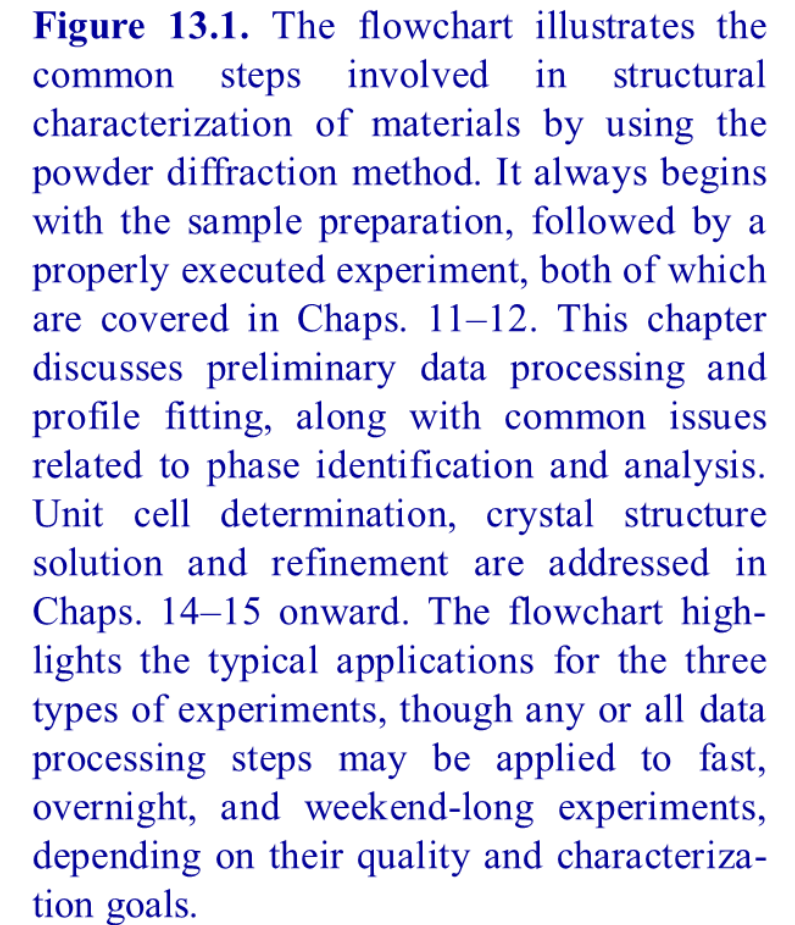




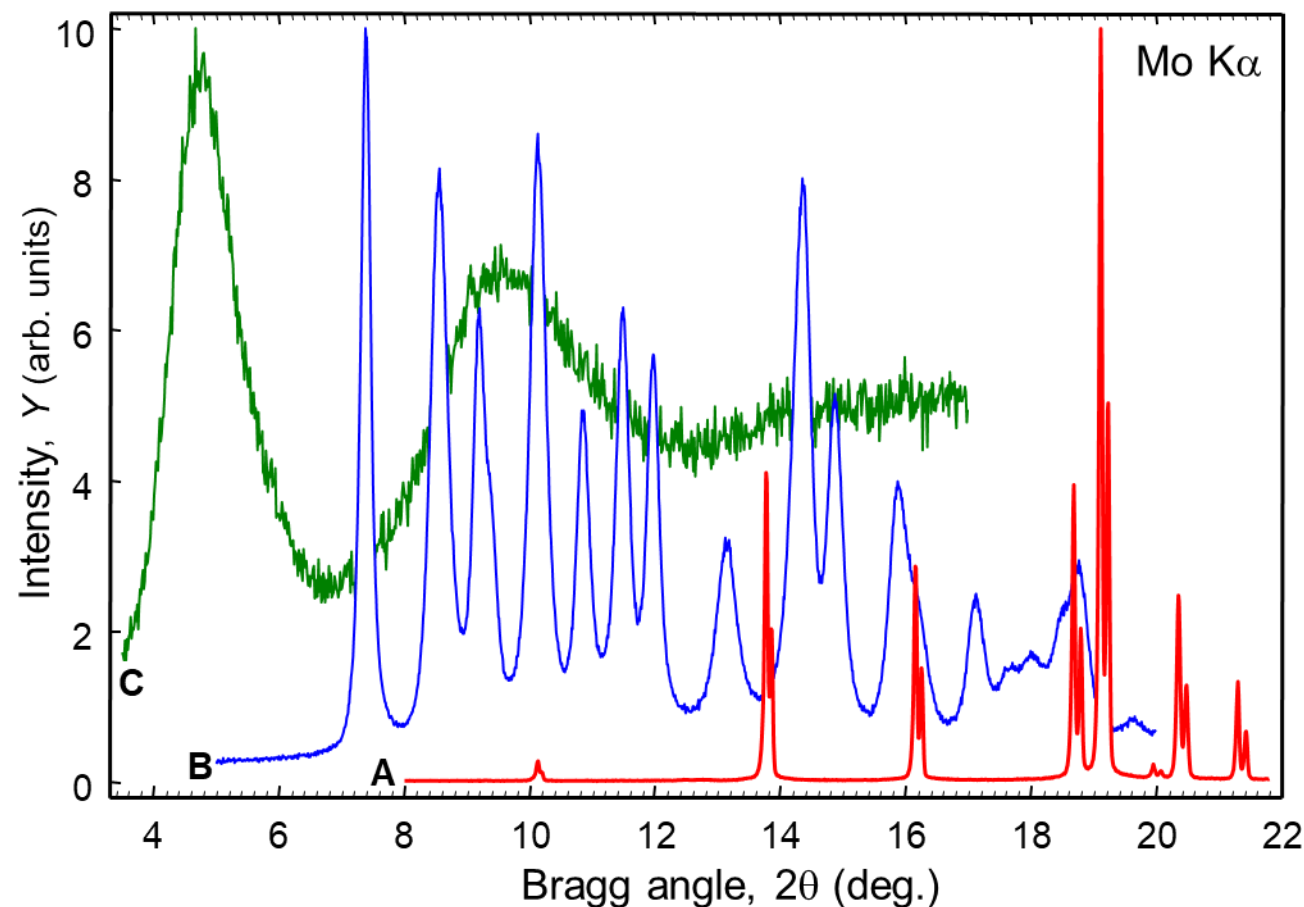
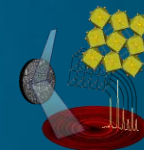


Figure 13.2. Fragments of powder diffraction patterns collected from three different materials on a Rigaku TTRAX rotating anode powder diffractometer using Mo $K\alpha$ radiation:

Pattern A (red) represents a material with excellent crystallinity: narrow and sharp Bragg reflections with $K\alpha_1/K\alpha_2$ doublets, becoming partially resolved at $2\theta \cong 14$.

Pattern B (blue) is also a crystalline material, however, its crystallinity is poor (and/or grain sizes are extremely small, and/or the material has been strained).

Pattern C (green) is collected from a material, which is clearly noncrystalline in a conventional sense: long-range order and periodicity are absent because no Bragg reflections have been observed.

