

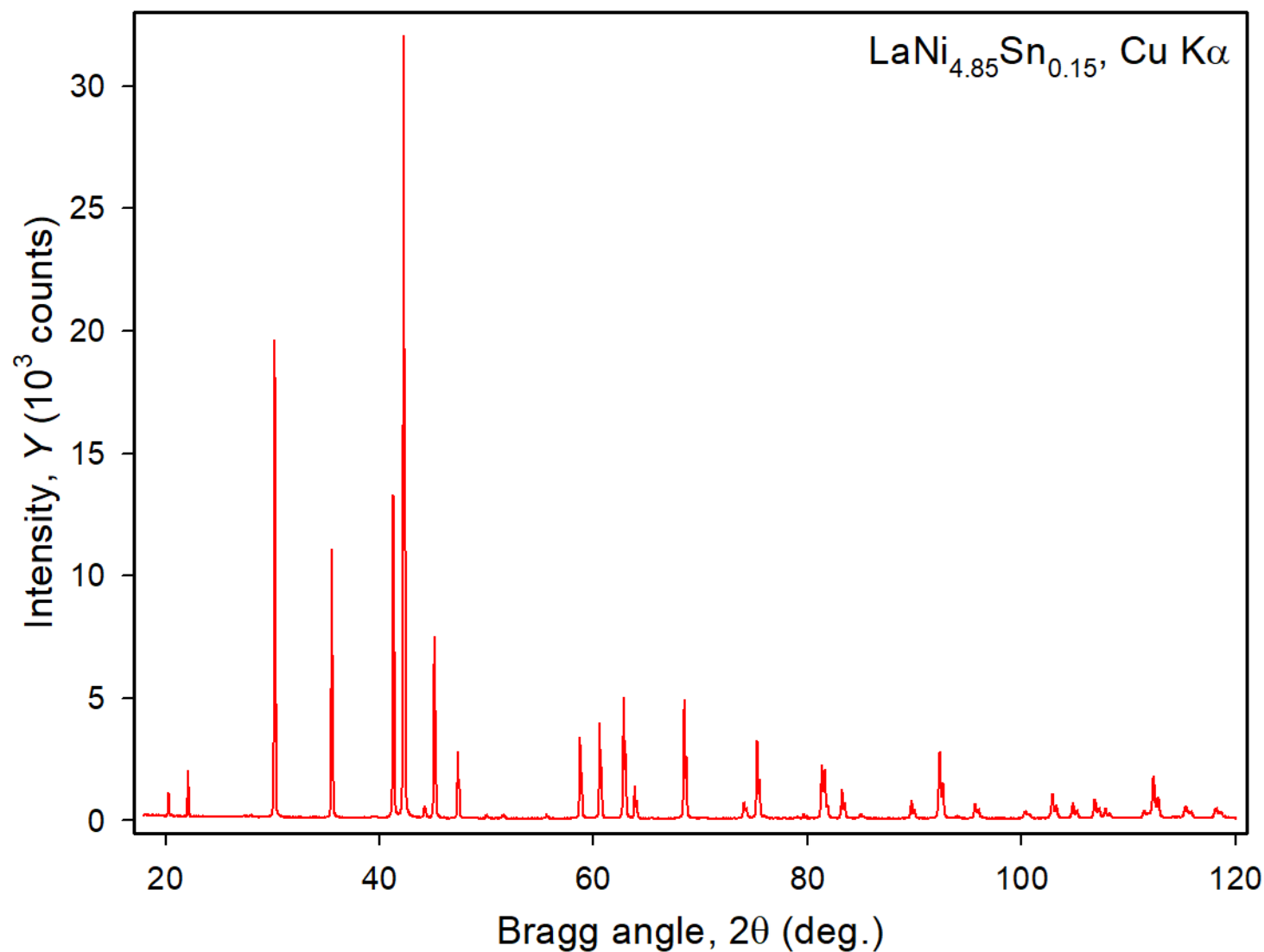
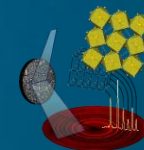


Figure 16.1. The powder diffraction pattern collected from a sample of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ using Cu K α radiation on a Rigaku TTRAX rotating anode diffractometer. The divergence slit was 0.75° and the receiving slit was 0.03° . The experiment was carried out in a continuous scanning mode with a rate $0.5^\circ/\text{min}$ and with a sampling step 0.02° . The powder used in this experiment was prepared by gas atomization from the melt and therefore, particles were nearly spherical (see inset in Figure 12.16)

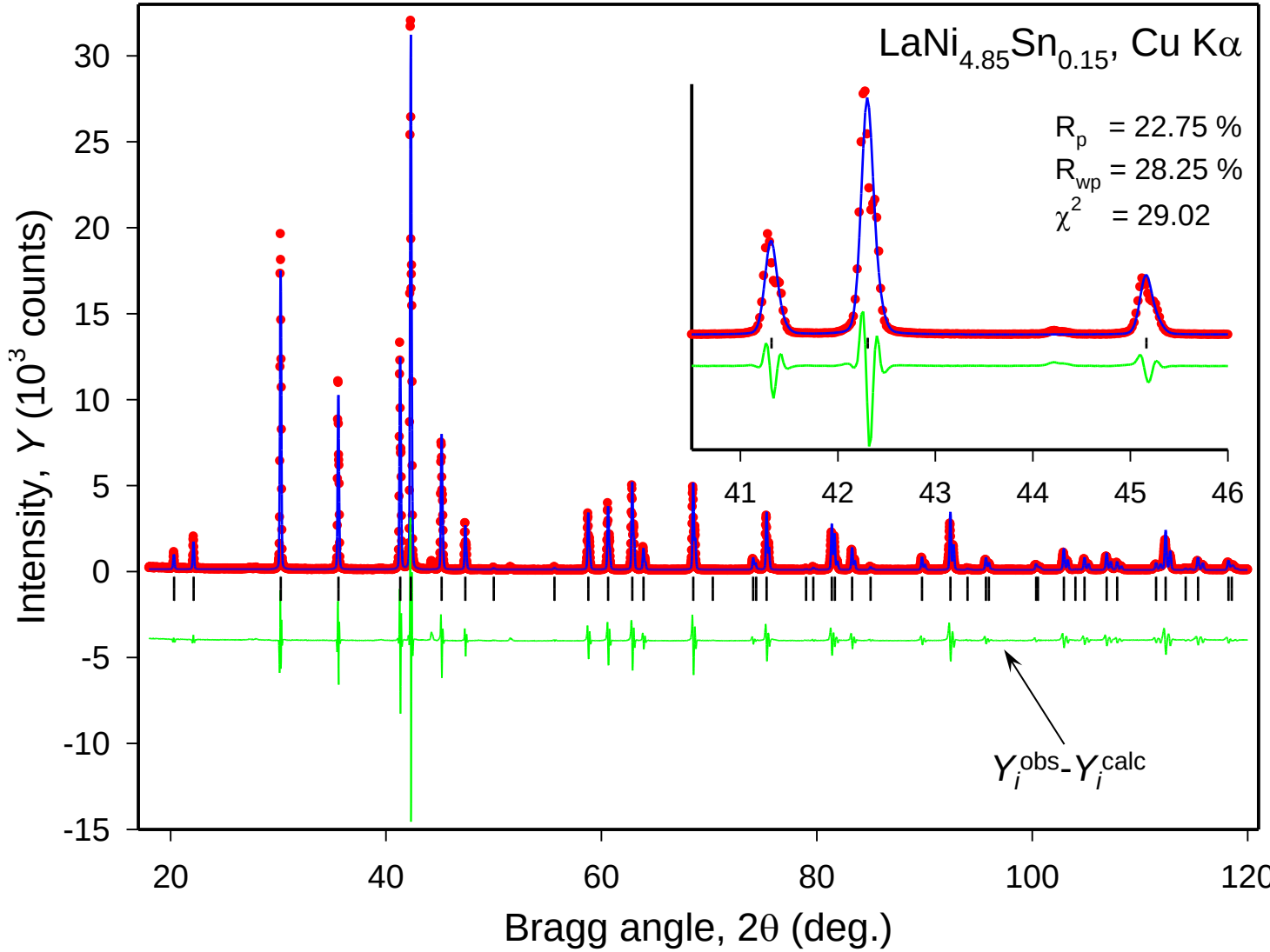
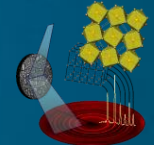


Figure 16.2. The observed (*red circles*) and calculated (*blue lines*) powder patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after a linear background has been refined. Peak-shape parameters were kept at their default values and lattice parameters were fixed at $a = 5.0421$, $c = 4.0118 \text{ \AA}$. The vertical bars located just below the background level indicate calculated positions of Bragg peaks for $\lambda \text{ K}\alpha_1$. Green curve in the bottom represents the difference $Y_i^{\text{obs}} - Y_i^{\text{calc}}$. The scales for the observed, calculated and difference plots are identical. The inset highlights details in the vicinity of the strongest Bragg peak. Same notations are maintained in all similar figures below and throughout the book

