

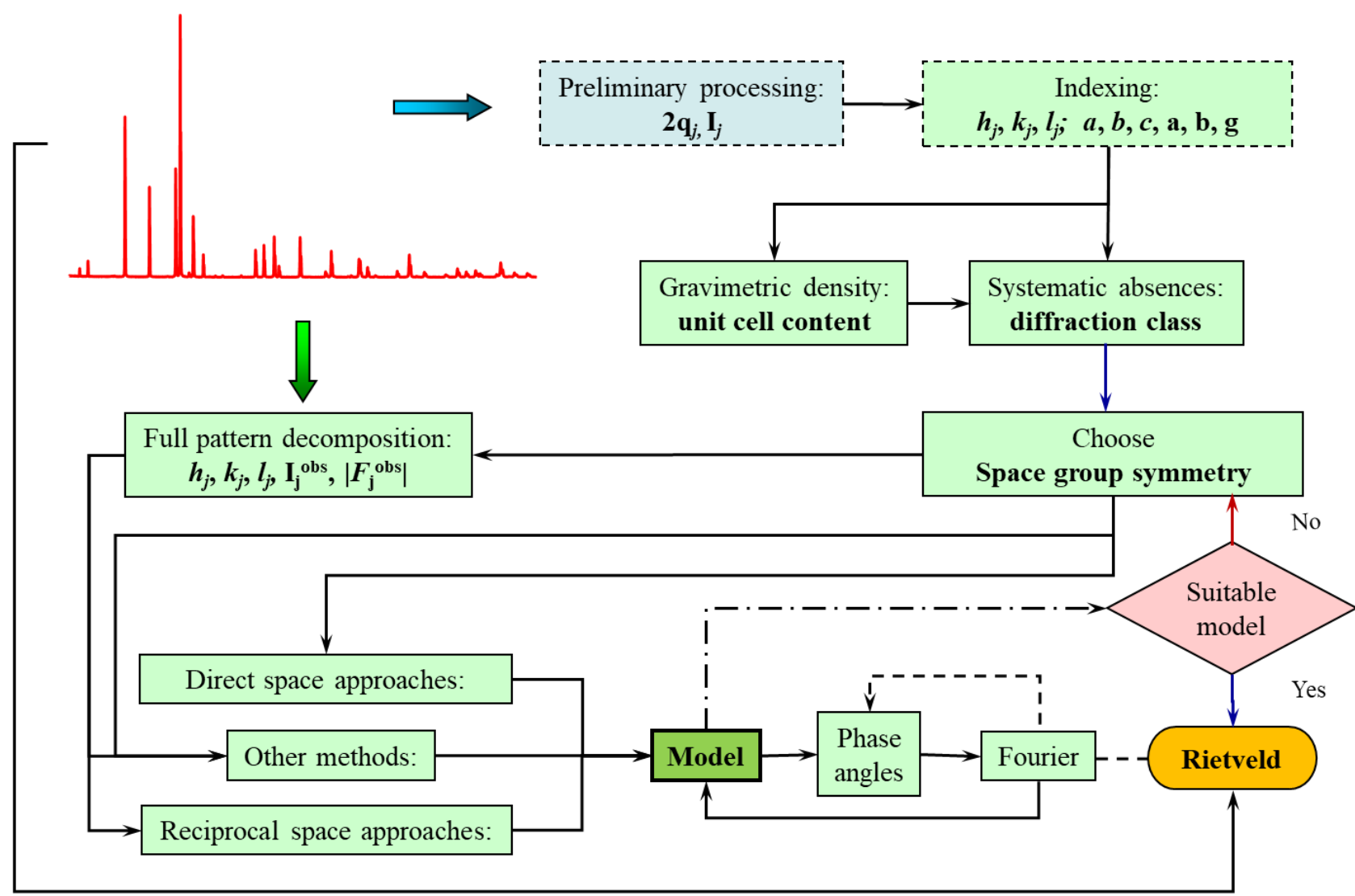
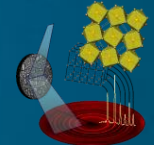


Figure 15.1. The flowchart illustrating crystal structure determination from powder diffraction data. Preliminary processing and indexing are described in Chaps. 13 and 14, respectively, and have been assumed accomplished at an earlier stage.

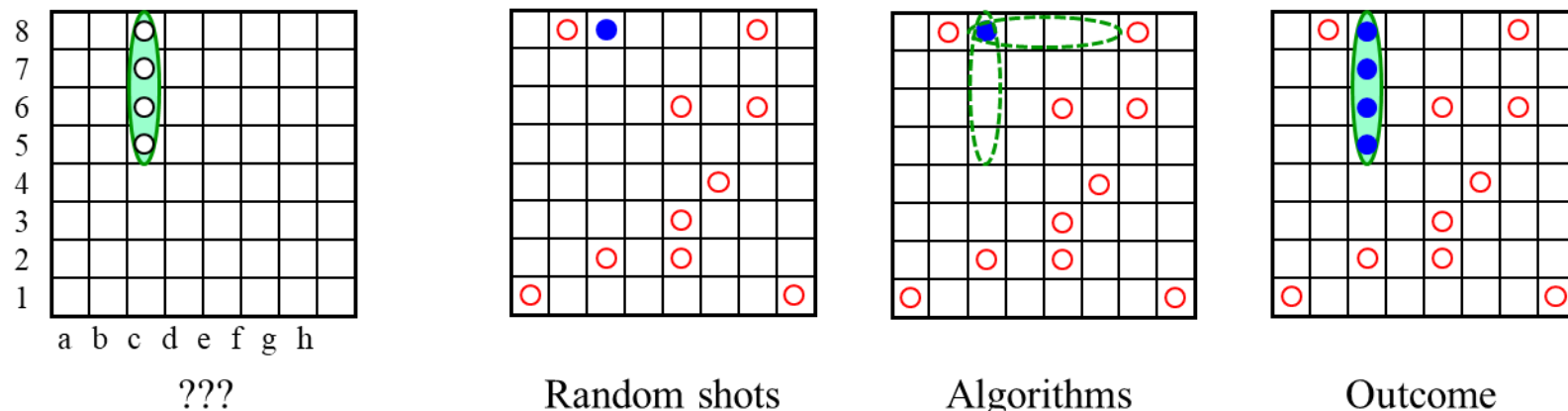
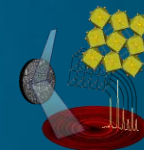
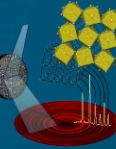


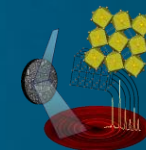
Figure 15.2. The Monte Carlo method illustrated as a game of battleship.

