2.6. Non-ambient-temperature powder diffraction

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2.6.1. Introduction

X-ray powder diffraction (XRPD) is a powerful tool for the *in situ* investigation of the evolution of a specimen during a non-ambient experiment and for studying structural changes such as lattice expansions and contractions, phase transformations, phase composition, material stability, and alterations in crystallite size. X-rays (and neutrons) are more penetrating than other analytical probes and thus are ideally suited to carrying out *in situ* studies. Many (if not most) polycrystalline materials undergo transformations under non-ambient conditions. If the aim of an experiment is to discover structure–property correlations, it is crucial that the correct structure be used; thus *in situ* diffraction experiments are almost mandatory. This chapter highlights the best ways to perform non-ambient experiments, describing the different equipment for slightly and heavily absorbing materials and the corresponding optical pathways.

The focus is on commercially available equipment for laboratory diffractometers and not on special equipment built at synchrotrons and neutron facilities.

2.6.2. *In situ* powder diffraction

The Latin phrase '*in situ*' literally means 'in position', but it is used in many contexts. In the field of X-ray powder diffraction there is no strict definition of this phrase. If the phrase is taken literally, all non-ambient experiments are *in situ*; the material stays 'in position' during the non-ambient experiment. The environment changes while transforming the sample by outside influences (Norby & Schwarz, 2008). Temperature changes give rise to many processes that can be monitored with or without different gas environments. The main processes that are monitored are the formation of new compounds, phase transformations, and structural changes such as lattice expansions and contractions. Increasingly, surface-layer properties such as stress and texture are studied. The characterization of variations in the crystallite size of nanomaterials is a more recent application.

In situ X-ray diffraction is still a growing research field owing to the introduction of line detectors and area detectors (see Chapter 2.5). These make it possible to measure a large part of the diffraction pattern at once, making the scanning time much shorter compared with a point detector. This speed significantly improves the data quality and reduces the risk of collecting uninterpretable data because of changes in the material under study during the measurement. Another advantage of these detectors is that static detector measurements can be performed, making time-resolved and/or temperature-resolved studies possible.

2.6.3. Processes of interest

Many applications of XRPD contribute to industrial and environmental process development. Some typical application areas are heat treatment and annealing, which are frequently used in the production of alloys, ceramics and polymers; the annealing process affects the strength and/or hardness of materials through microstructural changes. Calcination and sintering are used in the fields of catalysts, building materials and zeolites. Dehydration processes in pharmaceuticals are studied to determine the influence of local environment on the microstructure of drugs and how time affects the availability or preservation of the active pharmaceutical ingredient. These very important topics can be investigated in the case of hydration or dehydration with a humidity chamber. Such chambers control the relative humidity at the same time as the temperature, and are commercially available. Another important topic for the pharmaceutical industry (see Chapter 7.5) is the polymorphic transformations that occur under near- and non-ambient conditions. In nearly all fields from alloys to drugs, from building materials to catalysts, and from nanomaterials to single-crystal materials, structure and phase changes are studied during the operation of processes. Increasingly, non-ambient studies also include other parameters besides temperature and gas environment, for example pressure and humidity. Processes such as the charging and discharging of batteries (see Chapter 7.3) can also be seen as a non-ambient or perhaps better as an '*in operando*' process.

2.6.4. General system setup of non-ambient chambers

2.6.4.1. *Sample stage*

The main requirement for a good non-ambient chamber is that the specimen is cooled/heated homogeneously at a controllable rate. The temperature of the goniometer and other parts of the diffractometer should not be affected while operating the temperature stage. Different sample-stage designs are possible: direct heating/cooling *via* a strip or plate, or surround heating/cooling with an oven or gas convection for a capillary. The advantage of an environmental heater/cooler is the good temperature homogeneity, as there is heat transfer from all sides by radiation and gas convection around the sample or capillary. In contrast, when using a direct heater such as a heating/cooling strip or plate only one-side heat transfer to the sample is possible through the contact surface. An advantage of direct heaters/coolers is the ability to achieve very high and low temperatures and rapid temperature changes. Other differences are the more accurate sample-temperature measurement in an oven compared with a strip heater, where temperature gradients can be present in the strip and the sample attached to the strip heater. For high-temperature measurements with capillaries, the best choice is fused silica ('quartz') glass with a melting point of ~1973 K; for low-temperature measurements borosilicate glass capillaries are used. A typical hardware setup for a non-ambient X-ray diffraction experiment is shown in Fig. 2.6.1.

