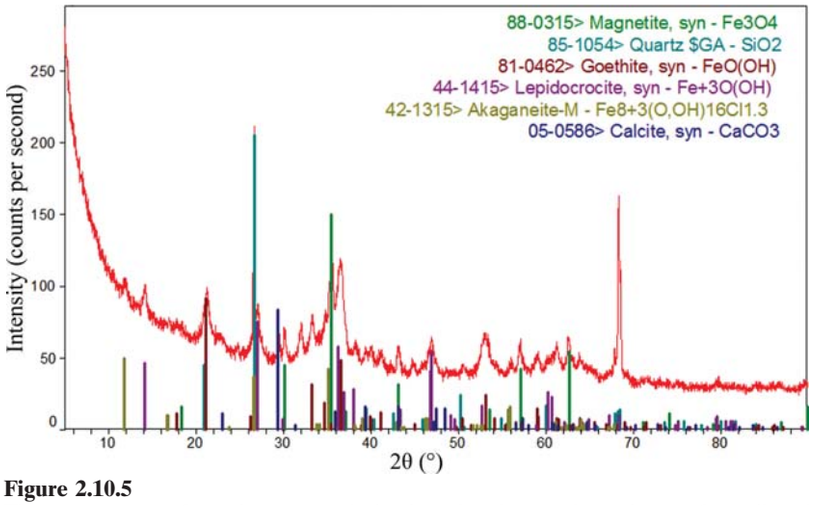

Figure 2.10.5
The appearance of specimen granularity in a hand-ground specimen of a railroad tank car corrosion deposit. The pattern was measured using a point detector. The intense sharp peak at ~68° 2θ turned out to come from a single crystal grain of sand at the surface of the specimen. The grain was detected by examination (after the measurement) in an optical microscope.

the crystallites to less than a few μm by milling. As shown in Fig. 2.10.4, rotating the coarse unmilled sample greatly improves the Debye rings compared with those seen in Fig. 2.10.2, but they are still not as uniform as those from the static milled sample in Fig. 2.10.3.

When using a point detector, granularity often manifests itself in the presence of a sharp (instrumental width) peak at relatively high diffraction angle. After a sharp peak at ~68° 2θ was observed in the pattern of a railroad tank car corrosion deposit (Fig. 2.10.5), examination of the specimen in an optical microscope indicated the presence of a single crystal grain of sand (quartz) on the surface. Re-grinding the specimen removed this artifact. Such sharp peaks tend to occur at relatively high diffraction angles, because at such angles the illuminated specimen area is smaller than at low angles, and the presence of a single crystal grain at the surface is relatively more important than when a larger area is illuminated.

An extreme example of granularity is provided by a hand-ground specimen of Scott's Moss Control Granules (Fig. 2.10.6). The even spacing of the strong peaks suggested severe preferred orientation, but examination of the specimen in an optical microscope (Fig. 2.10.7) revealed the presence of grains several tens of μm in size. Regrinding the sample in a McCrone micronizing mill reduced the crystallite size to a few μm (Fig. 2.10.7), and resulted in random powder data which could be used successfully in a Rietveld refinement (Fig. 2.10.8) and quantitative phase analysis.

An example of granularity at a synchrotron beamline is provided by $(Ba_{0.7}Sr_{1.3})TiO_4$ (Fig. 2.10.9). A Rietveld refinement using data collected from a static capillary specimen was unsuccessful. In an attempt to understand why, the diffractometer was driven to the 2θ angle of a strong peak, and a φ scan was carried out (rotating the capillary in steps). The intensity varied by a factor of five, as individual crystallites came into and out of diffracting position. Clearly, the intensities from such a measurement are not meaningful. When the capillary was rotated rapidly during a repeated φ scan, the intensity was constant and reliable.

Granularity can be encountered even in highly transparent organic specimens. A synchrotron pattern of 17α-estradiol showed that the sample was a mixture of the α-polymorph and an additional phase. Indexing the unknown peaks yielded the cell of the β-polymorph, the structure of which was unknown. The structure of the β-polymorph was solved using Monte Carlo simulated-annealing techniques, but the Rietveld refinement (Fig. 2.10.10) was not nearly as good as a Le Bail fit using the same cell and profile. The errors were then clearly in the structural model and/or the data. Examination of the specimen under an optical microscope revealed the presence of needles ~50 × 50 × 150–200 μm in size. Even the rapid rotation of the capillary specimen was not sufficient to obtain a powder average of such large crystallites.

Although granularity is normally considered to affect only the intensities of peaks, in extreme cases it can also affect the shapes. This is easily seen in a pattern from very coarse crystalline quartz in Fig. 2.10.11. The strange looking 101 reflection at 26.6° contains contributions from individual single crystals. When a wider view is taken, the relative intensities are distorted from those expected, similar to that seen in Fig. 2.10.2. Flat-plate data from highly-parallel-beam synchrotron beamlines are more (as opposed to less) susceptible, as shown by the comparison between flat-plate and capillary data of LaB_6 from the Australian Synchrotron in Fig. 2.10.12. Despite the use of ω-rocking and a Mythen position-sensitive detector, the flat-plate synchrotron data with 2–5 μm SRM660a LaB_6 crystallites show worse splitting of the Bragg peaks than lower-resolution laboratory data with 100 μm quartz crystallites.

The quantitative effect of particle statistics on diffraction results can be seen in Table 2.10.1. In the 15–50 μm sample the intensity varied from 4823 to 11 123 counts, which is a huge variation when trying to extract reliable intensities for analysis. Averaging over ten samples, the mean deviation was reduced from 18.2% to 1.2% when the smallest fraction of <5 μm was used. The absolute intensities of the largest fraction are significantly lower, which was attributed to extinction effects.

The source of this huge variation in errors can be understood more clearly when the theoretical treatment for quartz from

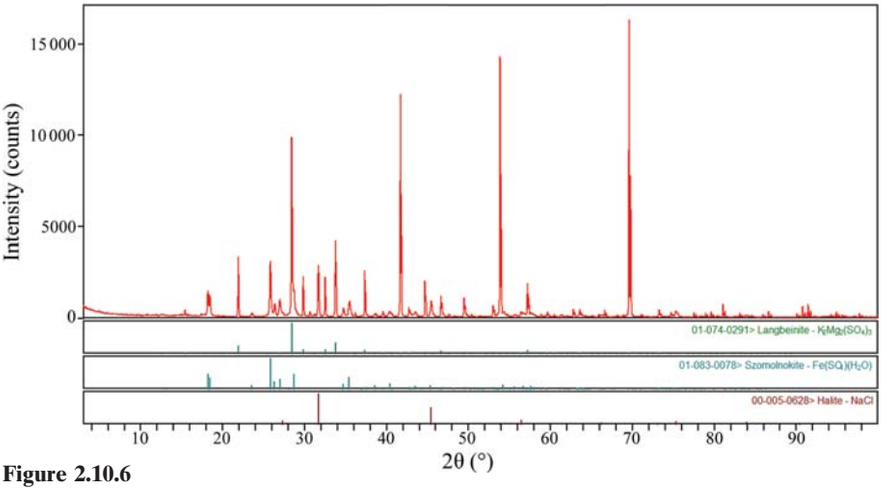

Figure 2.10.6
An extreme example of granularity. The pattern is of a hand-ground specimen of Scott's Moss Control Granules. No preferred orientation model could fit the langbeinite peaks.

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