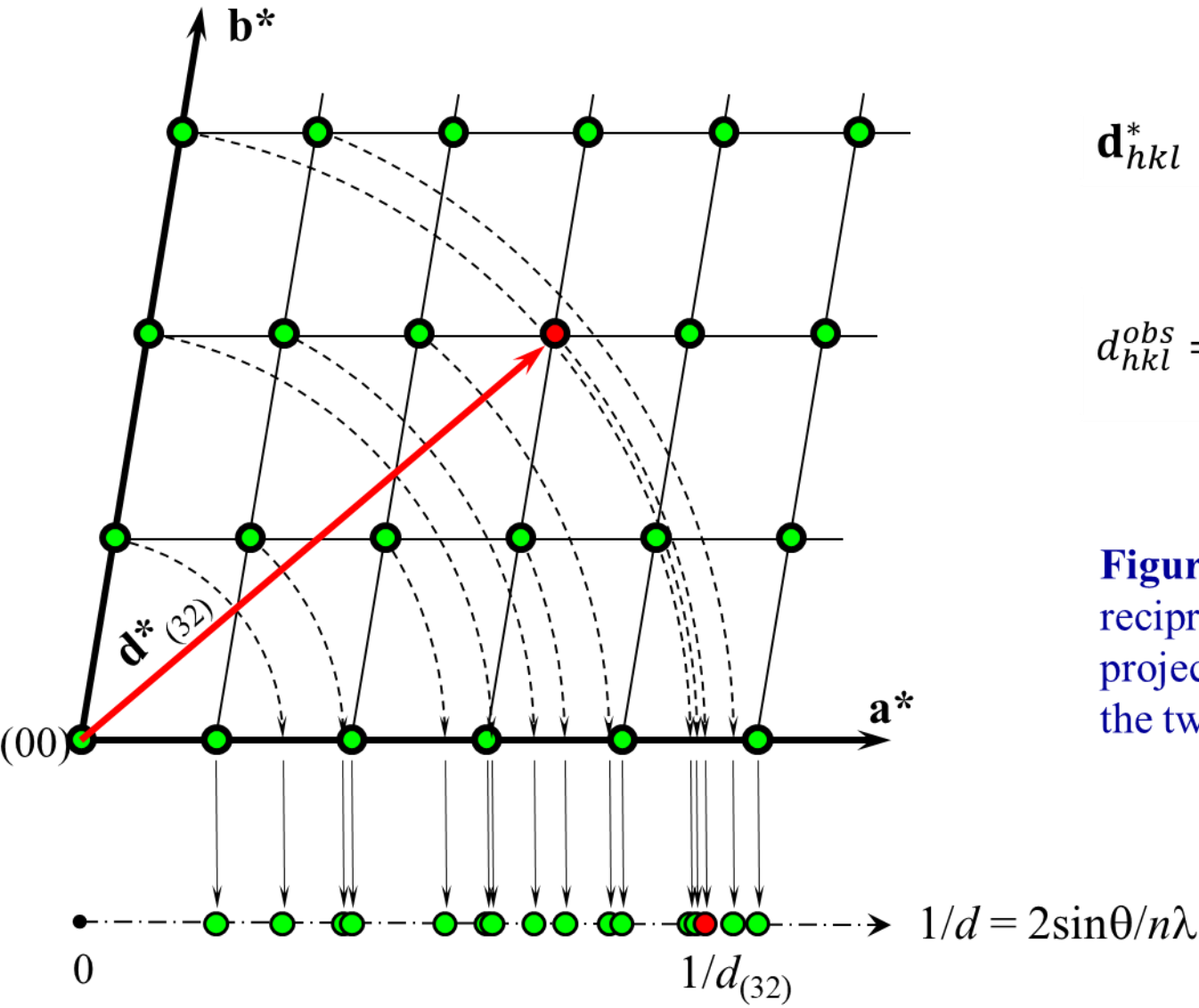
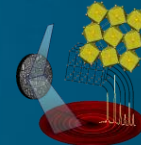




$$\mathbf{d}_{hkl}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

Eq. 14.1

$$d_{hkl}^{obs} = \frac{\lambda}{2 \sin \theta_{hkl}^{obs}}$$

Eq. 14.3

Figure 14.1. The illustration of a two-dimensional reciprocal lattice (*top*) and its one-dimensional projection on the $1/d$ axis (*bottom*). The scales in the two parts of the drawing are identical because

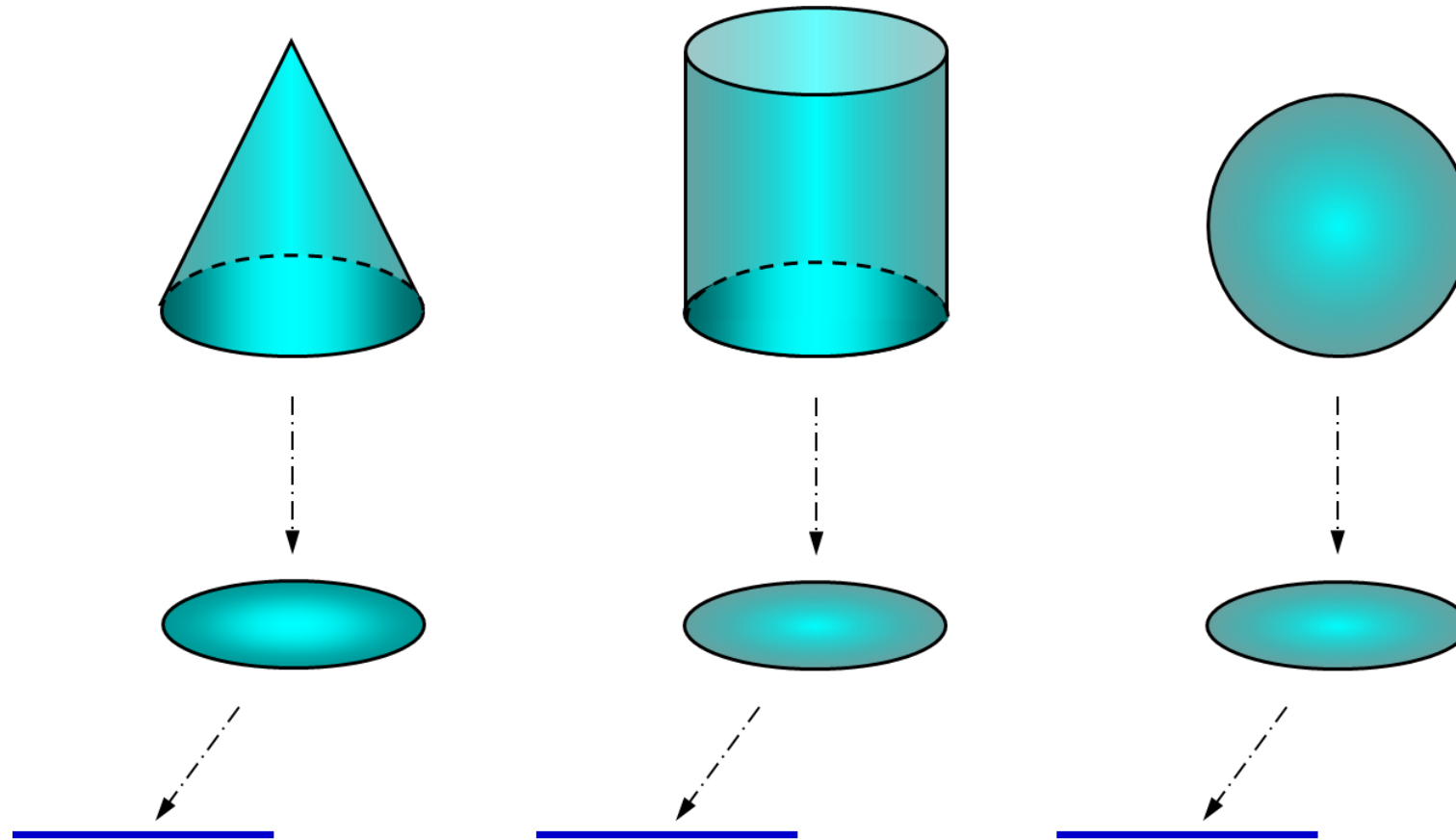
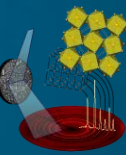


Figure 14.2. The illustration of three indistinguishable one- and two-dimensional projections obtained from three different three-dimensional objects. The projection directions are shown by *dash-dotted arrows*.

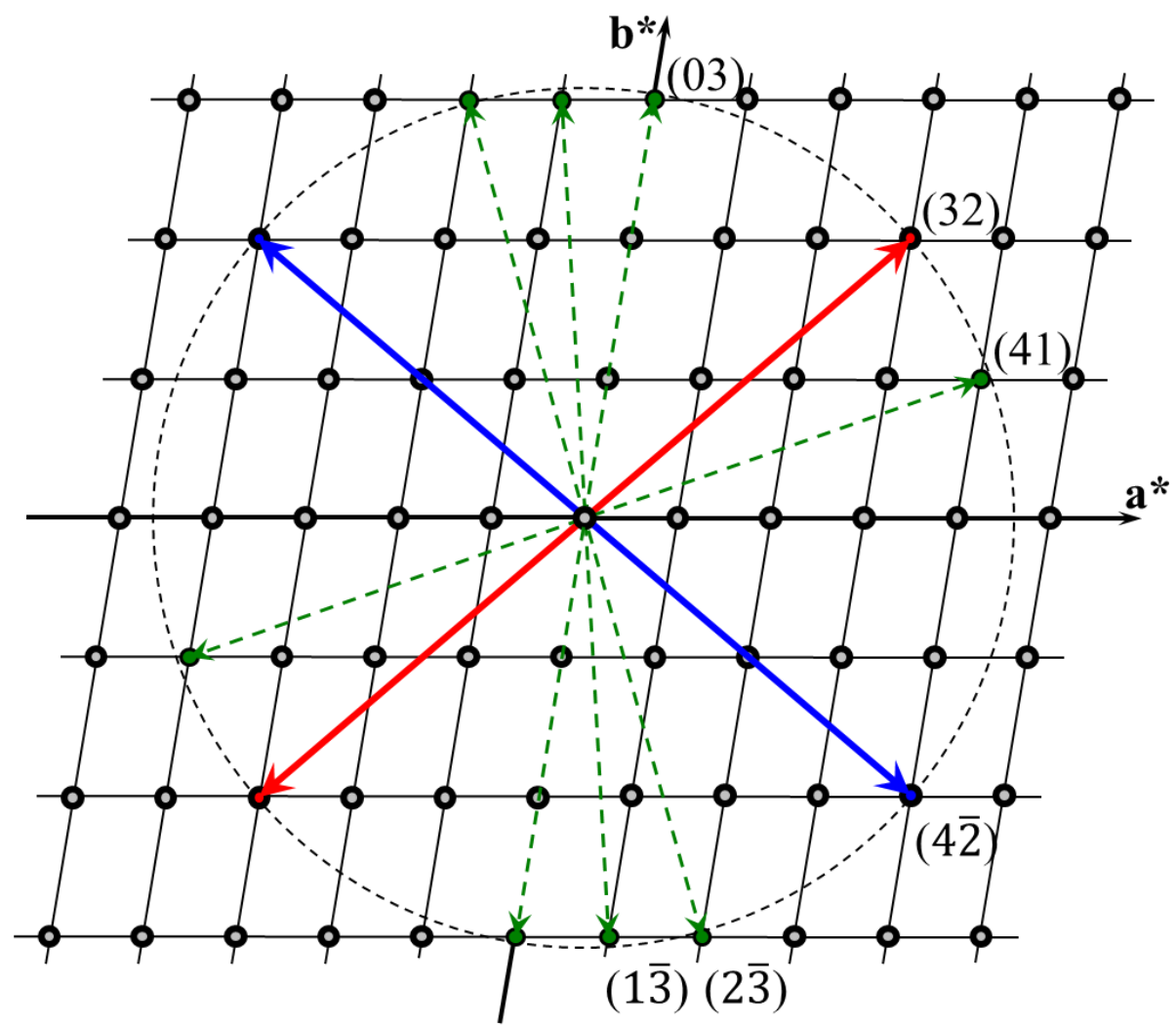
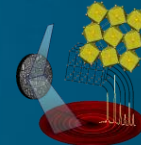


Figure 14.3. The illustration of a reciprocal lattice showing both the length and orientation of the reciprocal vector $\mathbf{d}_{(32)}^*$. A second vector in this lattice with identical length but different orientation is $\mathbf{d}_{(4\bar{2})}^*$ and the identity of their lengths is coincidental, i.e. not mandated by lattice symmetry. In addition, there are several vectors $[\mathbf{d}_{(03)}^*, \mathbf{d}_{(41)}^*, \mathbf{d}_{(2\bar{3})}^*$ and $\mathbf{d}_{(1\bar{3})}^*]$ with their lengths nearly identical to those of $\mathbf{d}_{(32)}^*$ and $\mathbf{d}_{(4\bar{2})}^*$.