2.6.4.2. *Temperature-control unit, process controller*

To control the temperature, a temperature controller with an integrated process controller is needed. For controlled heating/cooling it is necessary to continuously measure the actual temperature and compare it with the set temperature. Often, a standard industrial process controller is used to convert the signal from the temperature sensor into a temperature value, to display
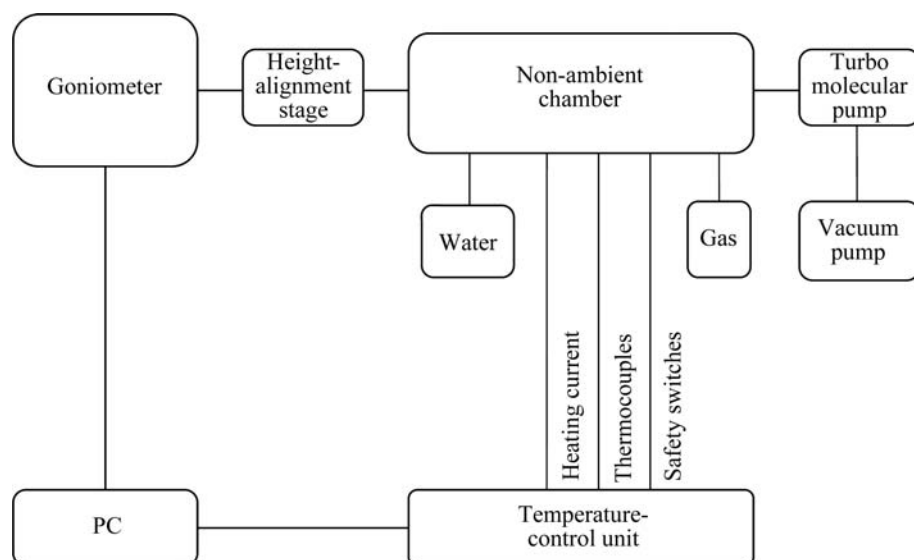
Figure 2.6.1
Typical hardware setup for a non-ambient X-ray diffraction experiment as described in Section 2.6.4; non-ambient chamber, temperature/process-control unit, vacuum/gas equipment, cooling water and goniometer with height-alignment stage connected to a PC.

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.
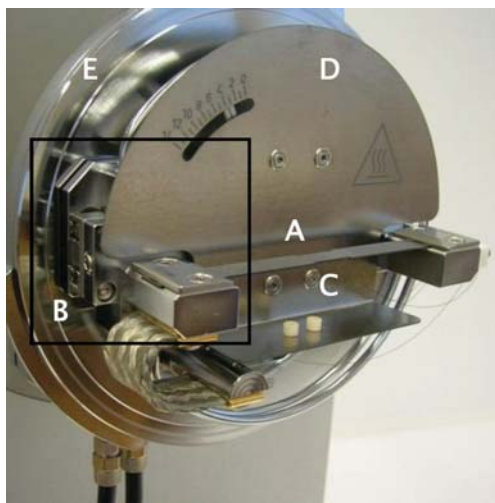
2. INSTRUMENTATION AND SAMPLE PREPARATION

