

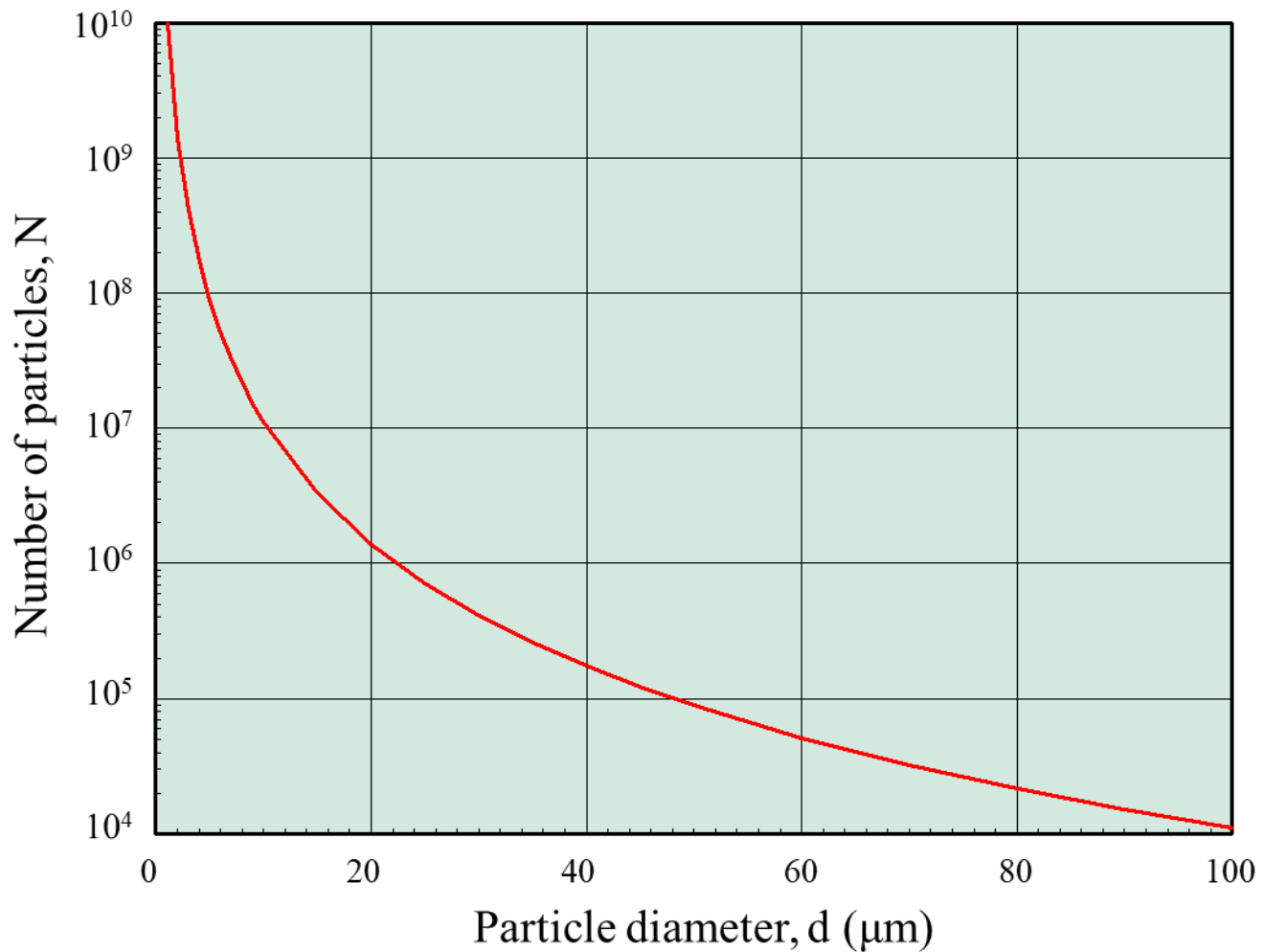
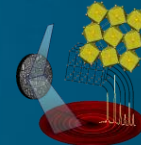


Figure 12.1. The total number of spherical particles in a cylindrical specimen 10 mm in diameter and 0.1 mm deep as a function of particle size assuming close packing of the spheres.

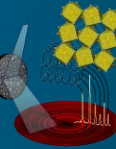


Figure 12.2. The tools most commonly used in sample preparation for powder diffraction experiments: agate mortar and pestle (*left*), and ball-mill vials made from hardened steel (*middle*) and agate (*right*).

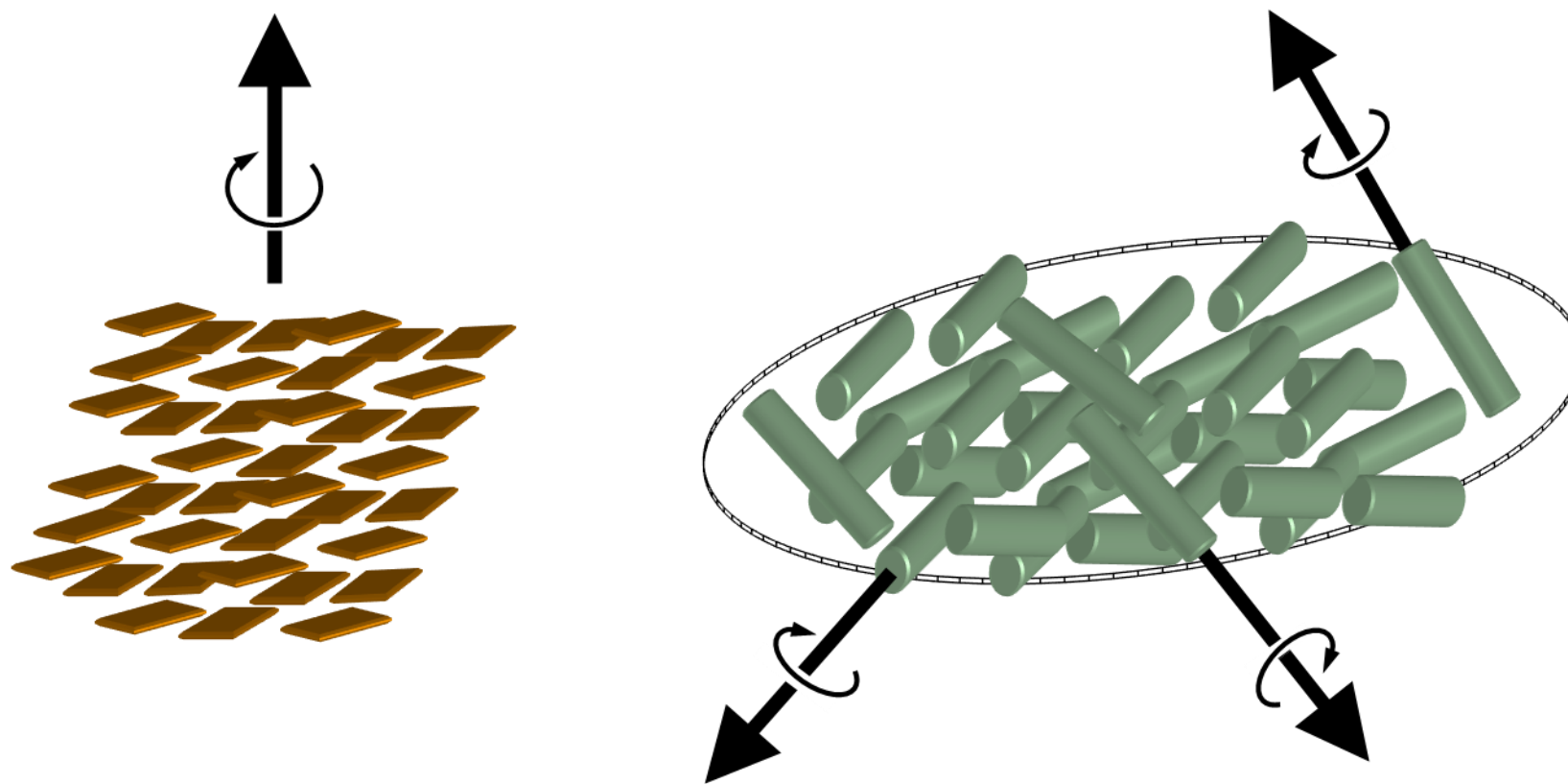
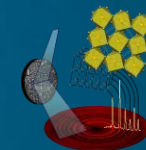


Figure 12.3. The two limiting cases of non-random particle orientation distributions due to distinctly anisotropic particle shapes: platelet-like (*left*) and needle-like (*right*) particles. The arrows indicate the directions around which the particles may rotate freely.

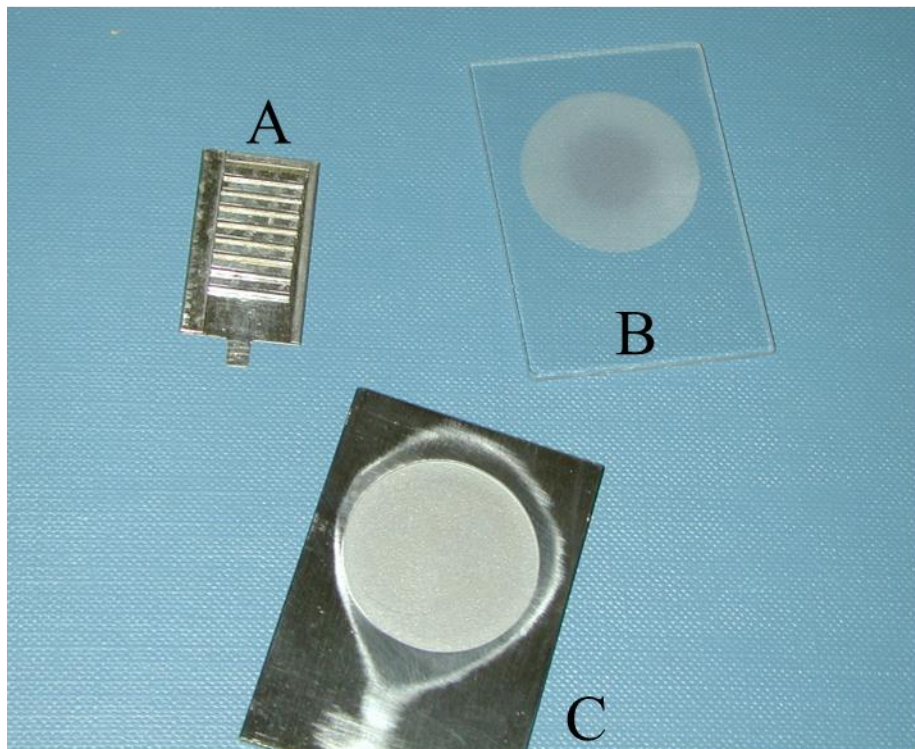
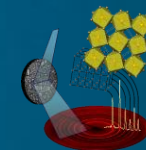


Figure 12.4. Examples of sample holders used with Bragg–Brentano geometry. **A** is platinum sample holder used in high temperature powder diffraction experiments. The fins seen in **A** are designed to improve heat conductivity and uniformity of powder temperature.

The fins seen in **A** are designed to improve heat conductivity and uniformity of powder temperature.

B is glass slide with a round area of about 1 inch in diameter sand blasted to improve randomization of particle orientations.

C is stainless steel sample holder with a ~0.5 mm deep cavity.

D is copper sample holder with a rectangular cavity to accommodate powder for low temperature high magnetic field experiments. The four screws shown in **D** are used to attach the sample holder to a cold finger.

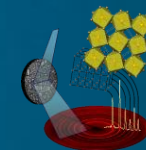


Figure 12.5. Examples of flat sample holders used in powder diffractometers with reflection geometry. The holder on the *left* has a cavity, which is filled with the powder. The holder on the *right* has a rough area, which accommodates a thin layer of the powder.

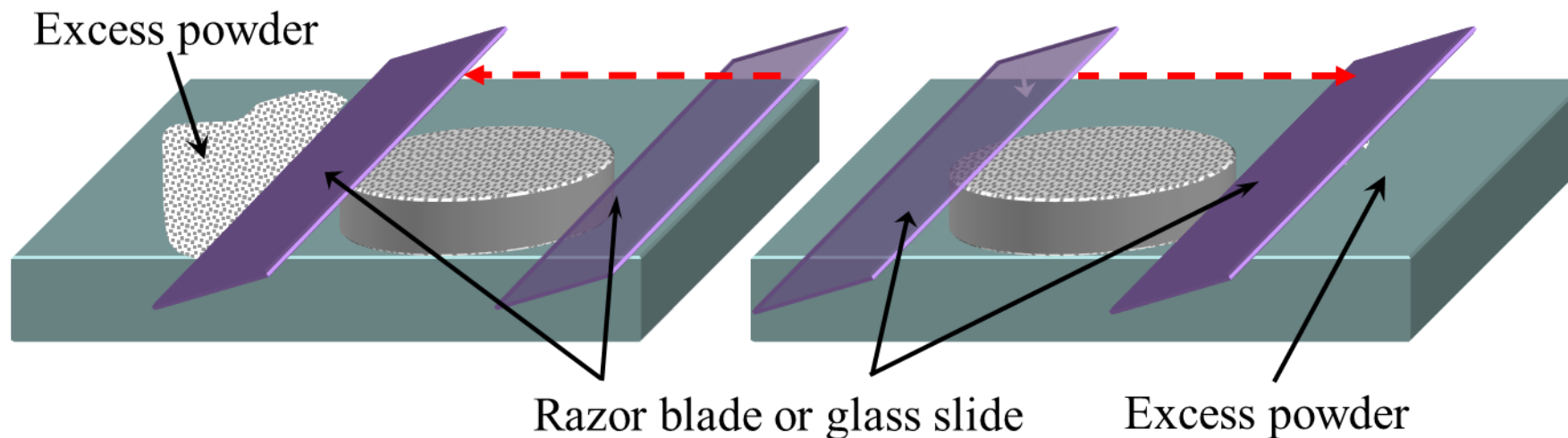
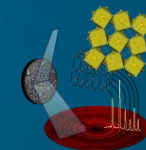


Figure 12.6. Excess powder is removed from the top of the sample holder with a single sweep by an edge of a razor blade or a glass slide. The direction of the sweep depends on the physical properties of the powder and is usually established by trial-and-error.