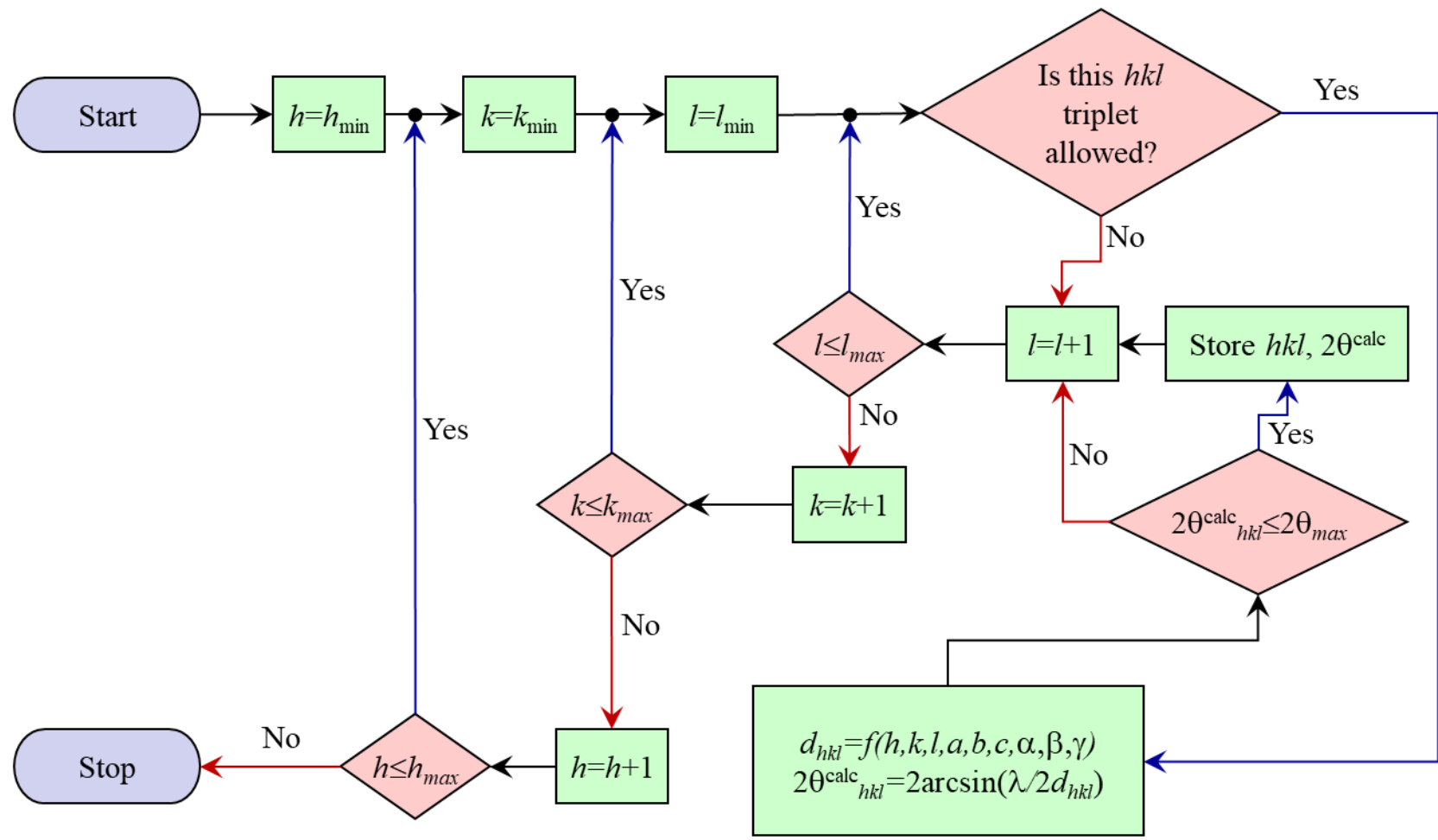
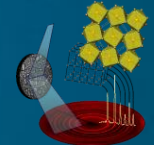
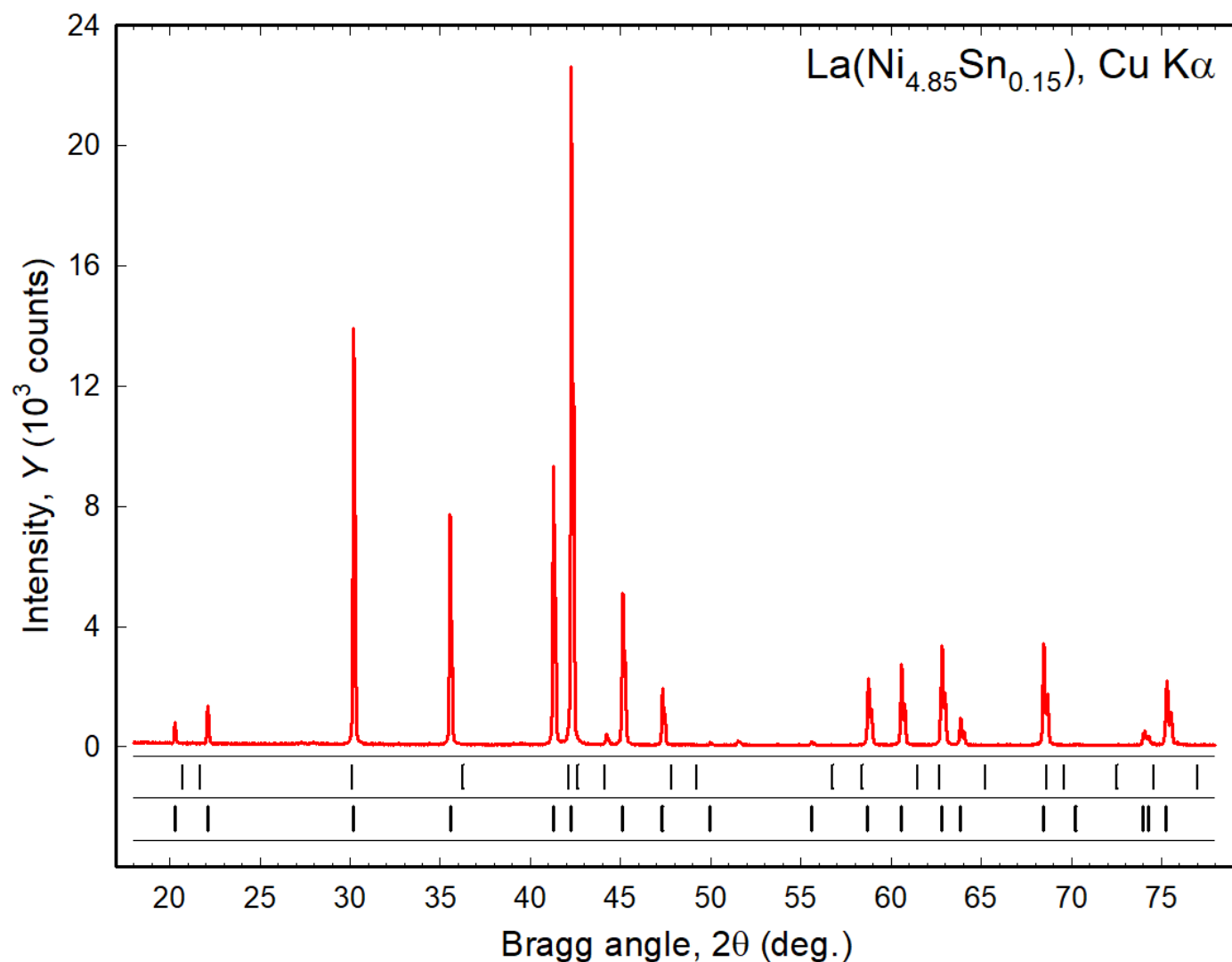
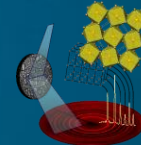


Figure 14.4. The flowchart illustrating a generic algorithm designed to generate all allowed combinations of Miller indices and compute Bragg angles from known unit cell dimensions.



$$\frac{1}{d^2} = \frac{4}{3} \times \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad \text{Eq. 14.4}$$

Figure 14.5. A fragment of the diffraction pattern collected from a LaNi_{4.85}Sn_{0.15} powder on a Rigaku TTRAX rotating anode powder diffractometer using Cu Kα_{1,2} radiation.

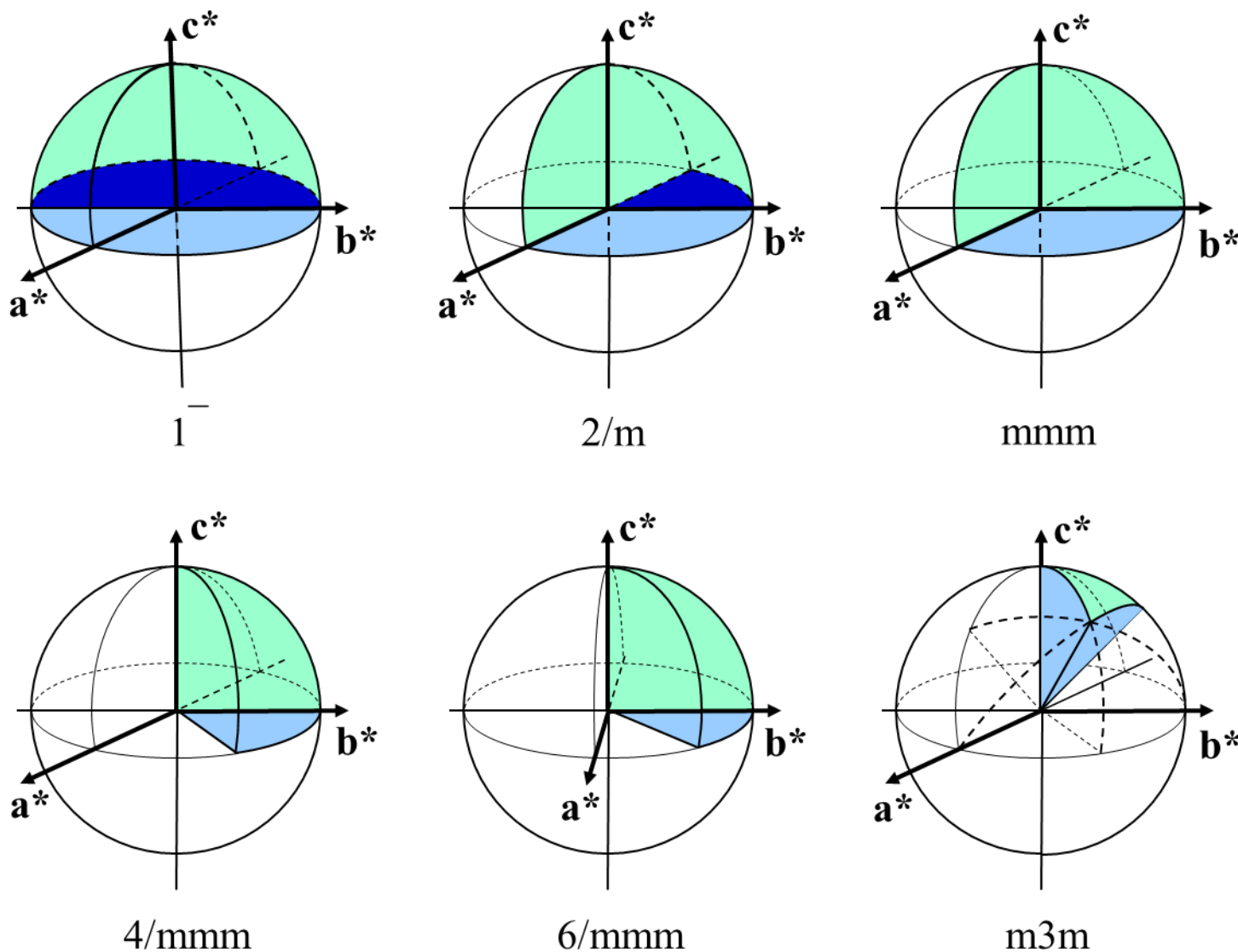
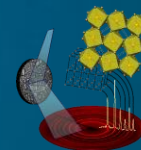


Figure 14.6. Schematic representations in the reciprocal space of the sphere volume fractions ($r = 1/\lambda$) where the list of hkl triplets should be generated in each of the six "powder" Laue classes.

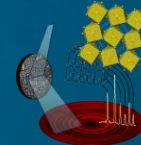


Table 14.7. Symmetrically independent combinations of indices in six "powder" Laue classes.

“Powder” Laue class	Range of indices and limiting conditions ^a	Independent fraction of sphere volume ^b
Triclinic, $\bar{1}$	$-h\dots+h; -k\dots k; 0\dots+l$	$\frac{1}{2}$
Monoclinic, $2/m$	$-h\dots+h; 0\dots k; 0\dots+l$	$\frac{1}{4}$
Orthorhombic, mmm	$0\dots+h; 0\dots+k; 0\dots+l$	$\frac{1}{8}$
Tetragonal, $4/mmm$	$0\dots+h; 0\dots+k; 0\dots+l; h \leq k$	$\frac{1}{16}$
Hexagonal (=Trigonal), $6/mmm$	$0\dots+h; 0\dots+k; 0\dots+l; h \leq k$	$\frac{1}{24}$
Cubic, $m\bar{3}m$	$0\dots+h; 0\dots+k; 0\dots+l; h \leq k; k \leq l$	$\frac{1}{48}$

^a The range and limiting conditions match the illustrations in Figure 14.6.
^b Any fraction of the sphere that is symmetrically equivalent to the shaded area in Figure 14.6 is acceptable.