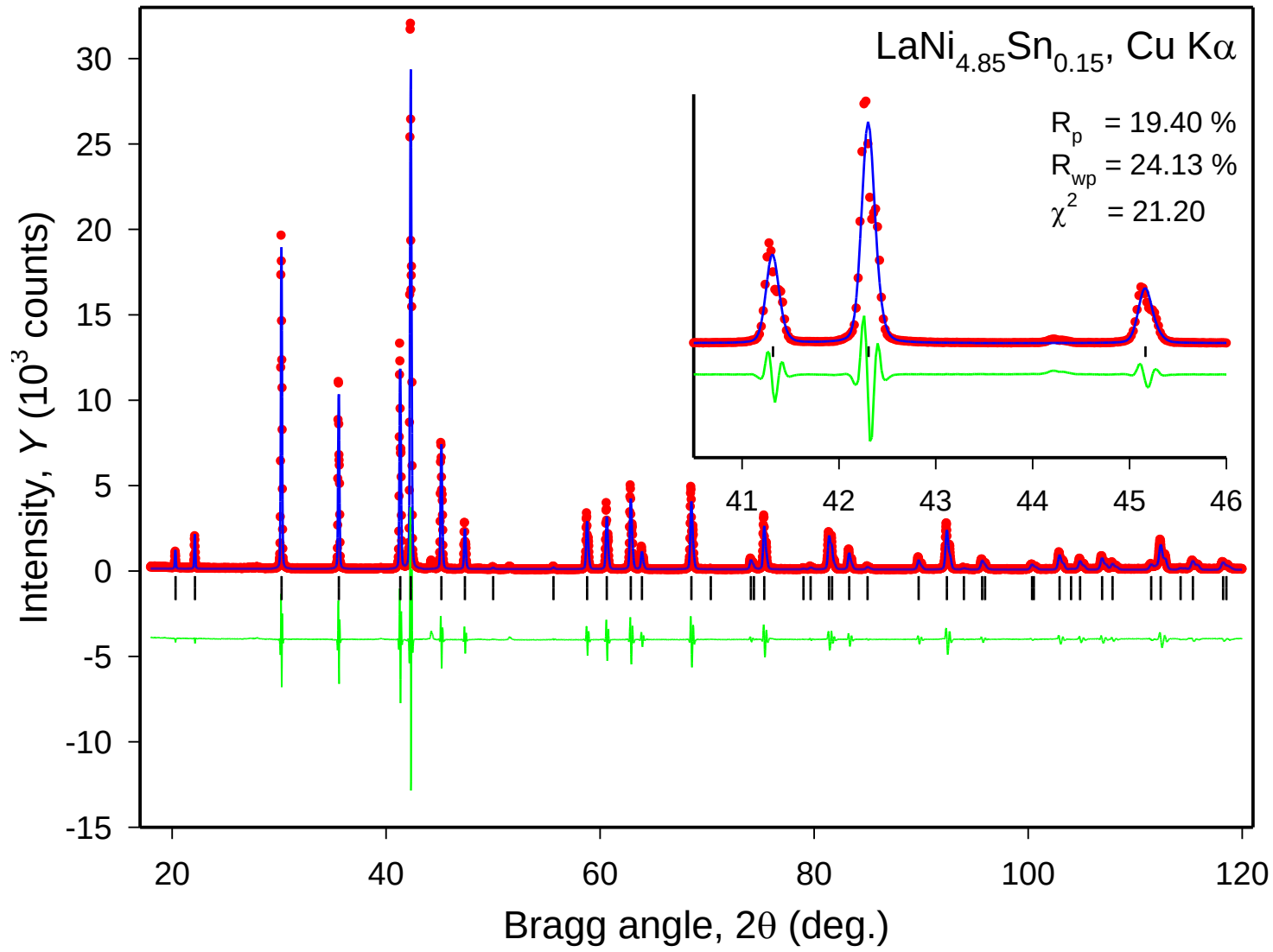
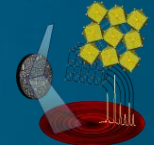


Figure 16.3. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after peak-shape parameters, U , V , W and η_0 , were refined together with linear background.

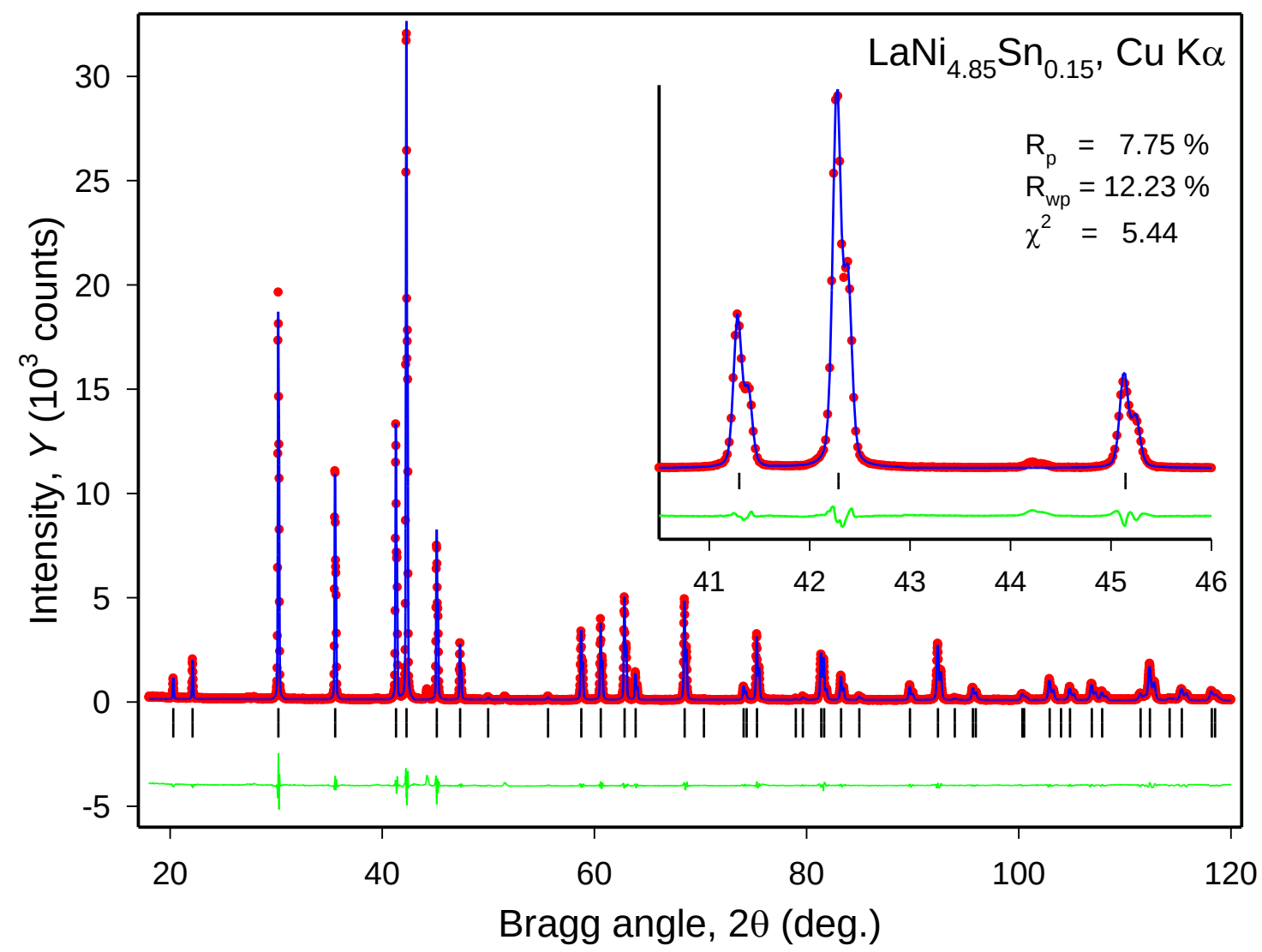
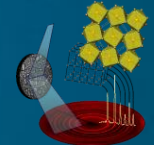


Figure 16.4. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after zero-shift and lattice parameters were included in the refinement.

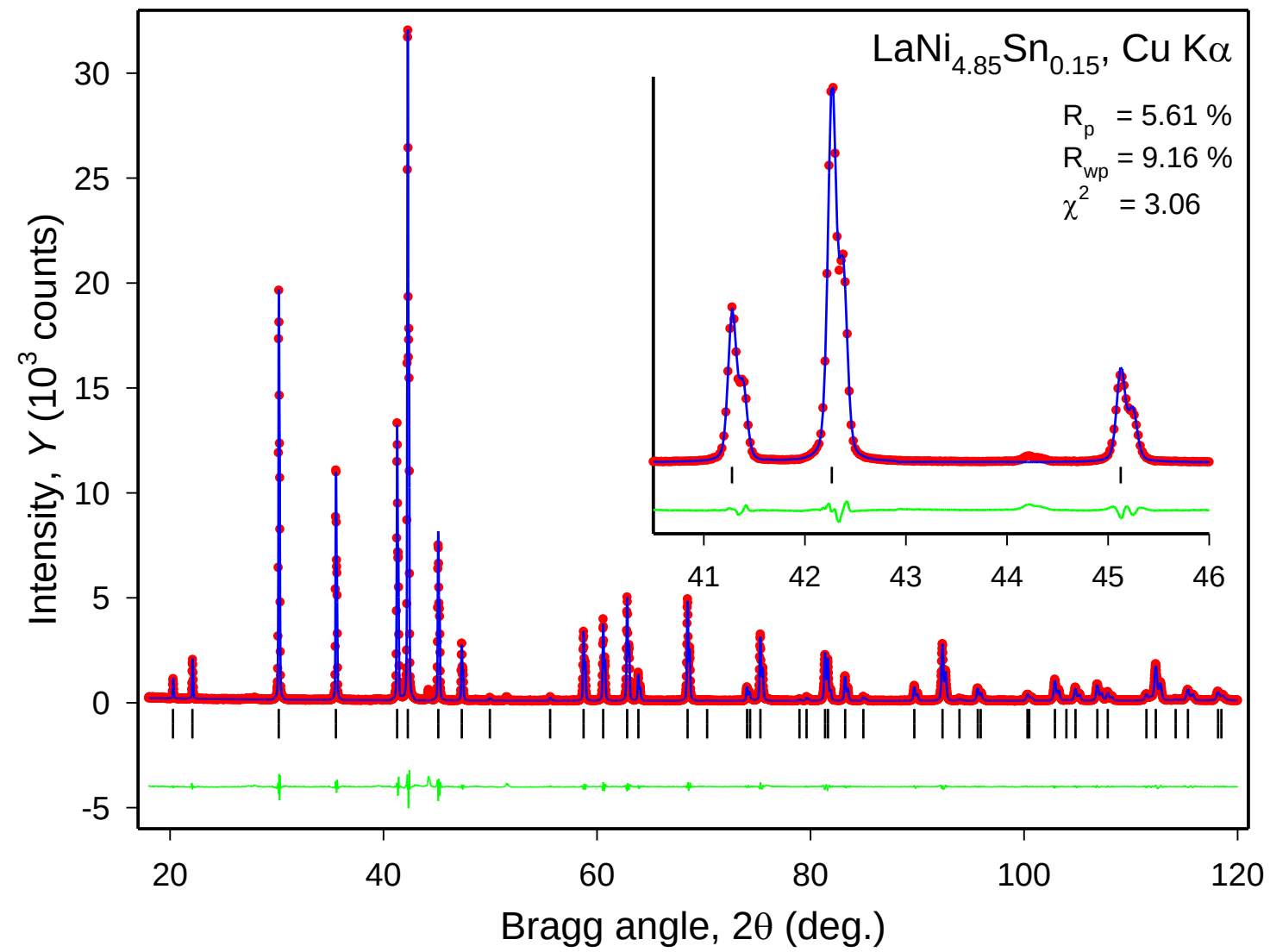
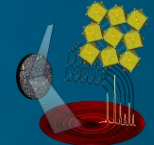


Figure 16.5. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after the polynomial background and asymmetry were refined together with lattice parameters, zero-shift and peak-shape parameters (U , V , W and η_0).

