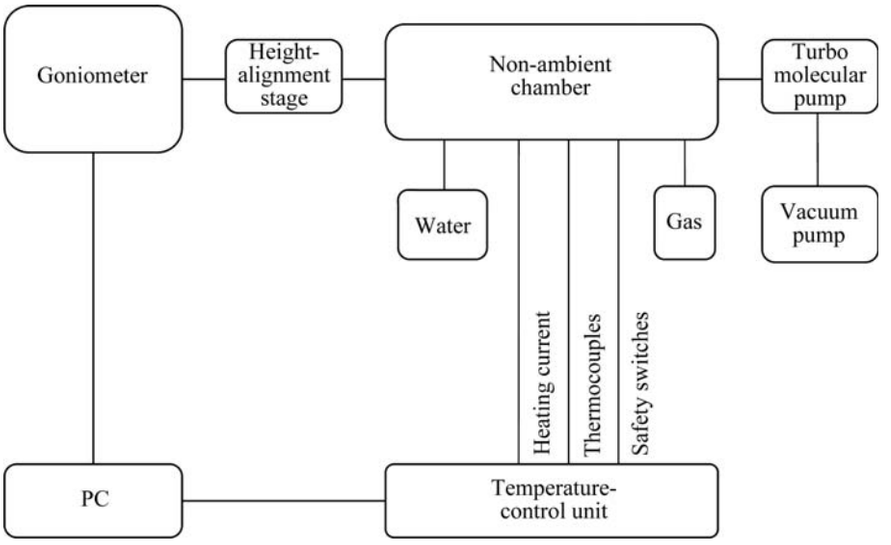

Figure 2.6.1
Typical hardware setup for a non-ambient X-ray diffraction experiment as described in Section 2.6.4; non-ambient chamber, temperature/process-control unit, vacuum/gas equipment, cooling water and goniometer with height-alignment stage connected to a PC.

the value, to send it to the control PC and to control the power for heating/cooling. In addition to controlling the sample conditions, the temperature-control unit (TCU) usually monitors other instrument components such as the cooling of the sample-stage housing and safety devices.

2.6.4.3. *Vacuum equipment, gas supply*

High-temperature X-ray diffraction measurements are often performed in vacuum or in an inert-gas atmosphere to avoid oxidation of the specimen or the sample support. Systems with a rotary pump typically achieve a vacuum of 10^{-2} mbar (where 1 mbar = 100 Pa); when adding a turbo molecular pump to the rotary pump, a vacuum of about 10^{-4} mbar can be reached. A low vacuum or a completely dry gas atmosphere, *e.g.* pure nitrogen (or helium, which has the advantage of a lower background in the diffraction patterns), is also needed for low-temperature experiments to avoid icing problems. Best practice is not to vent the flow of inert gas into the diffractometer enclosure or the laboratory atmosphere, but into the ventilation system (fume hood). Some local safety authorities may require such venting.

2.6.4.4. *Water cooling*

The housing of the sample stage must be kept close to room temperature to avoid heat transfer to the diffractometer and to ensure user safety. In most cases, water is used for this purpose, and the cooling water can be shared with the diffractometer.

2.6.4.5. *Diffractometer and height-compensation mechanism*

The non-ambient chamber has to be interfaced to the goniometer. Interfaces are available without and with a height-compensation mechanism; the latter can be manual or motorized.

When heating/cooling a specimen in an environmental heater, sample displacement is virtually unavoidable, mainly owing to the thermal expansion/contraction of the sample holder. It is possible to correct the temperature-dependent change of the sample position with a height-compensation mechanism (motorized z stage) or to model the displacement in the refinement software. When using a z stage that is controlled *via* software, the shifts in peak positions are only caused by the thermal lattice expansion/contraction of the sample under study. If no such mechanism is available, a parallel X-ray beam (which is not sensitive to sample displacement) can be used, but the resolution may be worse compared with measurements in para-focusing Bragg–Brentano geometry, and granularity may be significant. For strip heaters the displacement of the sample due to the strip is not so pronounced. If a peak of the material of the strip is visible in the diffractogram this can be used as a reference for height compensation if the thermal expansion of the strip material is also taken into account.