Assume that the unknown location of a *four-dot* battleship on the left represents a structure to be found. First a player makes some random shots (*empty red circles*) until the ship is hit once, shown as a *filled blue circle*. Next the player applies algorithms (i.e., a battleship is in the *vertical* or *horizontal* direction). Finally, based on the outcome of the random sampling and the algorithm, the player determines the location of the other player's ship, thus solving the structure.



Unconventional Direct, Reciprocal, and Dual Space Methods:

- **Genetic algorithm**
- **Maximum entropy** method
- **Maximum likelihood** method
- **Simulated annealing** method and its modification
 - **Parallel tempering**
- **Dual-space** methods:
 - **Charge flipping** algorithm

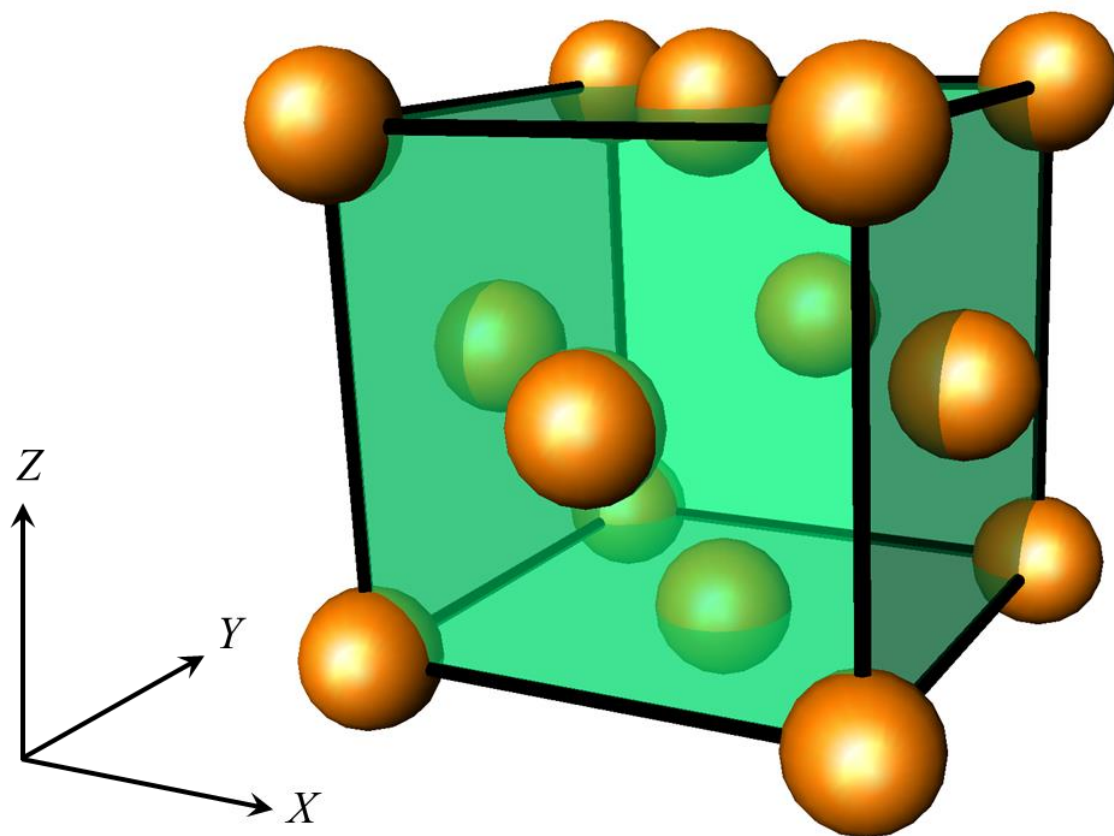
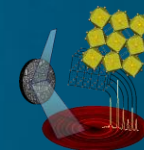


Full-pattern decomposition: Le Bail and Pawley methods:

$$\begin{aligned}
 Y_1 &= b_1 + \sum_{k=1}^m I_k [y_k(x_k) + 0.5y_k(x_k + \Delta x_k)] \\
 Y_2 &= b_2 + \sum_{k=1}^m I_k [y_k(x_k) + 0.5y_k(x_k + \Delta x_k)] \\
 &\dots \\
 Y_n &= b_n + \sum_{k=1}^m I_k [y_k(x_k) + 0.5y_k(x_k + \Delta x_k)]
 \end{aligned}
 \tag{Eq. 15.6}$$

Pawley method refined the intensity, while
Le Bail and Rietveld methods extract intensity as:

$$y_{k,i}^{obs} = p_{k,i} (Y_i^{obs} - b_i), \quad \text{where: } p_{k,i} = \frac{y_{k,i}^{calc}}{\sum_{k=1}^m y_{k,i}^{calc}}
 \tag{Eq. 15.7}$$

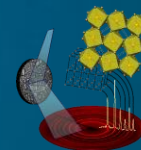


$$Z = \frac{m}{M} = \frac{\rho V}{M} \quad \text{Eq. 15.3}$$

$$Z = \frac{\rho V / 10^{24}}{M / 6.023 \times 10^{23}} = 0.6023 \frac{\rho V}{M} \quad \text{Eq. 15.4}$$

$$\rho = 1.66 \frac{ZM}{V} = 1.66 \frac{nzM}{V} \quad \text{Eq. 15.5}$$

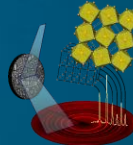
Figure 15.3. One unit cell in the crystal structure of elemental copper illustrating that a point located in a corner contributes $\frac{1}{8}$ of an atom, and a point located on a face contributes $\frac{1}{2}$ of an atom to the content of the unit cell. Similarly, a point located on an edge would contribute $\frac{1}{4}$ of an atom. Thus, the overall content of this unit cell is $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ Cu atoms.