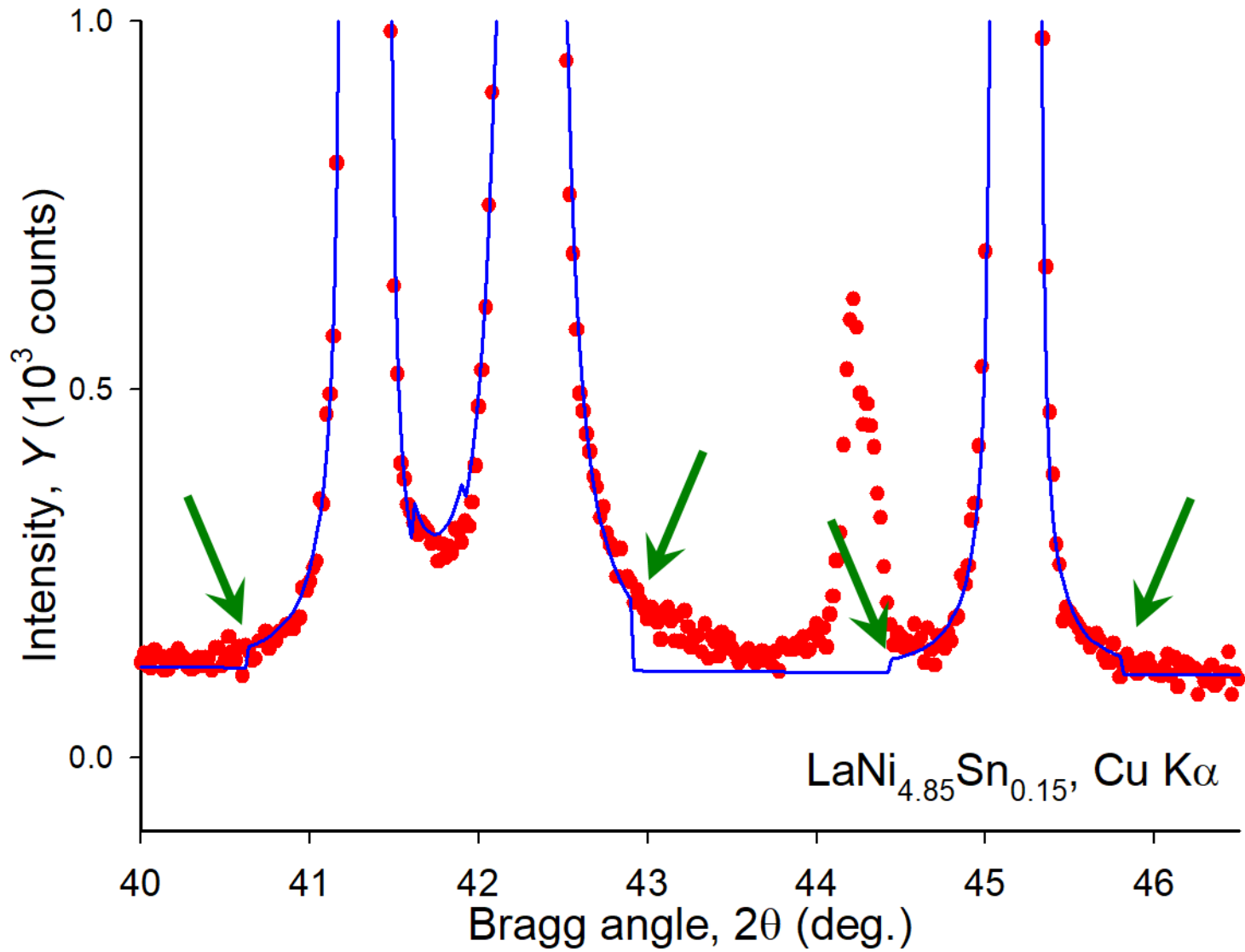
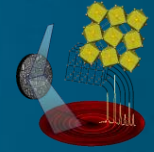


Figure 16.6. Expanded view of the bases of the strongest Bragg peaks indicating that peak ranges should be increased. The additional Bragg peak at $2\theta \cong 44.2^\circ$ is from Ni impurity.

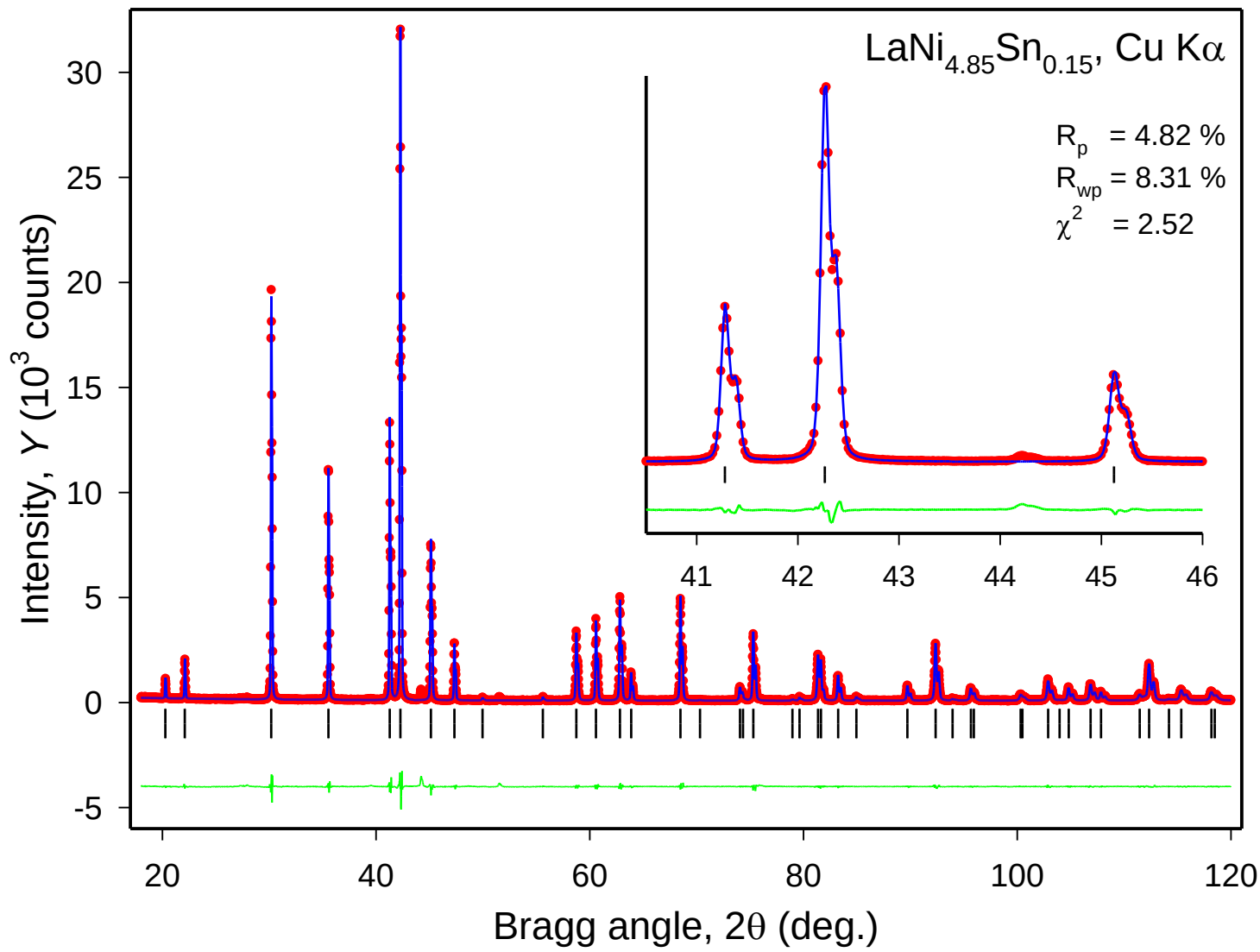
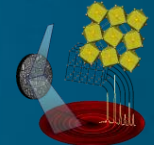


Figure 16.7. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after all parameters have been refined with the increased peak base widths