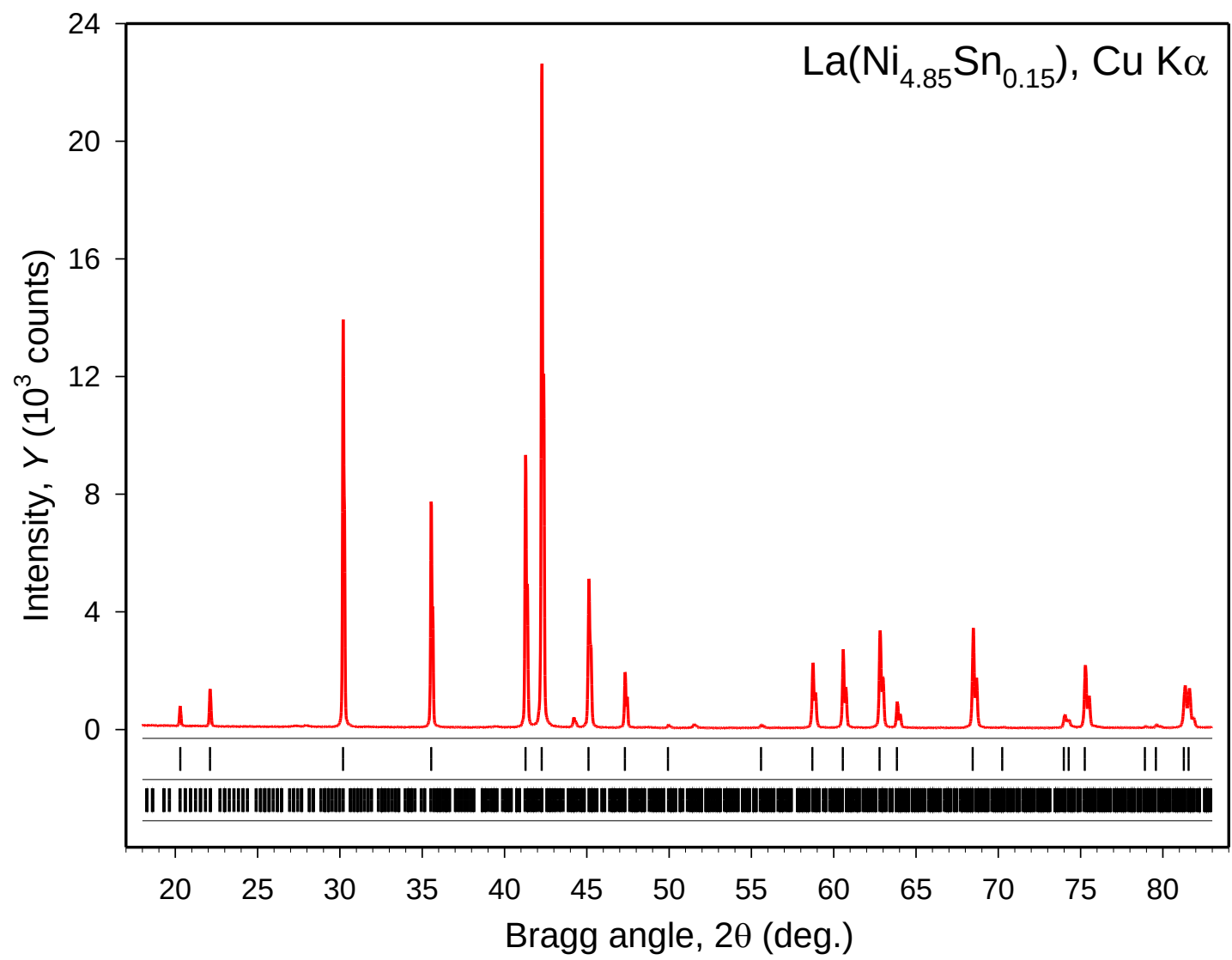
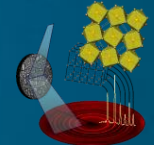
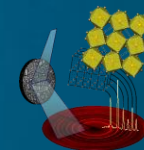


Figure 14.7. The illustration of an incorrect indexing of the powder diffraction pattern of LaNi_{4.85}Sn_{0.15}. The *upper set of vertical bars* corresponds to the locations of Bragg peaks calculated using the correct hexagonal lattice with $a = 5.0421$, $c = 4.0118$ Å. The *lower set of bars* represents dubious indexing using a large primitive cubic unit cell with $a=24.74$ Å.



Reliability of Indexing:

$$\varepsilon = \sum_{i=1}^N \left(2\theta_{h_i k_i l_i}^{obs} - 2\theta_{h_i k_i l_i}^{calc} \right)^2 \quad \text{Eq. 14.6}$$

The F_N and $M_{20}(M_N)$ Figures of Merit:

$$F_N = \frac{N}{N_{poss}} \times \frac{1}{|\overline{\Delta 2\theta}|} = \frac{N^2}{N_{poss} \sum_{i=1}^N |2\theta_i^{obs} - 2\theta_i^{calc}|} \quad \text{Eq. 14.7}$$

$$M_{20} = \frac{1}{N_{poss}} \times \frac{Q_{20}}{2|\overline{\Delta Q}|} = \frac{10Q_{20}}{N_{poss} \sum_{i=1}^{20} |Q_i^{obs} - Q_i^{calc}|} \quad \text{Eq. 14.9}$$

$$M_N = \frac{1}{N_{poss}} \times \frac{Q_N}{2|\overline{\Delta Q}|} = \frac{NQ_N}{2N_{poss} \sum_{i=1}^N |Q_i^{obs} - Q_i^{calc}|} \quad \text{Eq. 14.10}$$

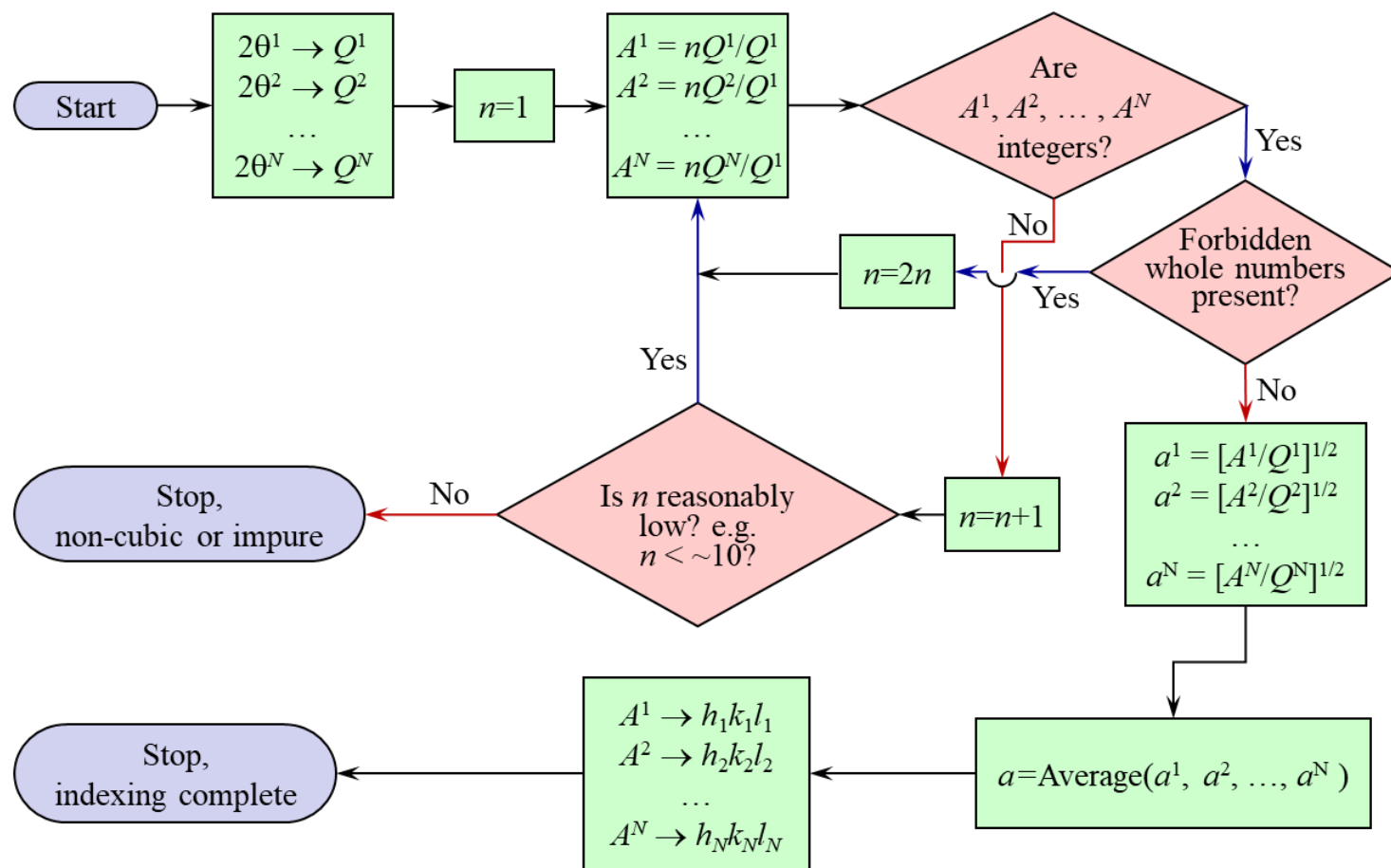
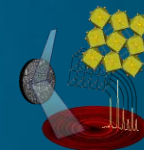


Figure 14.8. The flowchart illustrating the algorithm of the *ab initio* indexing when cubic symmetry is suspected. It is assumed that the array of Q -values is sorted in the ascending order from Q^1 to Q^N .

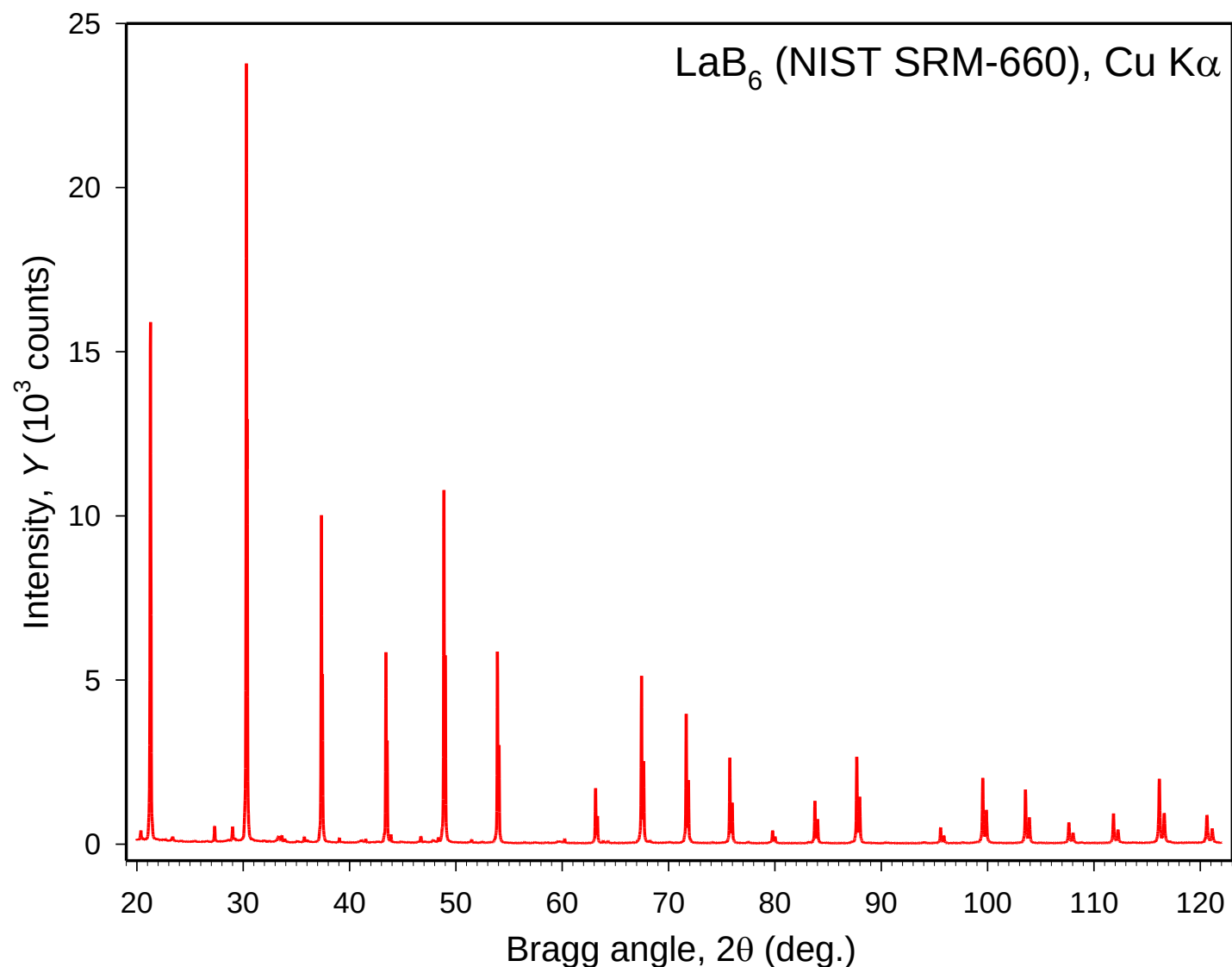
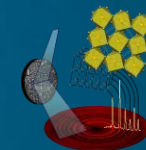


Figure 14.9. The X-ray powder diffraction pattern collected from SRM-660 LaB₆ powder on a Scintag XDS2000 powder diffractometer using Cu K α radiation.