Nonlinear Least Squares

$$\begin{aligned}
 & \frac{\partial f_1(x_1^0, \dots, x_m^0)}{\partial x_1} \Delta x_1 + \dots + \frac{\partial f_1(x_1^0, \dots, x_m^0)}{\partial x_m} \Delta x_m \cong y_1 - f_1(x_1^0, \dots, x_m^0) \\
 & \frac{\partial f_2(x_1^0, \dots, x_m^0)}{\partial x_1} \Delta x_1 + \dots + \frac{\partial f_2(x_1^0, \dots, x_m^0)}{\partial x_m} \Delta x_m \cong y_2 - f_2(x_1^0, \dots, x_m^0) \\
 & \dots \\
 & \frac{\partial f_n(x_1^0, \dots, x_m^0)}{\partial x_1} \Delta x_1 + \dots + \frac{\partial f_n(x_1^0, \dots, x_m^0)}{\partial x_m} \Delta x_m \cong y_n - f_n(x_1^0, \dots, x_m^0)
 \end{aligned}
 \tag{Eq. 15.9}$$

$$\Delta \mathbf{x} = (\mathbf{A}^T \mathbf{W} \mathbf{A})^{-1} (\mathbf{A}^T \mathbf{W} \mathbf{y})
 \tag{Eq. 15.10}$$



Nonlinear Least Squares (continue)

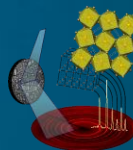
$$\Delta \mathbf{x} = \begin{pmatrix} x - x_1^0 \\ x - x_2^0 \\ \dots \\ x - x_m^0 \end{pmatrix} = \begin{pmatrix} \Delta x_1 \\ \Delta x_2 \\ \dots \\ \Delta x_m \end{pmatrix} \quad \text{Eq. 15.11}$$

$$\mathbf{y} = \begin{pmatrix} y_1 - f_1(x_1^0, \dots, x_m^0) \\ y_2 - f_2(x_1^0, \dots, x_m^0) \\ \dots \\ y_n - f_n(x_1^0, \dots, x_m^0) \end{pmatrix} \quad \text{Eq. 15.13}$$

$$\mathbf{W} = \begin{pmatrix} w_1^2 & 0 & \dots & 0 \\ 0 & w_2^2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & w_n^2 \end{pmatrix} \quad \text{Eq. 15.14}$$

$$\mathbf{A} = \begin{pmatrix} \frac{\partial f_1(x_1^0, \dots, x_m^0)}{\partial x_1} & \frac{\partial f_1(x_1^0, \dots, x_m^0)}{\partial x_2} & \dots & \frac{\partial f_1(x_1^0, \dots, x_m^0)}{\partial x_m} \\ \frac{\partial f_2(x_1^0, \dots, x_m^0)}{\partial x_1} & \frac{\partial f_2(x_1^0, \dots, x_m^0)}{\partial x_2} & \dots & \frac{\partial f_2(x_1^0, \dots, x_m^0)}{\partial x_m} \\ \dots & \dots & \dots & \dots \\ \frac{\partial f_n(x_1^0, \dots, x_m^0)}{\partial x_1} & \frac{\partial f_n(x_1^0, \dots, x_m^0)}{\partial x_2} & \dots & \frac{\partial f_n(x_1^0, \dots, x_m^0)}{\partial x_m} \end{pmatrix} \quad \text{Eq. 15.12}$$

$$\mathbf{x} = \mathbf{x}^0 + \Delta \mathbf{x} = \begin{pmatrix} x_1^0 + \Delta x_1 \\ x_2^0 + \Delta x_2 \\ \dots \\ x_m^0 + \Delta x_m \end{pmatrix} \quad \text{Eq. 15.15}$$



Nonlinear Least Squares (continue)

Standard uncertainty $\sigma(x_j)$:

$$\sigma(x_j) = \sqrt{\frac{(A^T W A)^{-1}_{jj} \sum_{i=1}^n w_i (y_i)^2}{n - m}}$$

Eq. 15.16

– $j = 1, \dots, m$

– n is the number of equations in Eq. 15.9,

– m is the number of parameters in Eq. 15.9

Marquardt damping (D):

$$\Delta \mathbf{x} = (\mathbf{A}^T \mathbf{W} \mathbf{A} + \lambda \mathbf{D})^{-1} (\mathbf{A}^T \mathbf{W} \mathbf{y})$$

Eq. 15.17

Correlation coefficients (ρ_{ij}):

$$\rho_{ij} = (A^T W A)^{-1}_{ij} / \sqrt{(A^T W A)^{-1}_{ii} (A^T W A)^{-1}_{jj}}$$

Eq. 15.18

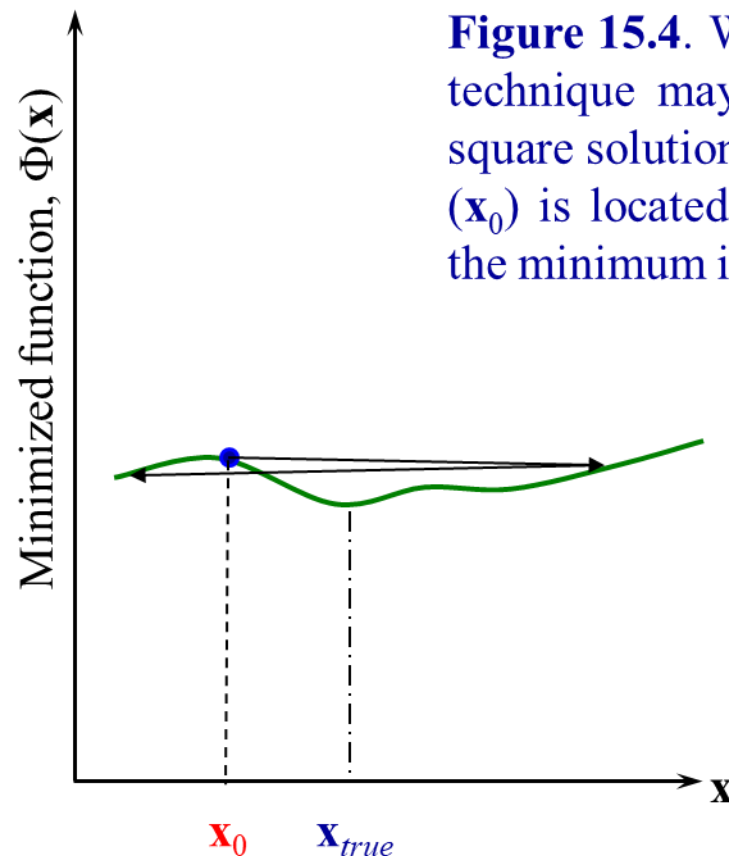
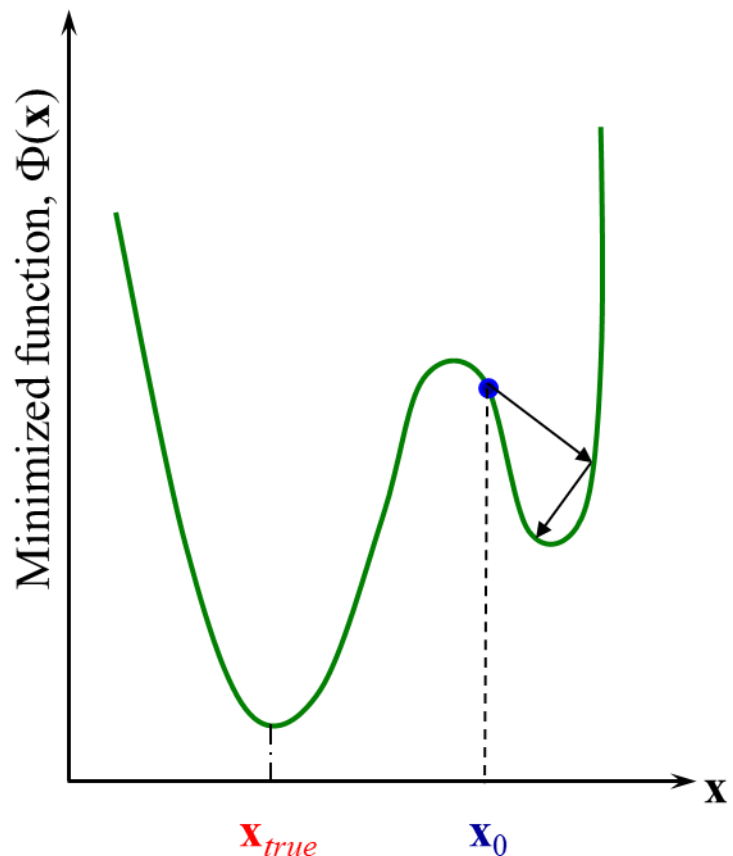
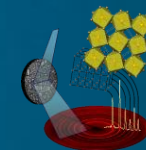