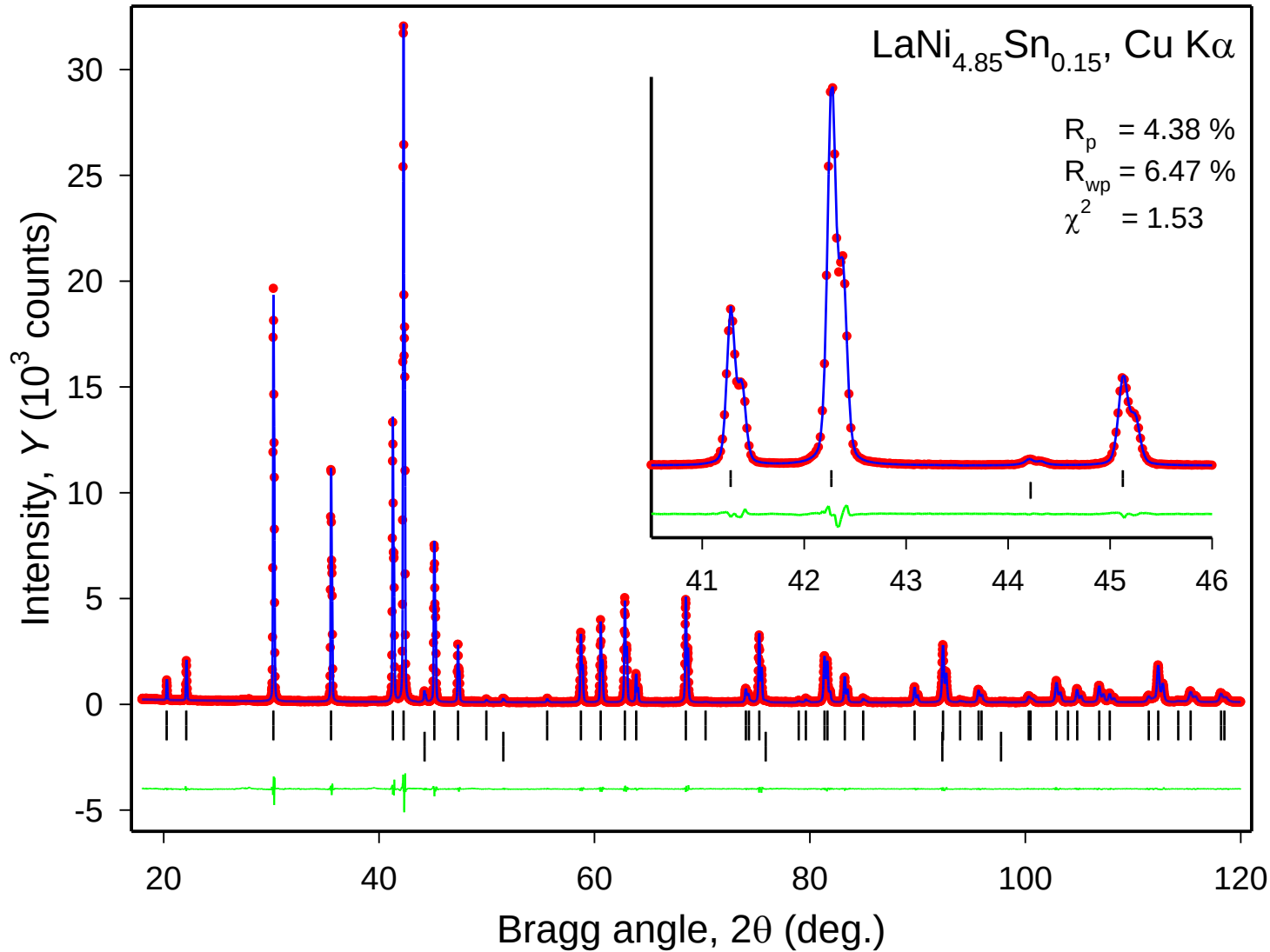
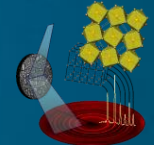


Figure 16.8. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after a second phase (solid solution of Sn in Ni) was included in the refinement. Considering the low background (the peak-to-background ratio exceeds 200 for the strongest Bragg peak at $2\theta \cong 42.3^\circ$), the final residuals are excellent.

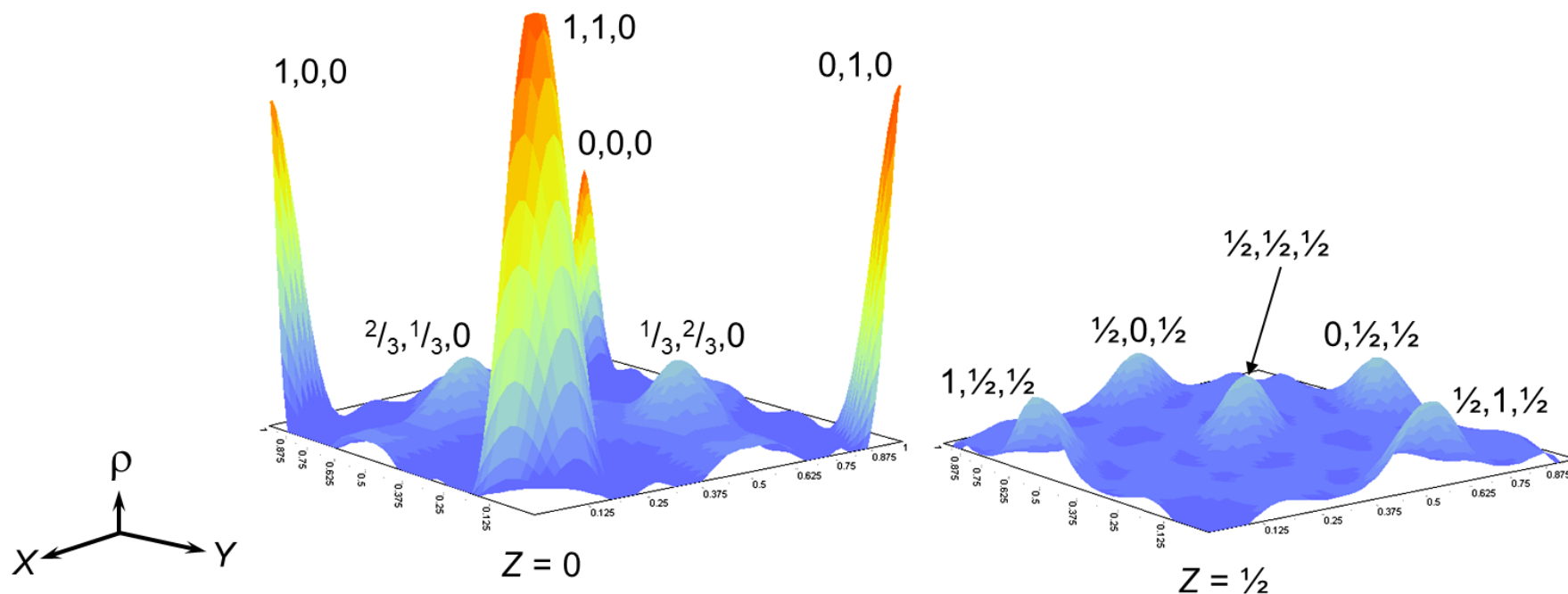
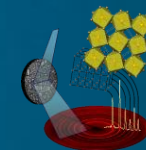


Figure 16.9. The cross-sections of the three-dimensional Fourier map of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ at $Z = 0$ (left) and at $Z = \frac{1}{2}$ (right) calculated using structure amplitudes listed in Table 16.3 and phase angles determined by the La atom placed in the 1(a) site. The triplets of numbers indicate the coordinates of the strongest peaks in the unit cell. The following groups of peaks are symmetrically equivalent to one another: 0,0,0; 1,0,0; 0,1,0 and 1,1,0 (all four correspond to the La atom in 1(a) and Peak No. 1 in Table 16.5); $\frac{1}{3}, \frac{2}{3}, 0$ and $\frac{2}{3}, \frac{1}{3}, 0$ (Peak No. 2 in Table 16.5), and $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $1, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, 1, \frac{1}{2}$ (Peak No. 3 in Table 16.5).

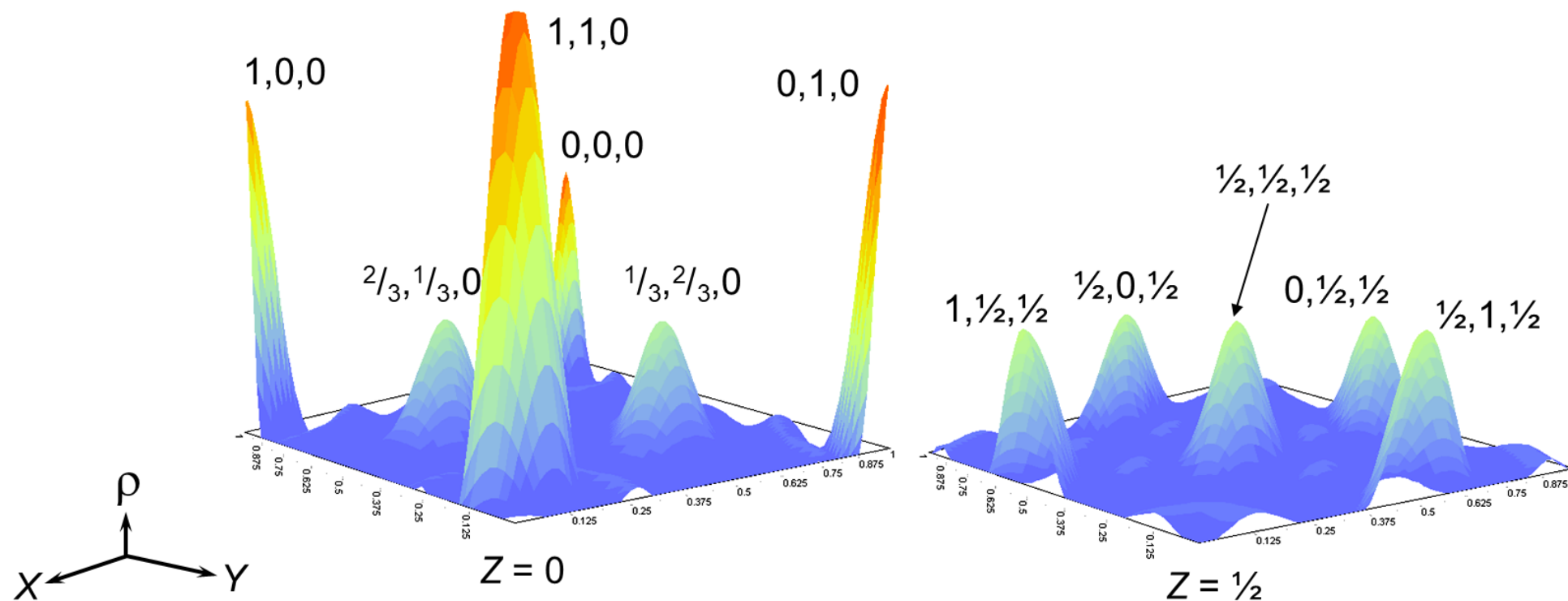
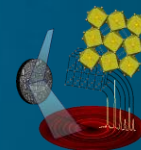


Figure 16.10. The cross-sections of the three-dimensional Fourier map of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ at $Z = 0$ (*left*) and at $Z = \frac{1}{2}$ (*right*) calculated using structure amplitudes listed in Table 16.3 and phase angles determined by the La atom placed in the 1(a) site and Ni atoms placed in the 2(c) and 3(g) sites. The notations are identical to Figure 16.9.