The ASCII data file with diffraction data is available online, file name *Ch14Ex02_CuKa.xy*.

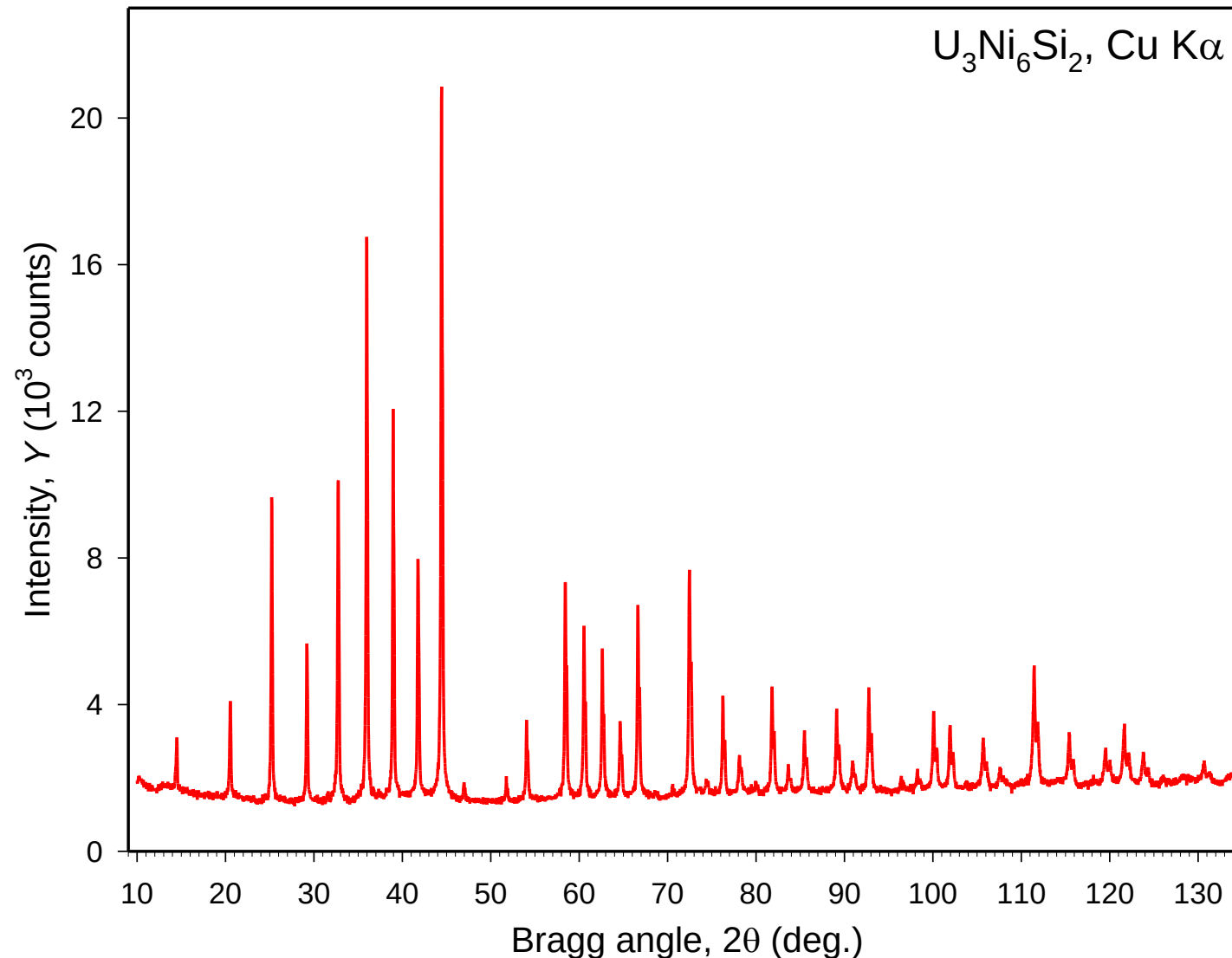
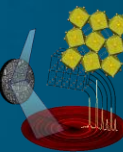


Figure 14.10. The X-ray powder diffraction pattern of U₃Ni₆Si₂ collected on an HZG-4a powder diffractometer using filtered Cu Kα radiation. The data were collected in a step scan mode with a step 0.02° of 2θ and counting time 25 sec.

The ASCII data file with the diffraction data is available online, file name *Ch14Ex03_CuKa.xy*.

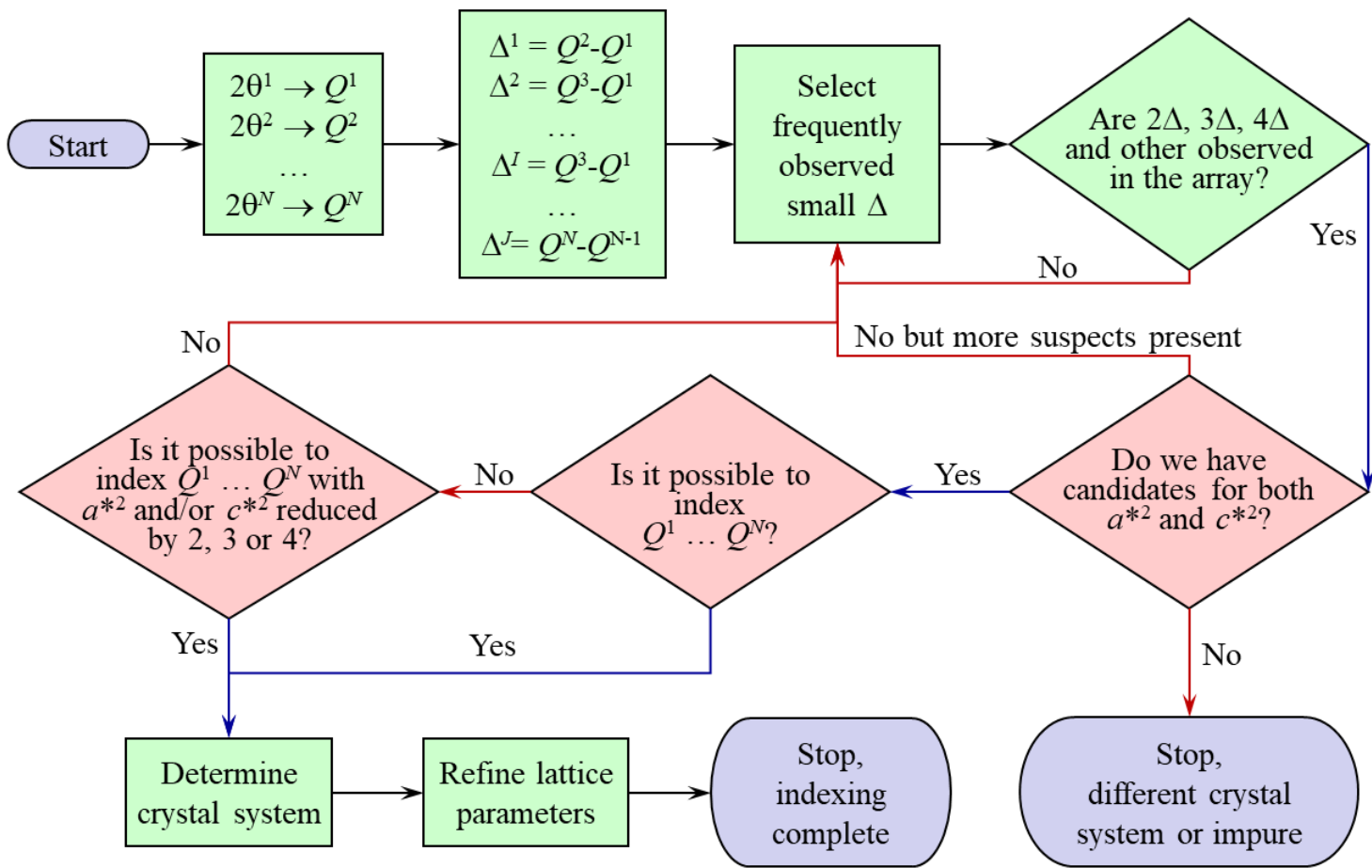
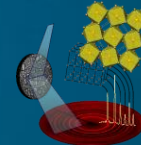


Figure 14.11. The flowchart illustrating the algorithm of the *ab initio* indexing assuming tetragonal or hexagonal symmetry of the reciprocal lattice.

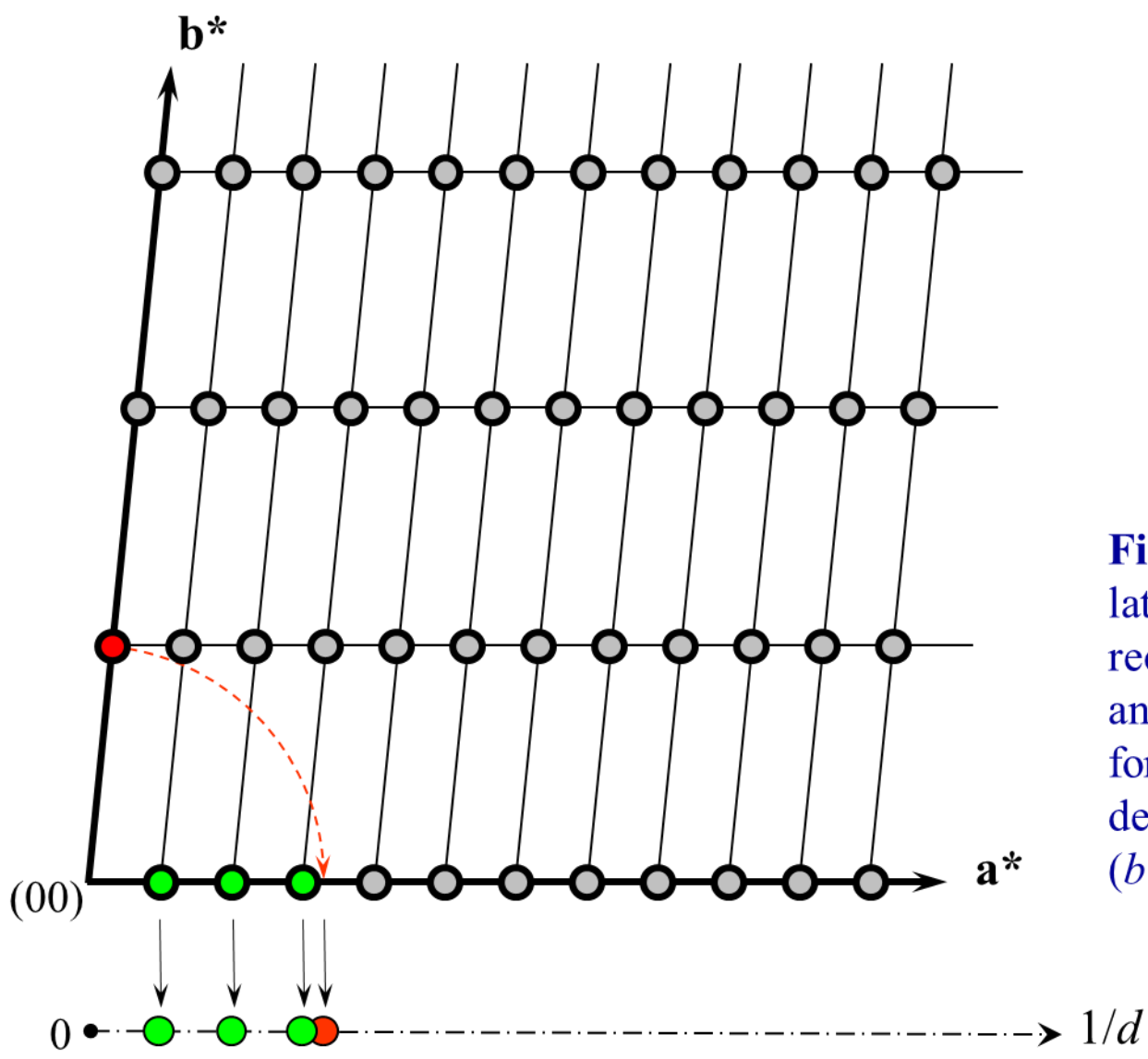
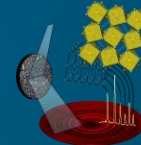
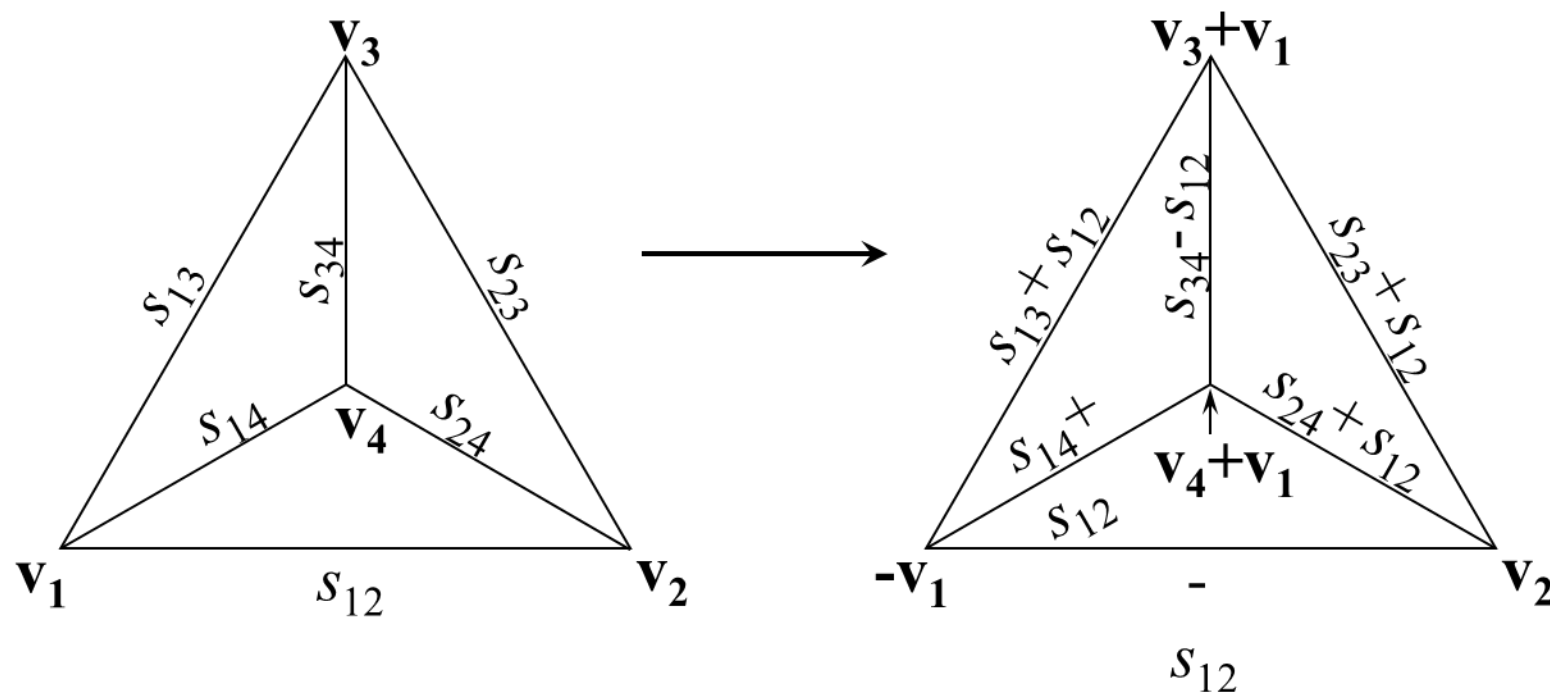
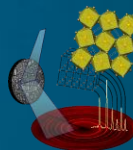