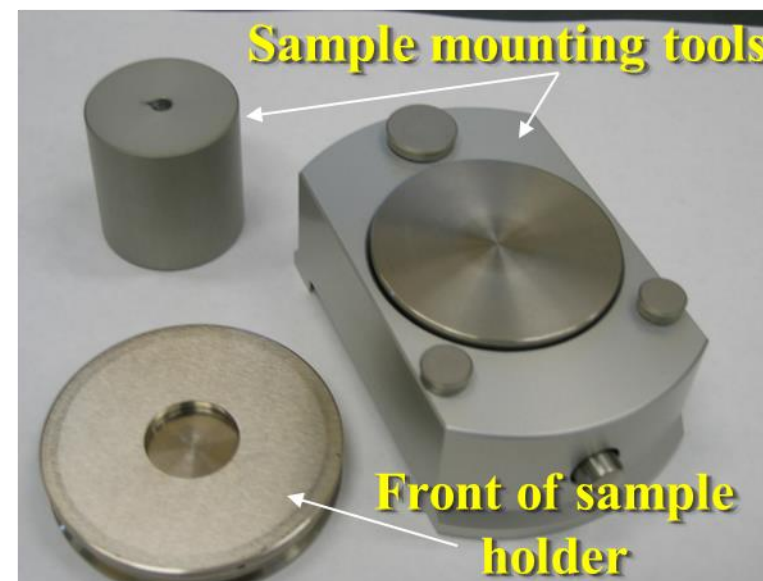
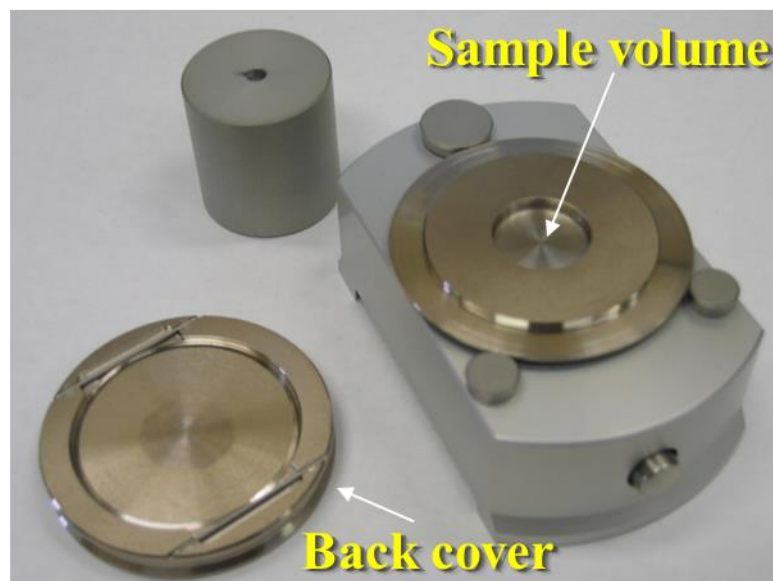
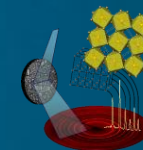


Figure 12.7. Tools used for back filling a sample holder with powder (sold by Malvern Panalytical). On the *left*, the front side of the sample holder is clamped on a support. After the sample volume is filled from the back side and packed, the front side of the holder couples to the back cover, and the sample holder is released from the clamping tool, as seen on the *right*.

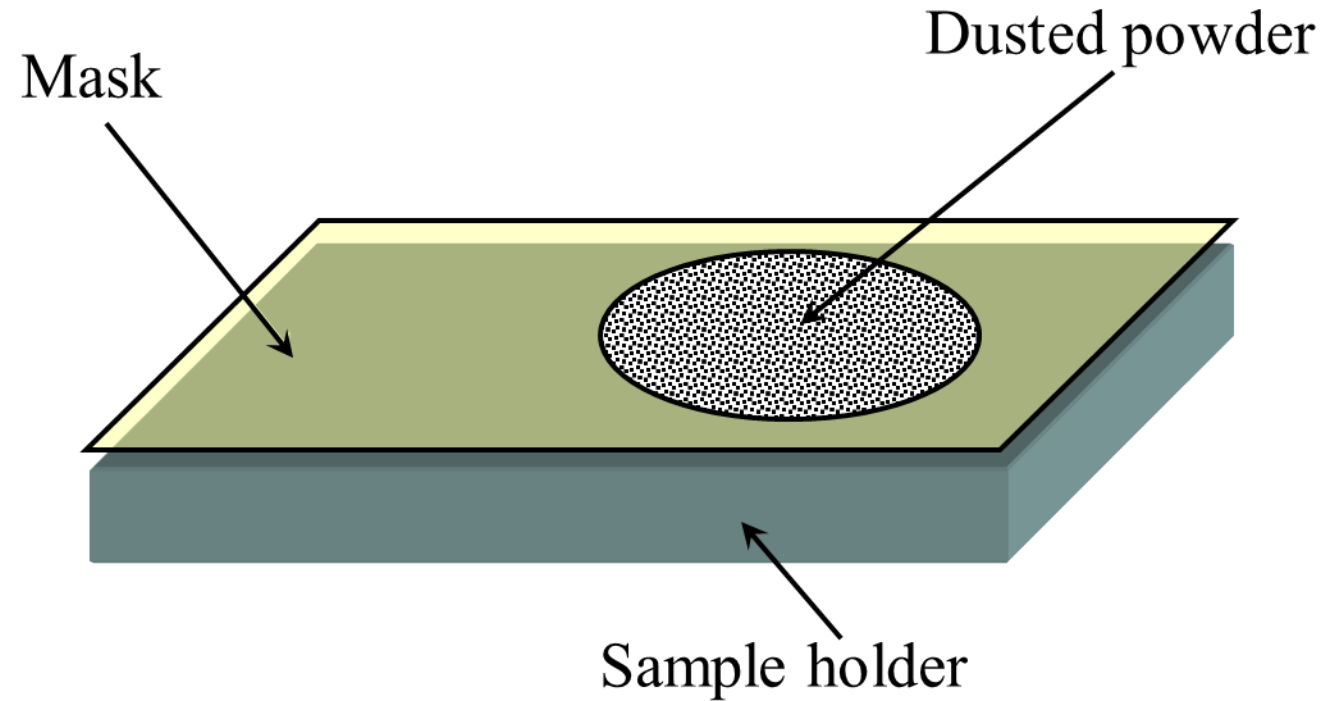
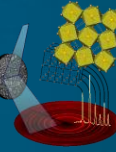
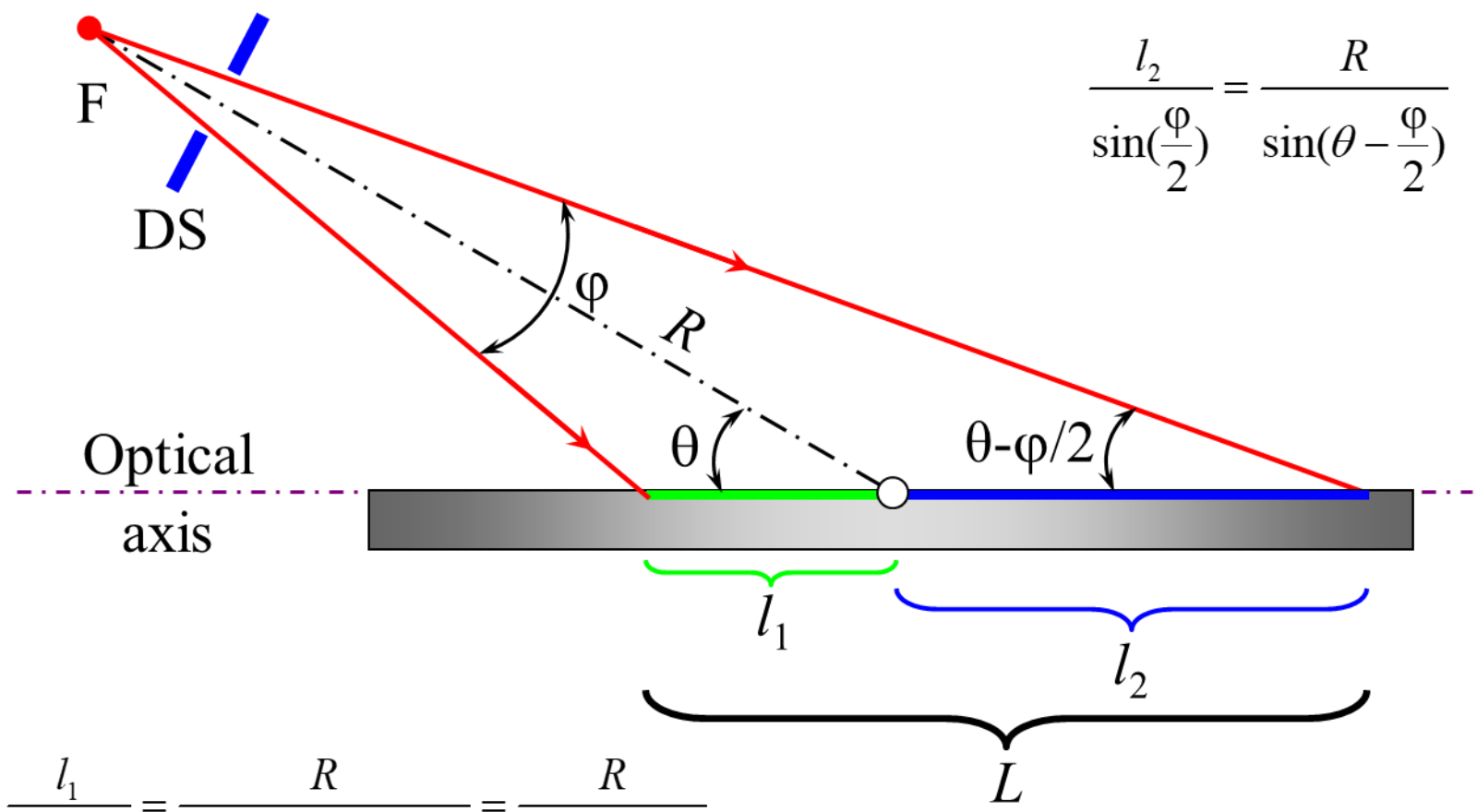
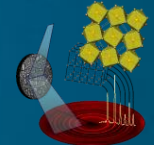


Figure 12.8. Sample for powder diffraction prepared by dusting ground powder on the sample holder covered with a mask.



$$\frac{l_2}{\sin(\frac{\varphi}{2})} = \frac{R}{\sin(\theta - \frac{\varphi}{2})}$$

$$\frac{l_1}{\sin(\frac{\varphi}{2})} = \frac{R}{\sin(180 - \theta - \frac{\varphi}{2})} = \frac{R}{\sin(\theta + \frac{\varphi}{2})}$$

Eq. 12.1: $L = l_1 + l_2 = \frac{R \sin(\frac{\varphi}{2})}{\sin(\theta + \frac{\varphi}{2})} + \frac{R \sin(\frac{\varphi}{2})}{\sin(\theta - \frac{\varphi}{2})} \cong \frac{\varphi R}{\sin \theta}$

Figure 12.9. The length of the incident beam projection, *L*, on the surface of the flat sample in Bragg–Brentano geometry. The location of the goniometer axis is indicated by the *open circle*.

F – focal point of the X-ray source, DS – divergence slit, R – goniometer radius, φ – angular divergence of the incident beam, θ – Bragg angle.

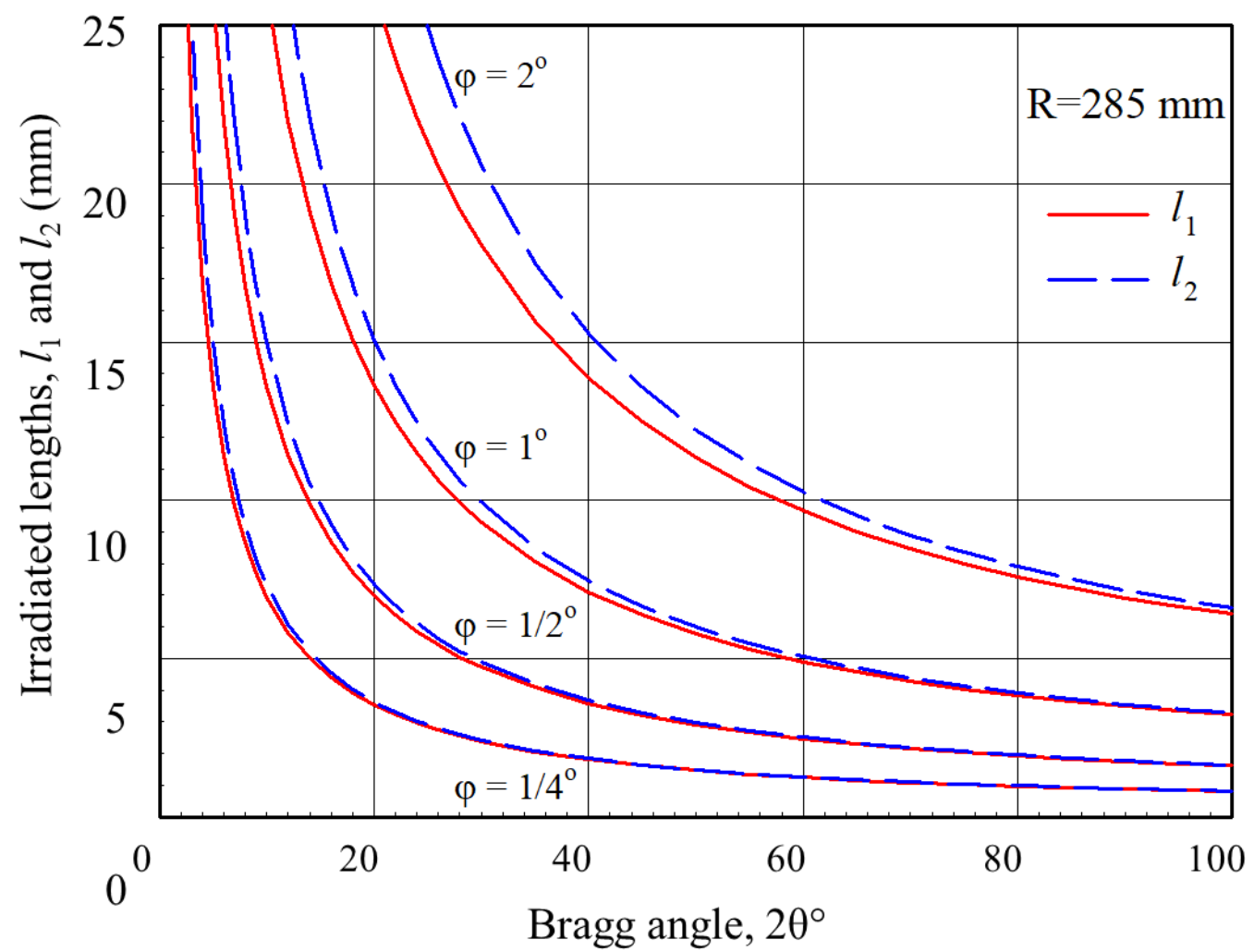
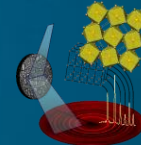
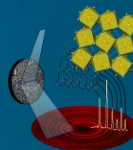


Figure 12.10. Irradiated lengths, l_1 and l_2 , of the flat specimen in the Bragg–Brentano geometry as functions of Bragg angle calculated using Eq. 12.1 for different angular divergences of the incident beam assuming goniometer radius, $R = 285 \text{ mm}$.