2.6.5. Specimen properties

In designing a non-ambient experiment the specimen properties must be taken into account; the holder material should not react with the sample. For flat sample geometry it is preferable that the specimen completely absorbs the X-ray beam. If the specimen is highly transparent, one can either use a thin specimen on a zero-background sample holder or use a capillary. For capillary measurements the X-ray beam must penetrate the capillary completely; if this is not the case, higher energy X-rays (such as Mo or Ag) can be used (Section 2.6.7.2). Every sample is unique, and a suitable solution must be devised.

2.6.6. High-temperature sample stages

A typical laboratory non-ambient setup consists of a non-ambient sample stage, often called a temperature chamber. The sample stage is mounted on a goniometer, preferably in a θ–θ configuration (Fig. 2.6.2). In this case the sample stays horizontal and there is no need to fear melting of the sample with the possibility of it dripping off/out of the sample holder.

A temperature-control unit, vacuum equipment, gas supply and water cooling have to be added to the system before it can be operational.

Figure 2.6.2
An Anton Paar HTK 1200N high-temperature oven chamber on a PANalytical Empyrean system equipped with a PIXcel3D detector.

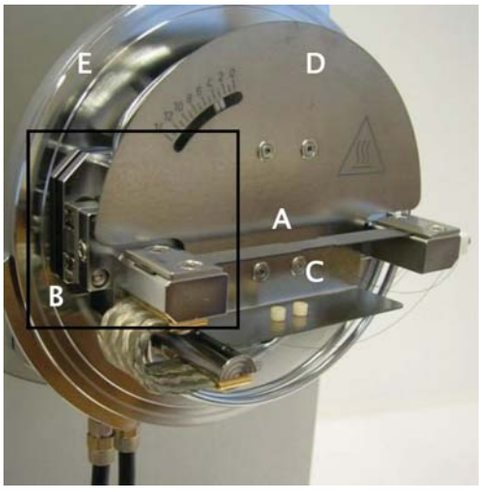

Figure 2.6.3
The interior of a typical strip-heater sample stage (Anton Paar HTK 2000N) with heating strip (A), mechanics to compensate strip expansion (B), thermocouple wires (C), heat shield (D) and water-cooled base plate (E).

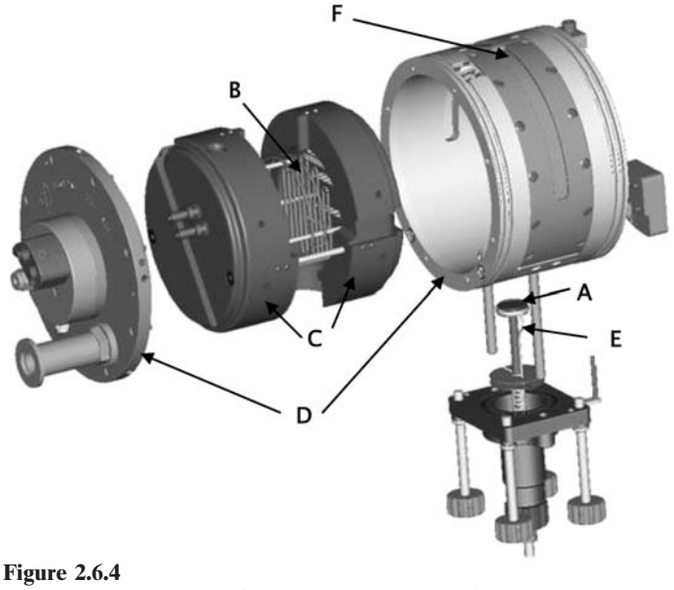

Figure 2.6.4
A typical furnace heater (Anton Paar HTK 1200N) consisting of sample holder (A), heater (B), thermal insulation (C), water-cooled housing (D), thermocouple (E) and X-ray window (F).