Figure 15.4. When the nonlinear least squares technique may fail in finding the best least-square solution: *left* – the initial approximation (x_0) is located near a false minimum; *right* – the minimum is poorly defined.

The *arrows* represent the possible outcomes of two least squares cycles. In the case on the *left* the minimization ends in a false minimum. In the case on the *right* the obtained shifts have correct signs but wrong magnitudes and instead of converging, their absolute values continue to increase. True solutions (i.e., global minima) are marked as x_{true} .

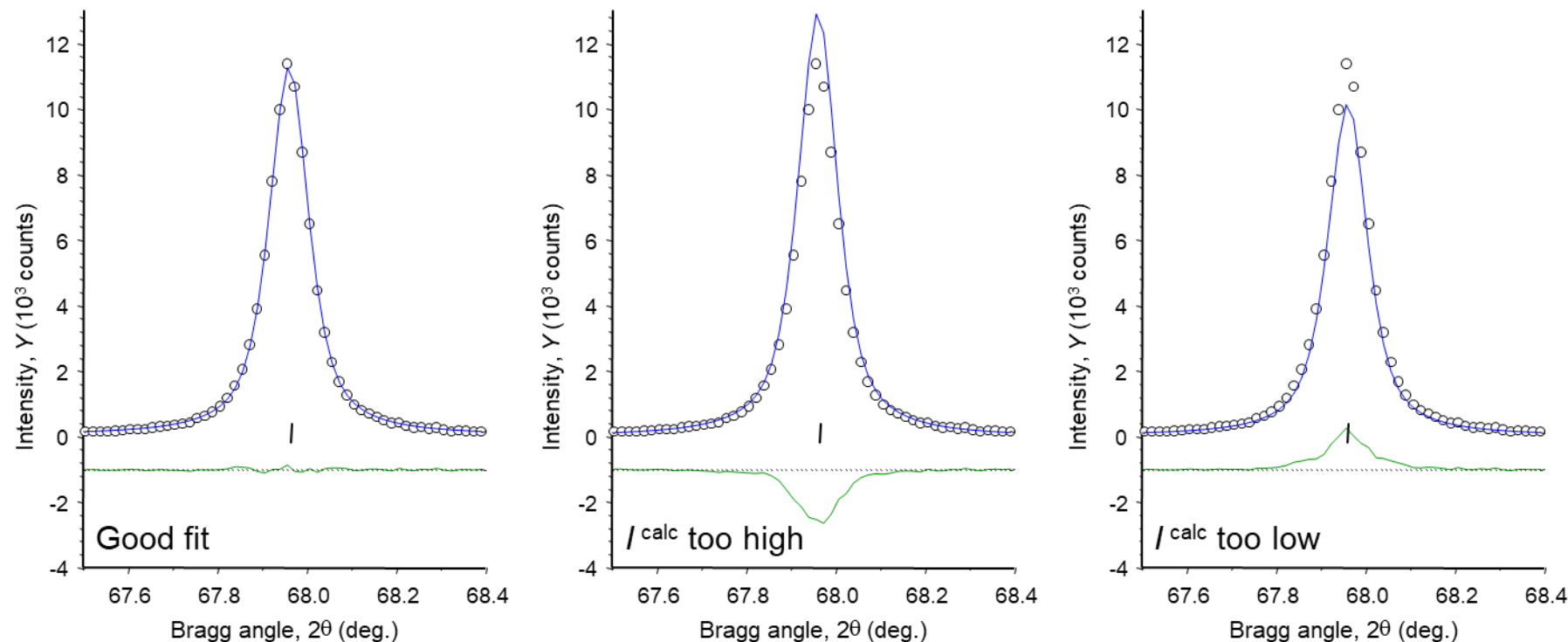
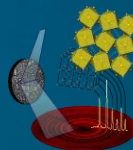


Figure 15.5. The observed (*circles*), calculated (*solid lines*), and difference (*solid lines at the bottom*) profiles.

The *dotted line at the bottom* corresponds to $Y_i^{obs} - Y_i^{calc} = 0$. The *short vertical lines* correspond to the calculated position of the Bragg peak. The *panel on the left* shows a good fit. The *panel in the middle* shows the result when the calculated integrated intensity is overestimated, while the *panel on the right* is for the underestimated integrated intensity.

