Zachariasen (1945) described an extinction correction (model) including terms relating to crystallite size, wavelength, structure factor and scattering angle. Extinction effects will be apparent with large crystallites and long wavelengths. Extinction effects are also greater for the more intense (low-angle) reflections, so extinction mimics the effects of small displacement parameters. In a single-phase system, unexpectedly low or even negative displacement parameters may be the only sign that extinction effects are present. In a multiphase system the effects of extinction will reduce the apparent phase fraction of the affected phase with respect to the rest of the sample. In fact, studying extinction experimentally is often done by using its effects on quantitative phase analysis to untangle the different effects (Cline & Snyder, 1987). The frequently high quality of natural quartz makes the quantitative phase analysis of mineral samples the most likely scenario for the appearance of extinction in a practical laboratory setting.

The wide range of wavelengths and wide range of $(\sin\theta)/\lambda$ used in time-of-flight (TOF) neutron diffraction makes extinction effects particularly pronounced. Consequently TOF data often require the application of an extinction correction (Sabine *et al.*, 1988). Constant-wavelength neutron diffraction frequently uses longer wavelengths than normally used in the laboratory or synchrotron beamlines, so the user must be aware of possible problems.

Despite the danger of 'message fatigue', the dependence of primary extinction on crystallite size adds yet another reason to reduce the crystallite sizes to the order of 1 µm or so. Theoretically, single-crystal silicon will exhibit extinction with copper radiation with crystallite sizes of 5 µm.

2.10.1.4. *Holders*

2.10.1.4.1. *Reflection sample holders*

In a laboratory setting these are the most common type of holders – normally for use in a Bragg–Brentano instrument. A wide variety of sample holders for different applications are available. Several different holders and techniques will be described, but there are some issues common to all holders in reflection geometry, particularly with Bragg-–Brentano geometry.

In Bragg–Brentano parafocusing geometry care should be taken that the surface of the sample is flat. If the surface is not flat the parafocusing condition is violated and will degrade the peak resolution and positions; in addition, surface roughness can affect the intensities. Where there is a cavity it seems straightforward to make sure that the sample surface is level with the top surface of the holder. The peak positions obtained in Bragg–Brentano geometry are very sensitive to specimen displacement; a vertical displacement of 20 µm in a typical diffractometer will shift the peaks by approximately 0.01° 2θ. The derivation of the equation for the effect of displacement on peak position is given in Fig. 2.10.31. The minus sign in the equation reflects the convention that the displacement is positive if it increases the radius of the diffracting circle, *i.e.* the sample is too low. Front-packed specimens are almost always too high, so the analyst needs to refine his/her technique to minimize the displacement errors.

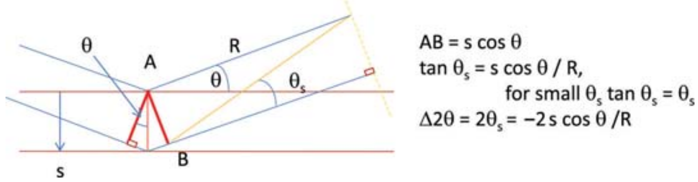

Figure 2.10.31
Derivation of the equation relating peak displacement to sample displacement (s) in parafocusing geometry. R is the goniometer radius.

Figure 2.10.32
A home-made top-loading zero-background silicon holder with a 0.5 mm deep cavity.

The sensitivity to specimen displacement is such that even dirt between the reference surface of the sample stage and the holder can produce a detectable peak shift. Dust accumulation inside a powder diffractometer is almost inevitable, so occasionally cleaning these surfaces is recommended.

Parallel-beam-geometry diffractometers have become popular in many laboratories because some of these problems are avoided. Although there are often some disadvantages in terms of peak resolution and grain sampling, they allow more flexibility in the mounting of specimens. For instance, rough sample surfaces and displacements do not cause the aberrations that are apparent in data from conventional parafocusing diffractometers when the same samples are analysed with a parallel-beam system.

Many different types of holders for reflection geometry are available commercially from the instrument vendors, but often home-made holders can be equally effective and customized for specific tasks. Most common are the different types of top-loading sample holders made from plastic or metal, often with a cavity to hold the sample. Commonly the cavities are larger or smaller than those offered by the vendors. The cavity may include some form of zero-background plate such as specially cut single-crystal silicon (Fig. 2.10.32) or quartz, although this does add a significant cost. Some quartz plates may exhibit forbidden reflections or contain inclusions, so they should be tested before use in a sample spinner.

In addition to the standard holders, more specialized holders may be bought or built, or indeed fabricated using a 3D printer. These include holders for air-sensitive samples (Fig. 2.10.33), back-loading (Fig. 2.10.34) and side-loading holders, holders for filter papers, clay samples *etc*. Any laboratory with a competent workshop can construct a wide variety of holders, including those for complex *in situ* work, which is discussed in Chapter 2.9. One common theme is that any material in the X-ray beam path must be kept to a minimum to reduce attenuation. Ideally any such material (such as the polymer dome of the air-sensitive holder shown in Fig. 2.10.33) should be as far away from the diffracting plane as possible. A secondary monochromator can be effective in stopping the parasitic scattering from reaching the detector, but with a PSD there is greater reliance on good design to reduce it as much as possible. A common approach with home-designed and -constructed sample holders for air- or moisture-sensitive samples is to cover the sample with a thin Kapton or Mylar film attached with a bead of silicone grease.