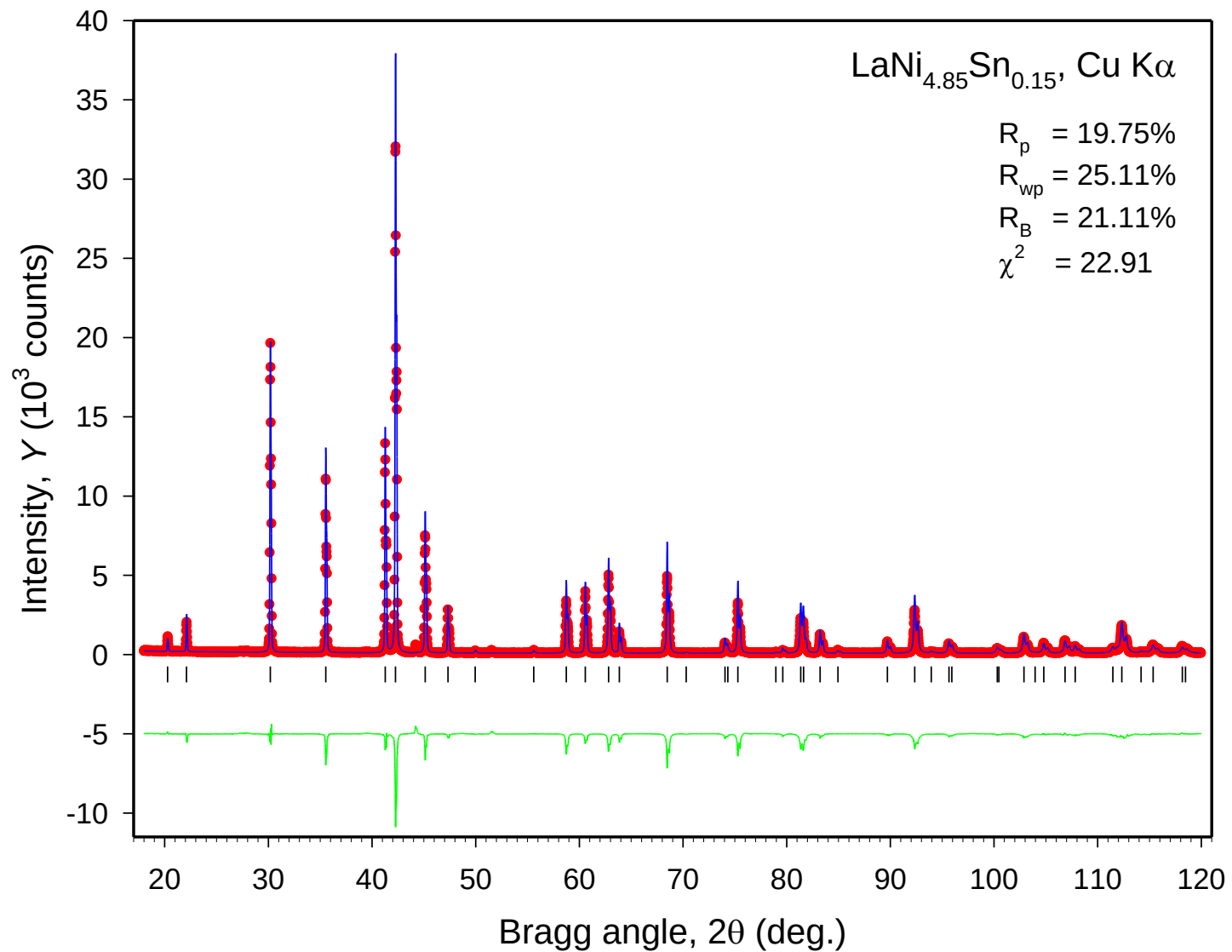
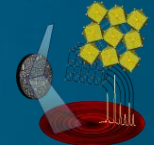


Figure 16.11. The observed (*open circles*) and calculated (*solid line*) diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$. Scattered intensity was calculated using instrumental and lattice parameters determined during Le Bail's refinement and default scale factor ($K = 0.01$). The difference, $Y_i^{obs} - Y_i^{calc}$, is displaced by -5,000 counts for clarity. *Vertical bars* in the lower part of the figure indicate calculated positions of the $\text{K}\alpha_1$ components of Bragg reflections in $\text{LaNi}_{4.85}\text{Sn}_{0.15}$.

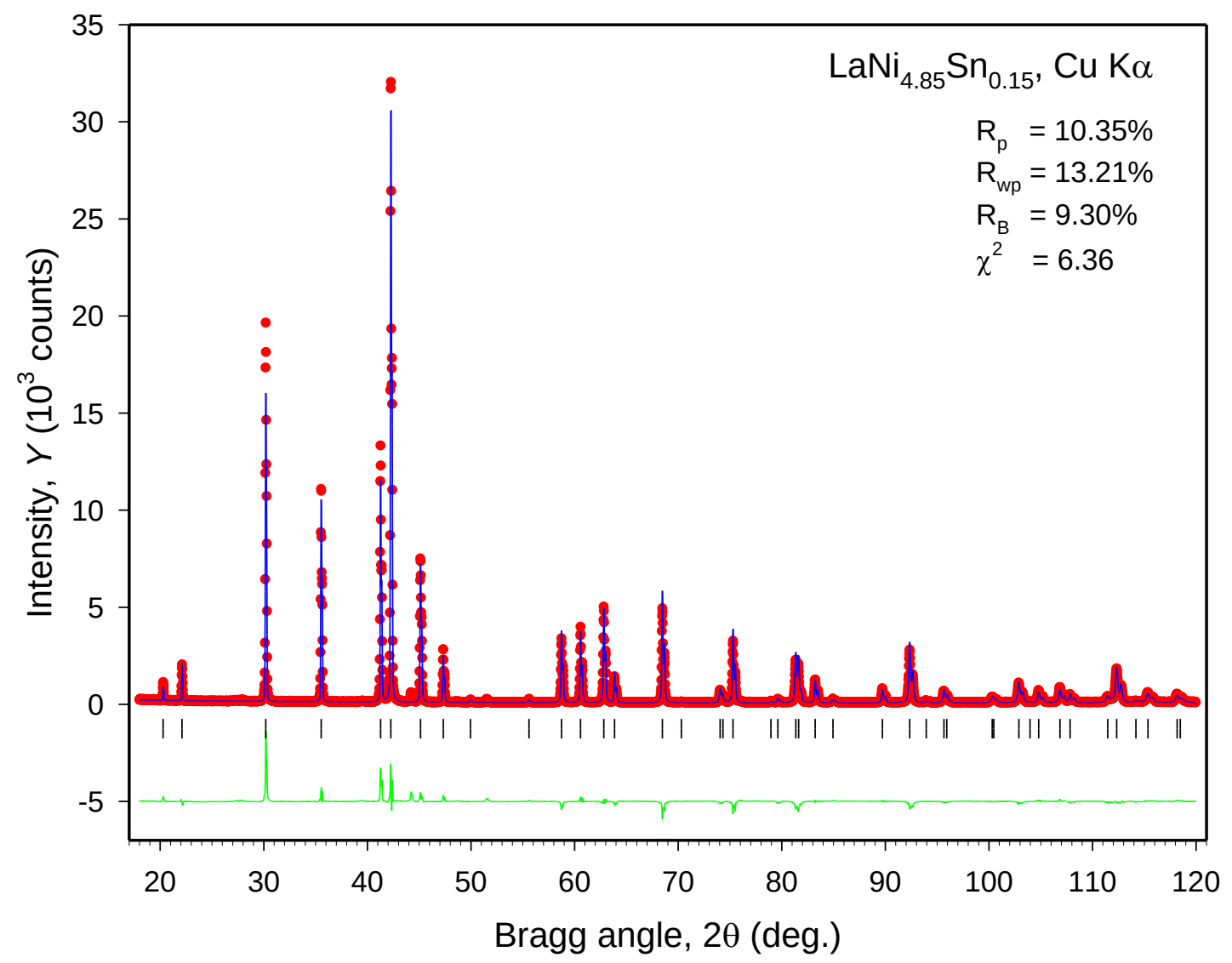
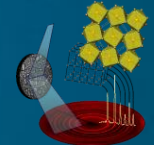


Figure 16.12. The observed and calculated diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$. The scattered intensity was calculated using scale factor, instrumental and lattice parameters determined during Rietveld refinement, and guessed overall atomic displacement parameter $B = 0.5 \text{ \AA}^2$. All notations are identical to Figure 16.11.

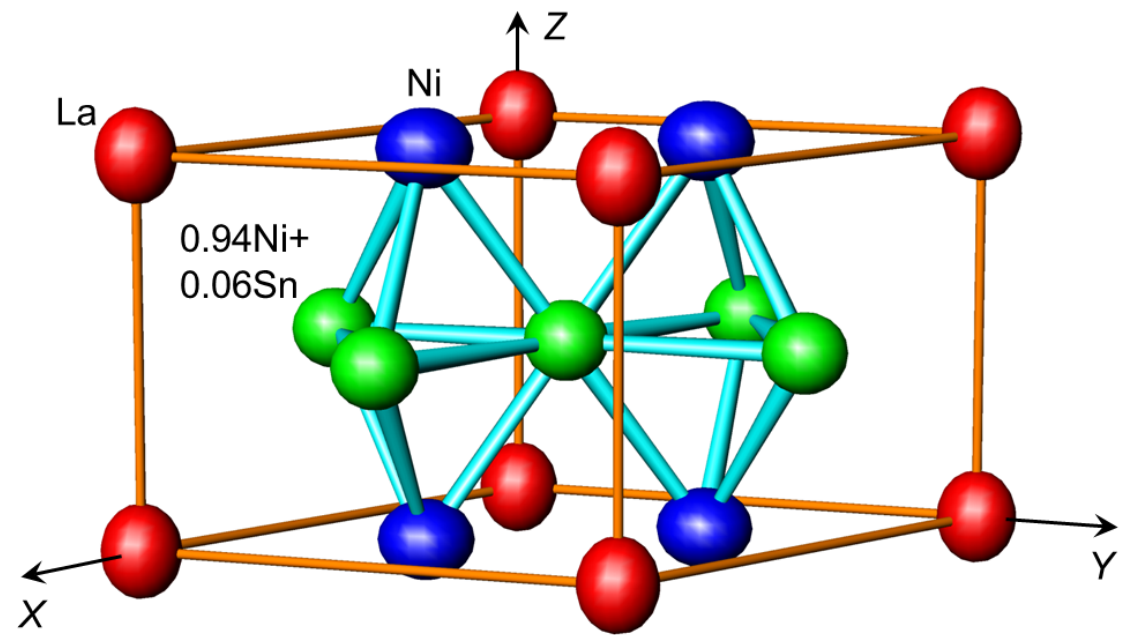
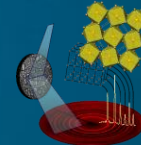


Figure 16.13. One unit cell of the crystal structure of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ as determined from Rietveld refinement. The model reflects the different distribution of the Ni and Sn atoms between 2(c) and 3(g) sites (dark- and light- gray, respectively). The displacement ellipsoids are shown at 99% probability.