Thickness and Uniformity:

Assuming that the absorption of **99.9 %** of the incident beam intensity represents complete opacity,

$$\frac{I_t}{I_0} = \exp(-2\mu_{\text{eff}}l) = 10^{-3} \quad \text{Eq. 12.2}$$

- I_0 and I_t are intensities of the incident and transmitted beams, respectively;
- μ_{eff} is the effective linear absorption coefficient (in mm^{-1}), which is specific for each sample and it should also account for the porosity of the powder;
- l is a beam path (in mm) through the sample and it is related to the sample thickness, t , as $l = t/\sin \theta$.

After solving Eq. 12.2, the minimum sample thickness (in mm) can be estimated from

$$t \cong \frac{3.45}{\mu_{\text{eff}}} \sin \theta_{\text{max}} \quad \text{Eq. 12.3}$$

Where: θ_{max} represents the maximum Bragg angle

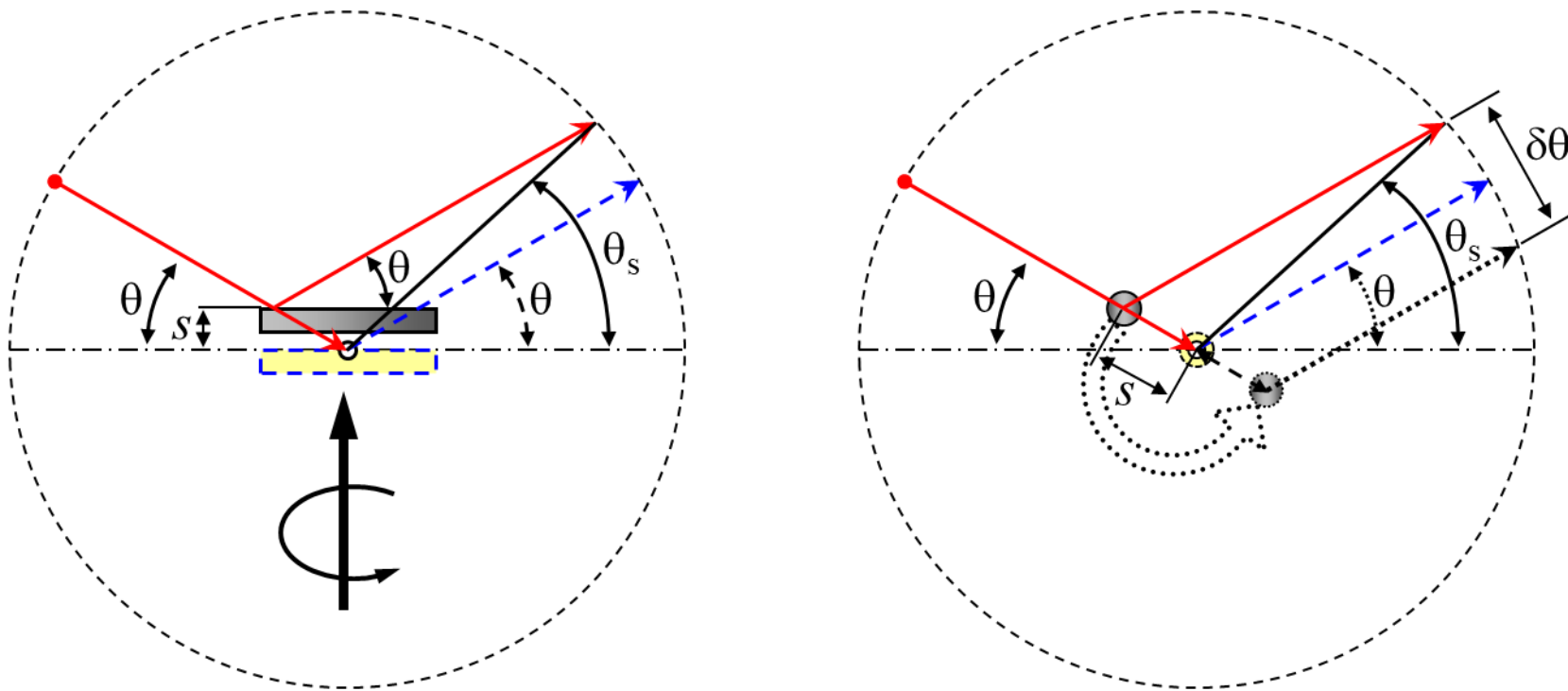
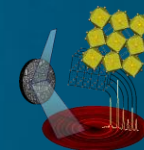
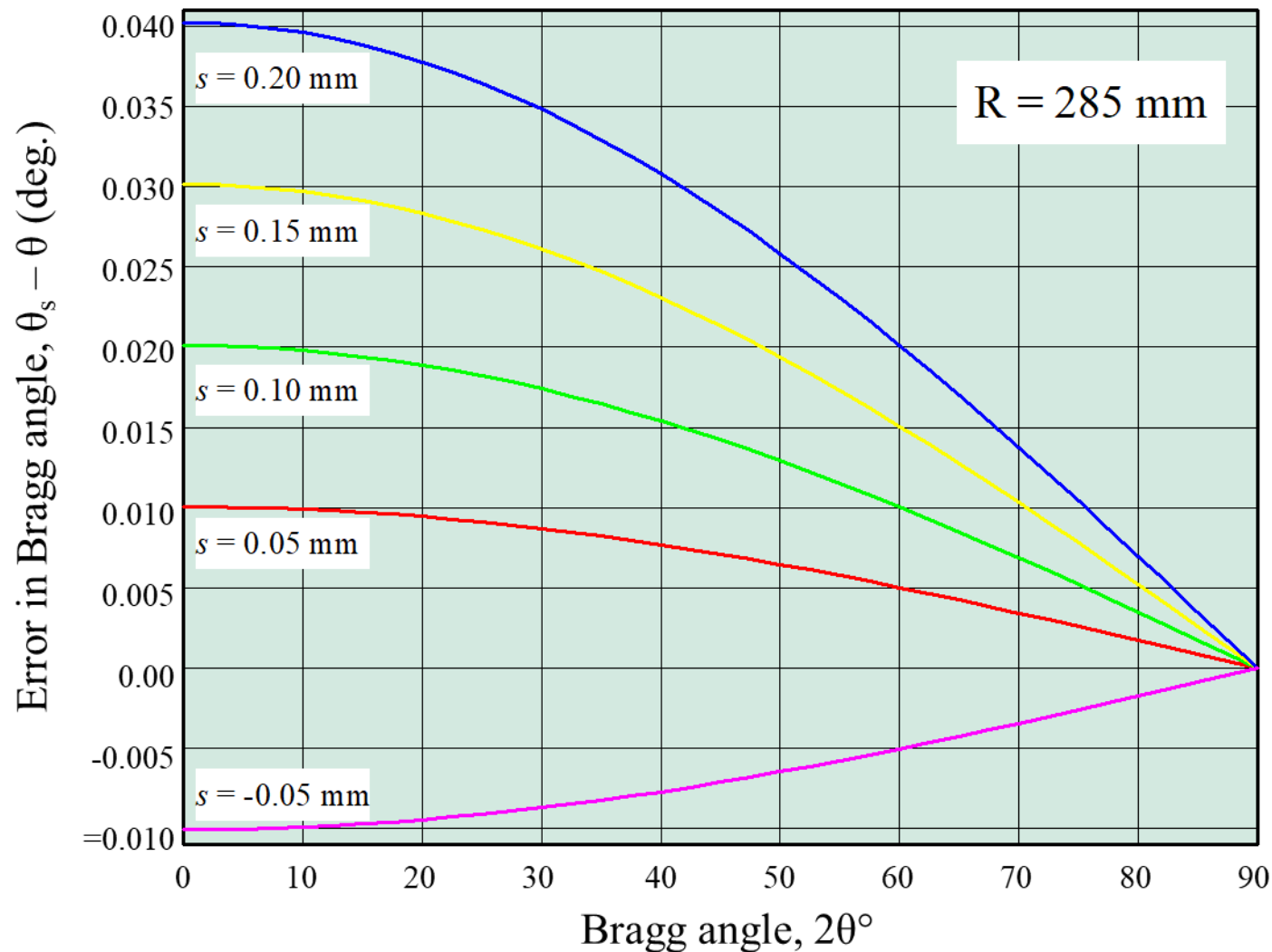
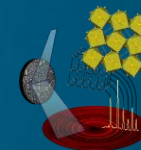


Figure 12.11. The effect of sample displacement by distance s from the goniometer axis on the measured Bragg angle, θ_s , in the Bragg–Brentano geometry (*left*) and in the transmission geometry (*right*). The goniometer axis is indicated by the small *open circle* in the center of the drawings. The optical axis is shown as the *dash-dotted line*. The ideal location of the sample is shown as the *light-shaded dashed rectangle* on the *left* and as the *light-shaded dashed circle* in the center of the drawing on the *right*.



$$\theta_s - \theta = \frac{s \cos \theta}{R} \quad \text{Eq. 12.4}$$

Figure 12.12. The effect of sample displacement, s , on the observed Bragg angles calculated from Eq. 12.4 assuming Bragg–Brentano geometry and goniometer radius $R=285$ mm. θ_s is the observed Bragg angle, θ is the Bragg angle in the absence of sample displacement.

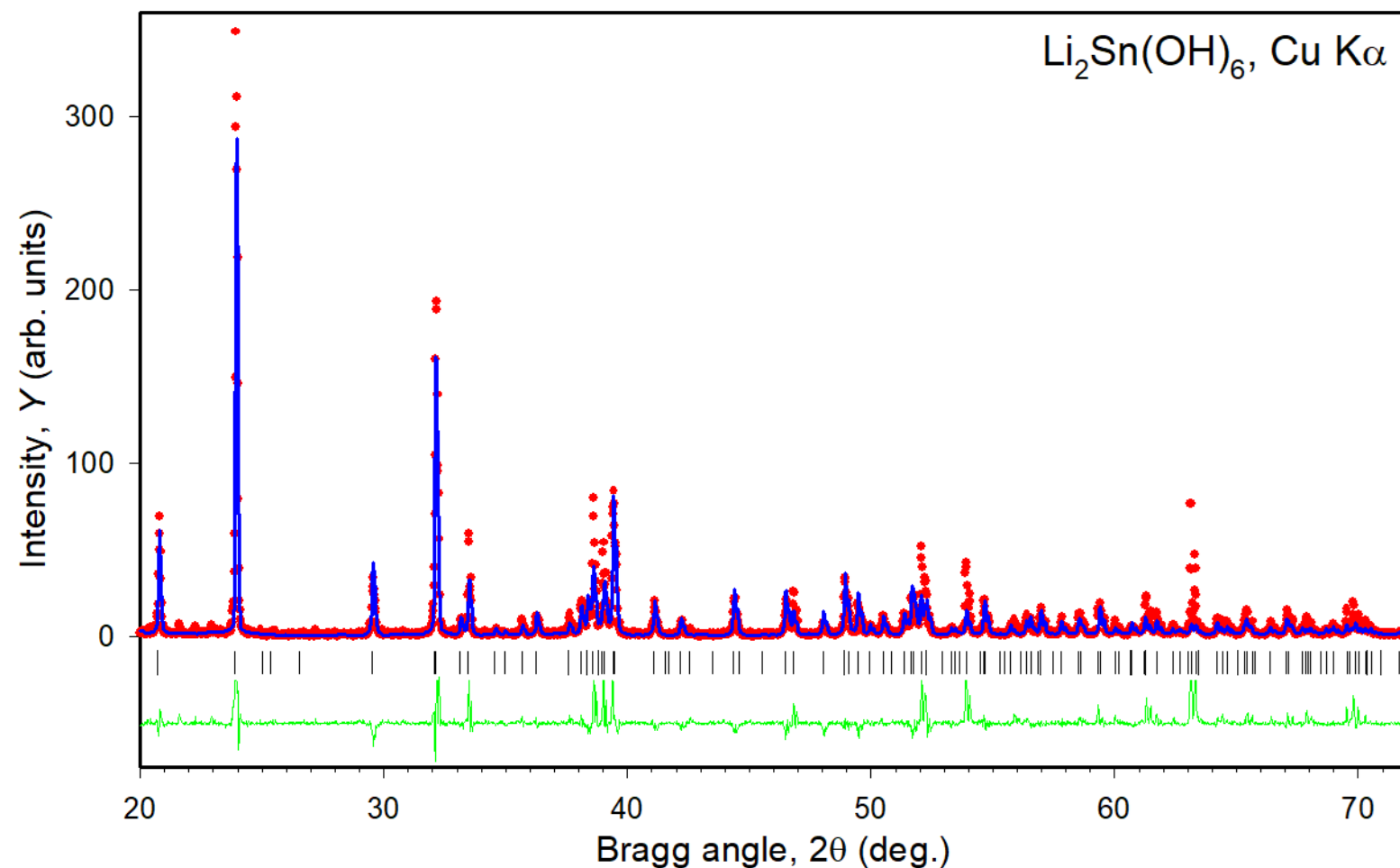
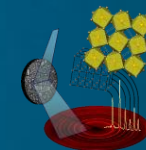


Figure 12.13. Coarsely ground powder and properly selected incident beam aperture. Experimental data are shown using *small red circles*; the calculated diffraction pattern is shown using *solid blue lines*. The difference $Y_{\text{obs}} - Y_{\text{calc}}$ is shown at the *bottom* of the plot in green and the calculated positions of Bragg peaks are marked using *vertical bars*. The data were collected without spinning the sample.