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).
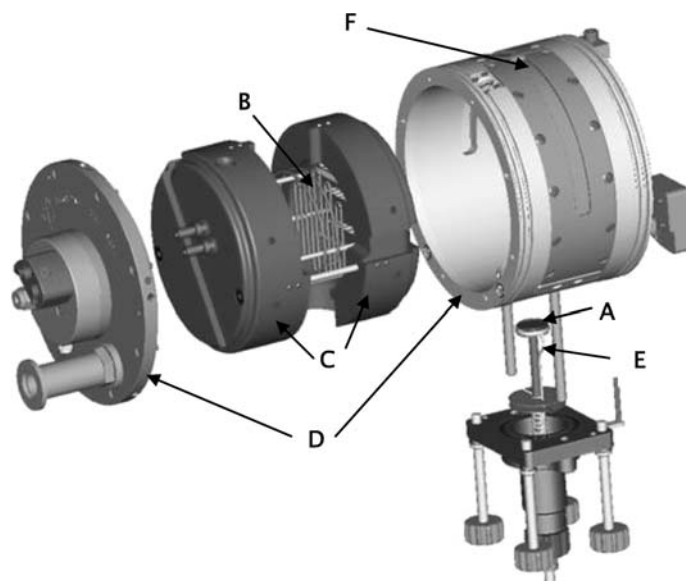

Figure 2.6.4
A typical furnace heater (Anton Paar HTK 1200N) consisting of sample holder (A), heater (B), thermal insulation (C), water-cooled housing (D), thermocouple (E) and X-ray window (F).

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. 2.6.5a). 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. 2.6.5b).

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
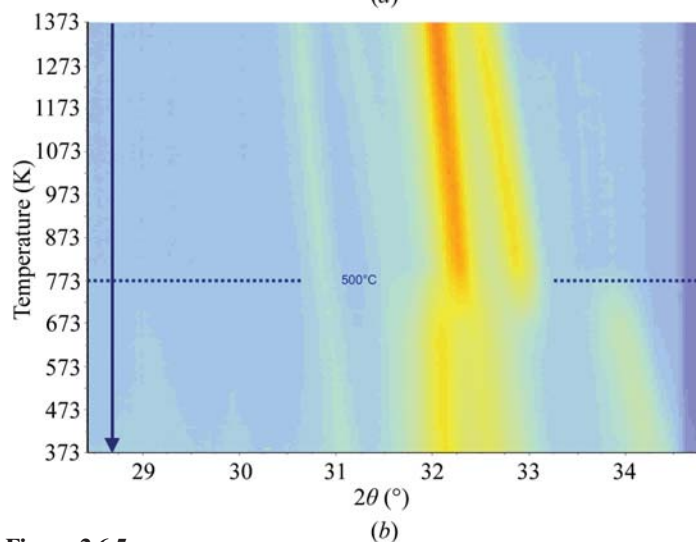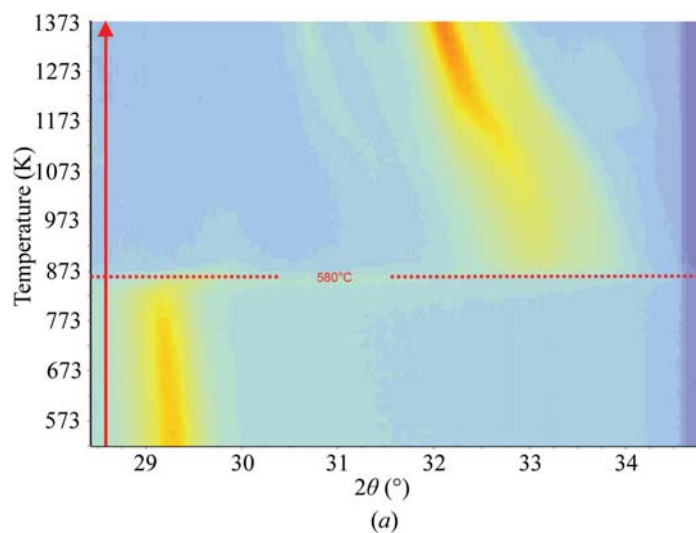
Figure 2.6.5
(*a*) Upon heating, CaCO$_3$ (the peak at about 29.3° in 2θ) reacts with SiO$_2$ (amorphous); at 853 K the new phase α'_L-Ca$_2$SiO$_4$ is formed (the peak between 33 and 32° in 2θ). (*b*) During cooling α'_L-Ca$_2$SiO$_4$ (the two peaks between 33 and 32° in 2θ), a different dicalcium silicate polymorph is formed at 773 K; this is β-Ca$_2$SiO$_4$.