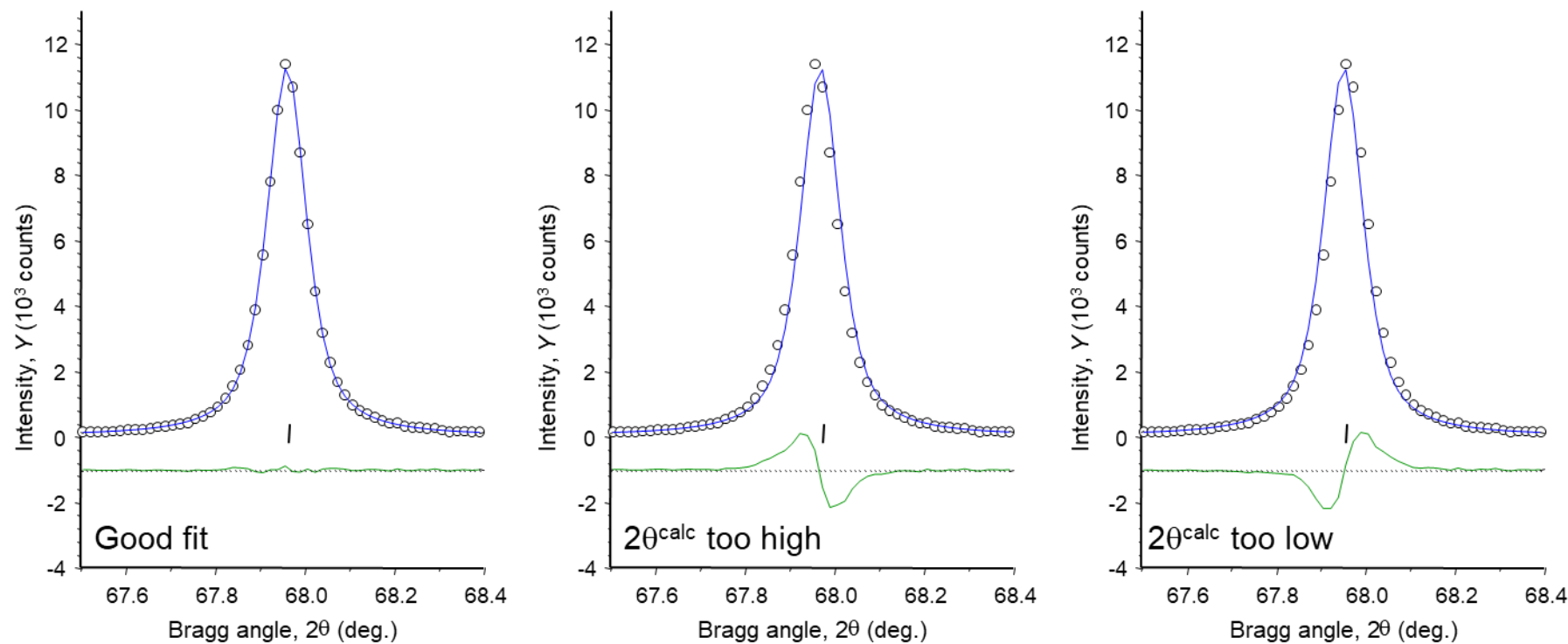
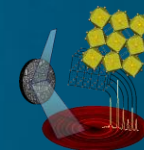


Figure 15.6. The *panel on the left* shows a good fit. The *panel in the middle* shows the result when the calculated Bragg angle is overestimated, while the *panel on the right* is for the underestimated Bragg angle. See Figure 15.5 for the explanation of notations.

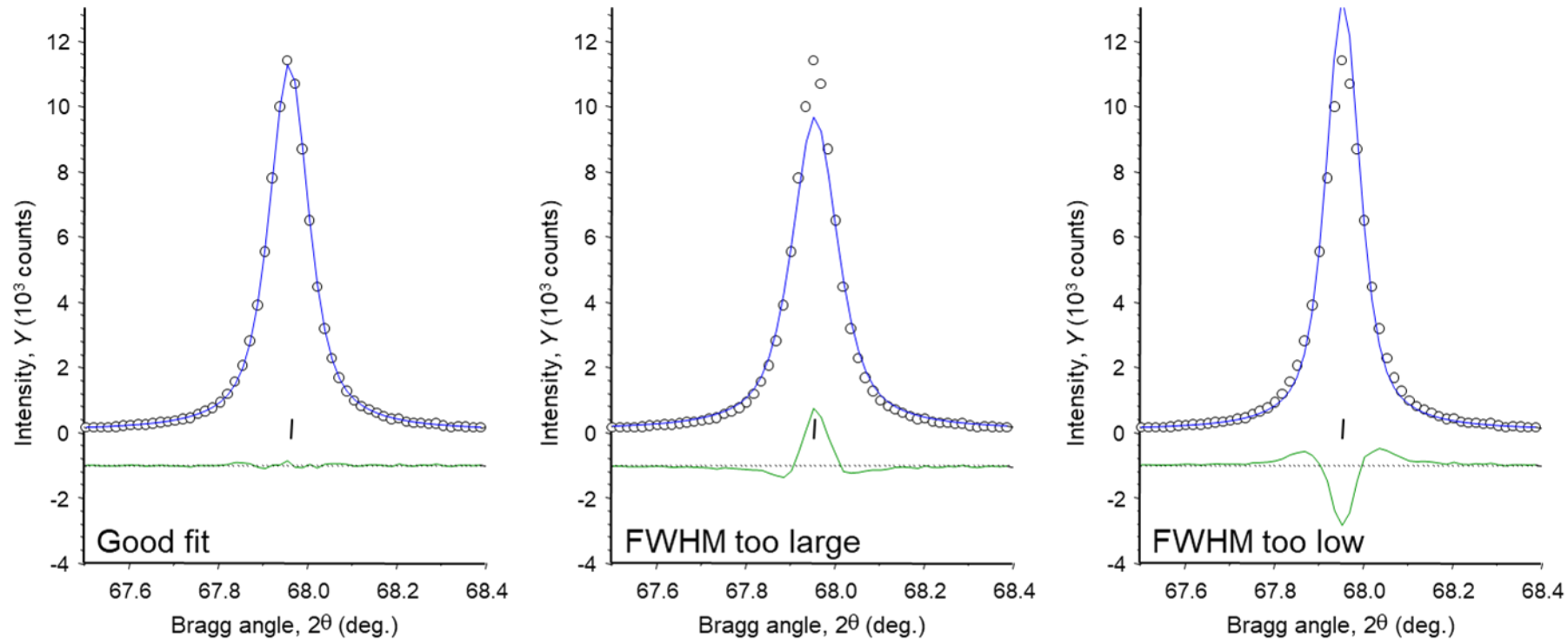
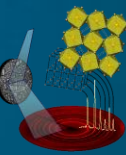


Figure 15.7. The *panel on the left* shows a good fit. The *panel in the middle* shows the result when the calculated FWHM is overestimated, while the *panel on the right* is for the underestimated FWHM. See Figure 15.5 for the explanation of notations.

