*International Tables for Crystallography* (2018). Vol. H, Section 2.6.7, pp. 153–154.

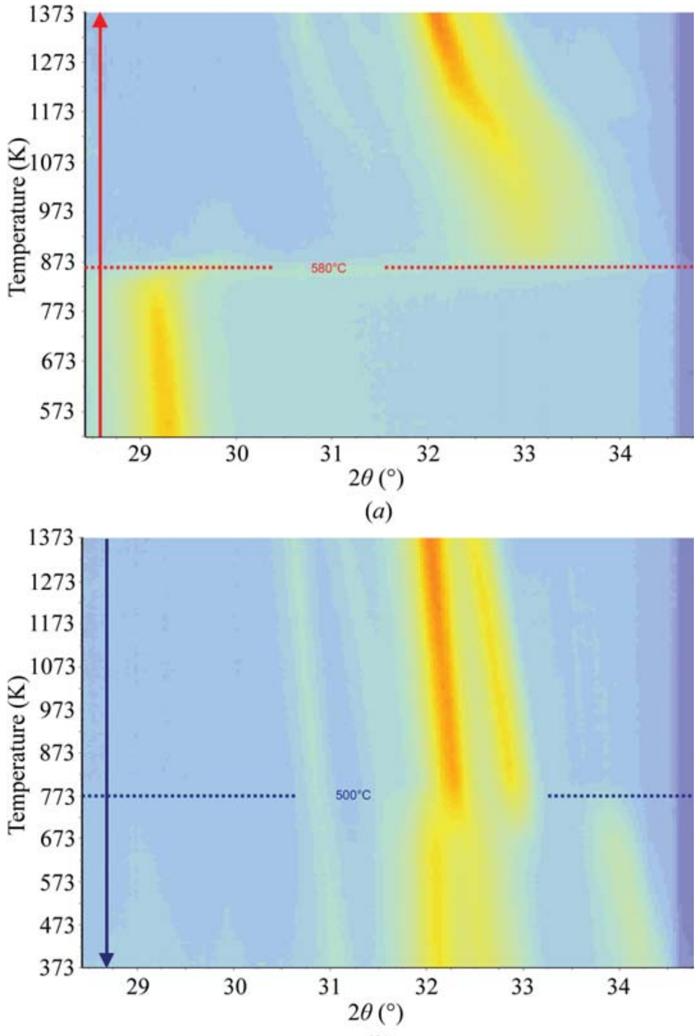

**Figure 2.6.5**
(*a*) Upon heating, $CaCO_3$ (the peak at about 29.3° in $2\theta$) reacts with $SiO_2$ (amorphous); at 853 K the new phase $\alpha'_L$-$Ca_2SiO_4$ is formed (the peak between 33 and 32° in $2\theta$). (*b*) During cooling $\alpha'_L$-$Ca_2SiO_4$ (the two peaks between 33 and 32° in $2\theta$), a different dicalcium silicate polymorph is formed at 773 K; this is $\beta$-$Ca_2SiO_4$.

*et al.*, 2006). Such a furnace can heat a specimen to >2000 K in air. A recent application of this furnace is the characterization of high-temperature phase transitions in $Zr_2P_2O_9$ (Angelkort *et al.*, 2013).

### 2.6.6.4. *Domed hot stage*

Sample stages with an X-ray transparent dome, such as the DHS 1100 domed hot stage manufactured by Anton Paar (Fig. 2.6.6), give another dimension to polycrystalline diffraction. The dome is made of highly transparent graphite. The transmission of the primary and diffracted beams depends on the wavelength used, and for Cu *Kα* radiation 65% is transmitted. The dome can be used on most of the commercially available modern multipurpose X-ray diffractometers with linear or two-dimensional detectors. Mounted on an *XYZ* table or a cradle, these sample stages can be used to study texture, stress/strain and other phase-induced changes in (for example) thin-film layers under non-ambient conditions.

*Example: thin films*. A great deal of research has been devoted to the development of gallium nitride (GaN)-based high-electron-mobility transistor (HEMT) structures (Kelekci *et al.*, 2012; Butté *et al.*, 2007). The structural quality of the layers and their interfaces is critical for the performance of the device (Teke *et al.*, 2009). Detailed knowledge of the effects of further process steps, such as thermal annealing, on these parameters is crucial. X-ray reflectivity can be used for monitoring, among other things, the layer thickness and (interface) roughness (Daillant & Gibaud, 2009). To monitor the annealing process, a wurtzite-type AlInN/AlN/GaN/ heterostructure was mounted on a DHS 1100 domed hot stage; 26 scans were made, each of which lasted 1 h and 59 min at a temperature of 823 K (Fig. 2.6.7). From these reflectivity measurements the activation energy could be calculated and compared with the results from X-ray diffraction data from a nominally identical structure (Grieger *et al.*, 2013). The same value was found for both experiments within 5%, giving valuable information about heterostructure layer and interface stability.

