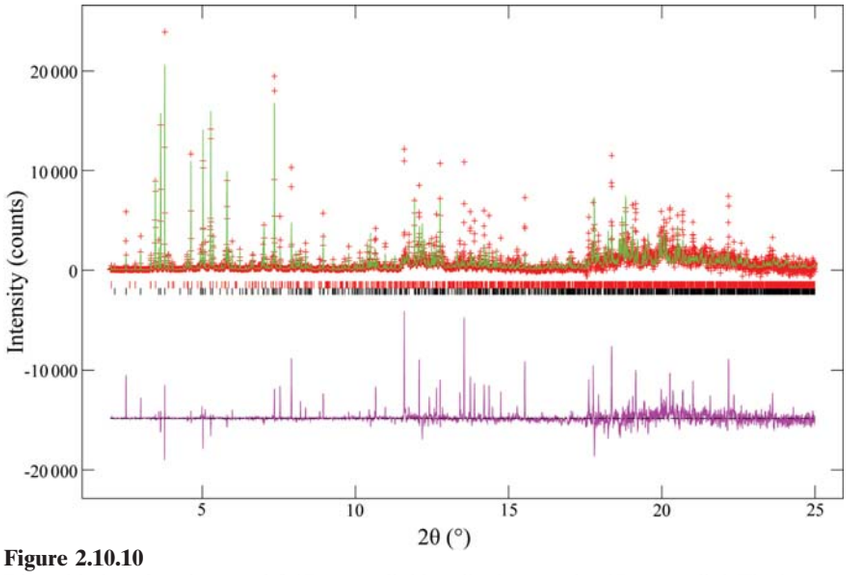

Figure 2.10.10
Rietveld plot of a mixture of β-17α-estradiol hemihydrate and α-17α-estradiol. The largest errors occur at the peaks of the β phase. Examination of the sample with an optical microscope revealed the presence of large single crystals. The rapid specimen rotation at the synchrotron beamline could not yield a powder average from such a coarse sample.

Kimmel, 1995), so is rarely sufficient on its own to solve problematic particle statistics.

Both the experimental data and theoretical treatment shown in Tables 2.10.1 and 2.10.2 show that with a typical laboratory setup, crystallites should ideally be in the range of a few μm in size to produce accurate intensity data. Reducing the crystallites to below 1 μm will improve the statistics further but may also induce crystallite-size and/or microstrain broadening depending on the instrument resolution. It is important to note that the crystallites must be uniformly small. Mineralogists often refer to 'rocks in dust', where there are a small number of very large crystallites scattered among the sample. Scattering of X-rays is sensitive to statistics by *volume*. A few very large crystallites will dominate (and probably distort) the resulting pattern, so the 'rocks in dust' scenario should be avoided whenever possible by correct specimen-preparation techniques.

As we have seen previously, the granularity can be seen visually in a 2D data set. If the researcher has access to a 2D detector this is the quickest way to assess a sample. However, where such a system is not available, an alternative is to use φ scans. In simple terms this involves taking data sets of a static specimen but rotating the specimen by a particular angle between data sets, for example at 0, 90, 180 and 270° in φ. Ideally the patterns should overlap exactly, although in practice one is looking for reproducible relative intensities, as the absolute intensities may change slightly. The examples used here are the so-called 'five fingers' of quartz. Although they are relatively weak reflections in the quartz pattern, three overlapping $K\alpha_{1,2}$ doublets provide a conveniently compact example. The three data sets shown in Fig. 2.10.13 are -400-mesh quartz (<38 μm), a commercial quartz with a size less than 15 μm and a sample milled to less than 5 μm. Optical micrographs of the -400 mesh and milled quartz samples are shown in Fig. 2.10.14.

The most obvious feature of the φ scans is that the reproducibility of the relative intensities is poor with the -400 mesh quartz sample. This has obvious consequences for any analytical technique relying on accurate peak intensities. All eight of the patterns from the micronized sample have practically identical relative peak intensities. It is worth comparing the similar results in the variability visible in Fig. 2.10.13 with the tabulated errors for the different methodology used for the data in Table 2.10.1.

The final approach to improving statistics is to increase the probability P that a crystallite is in the diffracting condition and visible to the detector. The latter is relevant today with 1D PSD detectors becoming more common, as the detector can simultaneously see multiple crystallite orientations at a particular incident beam angle, as shown in Fig. 2.10.15. P also increases with beam divergence; although there are many advantages of parallel-beam geometry, improving particle statistics is not one of them.

P is much higher with capillary transmission geometry than for reflection geometry. By rotating the specimen about an axis normal to the beam the effective number of orientations 'seen' by the detector increases greatly. This is the reason why a powder passing a 325-mesh sieve (<45 μm) almost always yields smooth

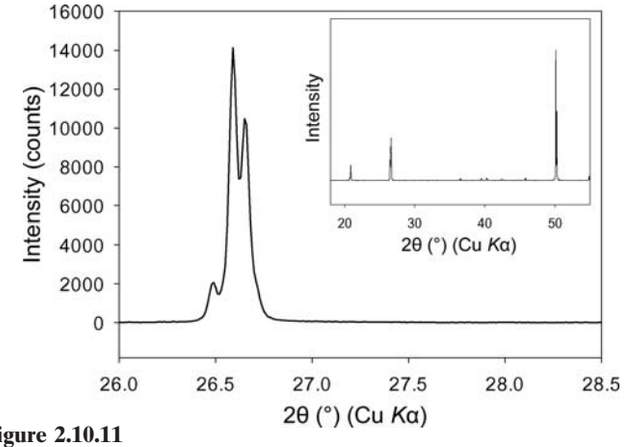

Figure 2.10.11
The main 101 reflection in data collected from a very coarse (~100 μm) highly crystalline quartz. The strange peak splitting is characteristic where there are very large crystallites present in the sample. The inset shows the diffraction pattern over a wider range and the strangely high intensity at 50° 2θ is caused by the detector intersecting a very intense diffraction spot similar to that seen in the lower part of Fig. 2.10.2.

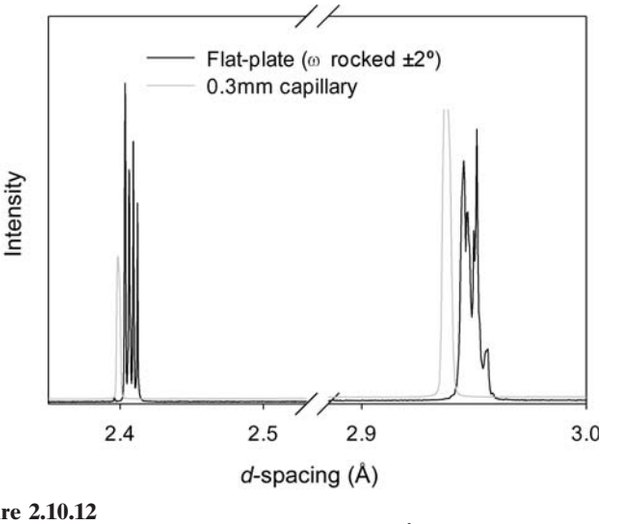

Figure 2.10.12
Comparison between capillary (0.3 mm, 0.8265 Å) and rocking flat-plate (strip heater, 1.2386 Å, ω ±2°) data from the Australian Synchrotron. Data courtesy of Ian Madsen, CSIRO.