Figure 14.12. The illustration of the two-dimensional lattice with one long (b^*) and one short (a^*) reciprocal lattice vectors. If the three lowest Bragg angle peaks (*filled circles*) are selected as a basis set for indexing, all of them are collinear and only depend on a^* . The remaining two lattice parameters (b^* and γ^*) cannot be determined from this basis set.



Eq. 14.25

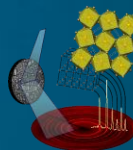
$$\mathbf{v}_1^{\text{ortho}} = \mathbf{v}_1 + \mathbf{v}_2$$

$$\mathbf{v}_2^{\text{ortho}} = -\mathbf{v}_1 + \mathbf{v}_2$$

$$\mathbf{v}_3^{\text{ortho}} = \mathbf{v}_3$$

$$s_{ij} = \mathbf{v}_i \cdot \mathbf{v}_j = |\mathbf{v}_i| |\mathbf{v}_j| \cos \alpha_{ij} \\ (\text{for } i \neq j)$$

Figure 14.13. The schematic of Delaunay-Ito transformation. *Left* – the four unit cell vectors ($\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_3$ and $\mathbf{v}_4$) are associated with the corners of the tetrahedron, while the six scalar products between the corresponding pairs of the vector (s_{12} through s_{34}) are linked to the edges of the tetrahedron. Assuming that $s_{12} > 0$, the transformation is carried out as shown on the *right*: the sign of s_{12} is changed; its value is subtracted from that on the opposite edge and added to those on all adjacent edges.



Niggli Reduction

$$\mathbf{v}_1 + \mathbf{v}_2 + \mathbf{v}_3 = \textit{minimum} \quad \text{Eq. 14.26}$$

$$\begin{aligned} &1) \, v_1 \leq v_2 \leq v_3 \\ &2) \, |s_{12}| \leq v_3/2 \\ &3) \, |s_{23}| \leq v_2/2 \\ &4) \, |s_{13}| \leq v_1/2 \\ &5) \, |s_{23} \pm s_{13}| \leq (v_1 + v_2 \pm 2s_{12}) \end{aligned} \quad \text{Eq. 14.27}$$

L. Zuo, J. Muller, M.-J. Phillippe, and G. Esling, A refined algorithm for the reduced-cell determination, Acta Cryst. **A51**, 943 (1995). <https://doi.org/10.1107/S0108767395006672>

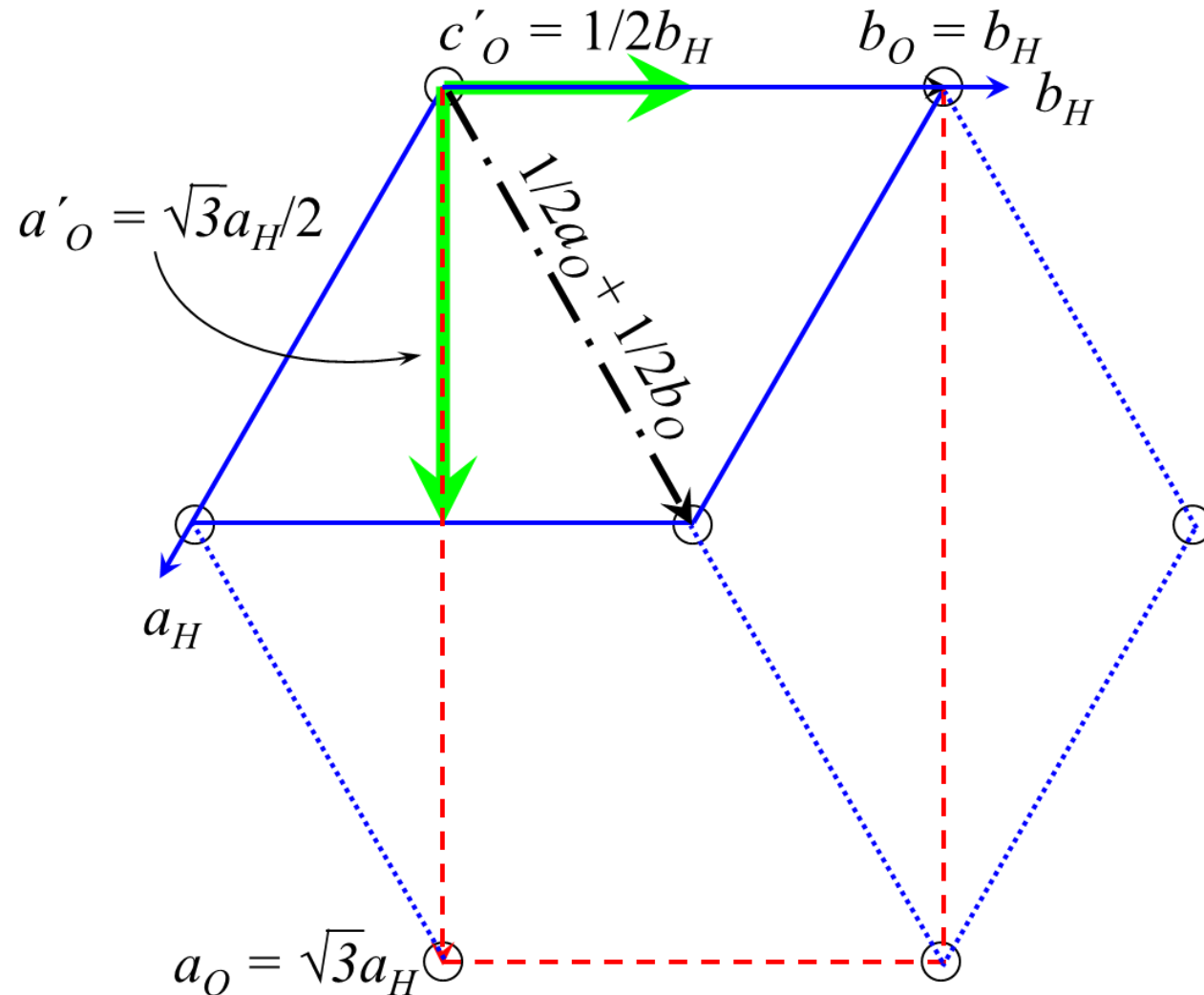
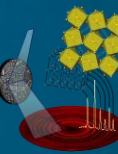


Figure 14.14. The relationship between the lattice parameters of the hexagonal unit cell (*blue solid and dotted lines*) and the related orthorhombic unit cell (*red dashed lines*). The unit cell parameter perpendicular to the plane of the projection is identical in both crystal systems. The smaller orthorhombic unit cell found using the DICVOL91 indexing program is indicated by the *thick green vectors* (a'_O and c'_O). Open circles show lattice points and the *black dash-dotted vector* illustrates the C-translation in the conforming orthorhombic lattice.

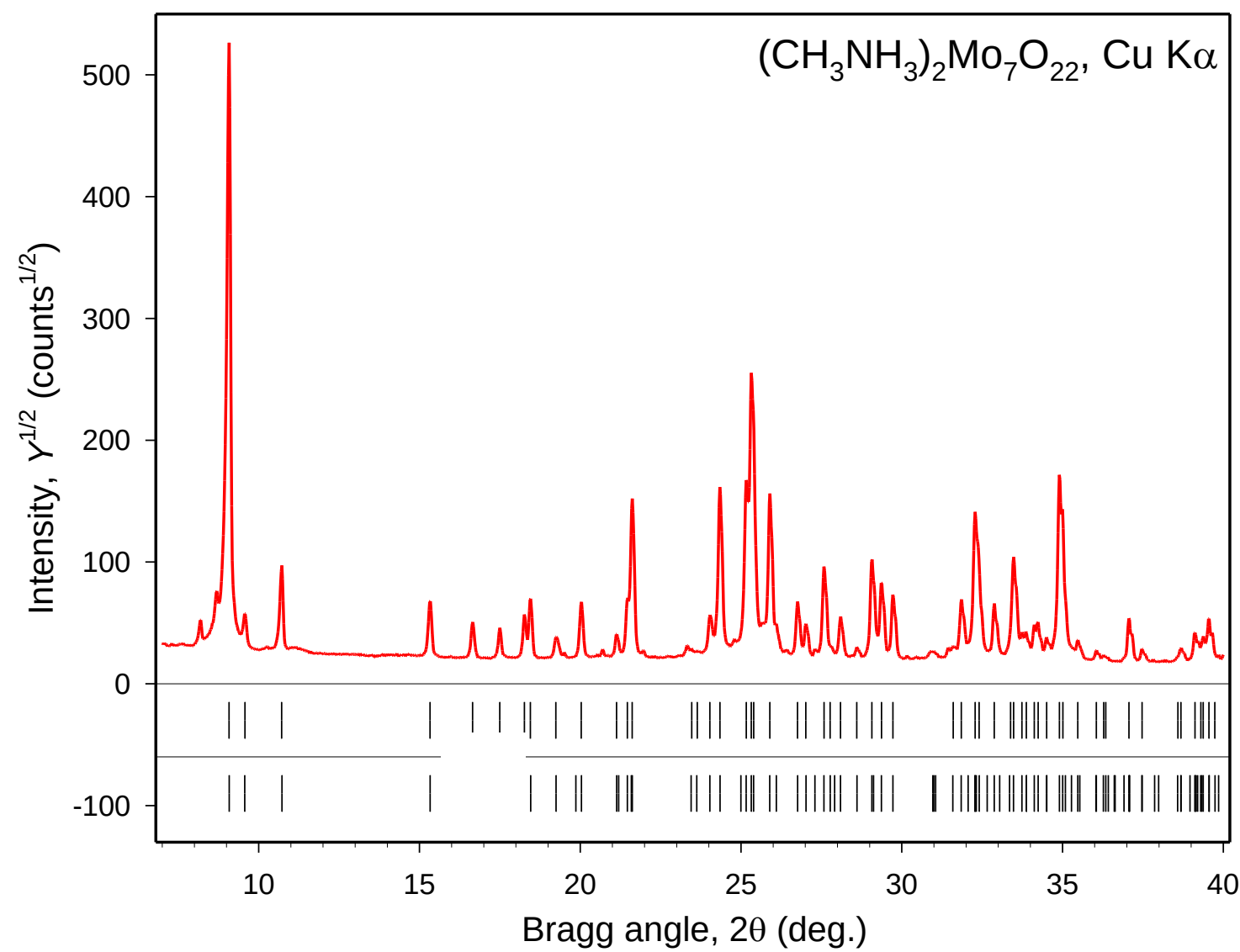
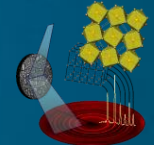