2.6.6.1. *Direct heating: strip heaters*

The highest temperatures can be reached with so-called strip heaters (Fig. 2.6.3). Commercial stages that can heat to up to 2573 K are available. Sample heating is performed with a high-current resistance heater. The specimen is placed directly on the strip or in a crucible on the strip. Typical strip materials are platinum (which can be heated in air to up to 1873 K) and tungsten (maximum temperature 2673 K), which requires a vacuum or an inert-gas atmosphere. Less common strip materials which have to be operated in vacuum or in an inert-gas atmosphere are graphite (maximum 1773 K), molybdenum (maximum 2173 K) and tantalum (maximum 2873 K). In addition to very high temperatures, these heaters offer very fast heating and cooling. The HTK 2000N from Anton Paar, for example, can reach up to 2573 K in 3 min. The temperature is measured with a thermocouple, which is usually welded to the heating strip. The main disadvantages of strip heaters are possible chemical reactions between the heating strip and sample, difficulties in measuring the sample temperature accurately and difficult sample preparation. Often, it is not the starting material that reacts but the products that form during heating. Another strip material can be chosen if reactions are known to occur. Inaccurate temperature measurements can be minimized by placing a second temperature sensor on top of the sample.

2.6.6.2. *Environmental heating: the oven*

The second common type of sample stage for high temperatures are oven heaters, also called environmental heaters (Fig. 2.6.4). An electrically heated wire is formed into a cage, which is surrounded with thermal insulation. The heater and insulation form a furnace which almost completely surrounds the sample, creating a very uniform temperature distribution on the inside and minimizing the heat transfer to the housing of the sample stage. Heat is transferred *via* radiation and convection to the sample. The sample is placed on a sample holder in the centre of the furnace, without direct contact with the heater. The sample temperature is measured with a thermocouple located close to the sample, providing accurate measurement of the sample temperature. In addition, it is possible to oscillate the sample to improve the data quality (by reducing granularity), and the user can measure (polycrystalline) solid samples as well as powder samples. In most cases, a long sample holder must be used to place the sample in the centre of the furnace. The thermal expansion of the sample holder while heating must be compensated for by z adjustment to avoid sample displacement (see Section 2.6.4.5). Windows for letting the X-rays enter and leave the chamber should preferably have no influence on the diffraction process. Different materials are available depending on the requirements of the non-ambient measurements. Kapton is the most commonly used window material, followed by graphite, aluminum and beryllium. Environmental heating is also one of two methods used to heat capillaries for X-ray diffraction with transmission geometry. The other option is heating the capillary with a gas flow.

Example: Cement. Cement consists of different calcium silicates (see Chapter 7.12). The exact phases that are present and their abundances determine important physical properties of a cement such as its strength. One of the phases in cement, belite (Ca_2SiO_4), exhibits rapid phase transitions. Fast transitions require good time resolution to detect short-lived intermediate phases and to follow the kinetics of fast phase transformations. An Anton Paar HTK 1200N oven was used for this experiment together with a PIXcel3D detector in static mode using a radius-reduction interface to allow snapshots to be taken over a 2θ range of 6° within a time frame of less than 1 min. Bragg–Brentano geometry was used to achieve a good resolution in 2θ and, to compensate for thermal expansion of the sample holder, an automatic height compensation was applied. On heating $CaCO_3$ with amorphous SiO_2 at 10 K min^{-1}, a solid-state reaction was seen at 853 K; α'_L-Ca_2SiO_4 is formed together with CO_2 (Fig. 2.6.5*a*). Dicalcium silicate exists in five polymorphic forms (Odler, 2000). During cooling, one of the other polymorphs of dicalcium silicate, β-Ca_2SiO_4, is formed, which has a different crystal structure and optical properties (Fig. 2.6.5*b*).

2.6.6.3. *Environmental heating: lamp furnace*

Another approach to designing an environmental chamber is the quadrupole lamp furnace developed by W. M. Kriven (Sarin

