of crystal positioning. In other words, the shaft φ and circle χ lie in the plane bisecting the angle formed by the incident beam and the reflection actually measured. The bisecting mode was optimal for avoiding collisions between the diffractometer shafts and detector, and also minimized absorption effects for most vertically mounted samples. However, these features are irrelevant for samples enclosed in a DAC. It was shown by Finger & King (1978) that the DAC absorption of the incident and reflected beams is a minimum when the Eulerian goniometer φ axis is not used and is always set to 0°. Hence, this is called the $\varphi = 0°$ mode. The $\varphi = 0°$ mode also minimizes the effect of the sample being shadowed by the gasket edges (Katrusiak, 2008). Moreover, in the $\varphi = 0°$ mode the DAC axis always lies in the diffraction plane of the diffractometer, which gives maximum access to the reciprocal-lattice nodes (Fig. 2.7.6).

The advent of area detectors facilitated high-pressure experiments considerably and extended the range of attainable conditions to simultaneous very high pressure and temperatures of several thousand kelvin. Single-crystal experiments are easier because the diffraction data can be recorded before the orientation matrix UB of the crystal is determined (Busing & Levy, 1967; Finger & King, 1978). The recorded data can thus be analysed after the experiment and all relevant structural models can be tested. The use of area detectors shortens the data-collection times for both single-crystal and powder diffraction measurements, and this is particularly efficient with the extremely intense X-ray beams provided by synchrotrons. In single-crystal experiments, several or even tens of reflections are partly scanned through or fully recorded in one image. Although these reflections are not each recorded at their optimum diffractometer settings, corresponding to the $\varphi = 0°$ mode setting described above, the redundancy of the data is increased and the intensities can be corrected for the absorption coefficients derived from differences between equivalent reflections. It is also advantageous that simultaneous diffraction events in the sample crystal and in one or both of the diamonds, which occur sporadically and weaken the recorded reflections, can be eliminated by comparing the intensities of the same reflection measured at several ψ angle positions as well as the equivalent reflections. Equivalent reflections measured at different positions are particularly useful for eliminating systematic errors in the data collection.

It is important that the so called 'run list', defining the diffractometer setting angles and scan directions for the detector exposures, takes into account the $\varphi = 0°$ mode of the DAC orientations, for which access to the DAC is still on average at its widest and the DAC absorption and gasket-shadowing effects are on average the smallest. Most importantly, such an optimum setting can be executed with a four-circle diffractometer, and cannot be done on simplified diffractometers with the φ shaft fixed at a χ angle of about 50°. Even fewer reflections can be accessed when the DAC is rotated about one axis only, which is still the case for some laboratory and synchrotron diffractometers.

2.7.9. Powder diffraction with the DAC

The DAC is often described as the workhorse of high-pressure research, owing to its versatile applications, low cost, easy operation and unrivalled attainable static pressure. However, the small size of the DAC chamber, containing sample volumes between 0.025 mm^3 for pressure to about 5 GPa, 0.005 mm^3 to about 10 GPa and less than 3×10^{-6} mm^3 for the megabar range, can be disadvantageous for powder diffraction studies. The disadvantages include the inhomogeneous distribution of temperature within the sample (particularly as it remains in contact with a diamond, which is the best known thermal conductor) and nonhydrostatic strain (often due to the technique of generating pressure by uniaxial compression of the chamber). In some samples close to the melting curve some grains increase in size at the expense of others, partly or fully dissolving, so the number of grains may be insufficient for obtaining good-quality powder diffraction patterns. This difficulty can be partly circumvented by rocking the DAC during the experiment about the ω axis. On the other hand, for a sample consisting of tens of grains it is possible to perform multi-grain analysis by merging the diffraction patterns to give the equivalent of single-crystal data. High-pressure powder diffraction patterns can also be affected by a low signal-to-noise ratio, too few crystal grains, and their preferential orientation in the DAC uniaxially compressed chamber. The preferential orientation is particularly significant when the grains are elongated and their compressibility is anisotropic; these effects can be further aggravated by the non-hydrostatic environment. Powder reflections are much weaker in intensity than the equivalent single-crystal reflections from the same sample volume. Small sample volumes are compensated for by the powerful beams available at synchrotrons. At present, high-pressure powder diffraction experiments are mainly carried out at synchrotrons by energy-dispersive (Buras *et al.*, 1997*a*,*b*; Baublitz *et al.*, 1981; Brister *et al.*, 1986; Xia *et al.*, 1990; Oehzelt *et al.*, 2002) and angle-dispersive methods (Jephcoat *et al.*, 1992; Nelmes & McMahon, 1994; Fiquet & Andrault, 1999; Crichton & Mezouar, 2005; Mezouar *et al.*, 2005; Hammersley *et al.*, 1996). Angle-dispersive methods are currently preferred to the energy-dispersive method owing to their higher resolution and simpler data processing. However, the energy-dispersive method requires less access for the X-ray beams probing the sample, and hence it is often preferred for studies in the megabar range (hundreds of gigapascals). For high-pressure powder diffraction studies in the laboratory, energy-dispersive methods are still preferred (Tkacz, 1998; Palasyuk & Tkacz, 2007; Palasyuk *et al.*, 2004). The main advantages of experiments at synchrotrons are:

(i) They have a very intense beam compared with traditional sealed X-ray tubes and modern micro-focus sources;
(ii) They offer the possibility of very narrow collimation of the beam, to a diameter of one or a few micrometres;
(iii) Very quick collection of high-quality diffraction data is possible, which is most useful for high-pressure and very high temperature data collections;
(iv) It is possible to measure diffraction data from very small samples, to reduce the dimensions of the DAC chamber and