Figure 14.15. Powder diffraction pattern of $(\text{CH}_3\text{NH}_3)_2\text{Mo}_7\text{O}_{22}$ collected on a Scintag XDS2000 diffractometer using $\text{Cu K}\alpha$ radiation in a step scan mode with $\Delta 2\theta = 0.02^\circ$ and counting time 30 sec. The square root of intensity is plotted as a function of Bragg angle for clarity. The two sets of *vertical bars* illustrate the following: *top* – positions of the observed Bragg peaks, *bottom* – the same calculated in the space group $\text{C}2/c$

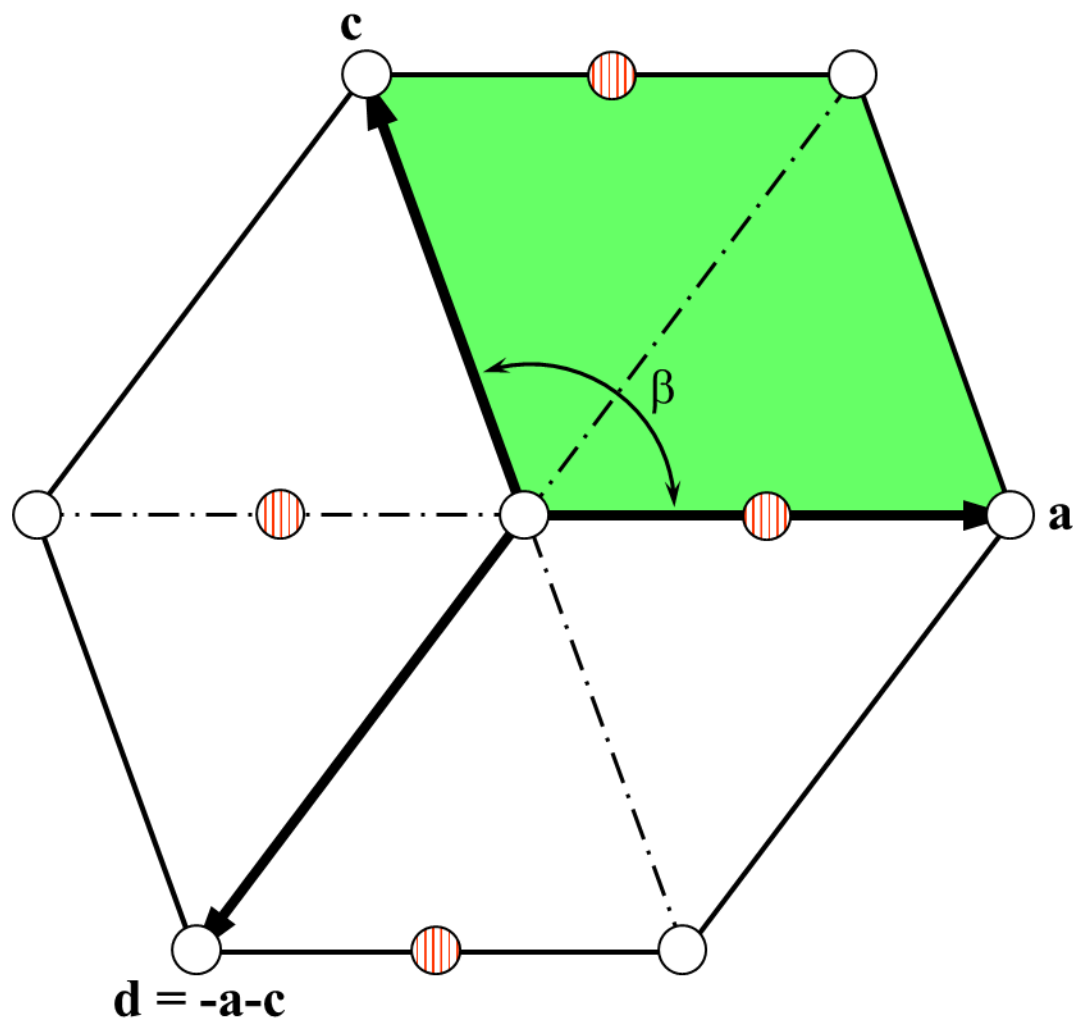
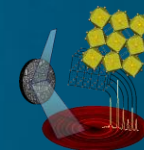


Figure 14.16. Alternative axes selection in the monoclinic crystal system. *Open and hatched points* represent lattice points. The *open points* are located in the plane, while the *hatched points* are raised by $\frac{1}{2}$ of the full translation in the direction perpendicular to the plane of the projection. Unit cells based on the vectors **a** and **c** or **a** and **d** correspond to a base-centered (C) lattice, while the unit cell based on the vectors **c** and **d** corresponds to a body-centered lattice.

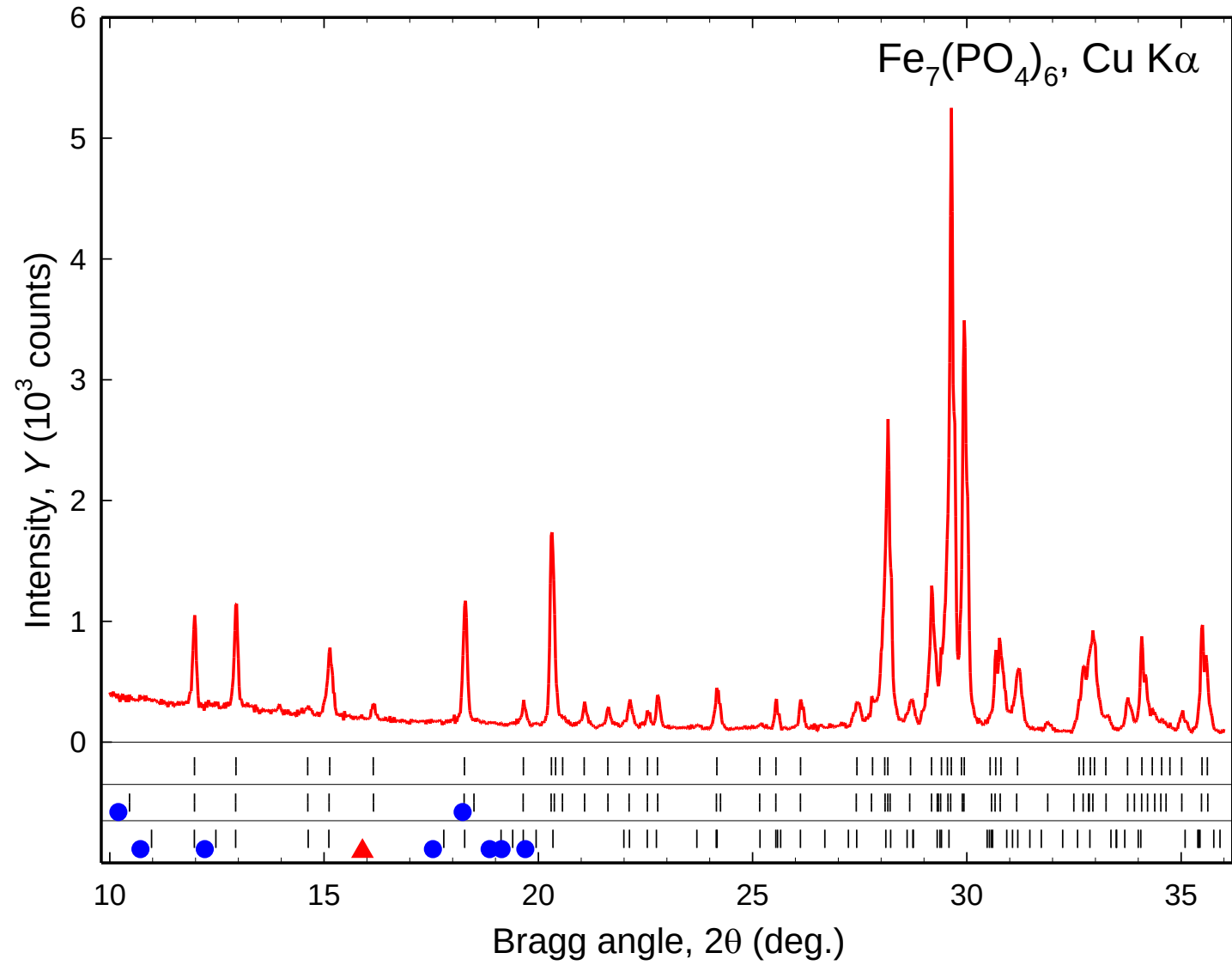
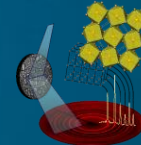
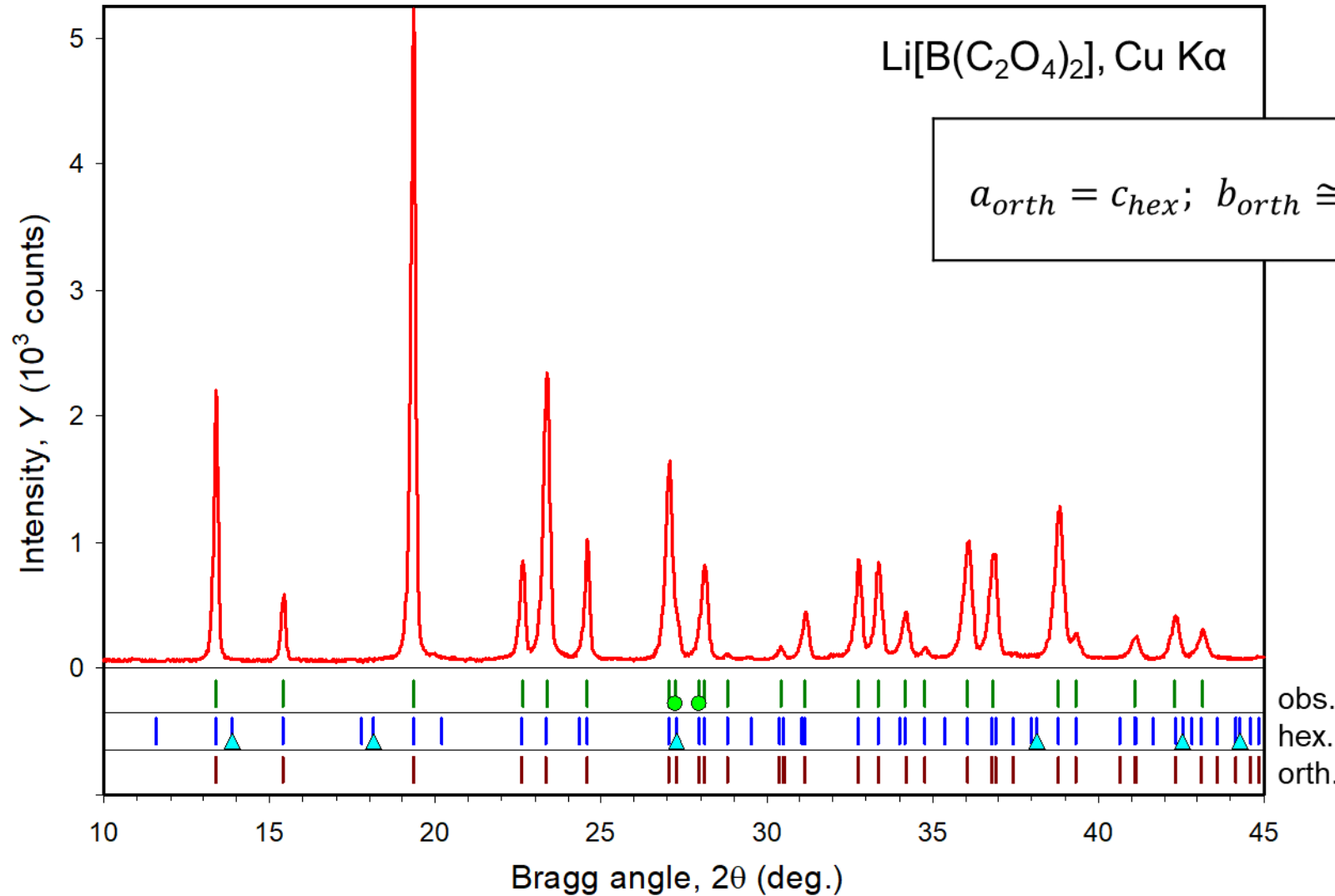
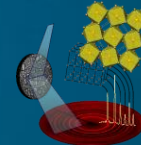


Figure 14.17. Powder diffraction pattern of $\text{Fe}_7(\text{PO}_4)_6$ collected on a Scintag XDS2000 diffractometer using $\text{Cu K}\alpha$ radiation in a step scan mode with $\Delta 2\theta = 0.02^\circ$ and counting time 30 s. The three sets of *vertical bars* illustrate the following: *top* – positions of the observed Bragg peaks, *middle* – positions of Bragg peaks calculated using ITO solution No. 1 (correct), and *bottom* – the same calculated using ITO solution No. 2 (incorrect); both solutions are listed in Table 14.24. *Blue circles* indicate unobserved reflections, and *red triangle* marks the only observed reflection below $2\theta = 20^\circ$, which remained unindexed in 2nd solution.