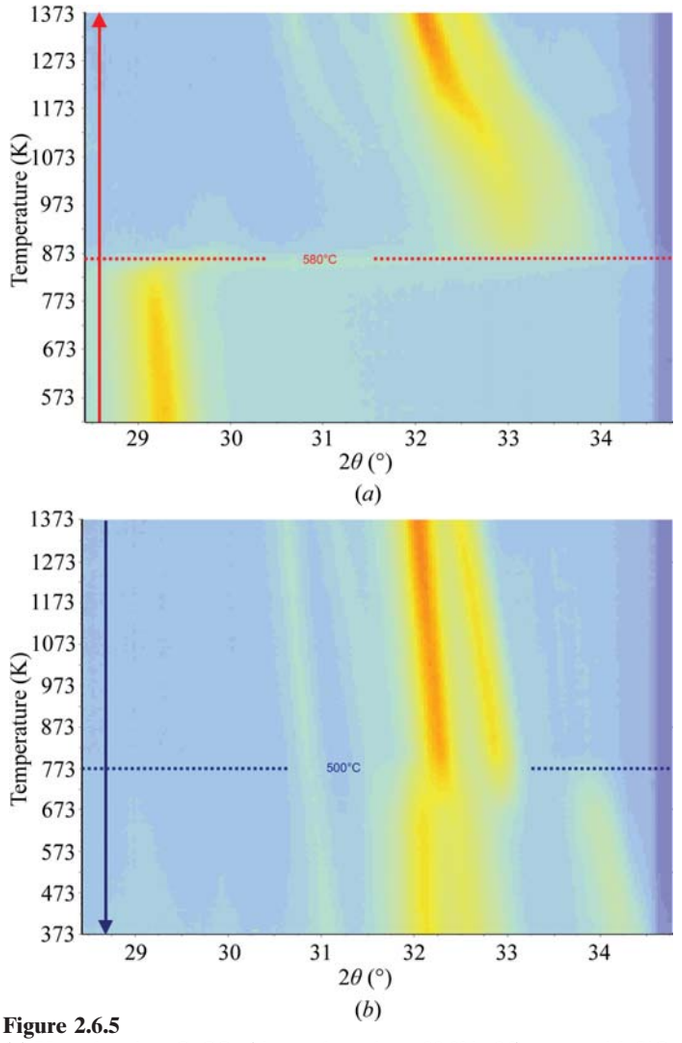

Figure 2.6.5
(*a*) Upon heating, $CaCO_3$ (the peak at about 29.3° in 2θ) reacts with SiO_2 (amorphous); at 853 K the new phase α'_L-Ca_2SiO_4 is formed (the peak between 33 and 32° in 2θ). (*b*) During cooling α'_L-Ca_2SiO_4 (the two peaks between 33 and 32° in 2θ), a different dicalcium silicate polymorph is formed at 773 K; this is β-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 $K\alpha$ radiation 65% is transmitted. The dome can be used on most of the commercially available modern multi-purpose 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

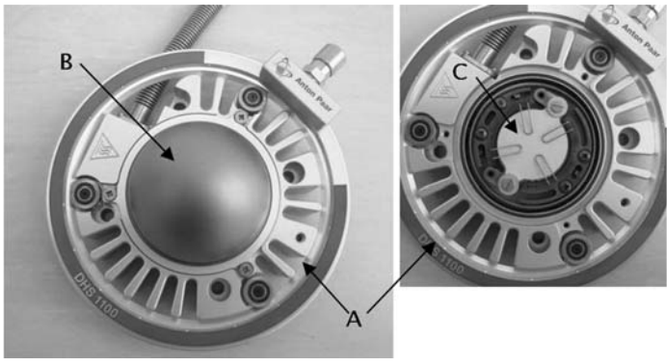

Figure 2.6.6
Sample-heating stage (Anton Paar DHS 1100) with lightweight, air-cooled housing (A), dome-shaped X-ray window (B) and heating plate with sample fixation (C).

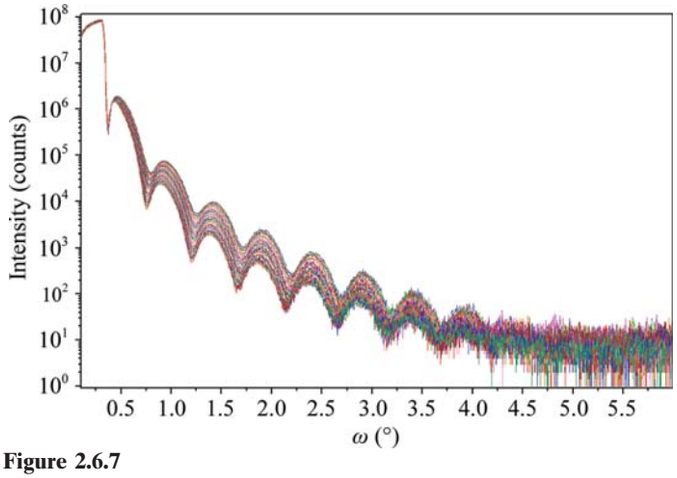

Figure 2.6.7
Monitoring of layer thickness and roughness by X-ray reflectivity measurements during annealing at 823 K.

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.

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-