La in 1(a): $b_{11}(\text{free}) = b_{22} = 2b_{12}; b_{33} - \text{free}; b_{13} = b_{23} = 0$
Ni in 2(c): $b_{11}(\text{free}) = b_{22} = 2b_{12}; b_{33} - \text{free}; b_{13} = b_{23} = 0$
Ni+Sn in 3(g): $b_{11}, b_{22}, b_{33} - \text{free}; b_{12} = 0.5b_{22}; b_{13} = b_{23} = 0$

Table 16.10. Structural parameters of the major phase ($\text{LaNi}_{4.85}\text{Sn}_{0.15}$), fully refined by the Rietveld method. The refined unit cell dimensions are: $a = 5.04228(6), c = 4.01170(5) \text{ \AA}$.

Atom	Site	x	y	z	g^a	$10^4 b_{11}^b$	$10^4 b_{22}^b$	$10^4 b_{33}^b$	$10^4 b_{12}^b$
La	1(a)	0	0	0	1	156(2)	156(2)	258(3)	78(1)
Ni1	2(c)	$\frac{1}{3}$	$\frac{2}{3}$	0	1	227(3)	227(3)	183(5)	113(1)
Ni2	3(g)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.944(2)	178(3)	174(4)	187(5)	87(2)
Sn	3(g)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.056(2)	178(3)	174(4)	187(5)	87(2)

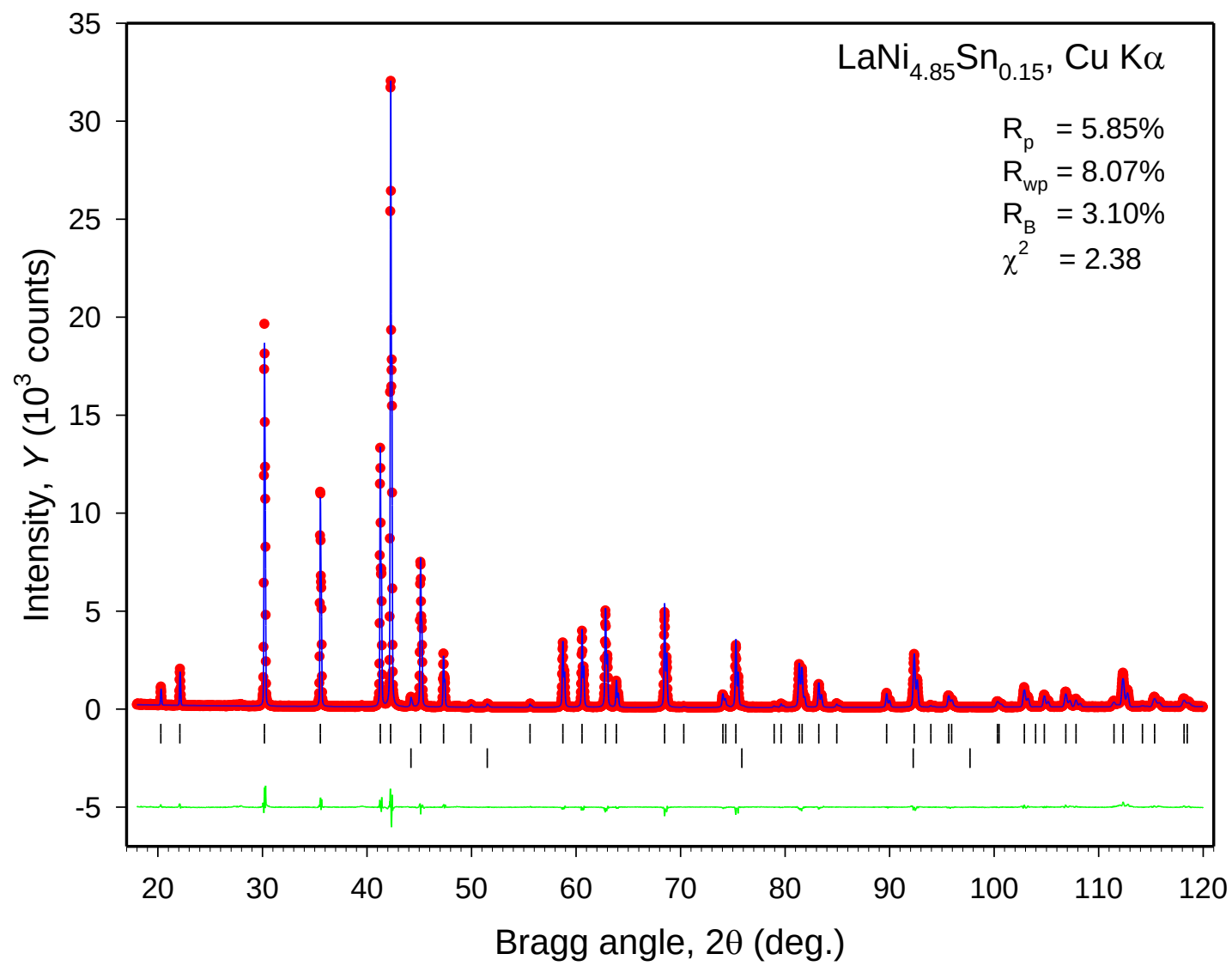
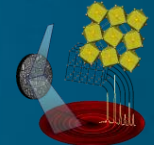


Figure 16.14. The observed and calculated diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after the completion of Rietveld refinement. Notations are identical to Figure 16.11 and the second set of vertical bars indicates the calculated positions of the $K\alpha_1$ components of Bragg peaks in the impurity phase (solid solution of Sn in Ni).

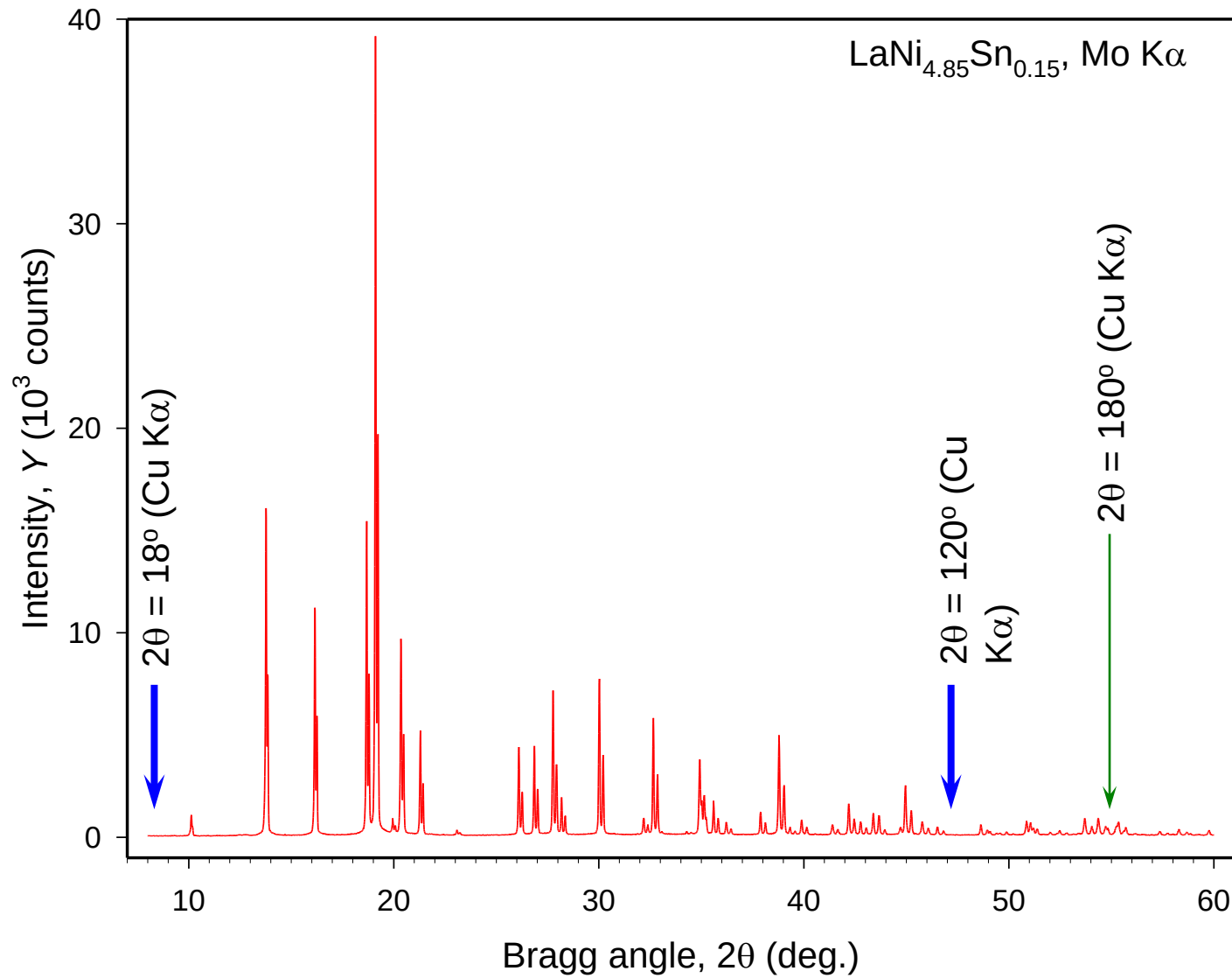
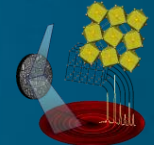


Figure 16.15. The X-ray powder diffraction pattern of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ collected on a Rigaku TTRAX rotating anode powder diffractometer using Mo $K\alpha$ radiation with a step $\Delta 2\theta = 0.01^\circ$.

The spherical $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powder was produced by high pressure gas atomization. The two short thick vertical arrows show the range of $\sin\theta/\lambda$ examined using Cu $K\alpha$ radiation (e.g. see Figure 16.1), and the *long thin vertical arrow* indicates the fundamental upper limit of the reciprocal space ($2\theta = 180^\circ$) accessible when using Cu $K\alpha$ radiation.