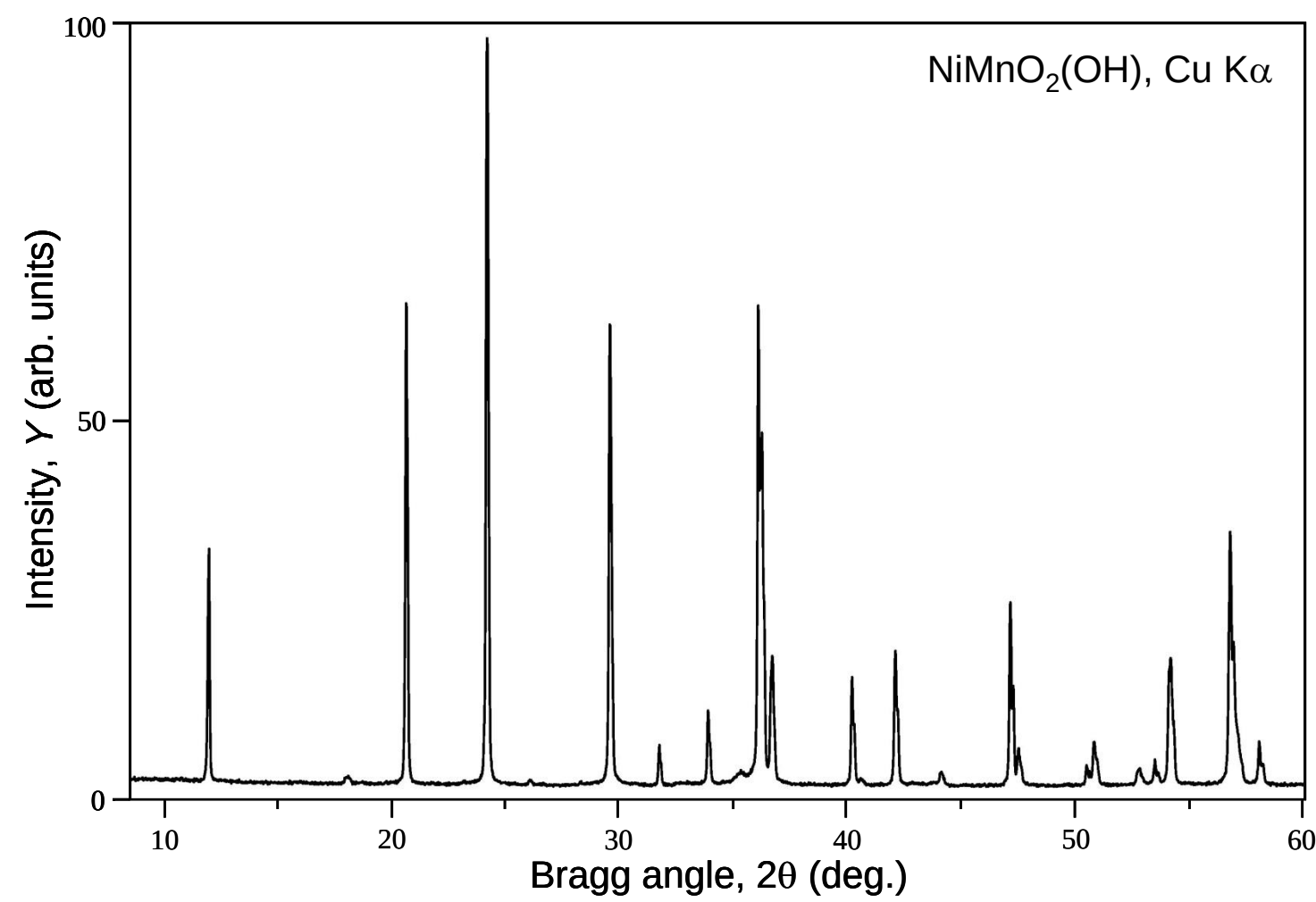
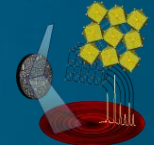


Figure 13.3. Powder diffraction pattern of the orthorhombic $\text{NiMnO}_2(\text{OH})$ collected on a Scintag XDS2000 powder diffractometer using $\text{Cu K}\alpha$ radiation. In this example, the background noise contributes a few percent to the highest measured scattered intensity.

