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.

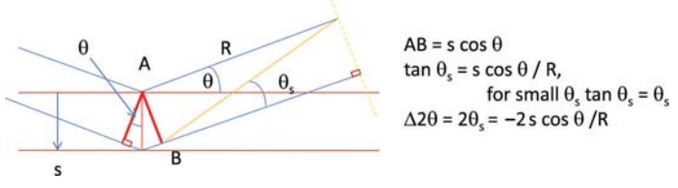

Figure 2.10.31
Derivation of the equation relating peak displacement to sample displacement (s) in parafocusing geometry. R is the goniometer radius.

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.

Figure 2.10.33
Commercial holder for air-sensitive samples. This particular holder for small samples has a flat silicon zero-background plate and a polymer dome which screws down against a rubber o-ring seal.

One of the most common questions asked by users of laboratory instruments is how to deal with small sample sizes. In an ideal world, a specialist microdiffraction system or capillary geometry could be used, but many laboratories do not have access to such equipment. How problematic such samples can be depends to some extent on the mass absorption coefficient of the sample. Conventional powder diffraction data relies on having a sample with an 'infinite sample depth'. However, that depth can be very small for samples with very high absorption coefficients. In those cases, spreading the sample in a very thin layer can still yield reasonable relative intensities across a large range of 2θ angles. With low-absorbing samples such as organics the relative intensities will drop off at higher angles as the sample is no longer

Figure 2.10.34
Filling a commercial back-loading sample holder. The holder is held against a base surface (sandpaper in this case) while filling, the back is replaced and then the holder is flipped over to reveal the sample surface once the clips are removed.

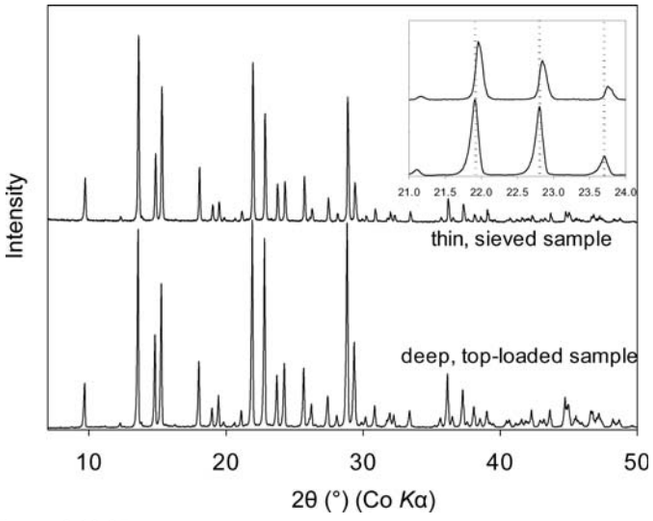

Figure 2.10.35
Data from powdered sucrose on a Bragg–Brentano instrument, with the peak intensities normalized to the first reflection. The thin sample was prepared by sieving onto a low-background silicon plate made slightly tacky using hairspray. The inset shows that there is a slight peak shift between the two data sets as well as the predicted decay in relative intensities with the thin sample with 2θ angle.

'infinitely thick', as shown in Fig. 2.10.35. However, the peak positions will be more accurate than with deeper samples because of the lack of transparency effects in thin samples. Consequently, it is not uncommon to obtain two data sets from such samples: from a thin sample to obtain good peak positions, and from a deep one to obtain better relative intensities. The details of sample penetration are given in Chapter 5.4.

Most modern holders are circular and the specimen is often loaded into a round cavity. As the beam 'footprint' is rectangular, this is not the most efficient use of the material, as a significant portion will always remain outside the beam. Prior to the introduction of sample spinners, square and rectangular cavities were quite common. It is good practice to know the footprint of the beam at various diffraction angles by observing the illuminated area of a fluorescent specimen. Should the material be in particularly short supply and sample spinning is not absolutely necessary, the powder may be mounted in the minimum rectangular shape to be illuminated by the incident beam. Such an approach may be combined with the use of motorized divergence slits to maintain a constant beam length on the sample. Although most analysis software assumes constant divergence slits, the correction is well known and implemented in most commercial software.

In order to avoid background from the sample holder, thin specimens are usually mounted on flat zero-background plates. It is useful to have the surface of the plate lower than the reference surface (50 μm is a common value) to minimize specimen displacement effects. In practical terms, thin samples are historically referred to as smear mounts. Slurry mounting using ethanol or acetone often yields a self-adhesive specimen, but it is tricky to obtain the correct slurry rheology to produce a non-lumpy, thin and even layer across the surface; surface roughness is often apparent in the pattern. Loose, friable samples may be problematic with spinning specimens or the tilting specimens in θ–2θ geometry. A number of materials have been used over the years to adhere thin powder samples to flat plates; common ones are thin smears of Vaseline or grease, but analysts often have their own favourites. The particular material used to stick the sample to the surface is often the result of testing a large number