Eq. 14.28

$$a_{orth} = c_{hex}; \quad b_{orth} \cong \frac{1}{2} a_{hex}; \quad c_{orth} \cong \sqrt{3} b_{orth} \cong \frac{\sqrt{3}}{2} a_{hex}$$

Figure 14.18. Powder diffraction pattern of Li[B(C₂O₄)₂]. The three sets of vertical bars illustrate positions of: top - observed Bragg peaks; middle - calculated for an incorrect hexagonal unit cell; bottom - calculated for a correct orthorhombic unit cell (Pnma); blue triangles - reflections extinct in P6₃/mmc; green circles - two peaks excluded from the.

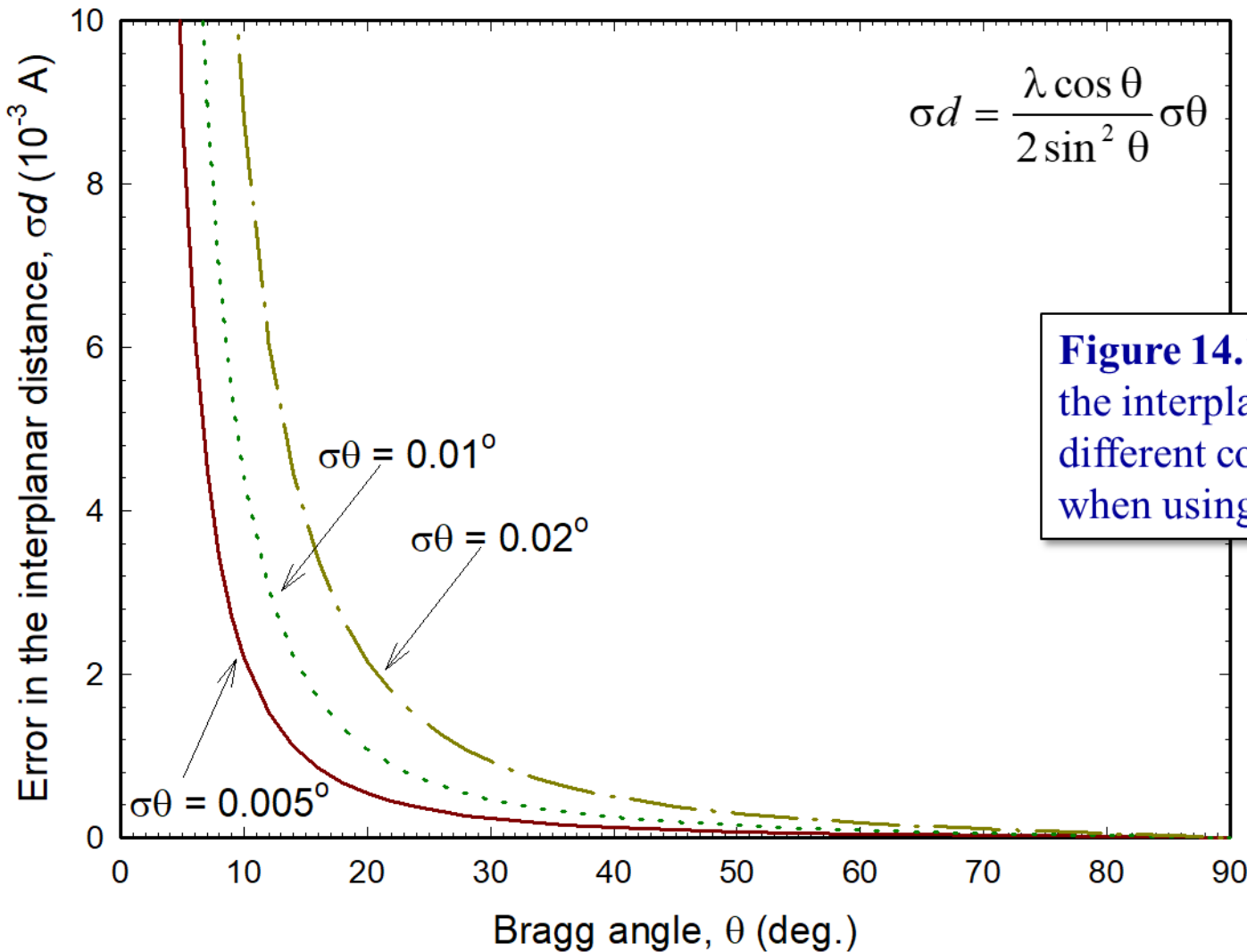
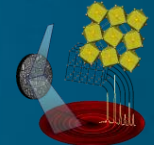


Figure 14.19. The dependence of the absolute error in the interplanar distance, σd , on Bragg angle for several different constant errors in the measured Bragg angle when using Cu $K\alpha_1$ radiation, $\lambda = 1.540593$ Å.

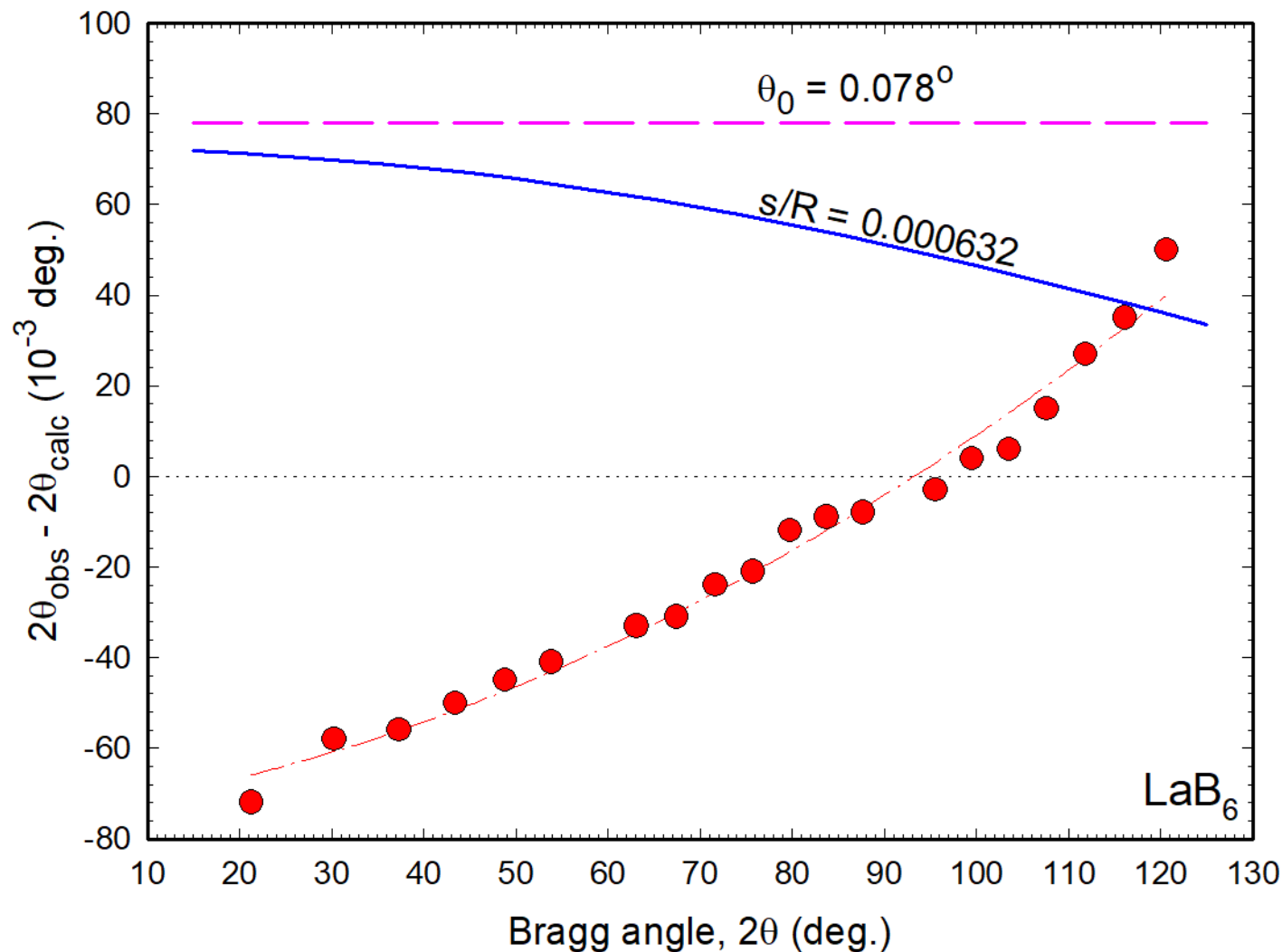
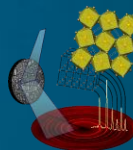


Figure 14.20. The differences between the observed and calculated Bragg angles after least squares refinement of the lattice parameter of LaB₆ without accounting for the presence of any kind of systematic error (*open circles*) using $a=4.1599(3)$ Å. The *dash-dotted line* drawn through the data points is a guide for the eye. The *solid line* represents corrections of the observed Bragg angles using the refined in the next step sample displacement error ($s/R = 0.00632$) and the *dashed line* represents a similar correction by using the determined zero-shift error ($\delta\theta_0 = 0.078^\circ$).

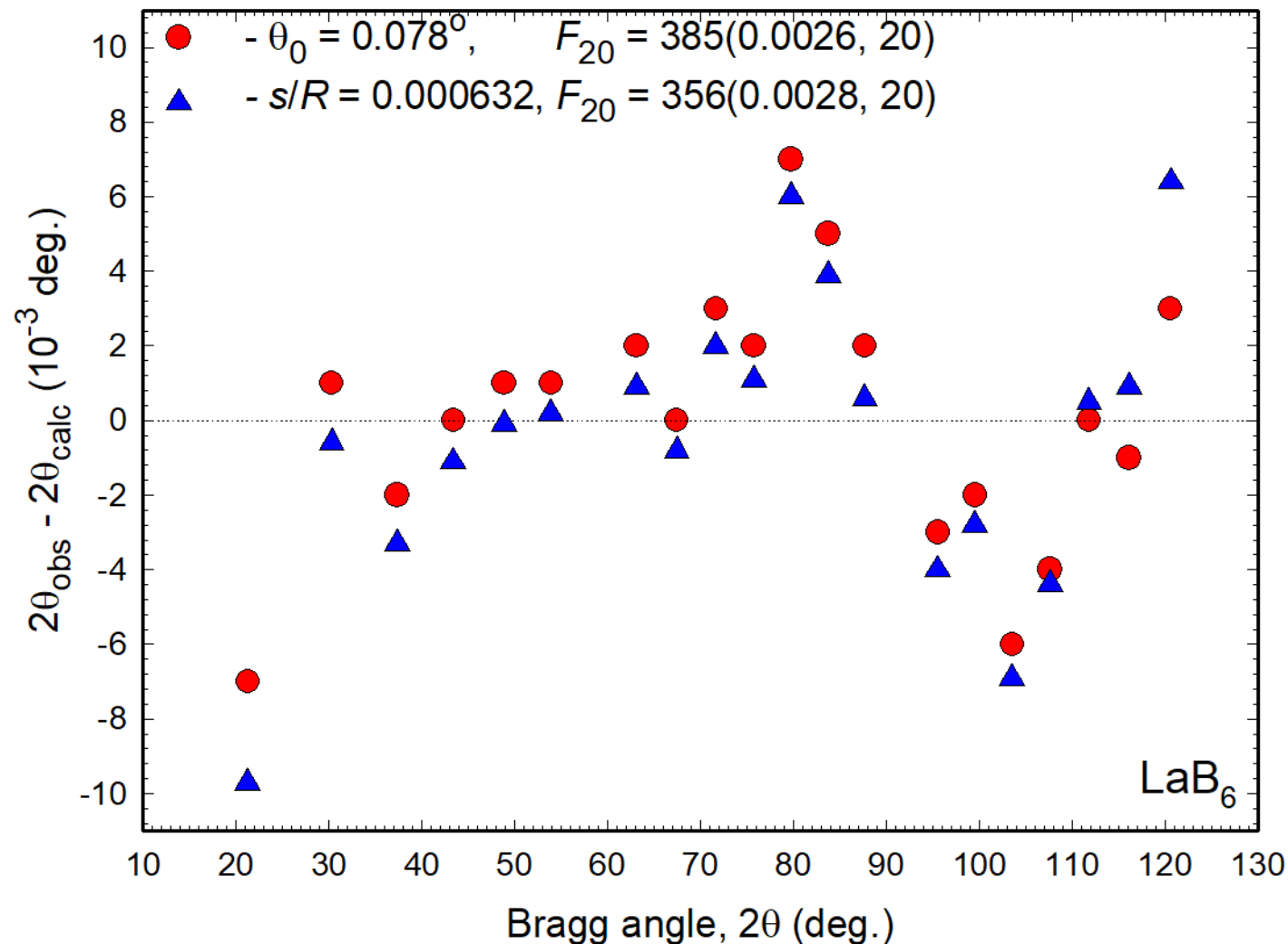
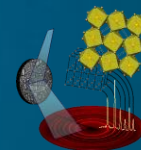


Figure 14.21. The differences between the observed and calculated Bragg angles after the least squares refinement of the lattice parameter of LaB₆ simultaneously with the zero-shift error (*red circles*) or simultaneously with the sample displacement error (*blue triangles*).