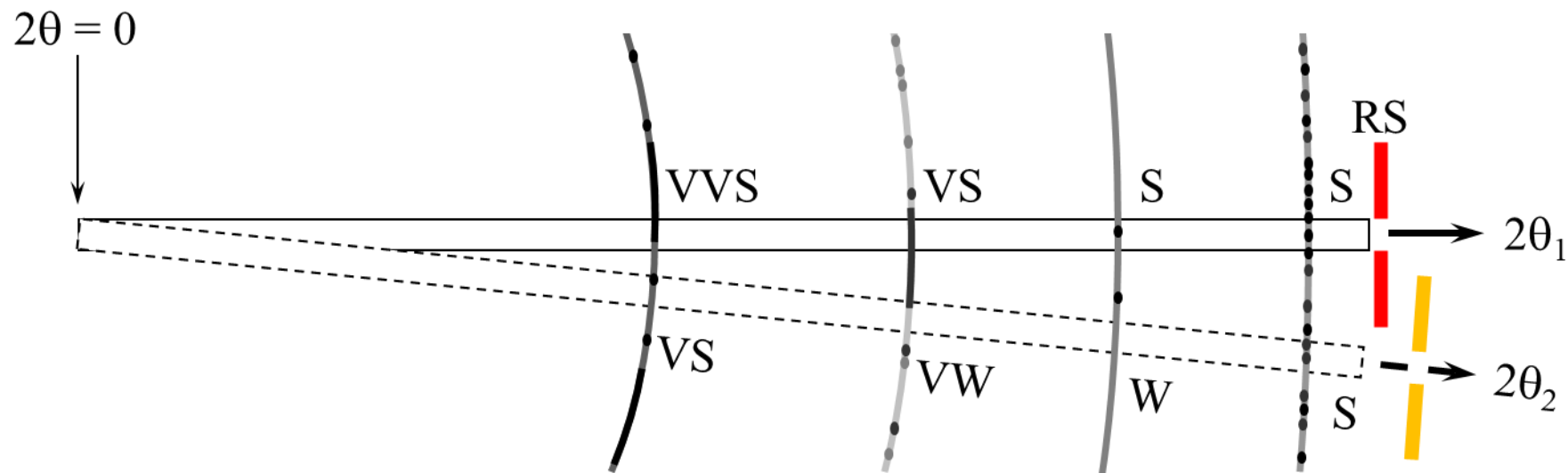
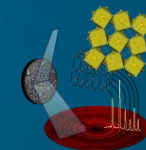


Figure 12.14. The model showing the spottiness of the first four distinct Debye rings in the X-ray film with the powder diffraction pattern of LuAu from Figure 11.1. The relative intensities of Bragg peaks vary considerably in the two directions shown as elongated rectangles (each direction represents the possible trace of the receiving slit traversing the Debye rings during data collection). The character notations in the figure characterize the expected measured intensity of Bragg peaks as follows: VVS – very very strong, VS – very strong, S – strong, W – weak and VW – very weak. RS is the receiving slit.

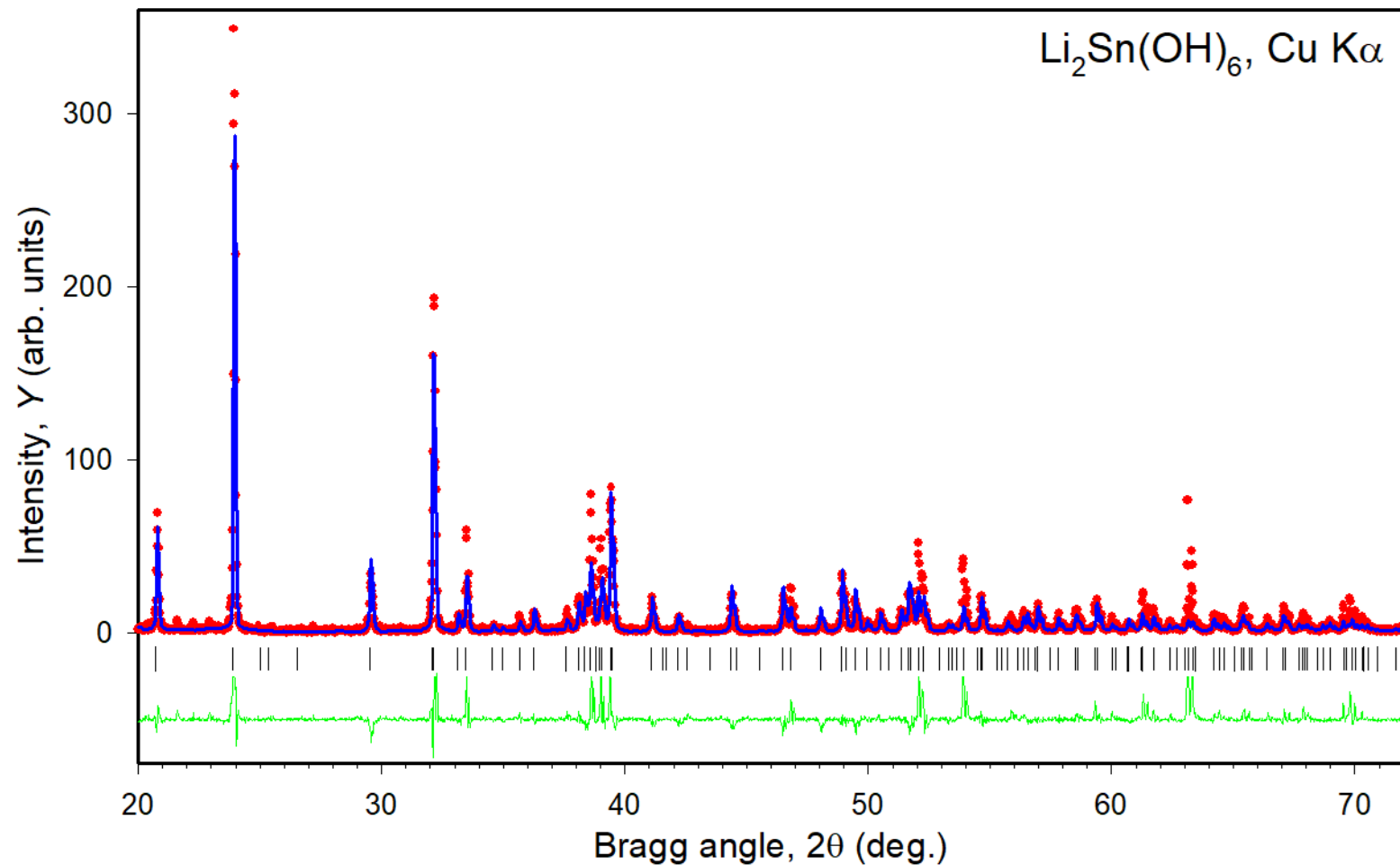
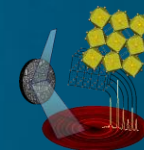


Figure 12.15. Coarsely ground powder and an improper incident beam aperture. The data were collected without spinning the sample.

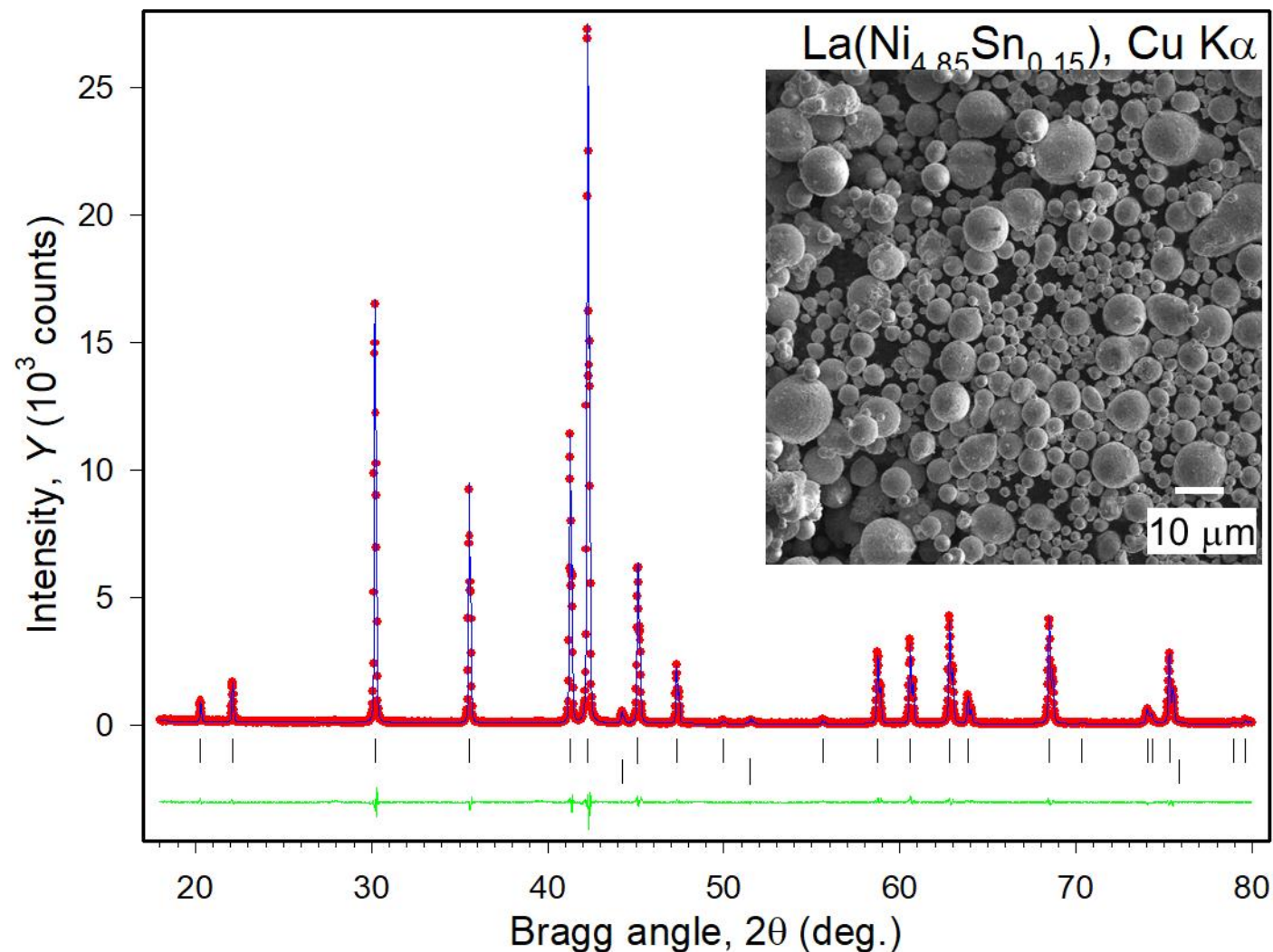
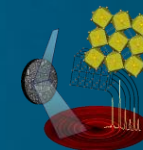
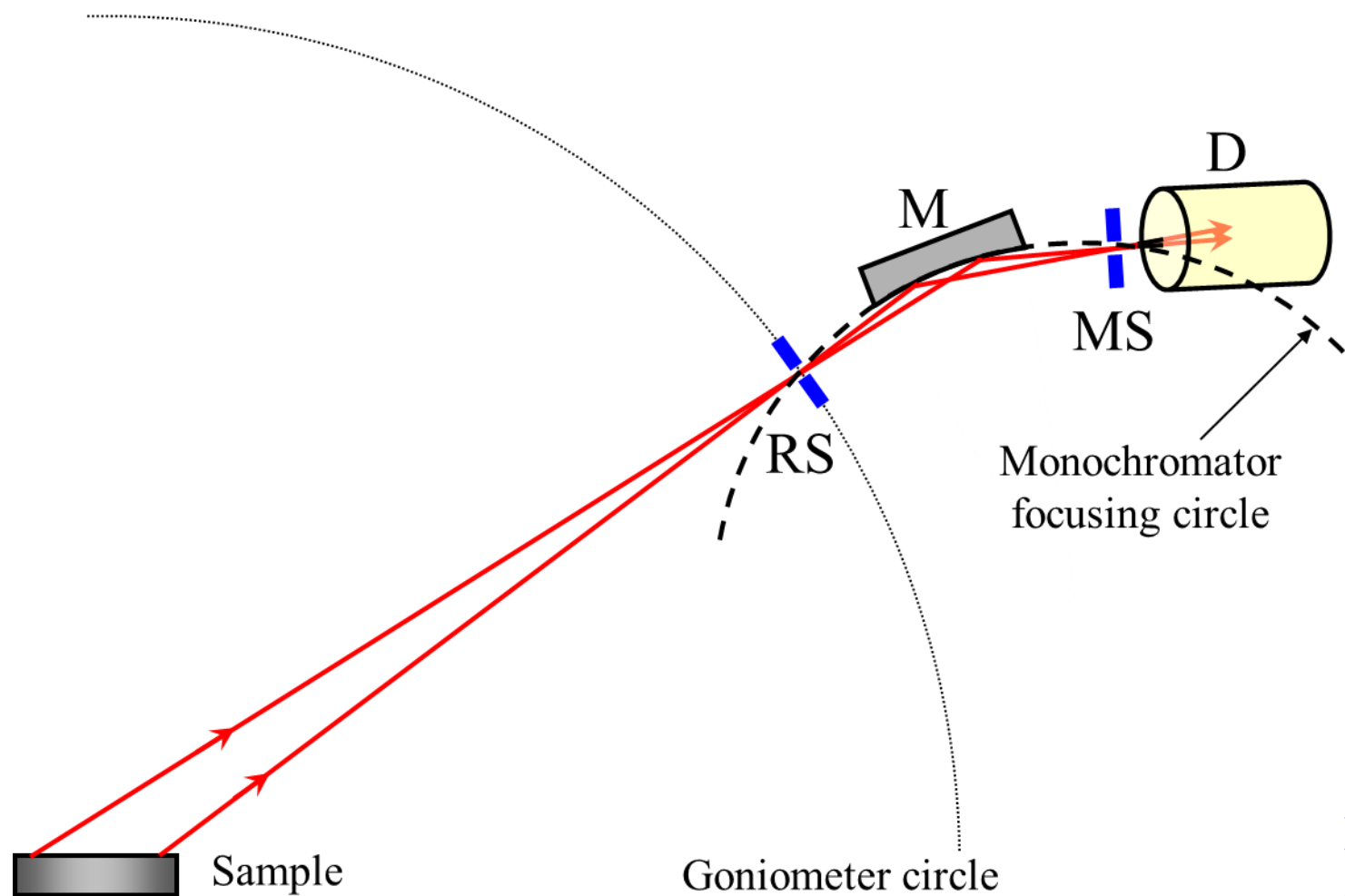
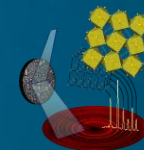


Figure 12.16. High quality, nearly spherical powder prepared by high-pressure gas atomization from the melt and proper sample length, L . The X-ray powder diffraction data were collected from a continuously spinning sample (20 mm diameter and 1 mm deep).