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$_2$P$_2$O$_9$ (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
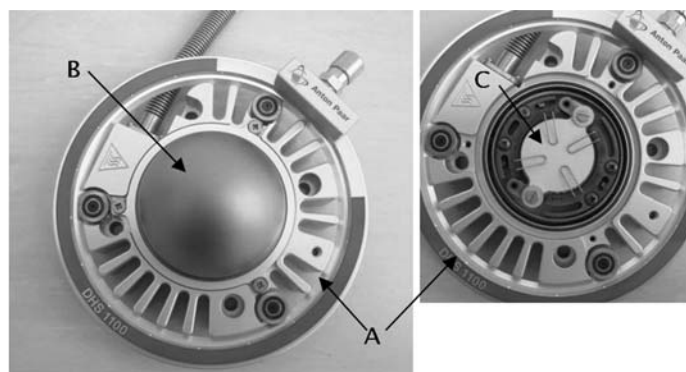

Figure 2.6.6
Sample-heating stage (Anton Paar DHS 1100) with lightweight, air-cooled housing (A), dome-shaped X-ray window (B) and heating plate with sample fixation (C).
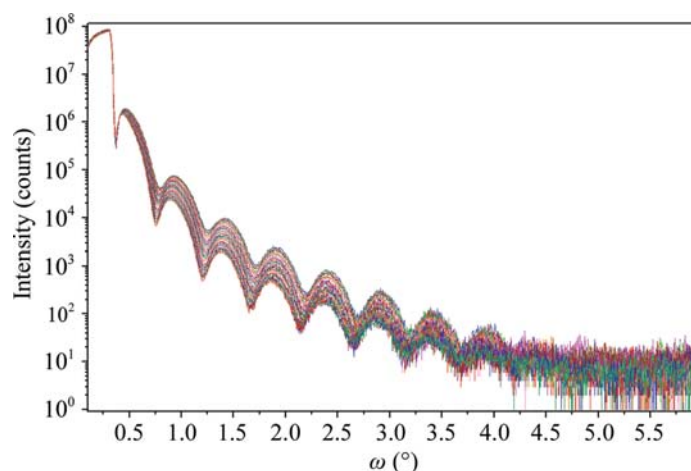

Figure 2.6.7
Monitoring of layer thickness and roughness by X-ray reflectivity measurements during annealing at 823 K.

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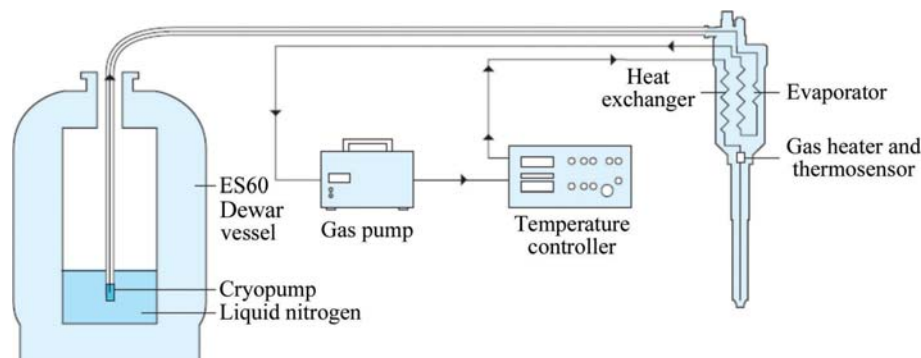
Figure 2.6.8
Schematic drawing of the Oxford Cryosystems cryostream setup.