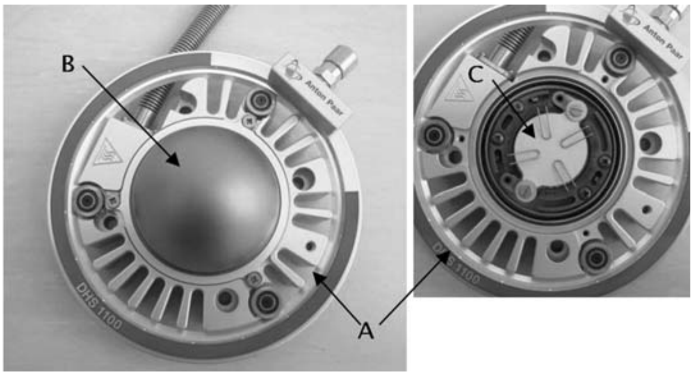

**Figure 2.6.6**
Sample-heating stage (Anton Paar DHS 1100) with lightweight, air-cooled housing (A), dome-shaped X-ray window (B) and heating plate with sample fixation (C).

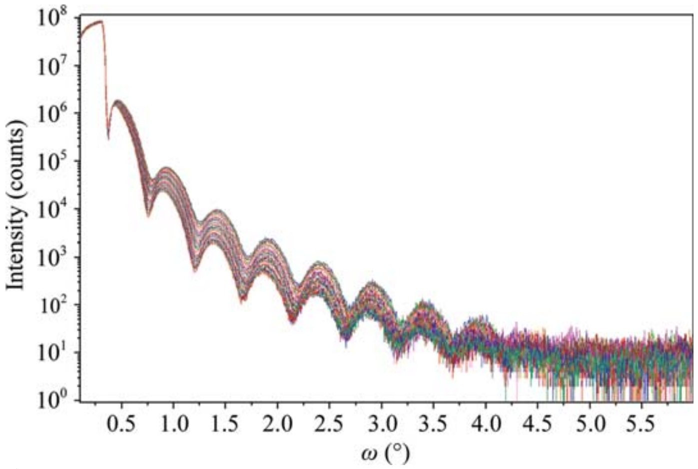

**Figure 2.6.7**
Monitoring of layer thickness and roughness by X-ray reflectivity measurements during annealing at 823 K.

## 2.6.7. Low-temperature sample stages

### 2.6.7.1. *Cryogenic cooling stages/cryostat*

For cryogenic experiments, liquid nitrogen (boiling point 77.4 K at 1 atm, where 1 atm = 101 325 Pa) or liquid helium (boiling point 4.3 K at 1 atm) is required (Weast, 1980). The most common types of chambers for medium-to-low temperatures are chambers with continuous-flow cooling. Here, a continuous flow of liquid nitrogen is provided from a Dewar storage vessel and the cooling process is controlled by a liquid-nitrogen controller. For lower temperatures helium is used. Helium is an expensive gas, and therefore a more economic method is to use a closed-

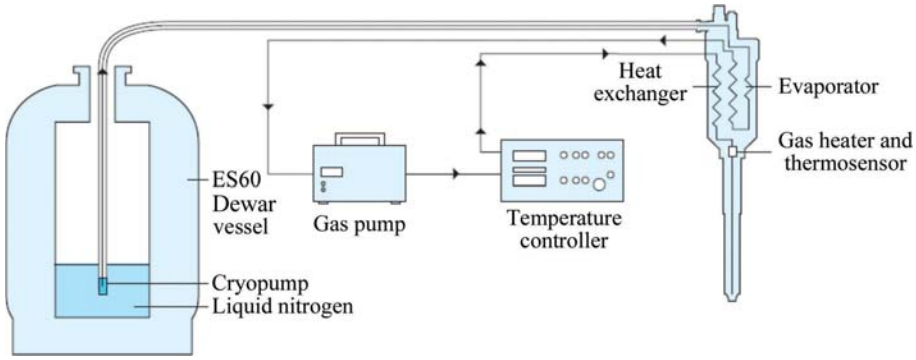

**Figure 2.6.8**
Schematic drawing of the Oxford Cryosystems cryostream setup.

cycle cryostat. This has the disadvantage that it consumes relatively large amounts of energy, but it does not need a continuous flow of helium and is also easy to use. The PheniX cryostat from Oxford Cryosystems is an example of such a chamber, which makes it possible to cool flat-plate powder samples to 20 K in just 35 min and to as low as about 12 K after a further 25 min. Recently, a group using beamline L11 at the Diamond Light Source synchrotron made some modifications to the PheniX cryostat to enable it to perform low-temperature Debye–Scherrer powder diffraction (Potter *et al.*, 2013). The original flat-plate sample holder in the cryostat was changed to a capillary sample holder.