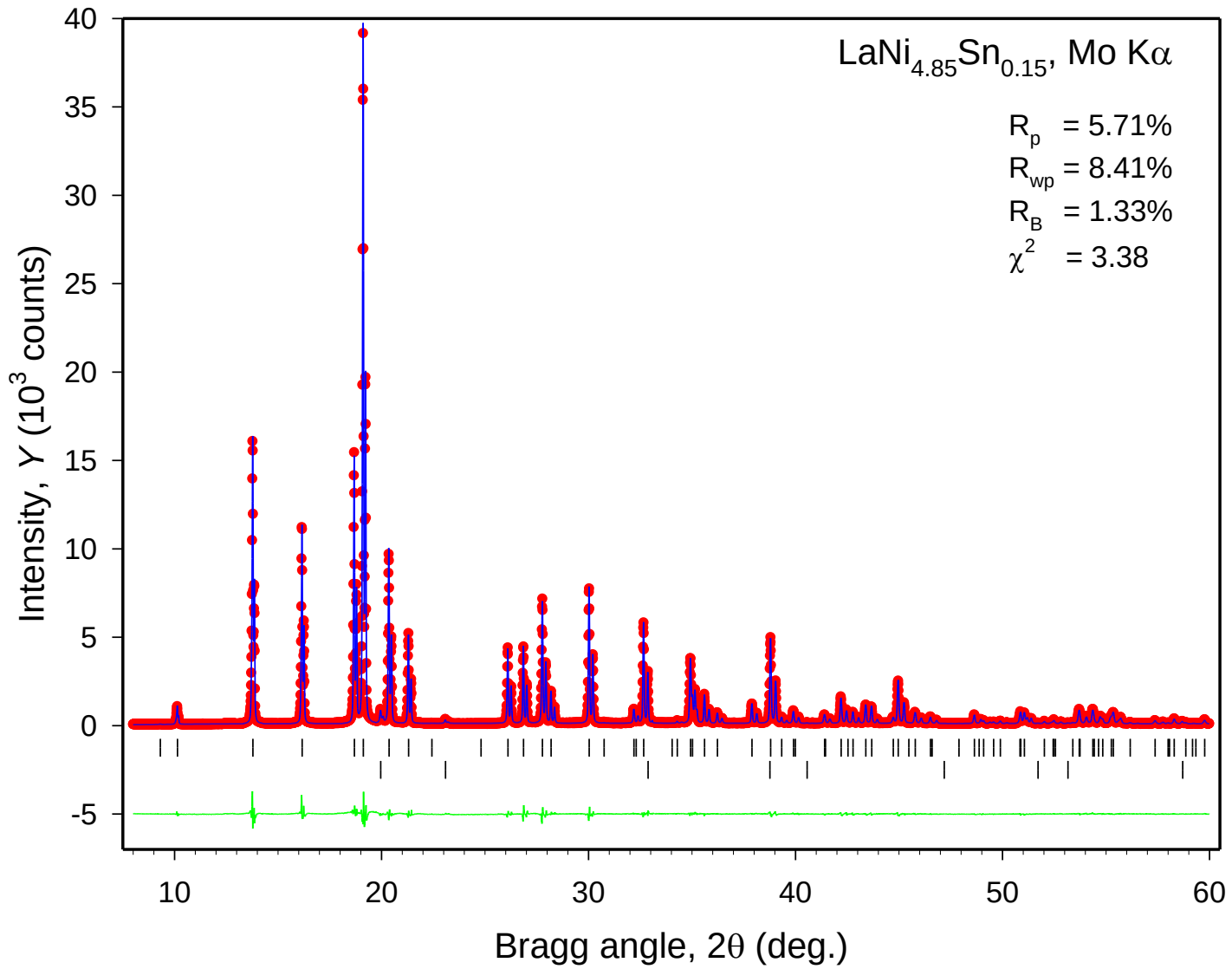
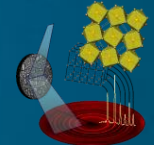


Figure 16.16. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after the completion of Rietveld refinement. Notations are identical to Figure 16.11. The second set of *vertical bars* indicates the calculated positions of the $K\alpha_1$ components of Bragg peaks in the impurity phase, which is a solid solution of Sn in Ni. The virtual absence of a Bragg peak at $2\theta \cong 9^\circ$ and the presence of the same reflection at $2\theta \cong 20^\circ$ when Cu K α radiation was employed (see Figure 16.14) is the result of differences in the anomalous scattering (see also Eqs. 9.15 and 9.22).

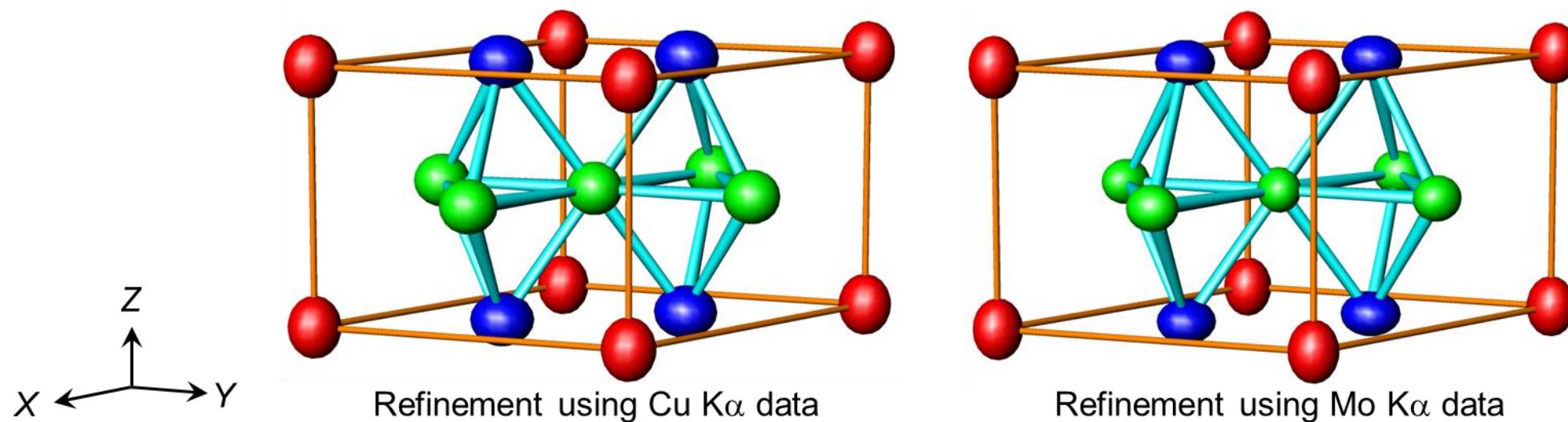
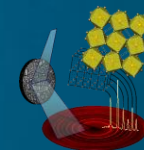
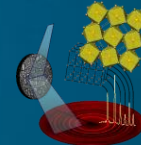


Figure 16.17. Atomic displacement ellipsoids in the crystal structure of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$, shown at 99% probability, as refined using Cu K α (*left*) and Mo K α (*right*) powder diffraction data.



Combined Rietveld refinement:

Minimized function:

$$\Phi = \sum_{s=1}^h \sum_{i=1}^{n_s} w_{s,i} [k_s(Y_{s,i}^{obs} - b_{s,i}) - K \sum_{j=1}^m I_j y_{s,j}(x_{s,j})]^2$$

Eq. 16.3

Table 16.14. Structural parameters of the major phase (LaNi_{4.85}Sn_{0.15}), fully refined by the Rietveld technique using the combined powder diffraction data collected employing Cu Kα and Mo Kα radiations from the same specimen. The refined unit cell dimensions are: *a* = 5.04430(3), *c* = 4.01292(3) Å. The following restrictions are imposed by symmetry: β₁₃ = β₂₃ = 0.

Atom	Site	x	y	z	g	10 ⁴ b ₁₁	10 ⁴ b ₂₂	10 ⁴ b ₃₃	10 ⁴ b ₁₂
La	1(a)	0	0	0	1	141(1)	141(1)	252(3)	71(1)
Ni1	2(c)	1/3	2/3	0	1	205(2)	205(2)	151(4)	103(1)
Ni2	3(g)	1/2	0	1/2	0.956(2)	142(2)	117(3)	139(3)	59(1)
Sn	3(g)	1/2	0	1/2	0.044(2)	142(2)	117(3)	139(3)	59(1)