- The inset shows the scanning electron microscopy image of the powder morphology.
- The powder contains a small fraction of a second phase, which is identified by the second row of vertical bars.



RS – receiving slit,
M – curved monochromator,
MS – monochromator scatter slit,
D – detector.

Figure 12.17. Monochromatization of the diffracted beam using a curved crystal monochromator.

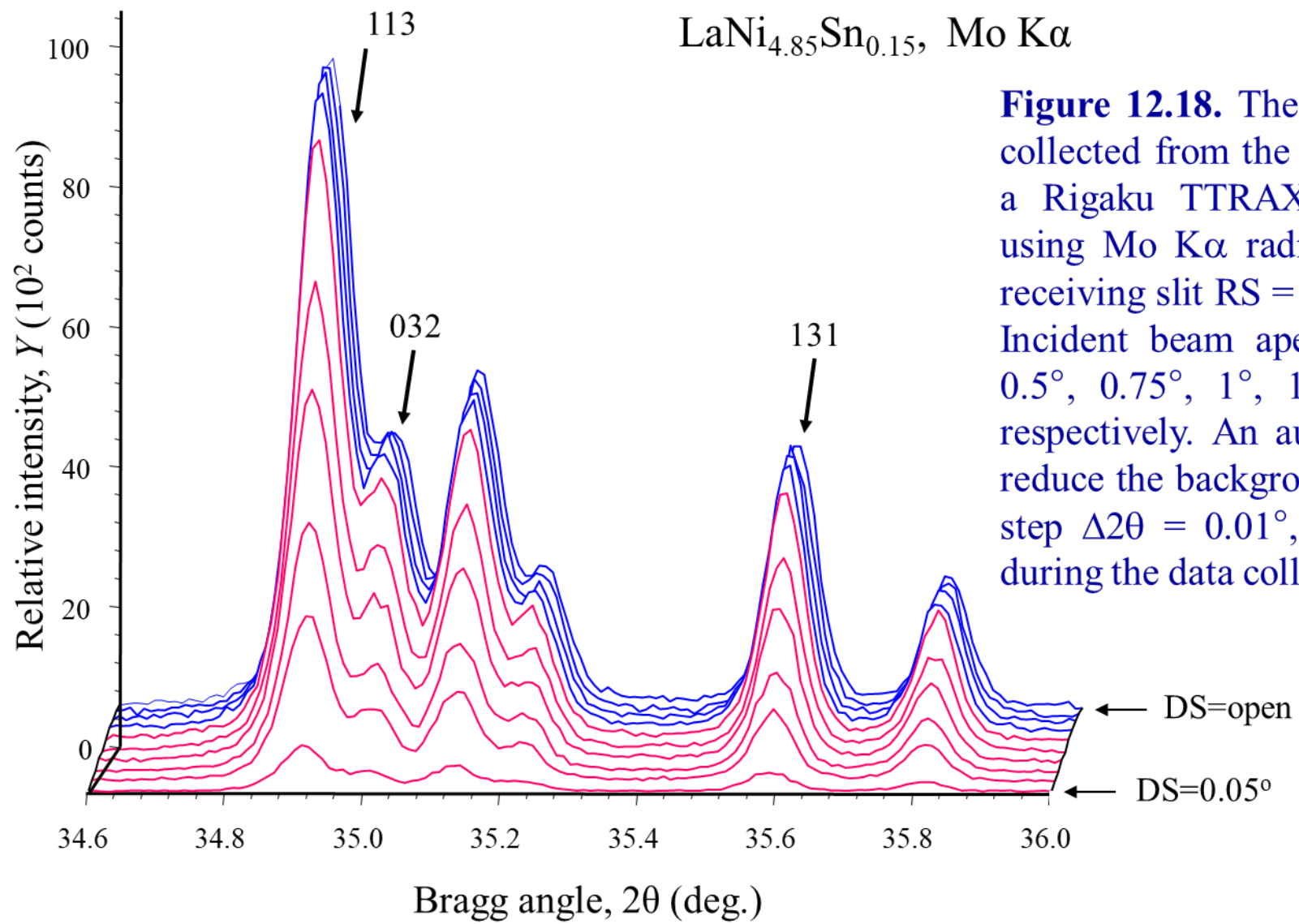
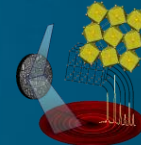


Figure 12.18. The set of X-ray powder diffraction patterns collected from the nearly spherical LaNi_{4.85}Sn_{0.15} powder on a Rigaku TTRAX rotating anode powder diffractometer using Mo K α radiation. Goniometer radius $R = 285 \text{ mm}$; receiving slit $RS = 0.03^\circ$; flat specimen diameter $d = 20 \text{ mm}$. Incident beam apertures were 0.05° , 0.17° , 0.25° , 0.38° , 0.5° , 0.75° , 1° , 1.5° , 2° , and completely opened ($\sim 5^\circ$), respectively. An automatic variable scatter slit was used to reduce the background. The data were collected with a fixed step $\Delta 2\theta = 0.01^\circ$, and the sample was continuously spun during the data collection.

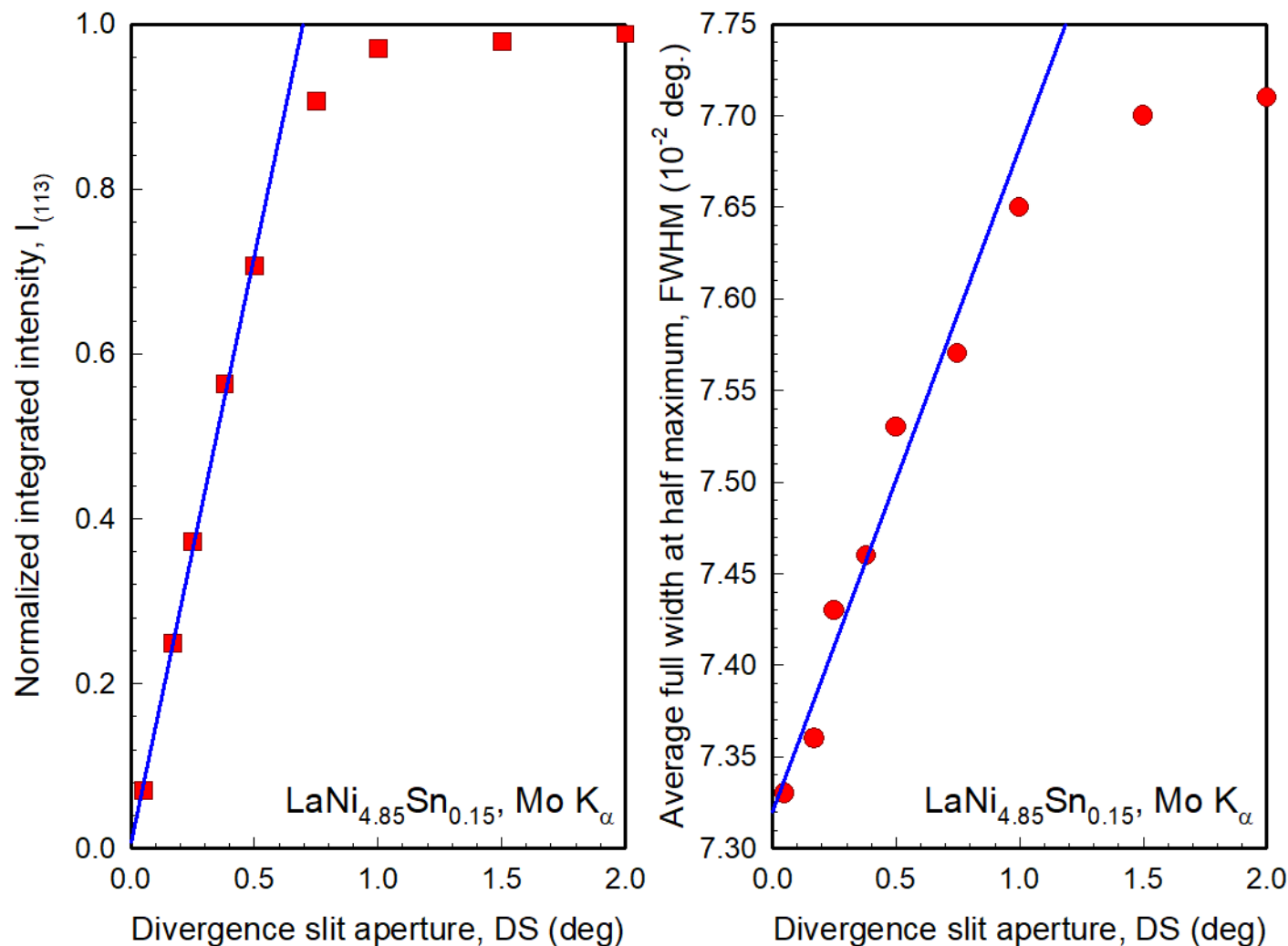
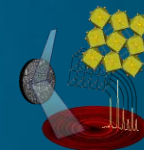


Figure 12.19. The normalized integrated intensity of the strongest peak (*left*) and the average full width at half maximum, FWHM, (*right*) of the three Bragg peaks shown in Figure 12.18, both as functions of the divergence slit aperture. The intensity of the strongest Bragg peak was normalized with respect to its value when the divergence slit was completely opened ($DS \cong 5^\circ$). The corresponding values at the completely opened divergence slit are not shown to clarify the behavior at low apertures.

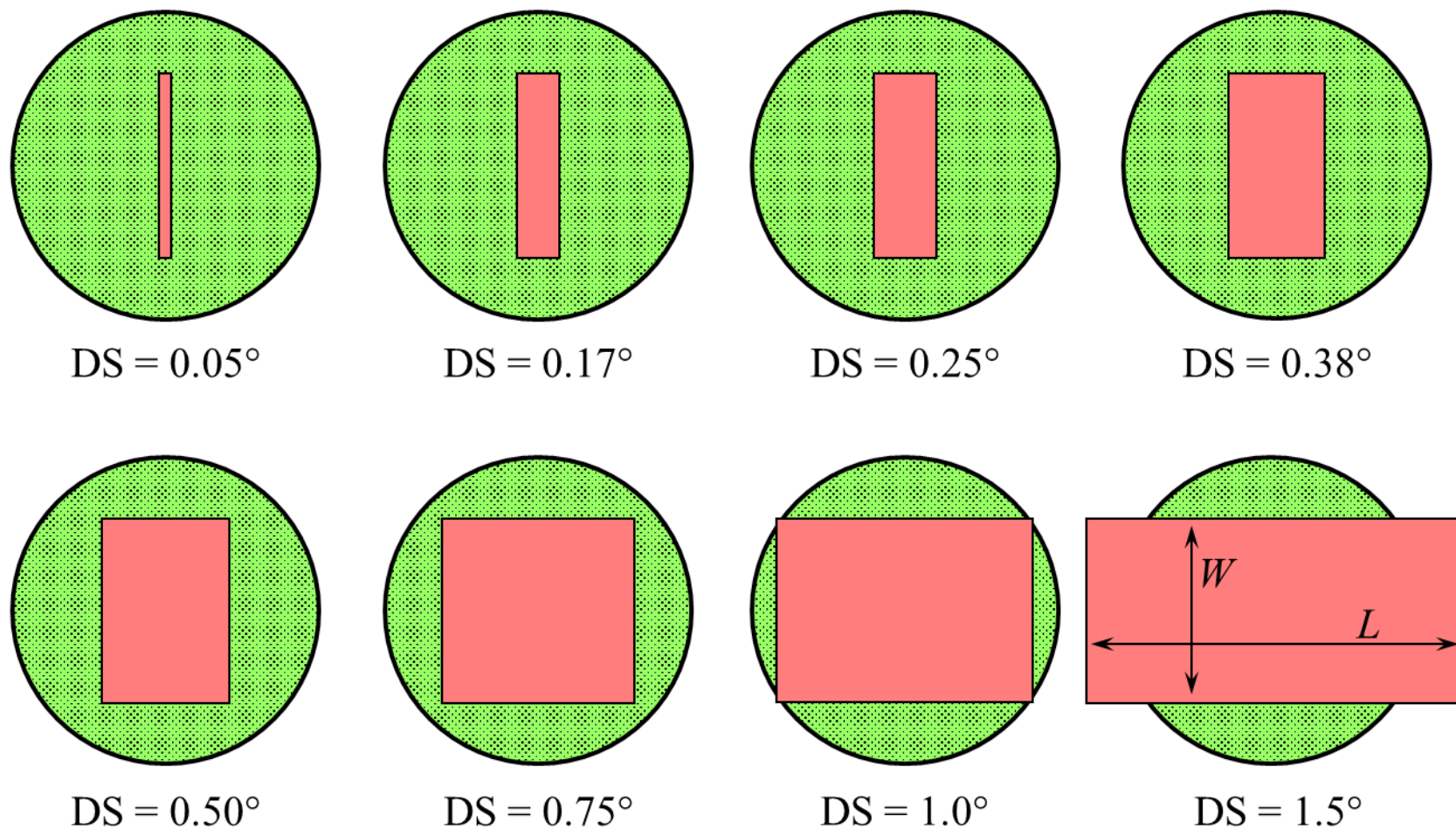
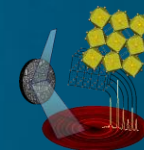


Figure 12.20. The projections of the incident beam (*pink rectangles*) on the sample surface (*green circles*) at $2\theta \cong 35^\circ$.