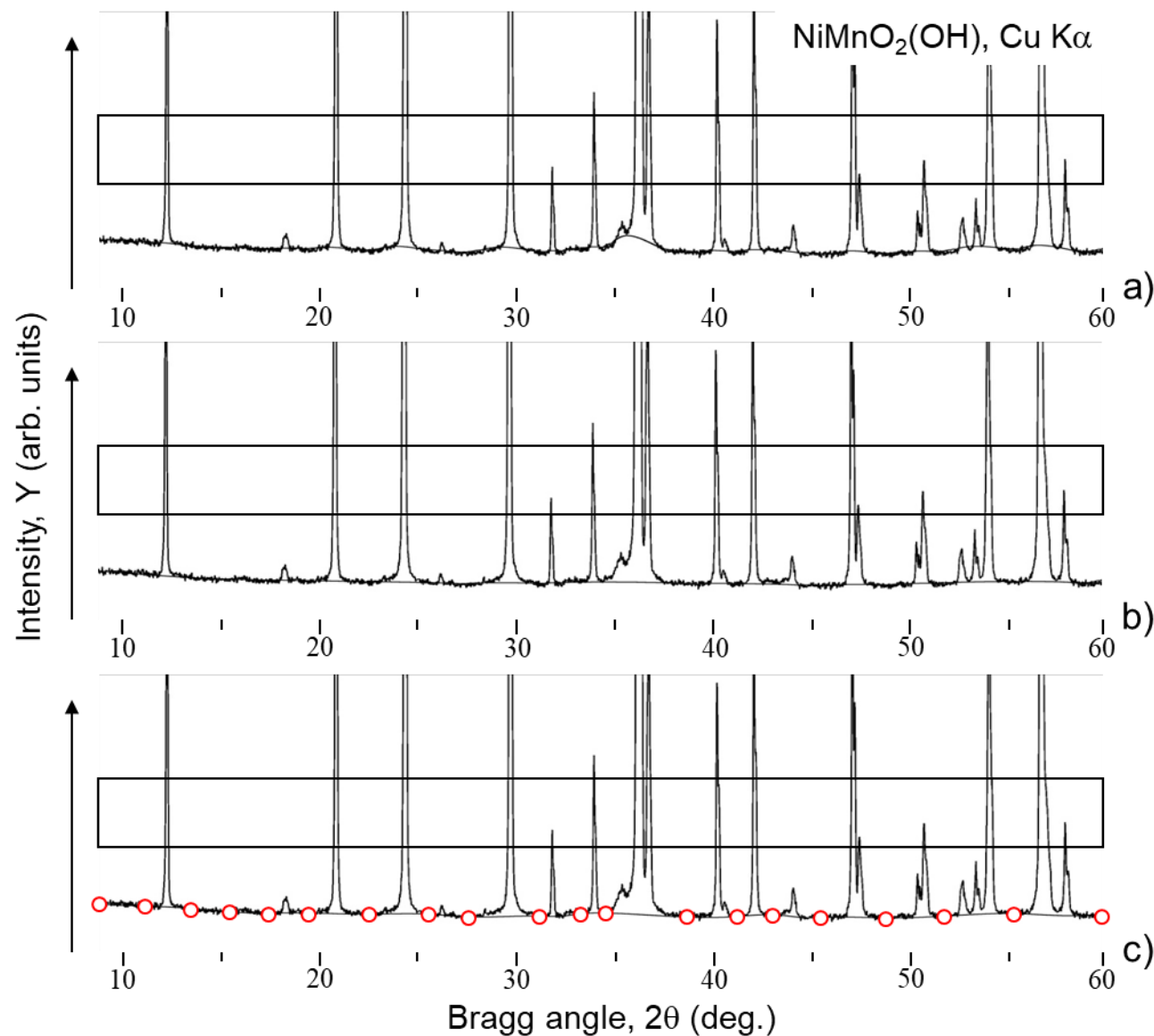
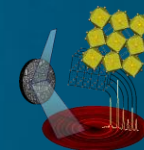


Figure 13.4. The powder diffraction pattern from Figure 13.3 shown with a different intensity scale. The background (thin lines at the bottom of each plot) has been approximated by means of (a) an automatic algorithm with the default box width of 1.5° ; (b) an automatic algorithm with a 4.0° box width; (c) background points selected manually as indicated by small circles.