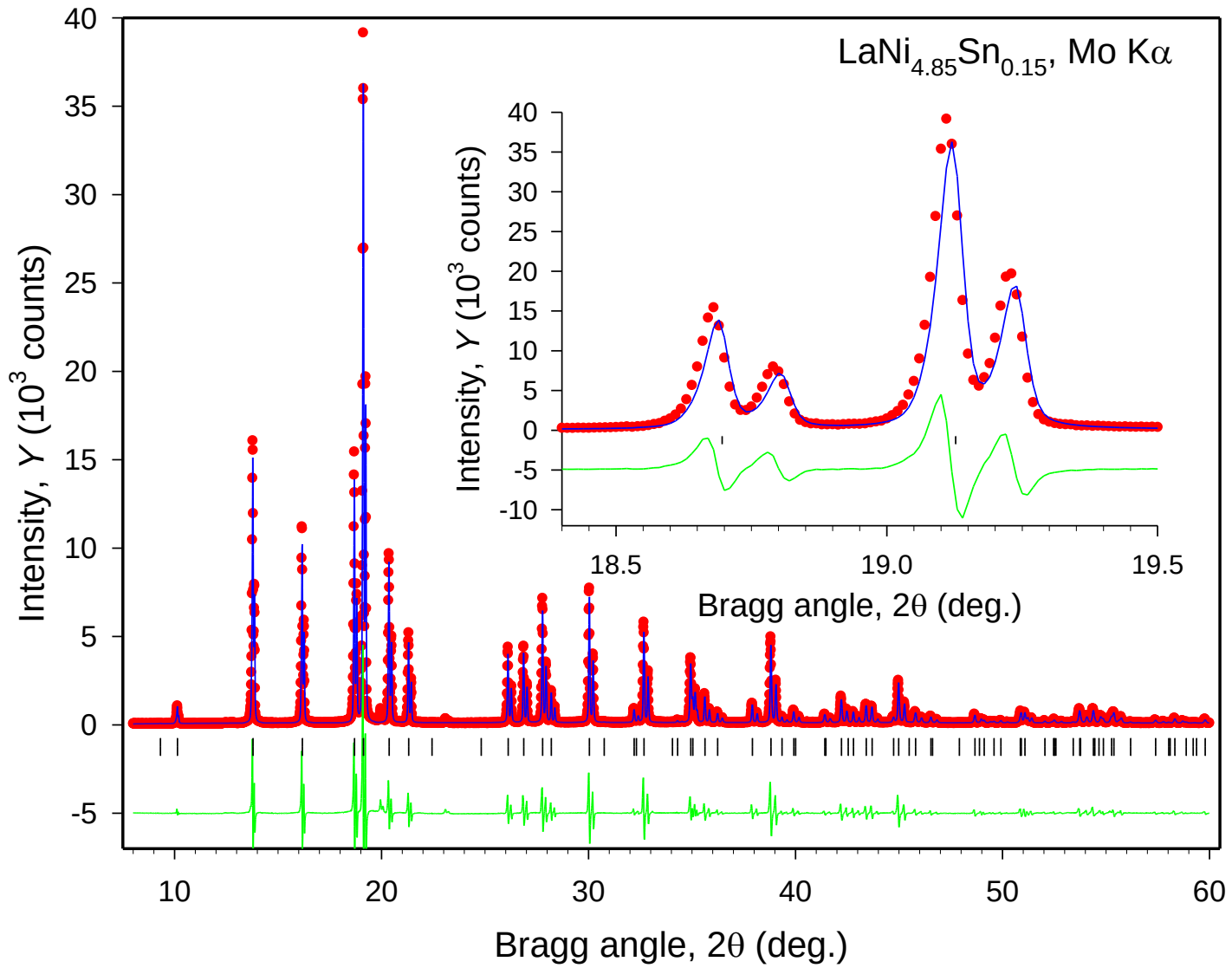
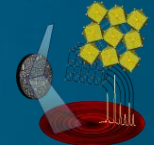


Figure 16.18. The observed (Mo $K\alpha$ radiation) and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ after combined refinement of scale factors only. The inset shows the expanded view between 18.4° and 19.5° of 2θ to illustrate the inaccuracy of lattice parameters.

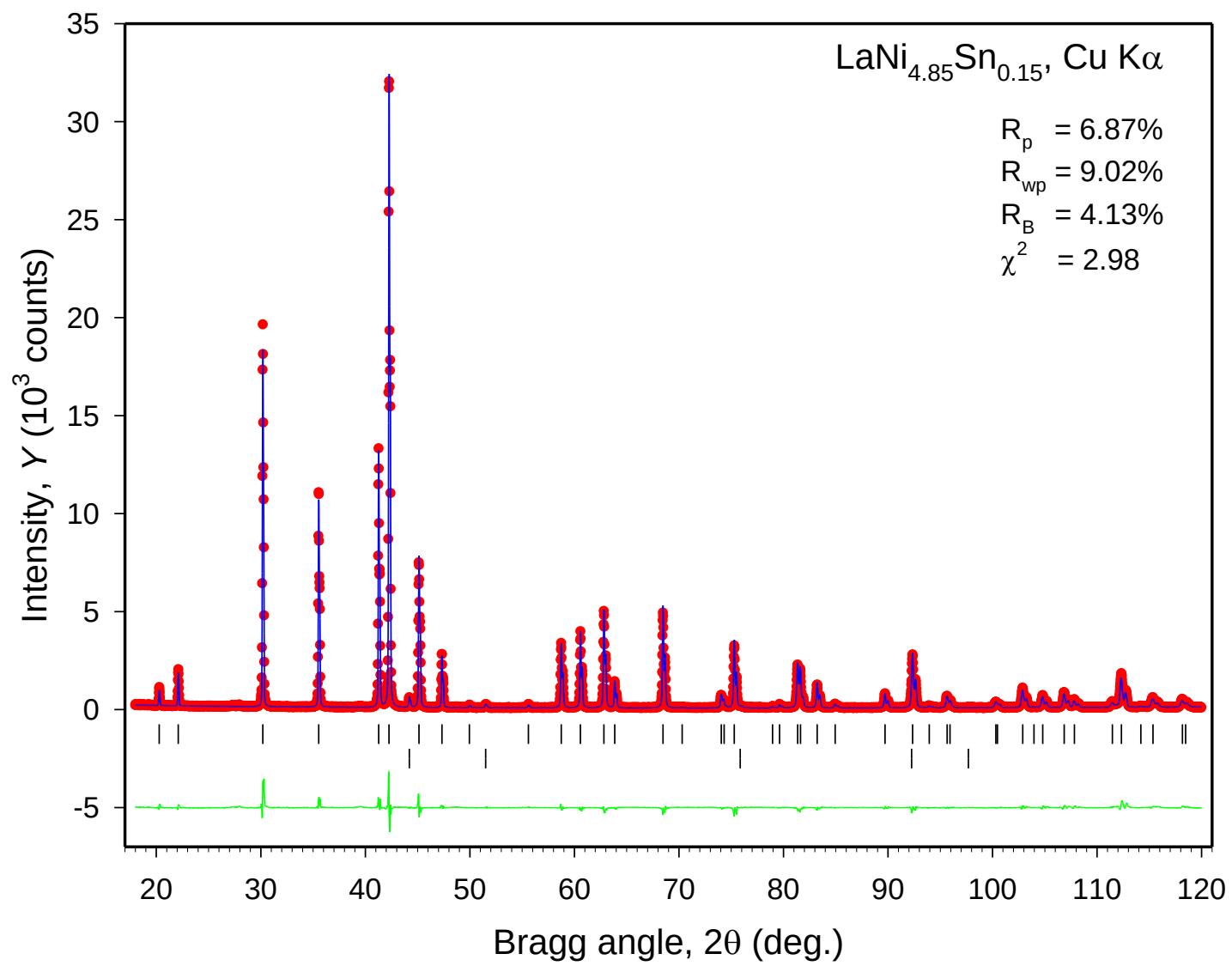
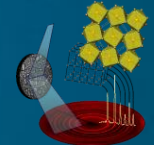


Figure 16.19. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ ($\text{Cu K}\alpha$ radiation) after the completion of the combined Rietveld refinement.

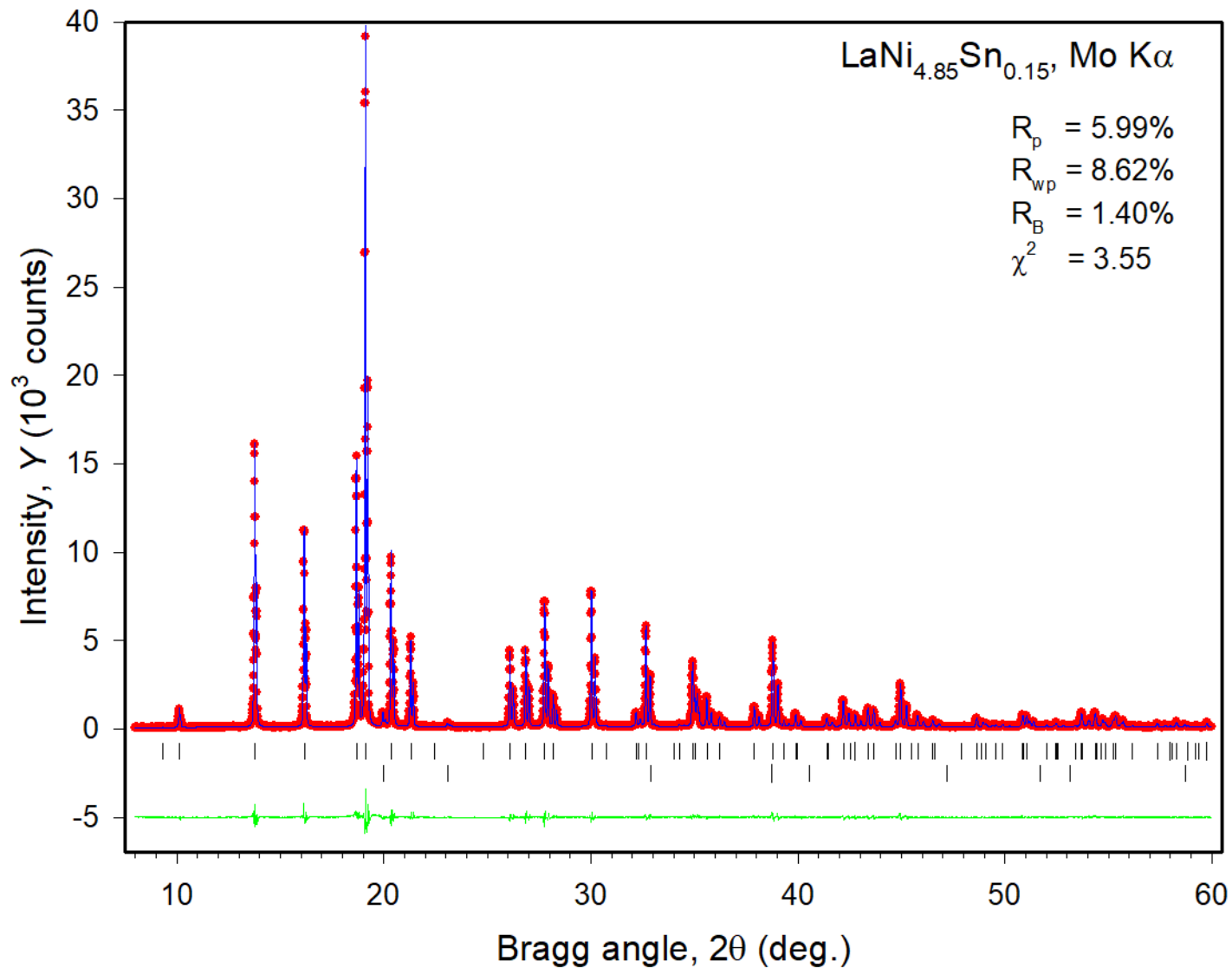
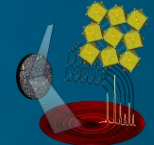


Figure 16.20. The observed and calculated powder diffraction patterns of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ (Mo $K\alpha$ radiation) after the completion of the combined Rietveld refinement.