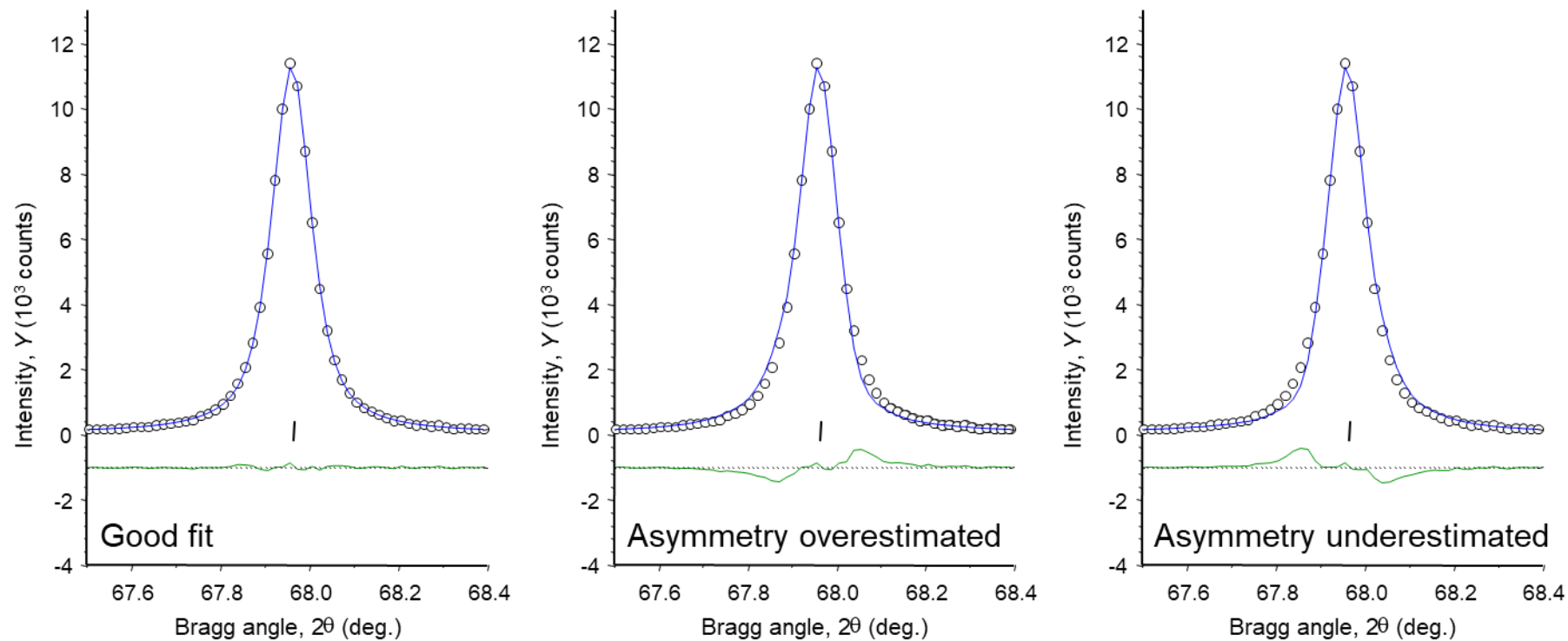
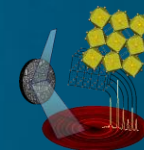


Figure 15.8. The *panel on the left* shows a good fit. The *panel in the middle* shows the result when peak asymmetry is overestimated, while the *panel on the right* is for the underestimated asymmetry. See Figure 15.5 for the explanation of notations.

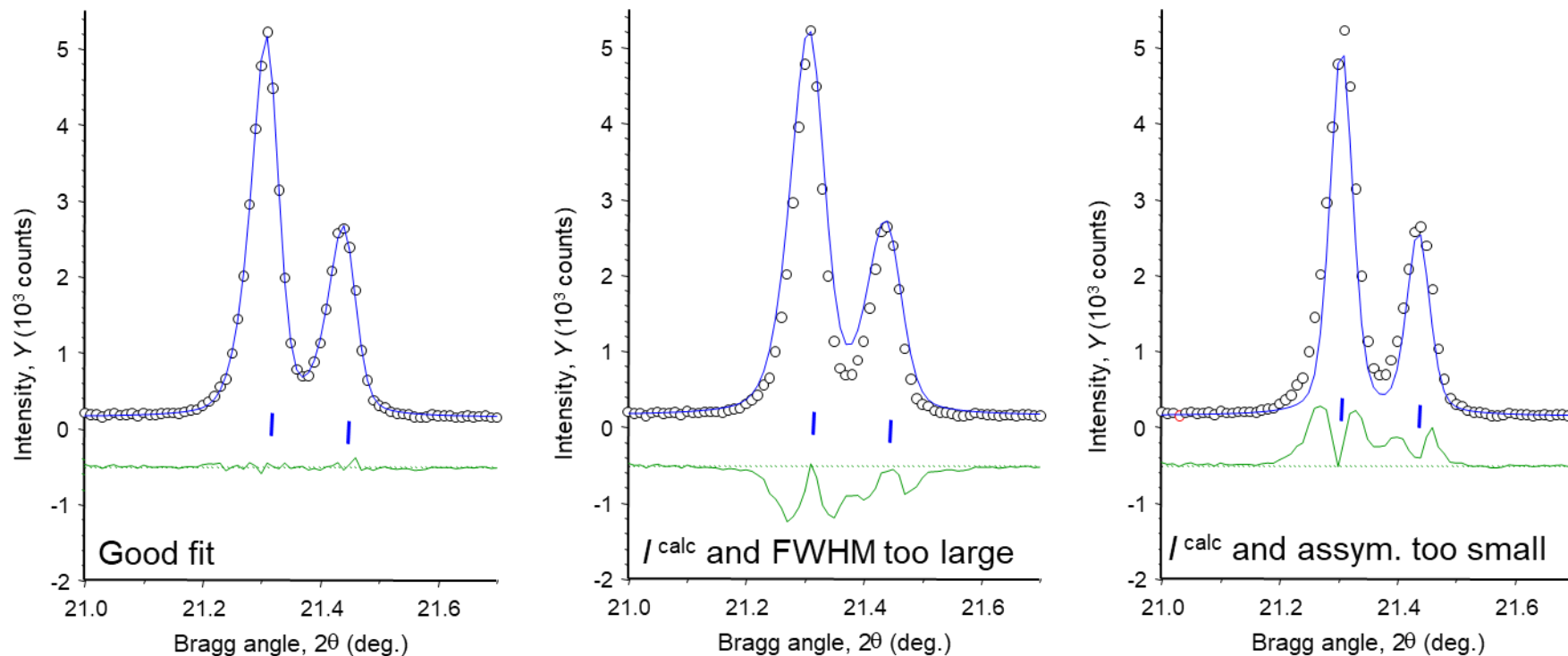
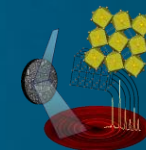
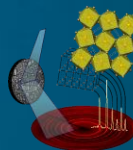


Figure 15.9. The *panel on the left* shows a good fit of a Mo $K\alpha_1/K\alpha_2$ doublet of the (021) Bragg peak of spherical $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powder. The *panel in the middle* shows the result when both peak intensity and full width at half maximum are overestimated, while the *panel on the right* is for the underestimated integrated intensity and asymmetry. See Figure 15.5 for the explanation of notations.