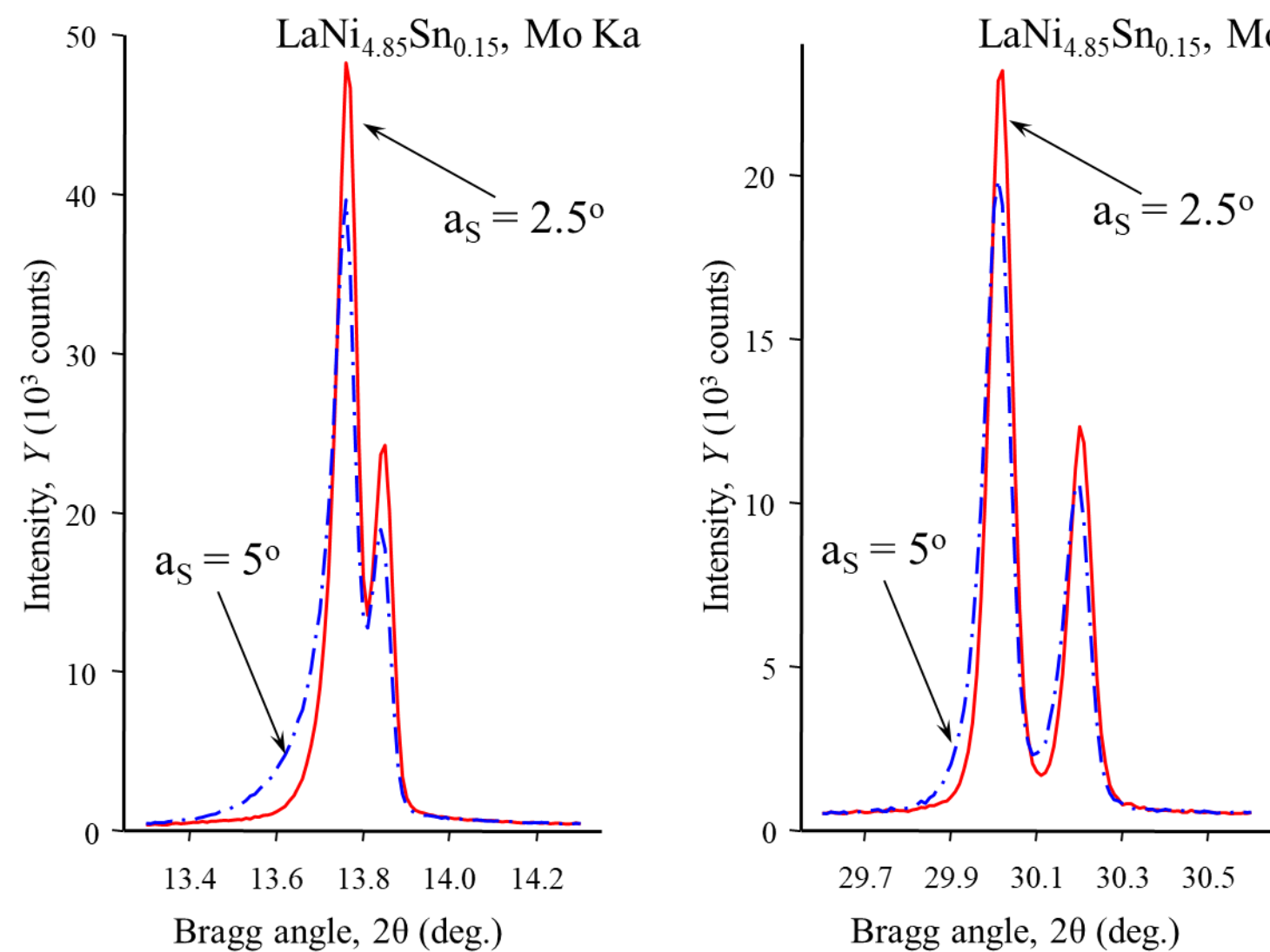
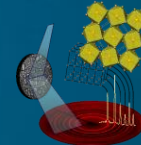


Figure 12.21. Two individual Bragg peaks observed in the diffraction pattern of the $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powder. The data were collected on a Rigaku TTRAX rotating anode powder diffractometer using MoK α radiation and two different sets of Soller slits controlling the axial divergence of the incident beam: $\alpha_S = 2.5^\circ$ (solid red lines) and $\alpha_S = 5^\circ$ (dash-dotted blue lines).

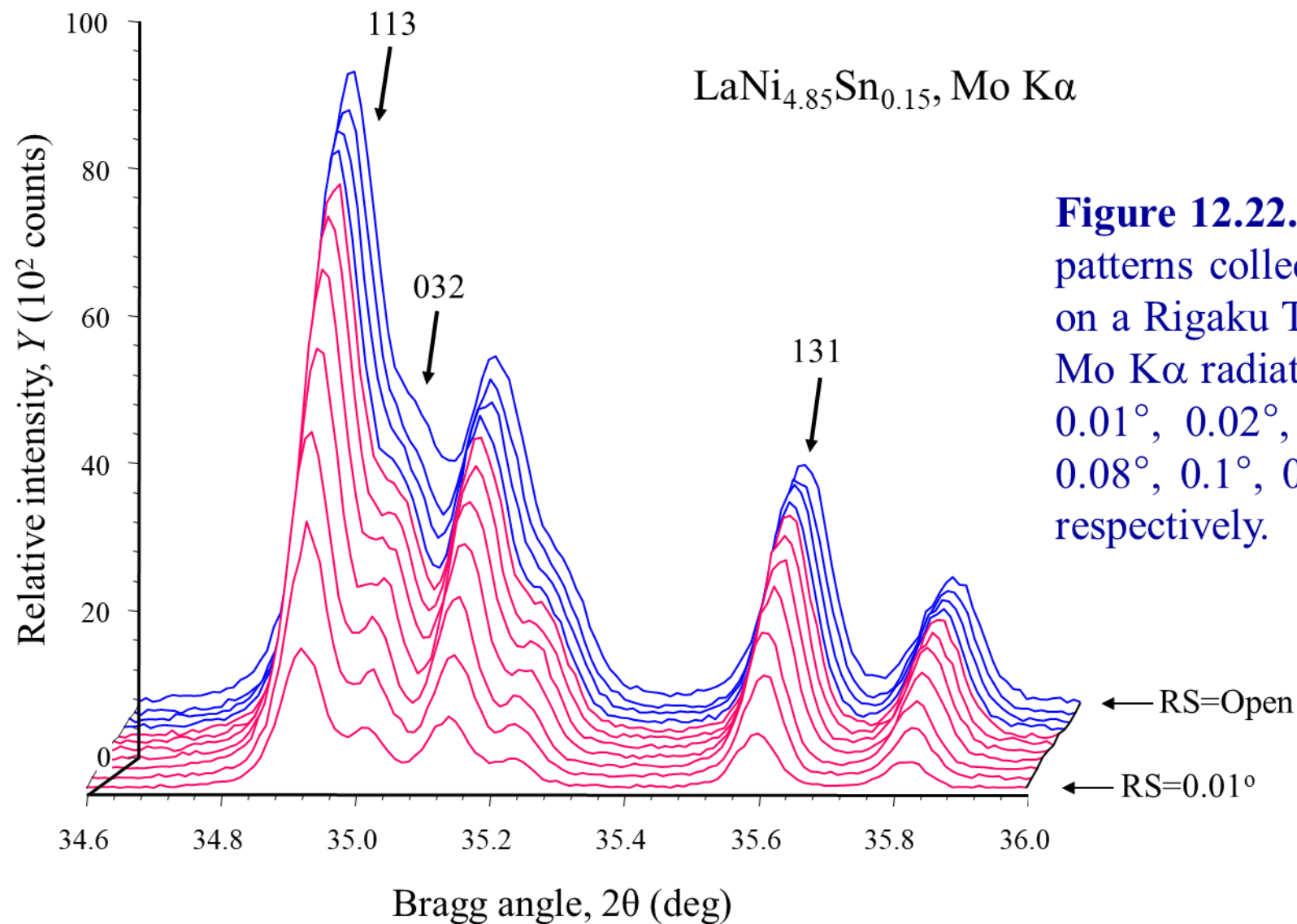
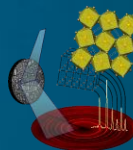


Figure 12.22. The set of X-ray powder diffraction patterns collected from the $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powder on a Rigaku TTRAX powder diffractometer using $\text{Mo K}\alpha$ radiation. Diffracted beam apertures were 0.01° , 0.02° , 0.03° , 0.04° , 0.05° , 0.06° , 0.07° , 0.08° , 0.1° , 0.12° and completely opened ($\sim 1^\circ$), respectively.

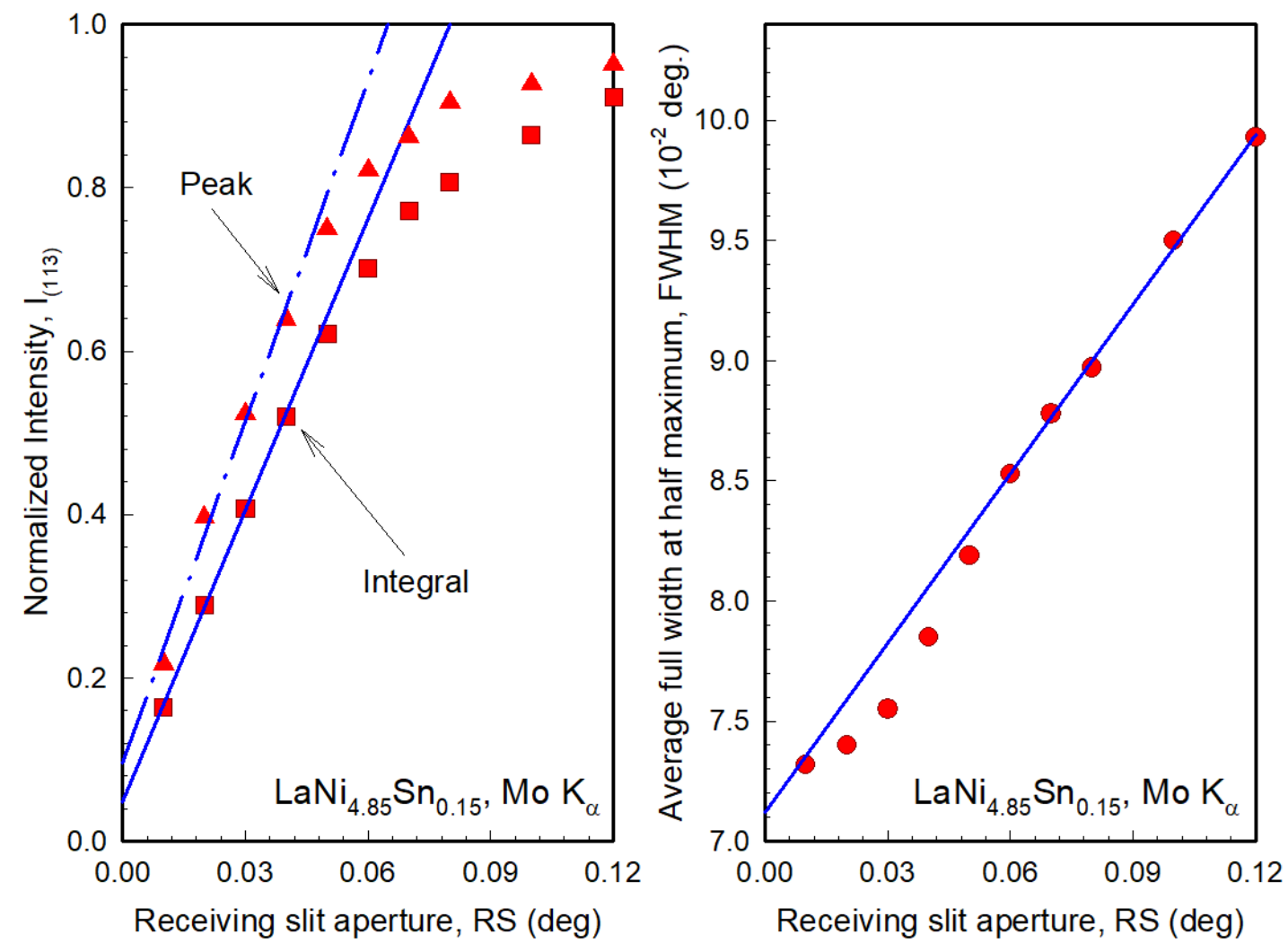
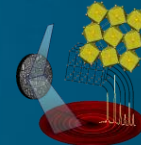


Figure 12.23. The intensity of the strongest peak (*left*) and the average full width at half maximum (*right*) of the three Bragg peaks shown in Figure 12.22, as functions of the receiving slit aperture. Both the integrated and peak intensities were normalized with respect to their values at the completely opened receiving slit ($RS \cong 1^\circ$). The corresponding values at the completely opened receiving slit are not shown to clarify the behavior at low apertures.