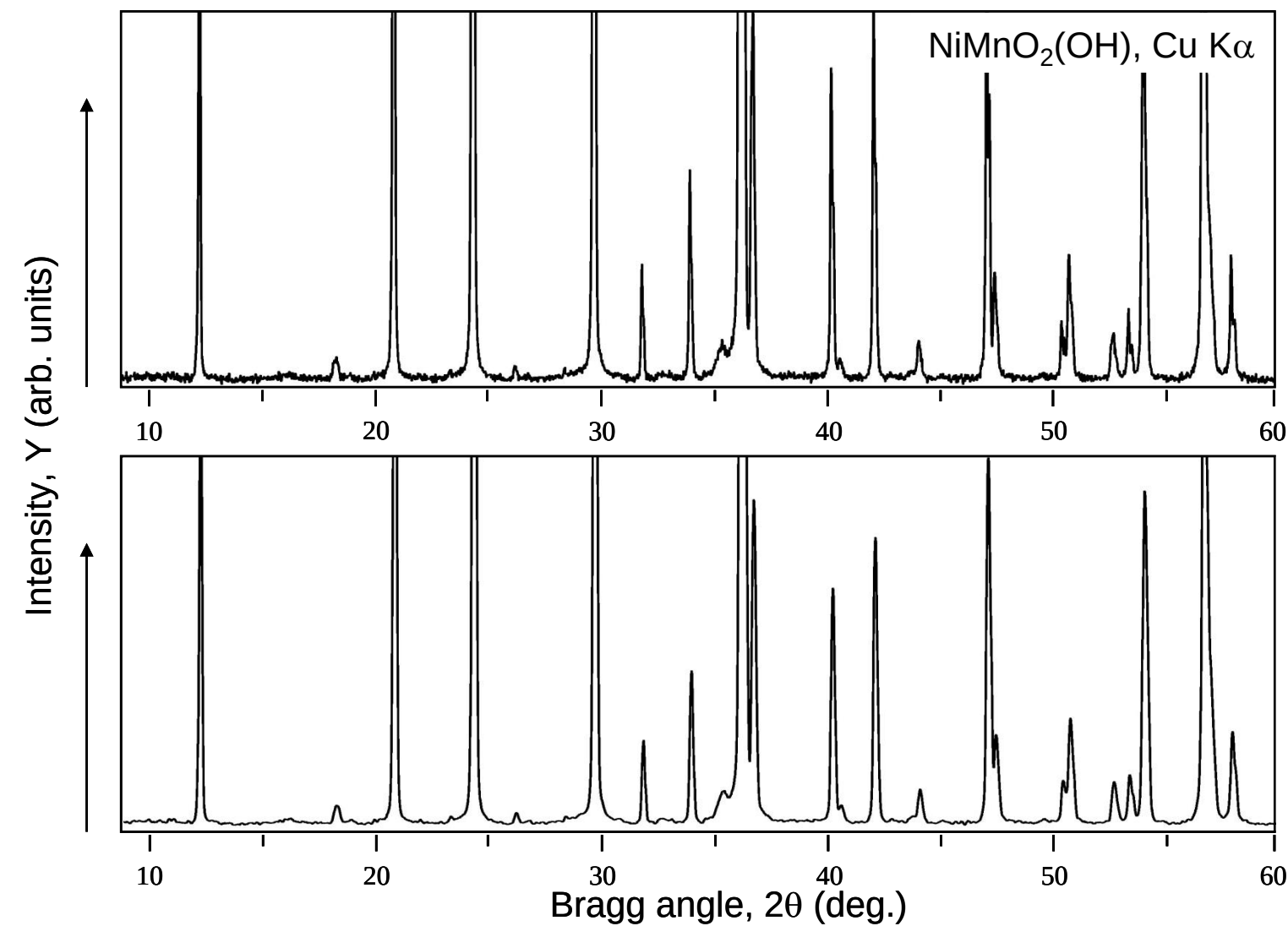
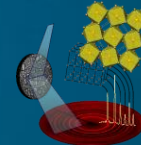


Figure 13.5. The powder diffraction pattern from Figure 13.3 with subtracted background prior to (*top*) and after (*bottom*) smoothing by using an analogue of Eq. 13.7 with 7 sequential data points.