Figures of Merit

$$R_p = \frac{\sum_{i=1}^n |Y_i^{\text{obs}} - Y_i^{\text{calc}}|}{\sum_{i=1}^n Y_i^{\text{obs}}} \times 100\% \quad \text{Eq. 15.19}$$

$$R_{wp} = \left[\frac{\sum_{i=1}^n w_i (Y_i^{\text{obs}} - Y_i^{\text{calc}})^2}{\sum_{i=1}^n w_i (Y_i^{\text{obs}})^2} \right]^{1/2} \times 100\% \quad \text{Eq. 15.20}$$

$$R_B = \frac{\sum_{j=1}^m |I_j^{\text{obs}} - I_j^{\text{calc}}|}{\sum_{j=1}^m I_j^{\text{obs}}} \times 100\% \quad \text{Eq. 15.21}$$

$$R_{\text{exp}} = \left[\frac{n - p}{\sum_{i=1}^n w_i (Y_i^{\text{obs}})^2} \right]^{1/2} \times 100\% \quad \text{Eq. 15.22}$$

$$\chi^2 = \frac{\sum_{i=1}^n w_i (Y_i^{\text{obs}} - Y_i^{\text{calc}})^2}{n - p} = \left[\frac{R_{wp}}{R_{\text{exp}}} \right]^2 \quad \text{Eq. 15.23}$$

– n is the total number of points measured in the powder diffraction pattern.

– Y_i^{obs} is the observed intensity of the i^{th} data point.

– Y_i^{calc} is the calculated intensity of the i^{th} data point.

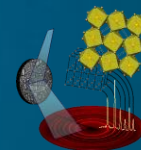
– w_i is the weight of the i^{th} data point, which is usually taken as $w_i = 1/\sigma_i = 1/Y_i^{\text{obs}}$.

– m is the number of independent Bragg reflections.

– I_j^{obs} is the “observed” integrated intensity of the j^{th} Bragg peak.

– I_j^{calc} is the calculated integrated intensity of the j^{th} Bragg peak.

– p is the number of free least squares parameters.



Figures of Merit (continue)

Durbin–Watson d -statistic:

$$d = \frac{\sum_{i=2}^n \left(\Delta Y_i / \sigma_i - \Delta Y_{i-1} / \sigma_{i-1} \right)^2}{\sum_{i=1}^n \left(\Delta Y_i / \sigma_i \right)^2} \quad \text{Eq. 15.26}$$

where $\Delta Y_i = Y_i^{obs} - Y_i^{calc}$ and σ_i is the corresponding statistical.

Parameter Q :

$$Q = 2 \left[\frac{n-1}{n-p} - \frac{3.0902}{\sqrt{n+2}} \right] \quad \text{Eq. 15.27}$$

where n and p are the number of experimental observations and free least squares parameters, respectively.
When:

$d < Q < 2$ – serial correlation is positive and sequential observations have the same sign;

$d > 4 - Q > 2$ – serial correlation is negative and sequential observations have opposite signs.

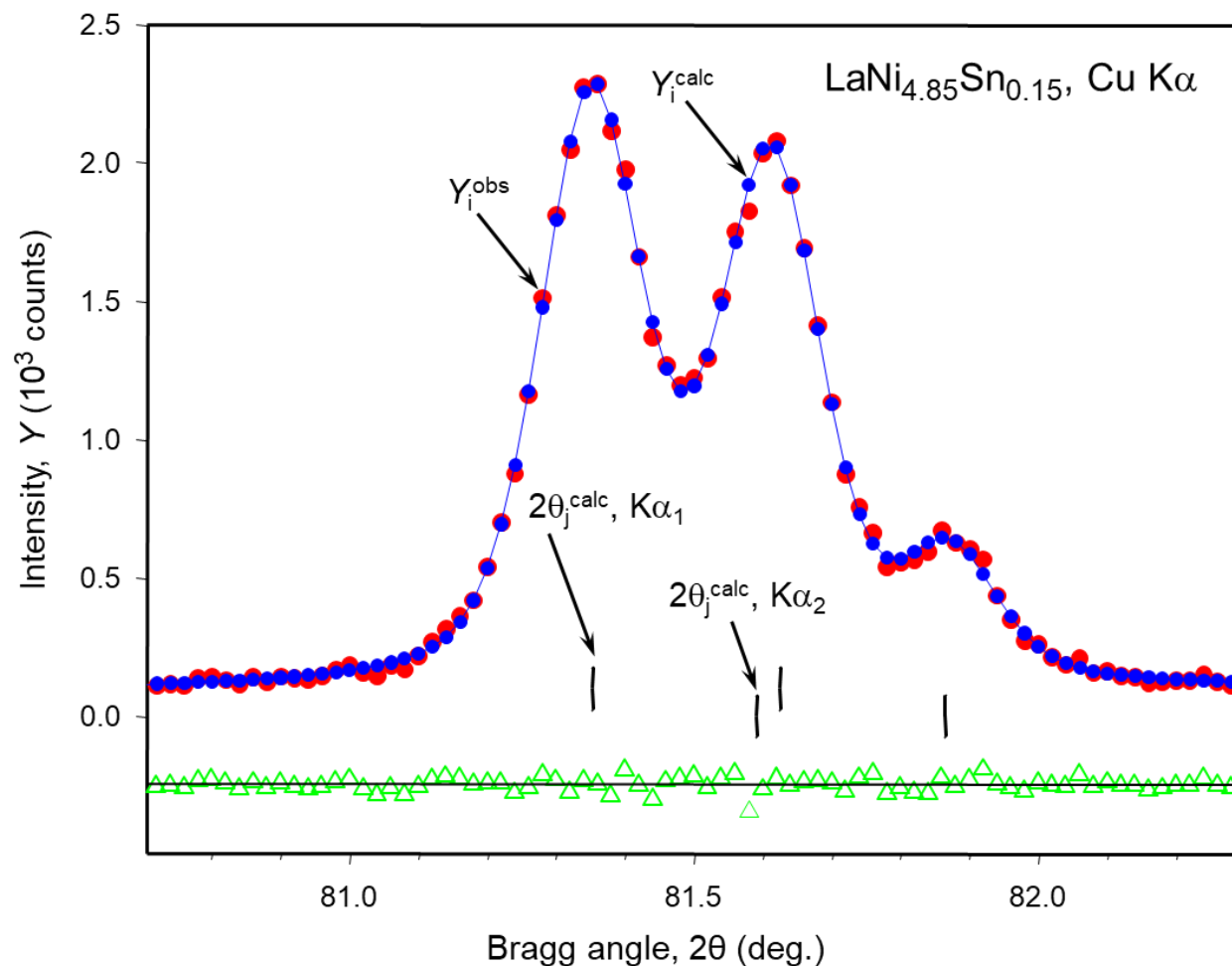
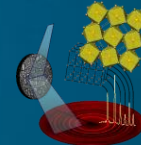
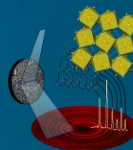