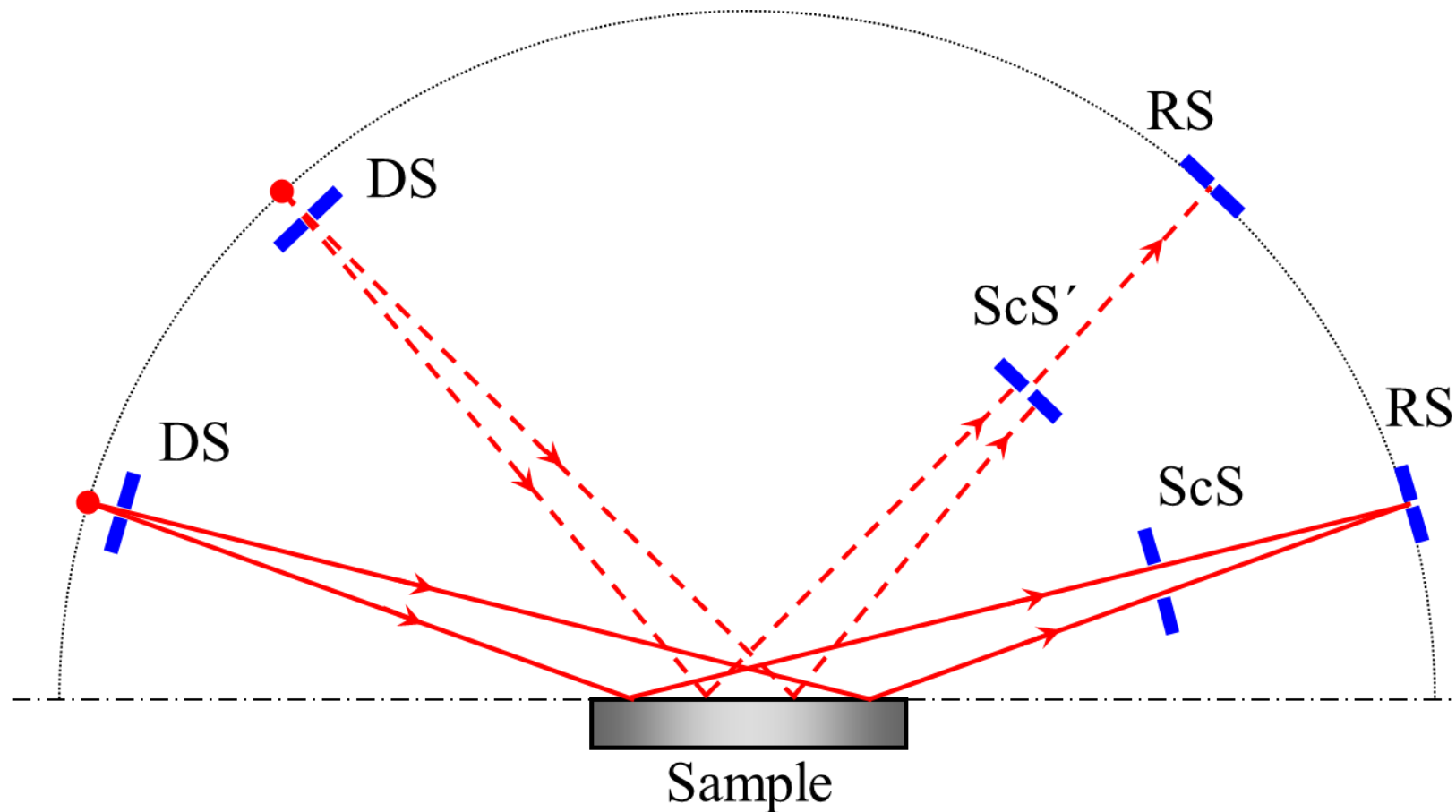
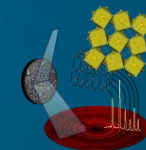


Figure 12.24. Examples of proper (ScS) and improper (ScS') selection of scatter slit aperture.

DS – divergence slits, RS – receiving slits.

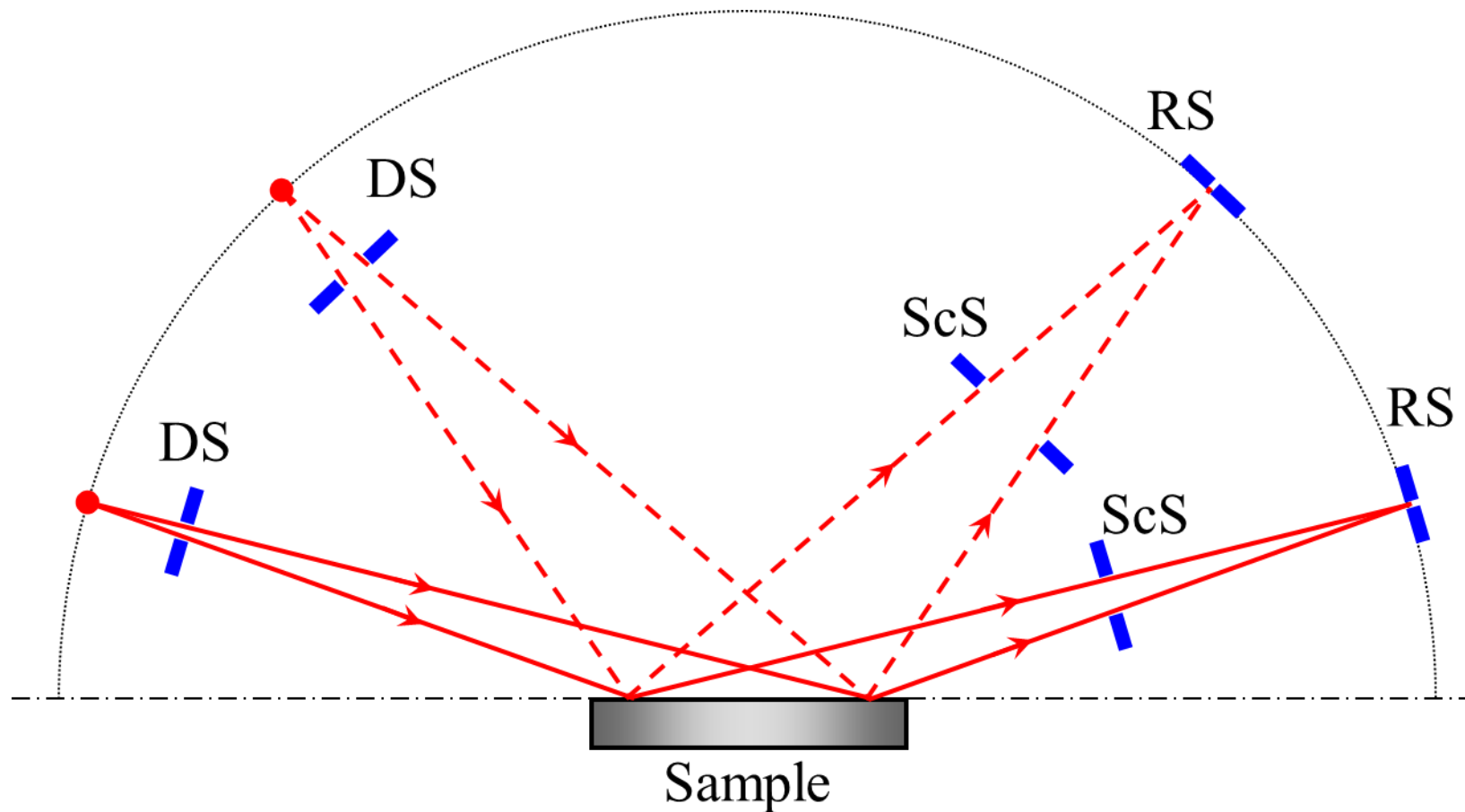
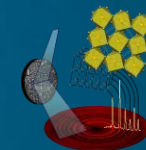


Figure 12.25. The schematic of goniometer optics during data collection using variable divergence and scatter slit apertures, which enables a constant irradiated area on the sample at any Bragg angle.

DS – divergence slit, ScS – scatter slit, RS – receiving slit.

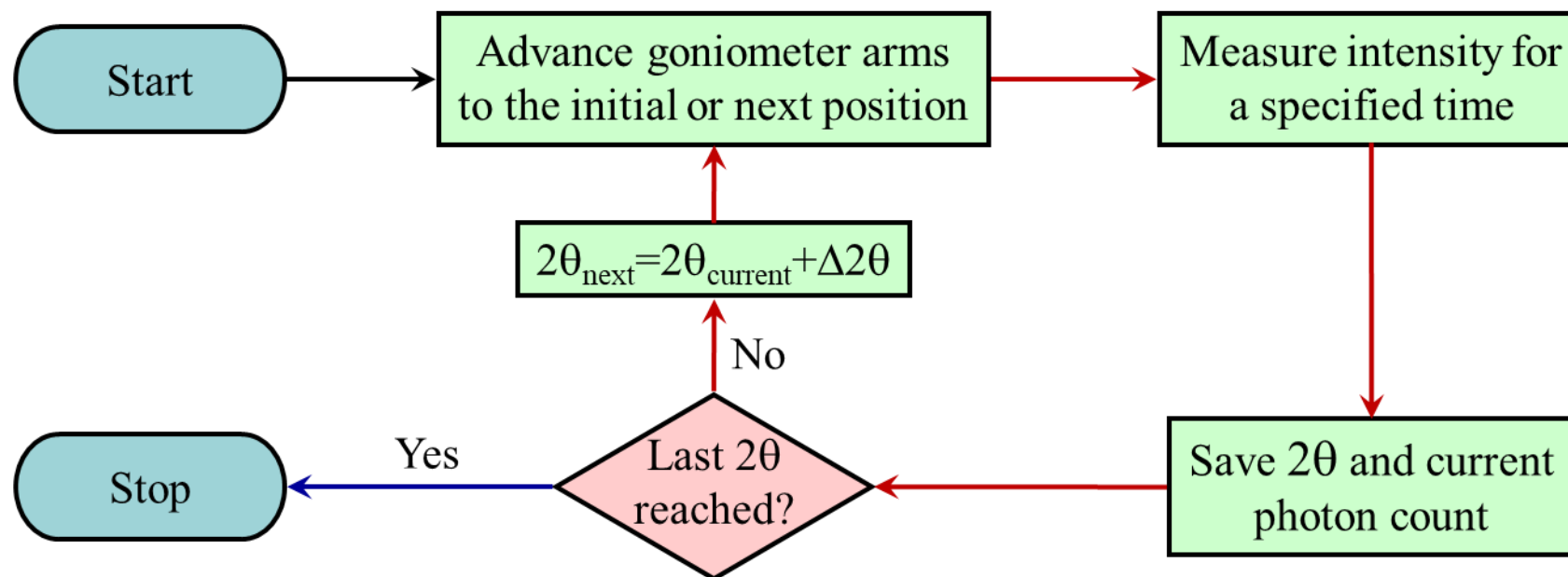
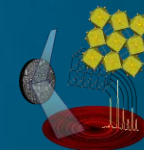
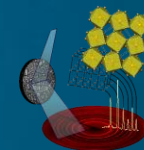


Figure 12.26. The flow chart visualizing a generic step scan data acquisition algorithm. The main loop is highlighted by using red arrows.



```
Instrument specific header  
Bragg angle 1, Number of accumulated counts 1[, Error 1]  
Bragg angle 2, Number of accumulated counts 2[, Error 2]  
Bragg angle 3, Number of accumulated counts 3[, Error 3]  
..., ...[, ...]  
Bragg angle N, Number of accumulated counts N[, Error N]
```

Figure 12.27. Example of powder diffraction data file format. Optional experimental errors in the measured intensity are shown in square brackets.

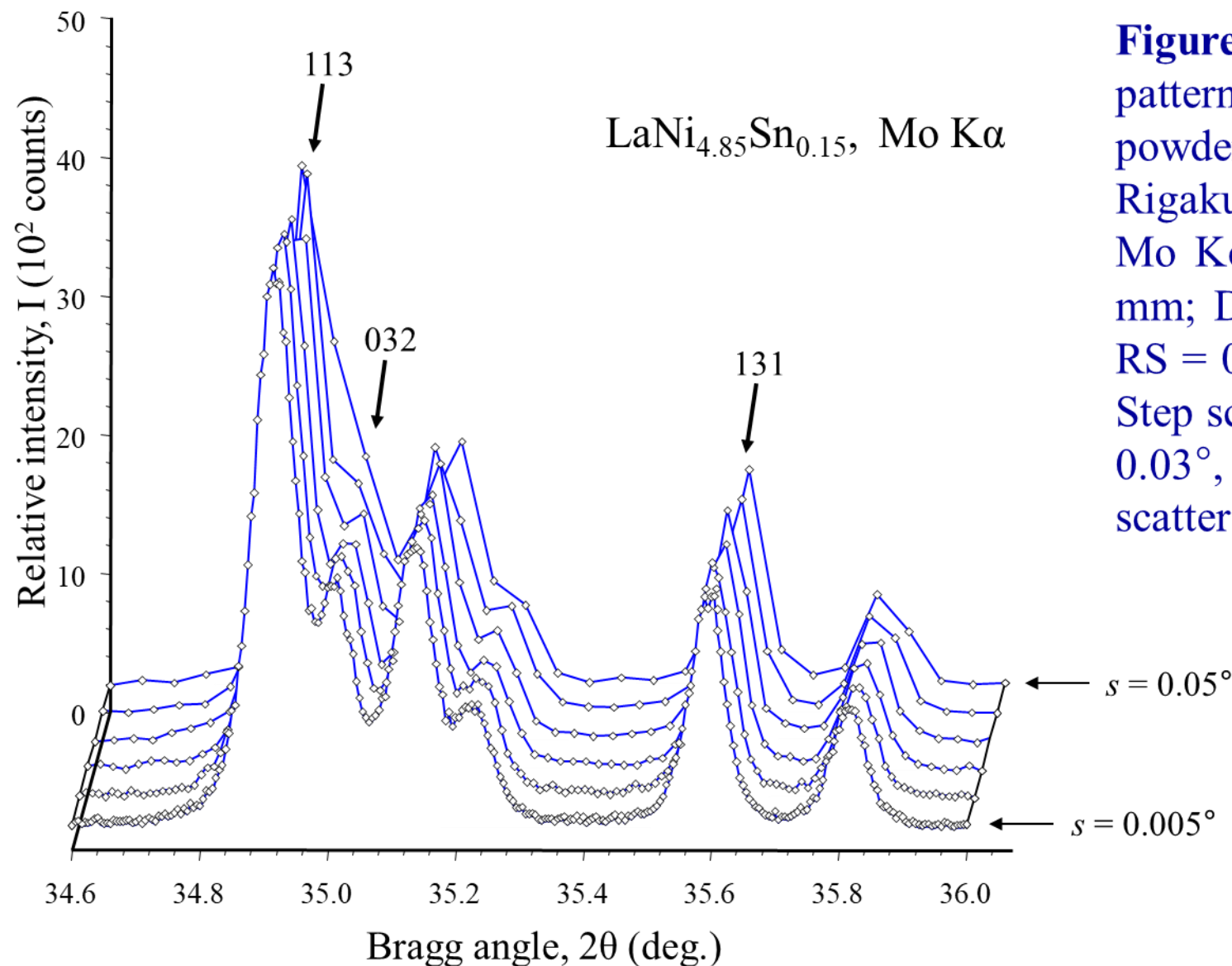
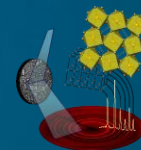


Figure 12.28. A set of X-ray powder diffraction patterns collected from the $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powder (see the inset in Figure 12.16) on a Rigaku TTRAX rotating anode powder using $\text{Mo K}\alpha$ radiation. Goniometer radius $R = 285$ mm; Divergence slit $\text{DS} = 0.5^\circ$; Receiving slit $\text{RS} = 0.03^\circ$; flat specimen diameter $d = 20$ mm. Step scan mode with steps 0.005° , 0.01° , 0.02° , 0.03° , 0.04° and 0.05° . An automatic variable scatter slit was used to reduce the background.