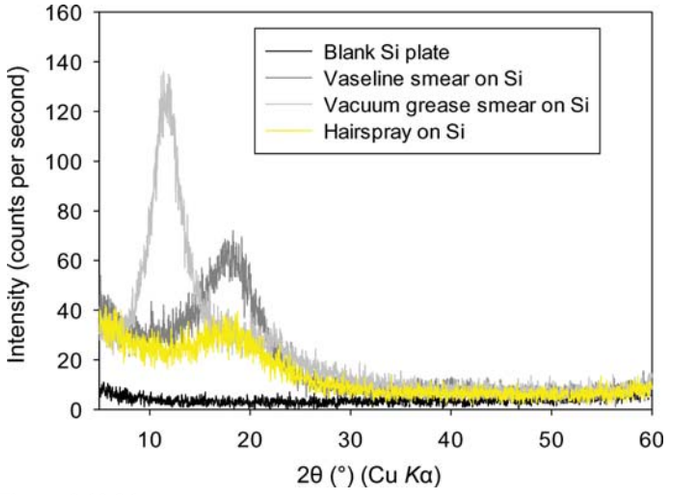

Figure 2.10.36
Diffraction pattern from a silicon-wafer zero-background holder, smears of Vaseline and Corning high-vacuum grease, and the surface treated with hairspray.

of options to find the one with the lowest background and fewest non-Bragg reflections. An unusual alternative is hairspray, which produces a tacky surface when applied correctly whilst having a minimal effect on the resulting diffraction pattern. The medium chosen may also depend on whether the sample must be recovered intact, as contamination with grease might not be acceptable. The effect on the background of different adhesion materials can be seen in Fig. 2.10.36. The Vaseline and vacuum grease smears add broad reflections at approx. 19 and 11° 2θ, respectively, with Cu $K\alpha$ radiation. Where data collection starts above the main portion of the peak the effect may be hardly noticeable, but could be problematic when starting at low 2θ angles. Such broad patterns are straightforward to model with a Debye (diffuse scattering) function, and it is not necessary to subtract them from the raw data.

Should the instrument have parallel-beam geometry, an alternative approach is to use a fixed incident-beam angle, more commonly known as grazing-incidence geometry. In this way the volume of sample illuminated is constant with angle, so in the absence of secondary diffractometer optics the relative intensities will match those expected with conventional geometry. An unfortunate effect of conventional grazing-incidence geometry with long slits is that the peak widths degrade significantly at lower incident angles (Toraya & Yoshino, 1994). It is possible to model the peak broadening in a Rietveld refinement (Rowles & Madsen, 2010) but it is not straightforward. Use of an appropriate secondary optic can avoid the peak-broadening problem but introduces a complex, geometry-dependent intensity correction (Toraya *et al.*, 1993).

2.10.1.4.2. *Transmission sample holders*

Transmission geometry of any type is best suited to samples with low absorption such as organics and polymers, and is preferred for such samples when available. Transmission geometry has advantages when data are required at low diffracting angles. While the beam often has to be stopped-down in reflection geometry to avoid overspilling the sample, this undesired attenuation of the beam is not required for transmission geometry. Another advantage common to both the foil and capillary transmission techniques is that a small quantity of a powdered sample is usually sufficient. Samples small enough to be problematic with reflection geometry will often be perfectly adequate for transmission.

Data collection in transmission geometry is best done with either a parallel-beam or focusing geometry; the focus should be at the detector. Data can be collected using a divergent-beam setup, but the intensities obtained are very low and the resolution is usually poor. Parallel-beam geometry has the advantage that it is able to perform reflection and transmission measurements equally well.

2.10.1.4.2.1. Flat foils

Although less commonly used with modern diffractometers, the foil-type transmission sample mounting was quite common in some older-style X-ray cameras. Sprinkling powders onto single-sided Scotch tape was sometimes used with instrumentation such as Hägg–Guinier cameras, but care should be taken as the quality of the tapes as diffraction substrates can vary wildly; the crystallinity of the polymer can be high or low, and the adhesive sometimes contains mineral inclusions, such as talc. In the modern diffractometer, foil-type transmission data can sometimes be collected using the same rotating sample stage as for reflection measurements. Simply turning the stage by 90° and using a different holder can be sufficient if the optical configuration is suitable for both reflection and transmission. For solid organic samples such as polymers this foil transmission geometry has significant advantages because of the lack of transparency effects. It is worth noting, however, that the processing of polymers can induce significant texture, such that the data collected from a film in reflection geometry will not necessarily be identical to those collected in transmission. Should a reproducible pattern independent of geometry be required, then steps should be taken to reduce the sample to a true random powder and/or a 2D detector should be used.

With powder samples the technique requires the use of a transparent substrate, usually in the form of a thin polymer film or foil. In an analytical laboratory the easiest place to find such a substrate is the X-ray fluorescence laboratory, where very thin X-ray transparent polymer films are used for both sample supports and covers for liquid cells. Some of the materials used in these applications are familiar in the diffraction community as windows, *i.e.* Mylar and Kapton, but others such as polypropylene are not. The substrate will obviously add to the background, but a good substrate from a diffraction standpoint combines transparency with a lack of sharp features in the diffraction pattern. This makes fitting the background much easier. Any holder must be capable of stretching or holding the film flat across an opening for the X-ray beam. A commercial version of a foil-type holder is shown prior to assembly in Fig. 2.10.37. Example data from three different XRF films are shown in Fig. 2.10.38, together with that from a thicker Kapton foil commonly used as window material. It is notable that, despite the two 7.6 μm Kapton films being almost twice as thick as the Mylar or polypropylene films, the scattering from them is almost identical. The lack of any distinctive, sharp features above 6° 2θ in the Kapton films makes them attractive in this region, but for low-angle data Mylar is probably the better choice. Although giving a generally higher background, the thicker 50 μm Kapton foils can be used very successfully (see Fig. 2.10.39). Despite the greater attenuation they are much easier to handle, as their greater stiffness and weight makes them less susceptible to static electricity.

One advantage of transmission foil mounts is the small amount of sample required. In a similar way to producing smear mounts