Figure 15.10. A fragment of a powder diffraction pattern of $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ collected on a Rigaku TTRAX rotating anode powder diffractometer using $\text{Cu K}\alpha$ radiation with a step $\Delta 2\theta = 0.02^\circ$. The observed scattered intensity (Y_i^{obs}) is represented by *red circles*; calculated intensity (Y_i^{calc}) is shown by *blue circles* connected with *thin solid line*. The differences between the observed and calculated intensities are depicted by *green triangles*. A *thick solid line* across the triangles corresponds to $Y_i^{\text{obs}} - Y_i^{\text{calc}} = 0$. The differences between the observed and calculated intensities are typically plotted on the same scale as Y_i^{obs} and Y_i^{calc} , with a constant vertical displacement for clarity. *Vertical tick marks* indicate the calculated positions of Bragg peaks.



Fundamentals of the Rietveld Method

For a single wavelength experiment:

$$\Phi = \sum_{i=1}^n w_i (Y_i^{obs} - [b_i + K \sum_{j=1}^m I_j y_j(x_j)])^2 \quad \text{Eq. 15.30}$$

For dual wavelength ($K\alpha_1 + K\alpha_2$):

$$\Phi = \sum_{i=1}^n w_i (Y_i^{obs} - [b_i + K \sum_{j=1}^m I_j \{y_j(x_j) + 0.5y_j(x_j + \Delta x_j)\}])^2 \quad \text{Eq. 15.31}$$

Weights:

$$w_i = [Y_i^{obs}]^{-1} \quad \text{Eq. 15.32}$$

For dual wavelength and several phases:

$$\Phi = \sum_{i=1}^n w_i (Y_i^{obs} - [b_i + \sum_{l=1}^p K_l \sum_{j=1}^m I_{l,j} \{y_{l,j}(x_{l,j}) + 0.5y_{l,j}(x_{l,j} + \Delta x_{l,j})\}])^2 \quad \text{Eq. 15.34}$$

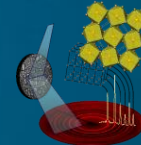
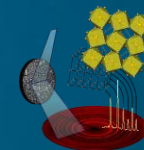


Table 15.2. A suggested parameter turn-on sequence in a single-phase, single-pattern Rietveld refinement using constant wavelength X-ray or neutron data.

Parameter or group of parameters	Linear	Stable	Comment	Sequence
Phase scale	Yes	Yes	a	1
Specimen displacement	No	Yes	b	1
Linear background	Yes	Yes	c	2
Lattice parameters	No	Yes	d	2
More background	Generally no	Fairly	c	2 or 3
profile parameter W	No	Poorly	e	3 or 5
Coordinates of atoms	No	Fairly	f	3
Preferred orientation	No	Fairly	f	4, if at all
Population and isotropic ADPs	No	Varies	Correlated	5
U, V, other profile parameters	No	No	e	Last
Anisotropic ADPs	No	Varies		Last, if at all
Zero shift	No	Yes	b	1, 5, if at all



Restraints:

$$\begin{aligned}
 \Phi = & \sum_{i=1}^{N^y} w_i^Y (Y_i^{obs} - Y_i^{calc})^2 + f^c \sum_{i=1}^{N^c} w_i^c (c_i^{obs} - c_i^{calc})^2 \\
 & + f^\delta \sum_{i=1}^{N^\delta} w_i^\delta (\delta_i^{exp} - \delta_i^{calc})^2 + f^\alpha \sum_{i=1}^{N^\alpha} w_i^\alpha (\alpha_i^{exp} - \alpha_i^{calc})^2 \\
 & + f^p \sum_{i=1}^{N^p} w_i^p (-p_i^{calc})^2 + f^P \sum_{i=1}^{N^P} w_i^P (-P_i^{calc})^2 \\
 & + f^z \sum_{i=1}^{N^z} w_i^z (-z_i^{calc})^2 + \dots
 \end{aligned}
 \tag{Eq. 15.35}$$

Chemical composition:

$$c^{calc} = \sum_{i=1}^n s_i m_i g_i \tag{Eq. 15.36}$$

c – chemical composition or charge balance,

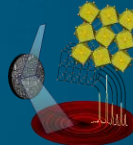
δ – distances,

α – valence angles,

p – displacement from a plane,

P – positive Pawley extracted integrated intensity,

z – positive pole figure



Rigid Bodies:

Tensor **U** from the
TLS parameters:

$$\mathbf{T} = \begin{pmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{pmatrix}, \mathbf{L} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{12} & L_{22} & L_{23} \\ L_{13} & L_{23} & L_{33} \end{pmatrix}, \text{ and } \mathbf{S} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \quad \text{Eq. 15.41}$$

$$\mathbf{U}_i = \mathbf{T} + \mathbf{A}_i \mathbf{S} + \mathbf{S}^T \mathbf{A}_i^T + \mathbf{A}_i \mathbf{L} \mathbf{A}_i^T \quad \text{Eq. 15.42}$$

$$\mathbf{A}_i = \begin{pmatrix} 0 & Z_i & -Y_i \\ -Z_i & 0 & X_i \\ Y_i & -X_i & 0 \end{pmatrix} \quad \text{Eq. 15.43}$$

$$U_{ij} = \frac{(\mathbf{gUg})_{ij}}{\sqrt{g_{ii}g_{jj}}}, \text{ where } \mathbf{g} = \begin{pmatrix} a^{*2} & a^*b^* \cos \gamma^* & a^*c^* \cos \beta^* \\ a^*b^* \cos \gamma^* & b^{*2} & b^*c^* \cos \alpha^* \\ a^*c^* \cos \beta^* & b^*c^* \cos \alpha^* & c^{*2} \end{pmatrix} \quad \text{Eq. 15.44}$$