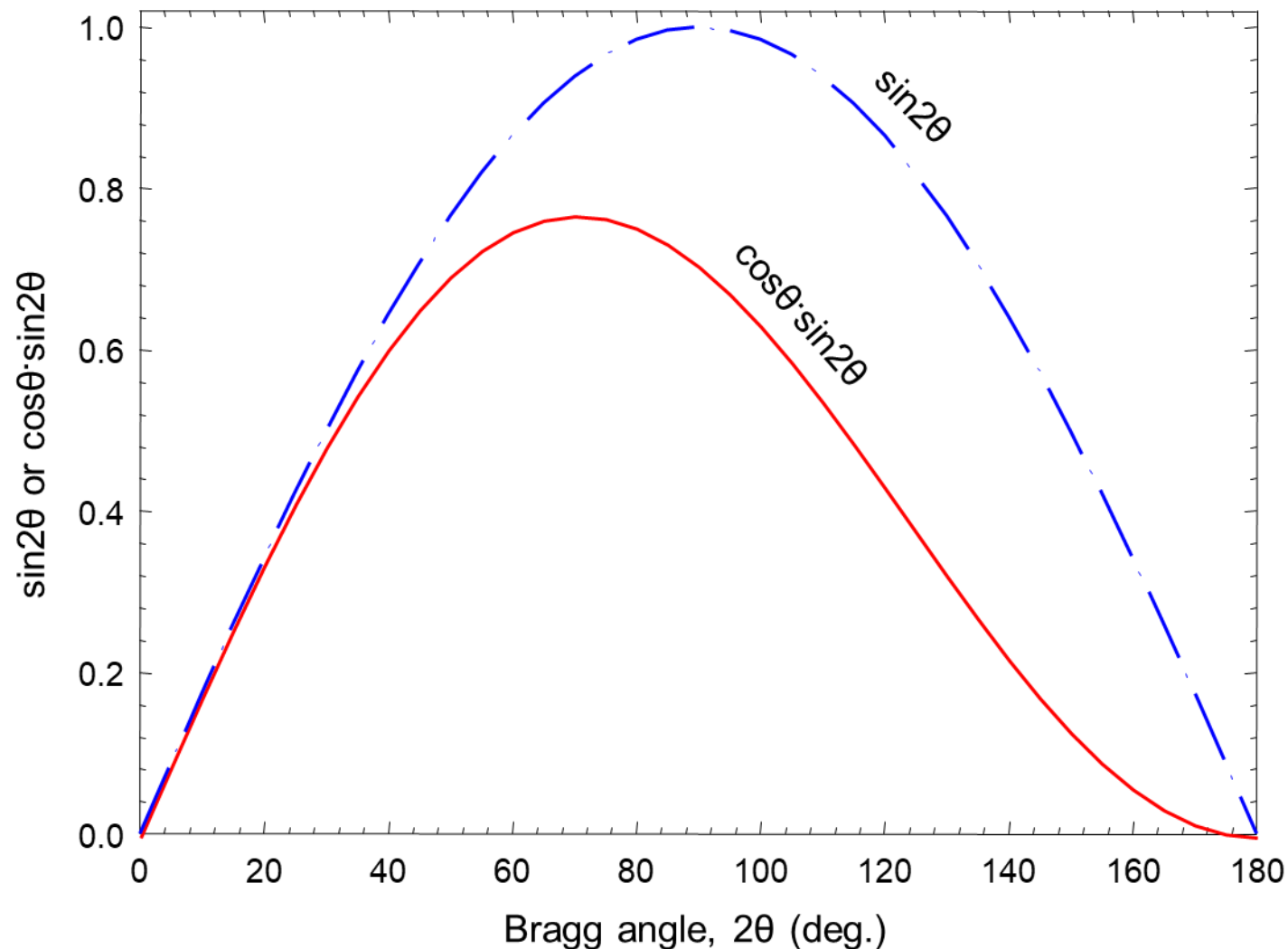
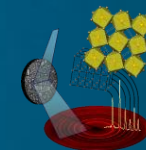


Figure 14.22. The behavior of $\cos \theta \sin 2\theta$ (sample displacement, Eq. 14.56) and $\sin 2\theta$ (zero-shift, Eq. 14.57) as functions of Bragg angle. The two functions show similar behavior, especially at low Bragg angles and therefore, the two parameters strongly correlate with one another when both are simultaneously included in the least squares refinement.

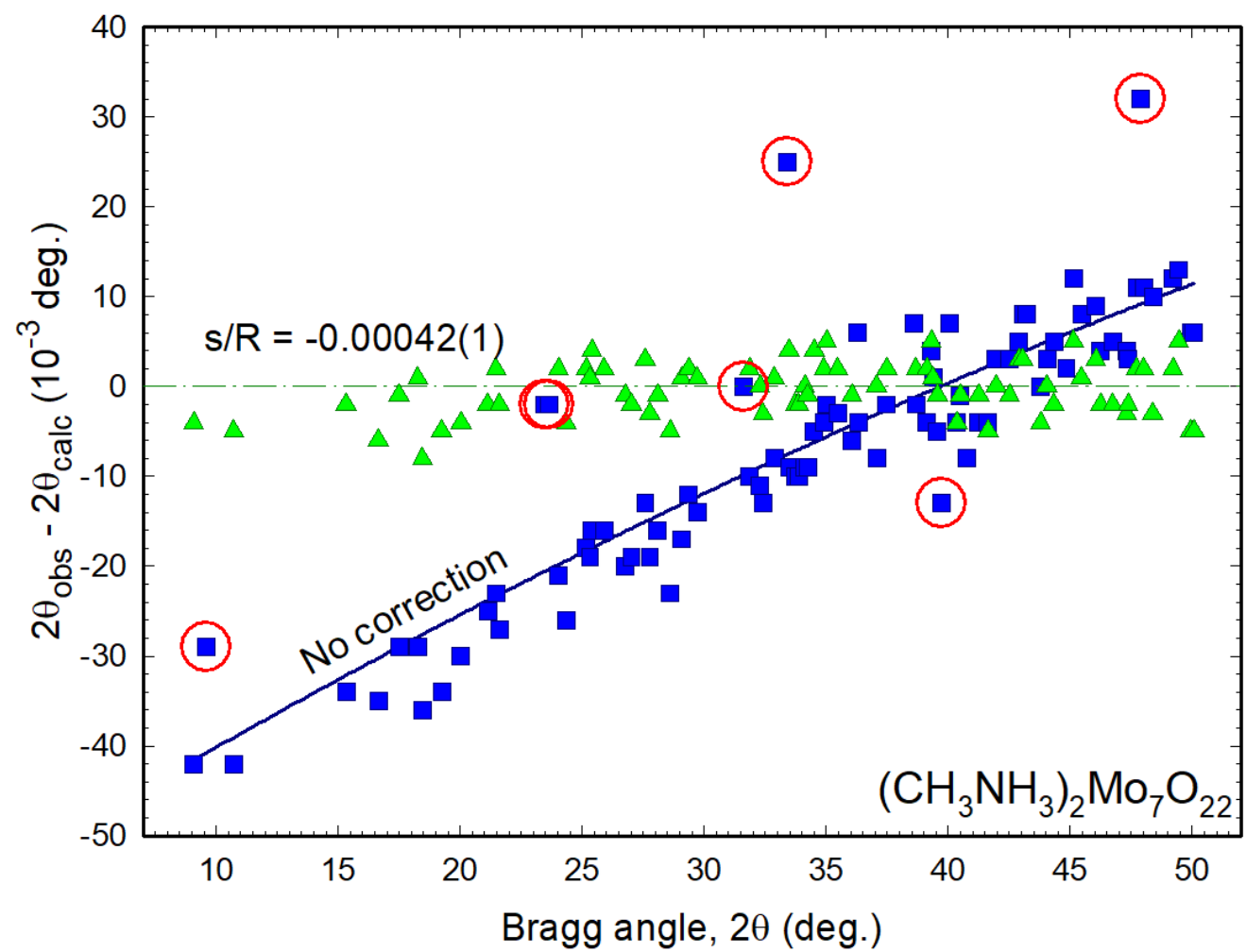
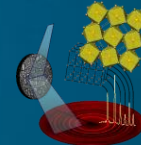


Figure 14.23. Differences between the observed and calculated Bragg angles after the least squares refinement of lattice parameters of the monoclinic $(\text{CH}_3\text{NH}_3)_2\text{Mo}_7\text{O}_{22}$. The *blue squares* and *green triangles* correspond to refinements without and with the sample displacement correction, respectively. The data points enclosed inside red circles were excluded from the second refinement due to the low intensity, strong overlap and, therefore, low accuracy of the corresponding observed Bragg angles.

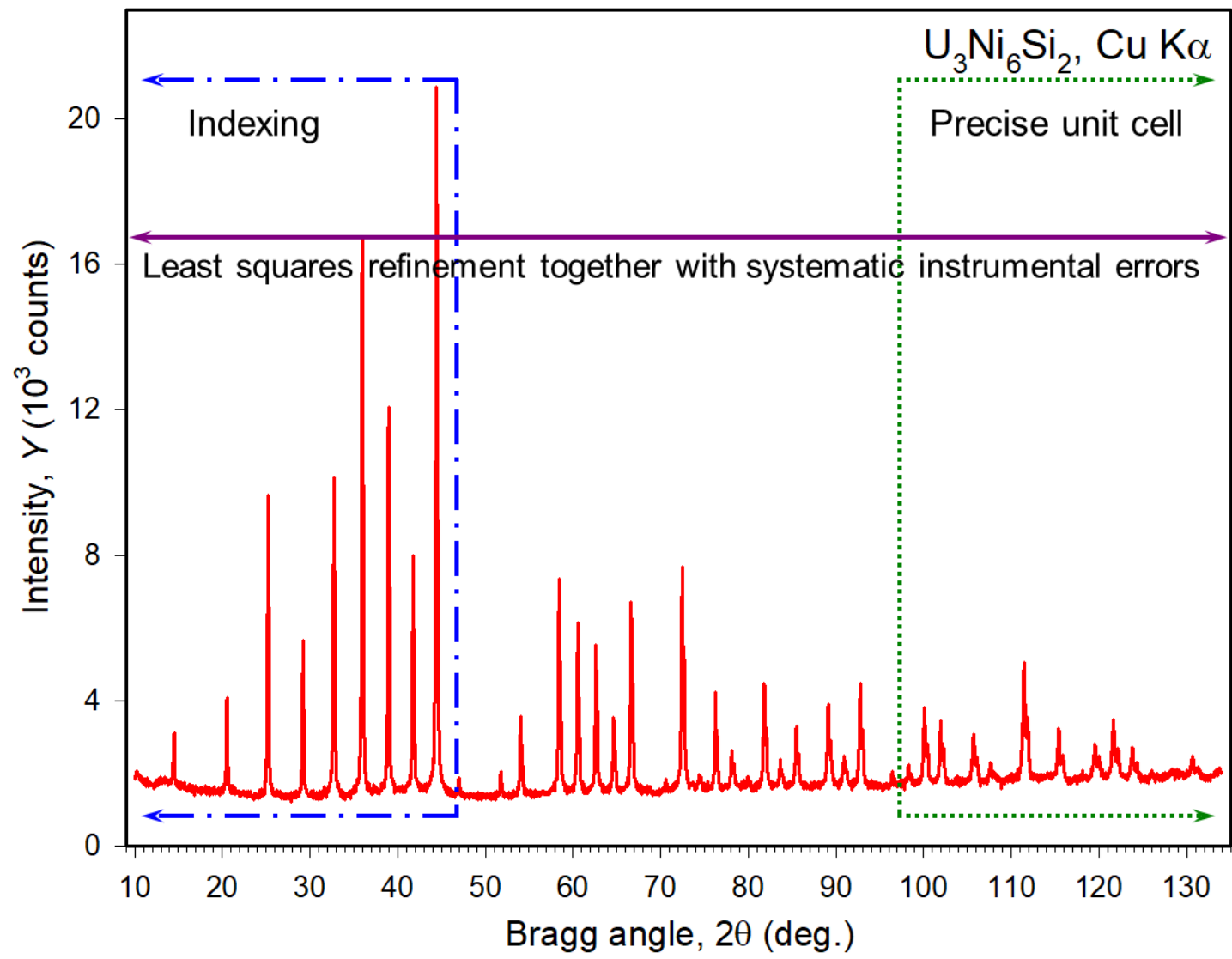
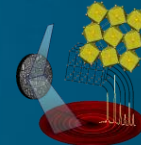


Figure 14.24. The X-ray powder diffraction pattern of U₃Ni₆Si₂ (see also Figure 14.10), illustrates regions critical for successful indexing and precise determination of unit cell dimensions. The boundaries of both the low and high Bragg angle regions are diffuse and can vary from one pattern to another.