### 2.6.7.2. *Cryogenic cooling stages/cryostream*

The cryostream from Oxford Cryosystems (Cosier & Glazer, 1986) cools the sample in a different way (Fig. 2.6.8). Originally developed for single-crystal X-ray diffraction experiments, it is currently also used to cool/heat capillaries in Debye–Scherrer experiments (Fig. 2.6.9). To prevent atmospheric moisture from freezing on the capillary, the cryogenic nitrogen-gas stream is shrouded in a second dry gas stream. When the two flows are balanced, the outer stream protects the inner nitrogen stream and temperatures as low as 80 K can be reached without ice formation on the capillary. The main advantage of measuring a powder sample in a capillary (transmission geometry) in contrast to flat-plate reflection geometry is minimization of preferred orientation of the sample. Attention must be paid, as in all non-ambient measurements, to temperature gradients in the sample. A short capillary is therefore advisable to minimize the occurrence of a gradient along the capillary.

For absorbing samples, hard radiation must be used to completely penetrate the capillary. Another possibility is to use capillaries with very small diameters, but this is not always very easy and filling them can be time consuming.

*Example: buckminsterfullerene*. An example that demonstrates the capability of the pair distribution function (PDF) method to independently probe the short-range and long-range atomic ordering in materials is $C_{60}$, also known as ($C_{60}$-$I_h$)[5,6]fullerene, fullerene or buckyball (Egami & Billinge, 2003). A buckyball molecule consists of 60 C atoms arranged on the vertices of a soccer-ball-like frame. At room temperature the $C_{60}$ molecules are arranged in a face-centred cubic (f.c.c.) lattice and they assume completely random orientations as a result of thermal energy.

For long-range atomic order to be present, the atoms of the $C_{60}$ molecules must remain in the same crystallographic position, which is not the case at room temperature. The time-averaged structure of the material can be represented as an f.c.c. structure, with space group $Fm\bar{3}m$, of uniform hollow balls with a diameter of about 7.1 Å. On cooling through 260 K a first-order structural phase transition occurs; the random rotation of each $C_{60}$ molecule becomes slower and is now best described as a librational motion (Brown *et al.*, 2005). The phase transition is accompanied by a sudden contraction of the cubic lattice parameter and the long-range order can be described with a primitive cubic lattice (space group $Pa\bar{3}$).

Fig. 2.6.10 shows the atomic PDF at room and low temperature; only the short distances within the balls are clearly observed at room temperature (Reiss *et al.*, 2012). The correlation between atoms of neighbouring molecules cannot be seen, but ball–ball correlations are visible at larger distances. The low-temperature measurement shows similar peaks below 7.1 Å as the ambient measurement, but above 7.1 Å peaks are visible that result from distances from C atoms in one $C_{60}$ molecule to C atoms in another $C_{60}$ molecule.

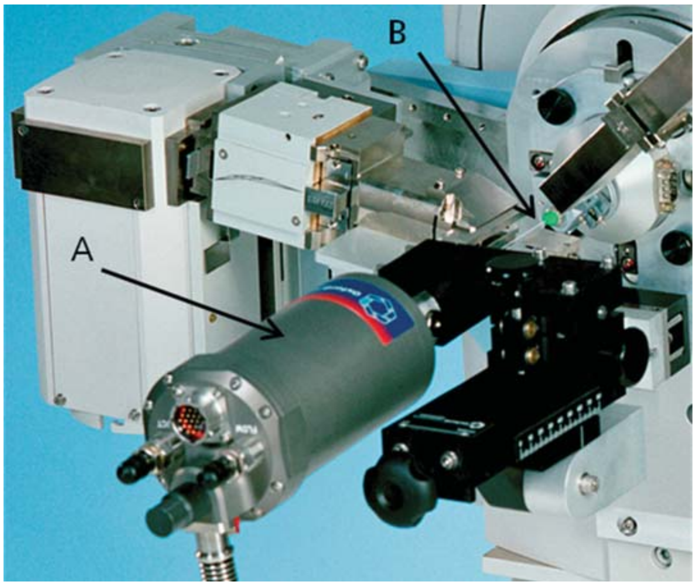

**Figure 2.6.9**
Oxford Cryostream (A) mounted on a PANalytical diffractometer for cooling a capillary (B).

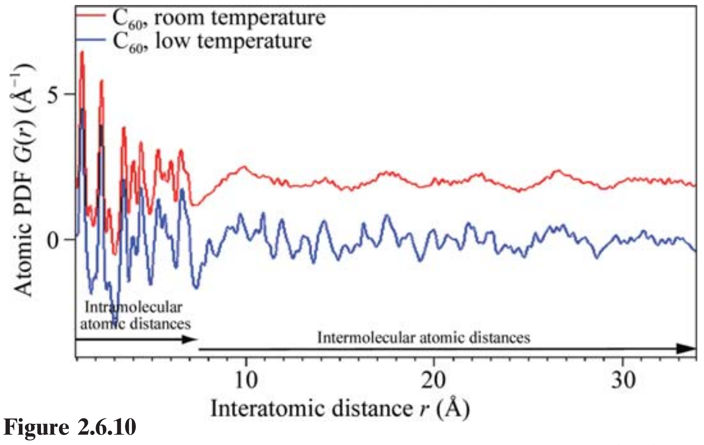

**Figure 2.6.10**
Atomic pair distribution function of $C_{60}$ at room temperature (red) and at 100 K (blue).