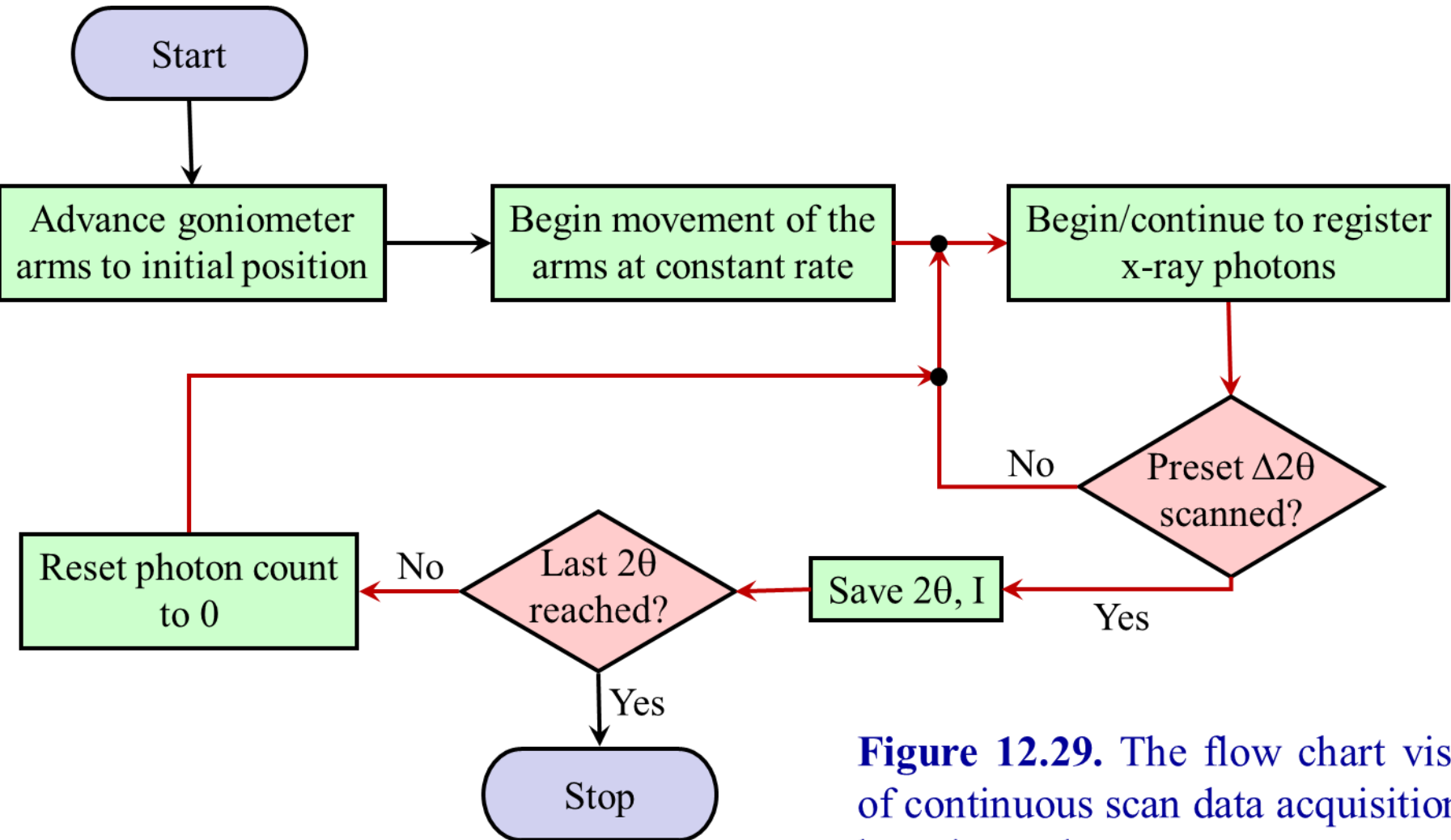
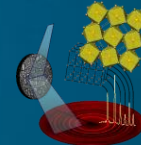


Figure 12.29. The flow chart visualizing a generic algorithm of continuous scan data acquisition. Main loops are highlighted by using red arrows.

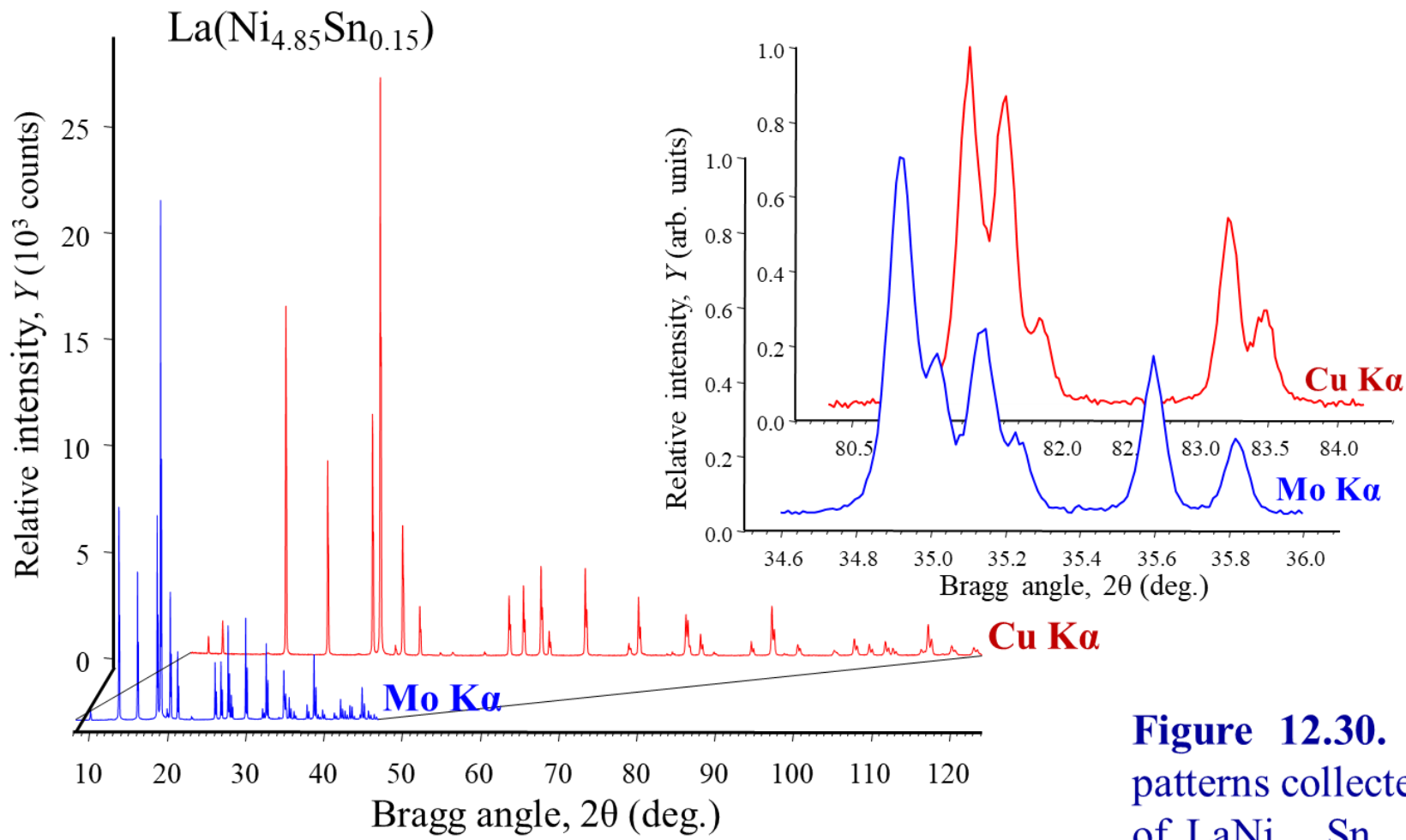
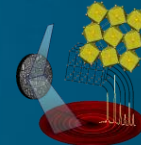
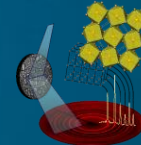


Figure 12.30. Two X-ray powder diffraction patterns collected from nearly spherical particles of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powder on a Rigaku TTRAX rotating anode powder diffractometer using $\text{MoK}\alpha$ and $\text{CuK}\alpha$ radiations.



$$R_{\text{obs}} = \sum_{i=1}^n \sigma_i / \sum_{i=1}^n N_i \times 100\% \quad \text{Eq. 12.10}$$

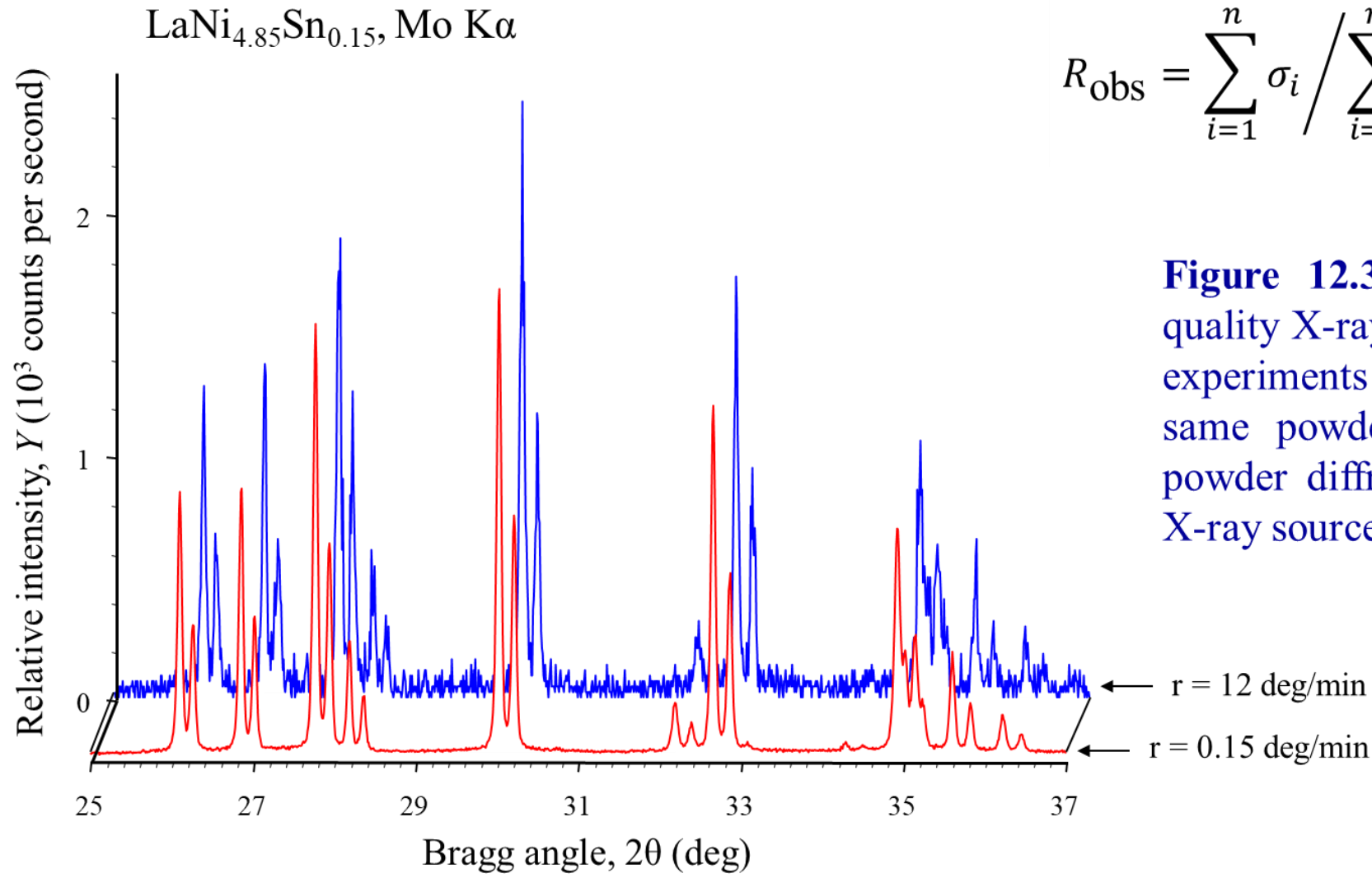


Figure 12.31. The example of different quality X-ray powder diffraction data. Both experiments were carried out using the same powdered specimen and the same powder diffractometer with rotating anode X-ray source but with different scan rates.

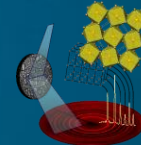


Table 12.1. Effect of counting time on the statistical error during a single measurement.

Photon flux (counts per second)	Counting time (s)	Number (N) of registered counts	Spread = $\sqrt{N}$ (counts)	Error at 90% confidence (%)
100	1	100	10	16.4
100	25	2,500	50	3.3

Poisson probability distribution: $\sigma = \sqrt{N}$ **Eq. 12.8**

The corresponding error, ε , in an individual measurement depends on the confidence level and is given as

$$\varepsilon = \frac{Q\sigma}{N} = \frac{Q}{\sqrt{N}} \times 100\% \quad \text{Eq. 12.9}$$

where $Q = 0.67, 1.64, 2.59$, and 3.09 for the 50, 90, 99 and 99.9% confidence levels,