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 forma-
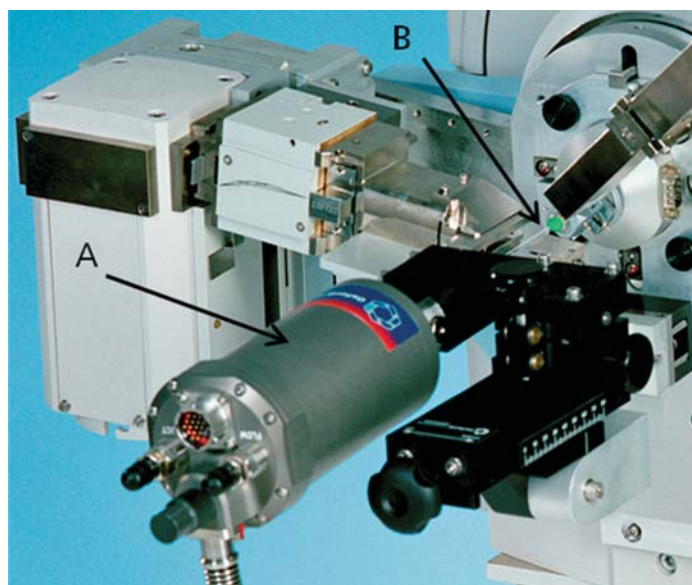

Figure 2.6.9
Oxford Cryostream (A) mounted on a PANalytical diffractometer for cooling a capillary (B).

tion 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 $(C_{60}\text{-}I_h)$[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.
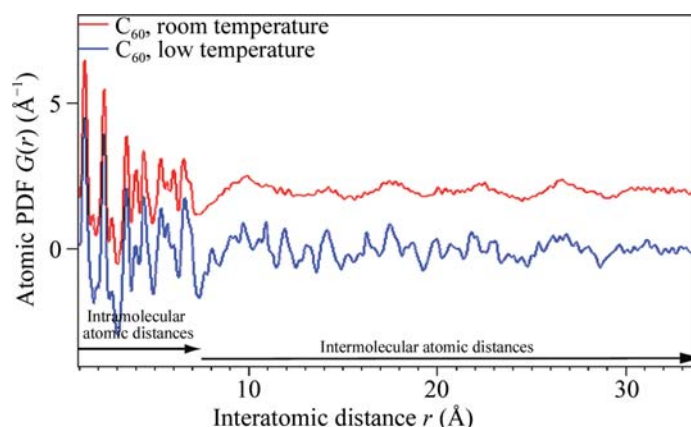

Figure 2.6.10
Atomic pair distribution function of C_{60} at room temperature (red) and at 100 K (blue).

2.6.8. Temperature accuracy

The accuracy of the temperature measurement of a non-ambient device has to be determined before starting a non-ambient experiment. At present no certified temperature standards for X-ray powder diffraction are available, only commonly used reference materials. A list of these materials can be found at https://www.xrayforum.co.uk/ and https://bl831.als.lbl.gov/~jamesh/pickup/Snell_SG_change_table.pdf.

A common method for validation of a non-ambient chamber is by determining the thermal expansion coefficient of a reference material as a function of temperature. Another is to determine the transition temperature of well known phase transformations. A third method is the so-called 'differential thermal expansion' method (Drews, 2001). This method utilizes the relative thermal expansion of two diffraction peaks. These peaks can be from the same or different reference material(s) but must be found in a narrow angular range and have different thermal expansion behaviour. Using only the relative separations of the peaks that are closely spaced eliminates the need for full pattern refinement to take into account geometrical aberrations and makes this method fast.

2.6.9. Future

A whole new field of non-ambient experiments has opened up with the study of new applications such as non-ambient PDF (see Section 2.6.7.2) and non-ambient SAXS measurements. And what happens in the nano world when large-scale models no longer hold at ambient and non-ambient temperatures? The future will tell; non-ambient diffraction/scattering experiments are more relevant now than ever before.

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