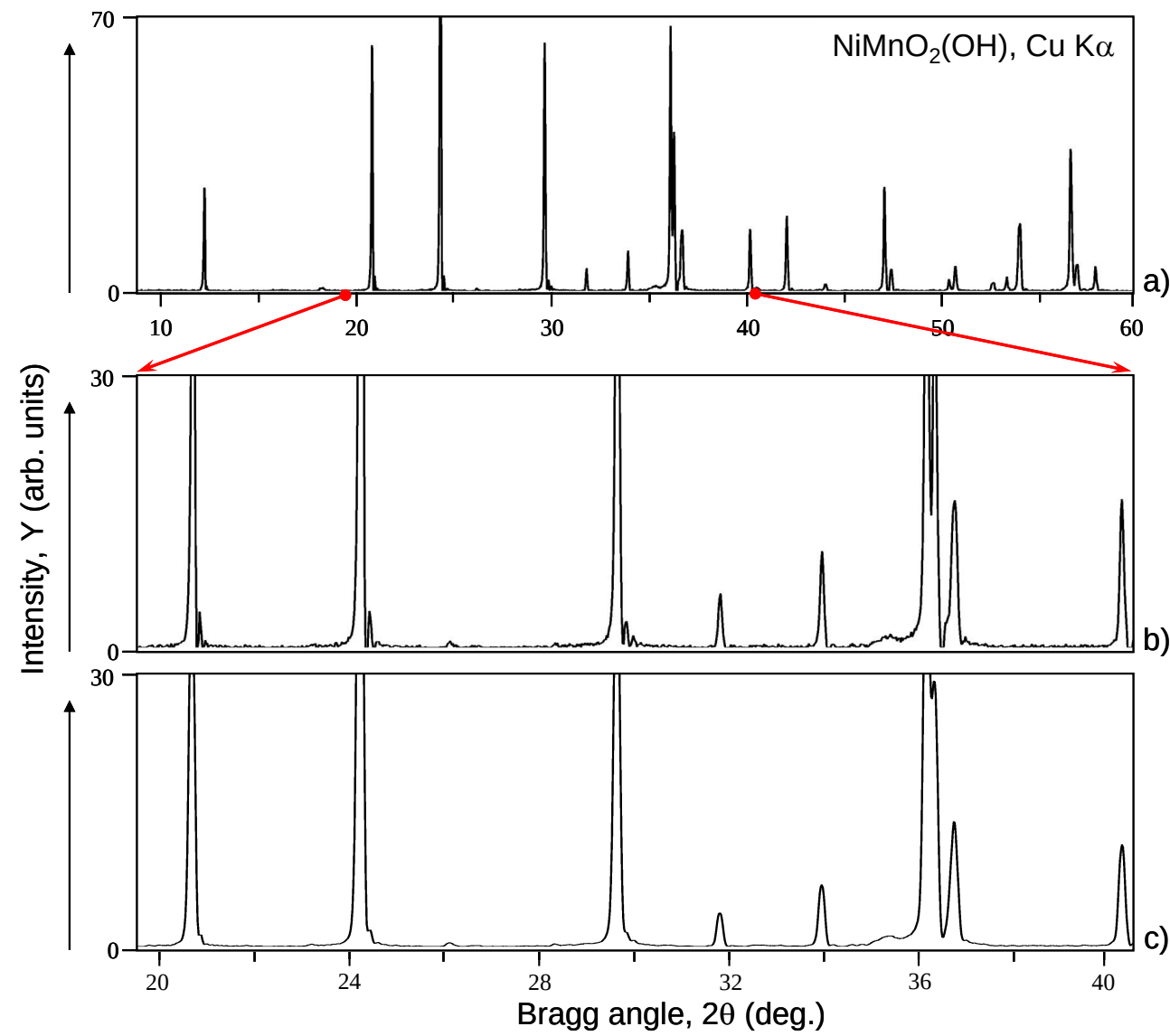
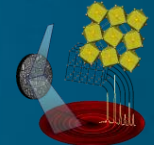
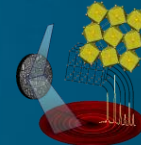


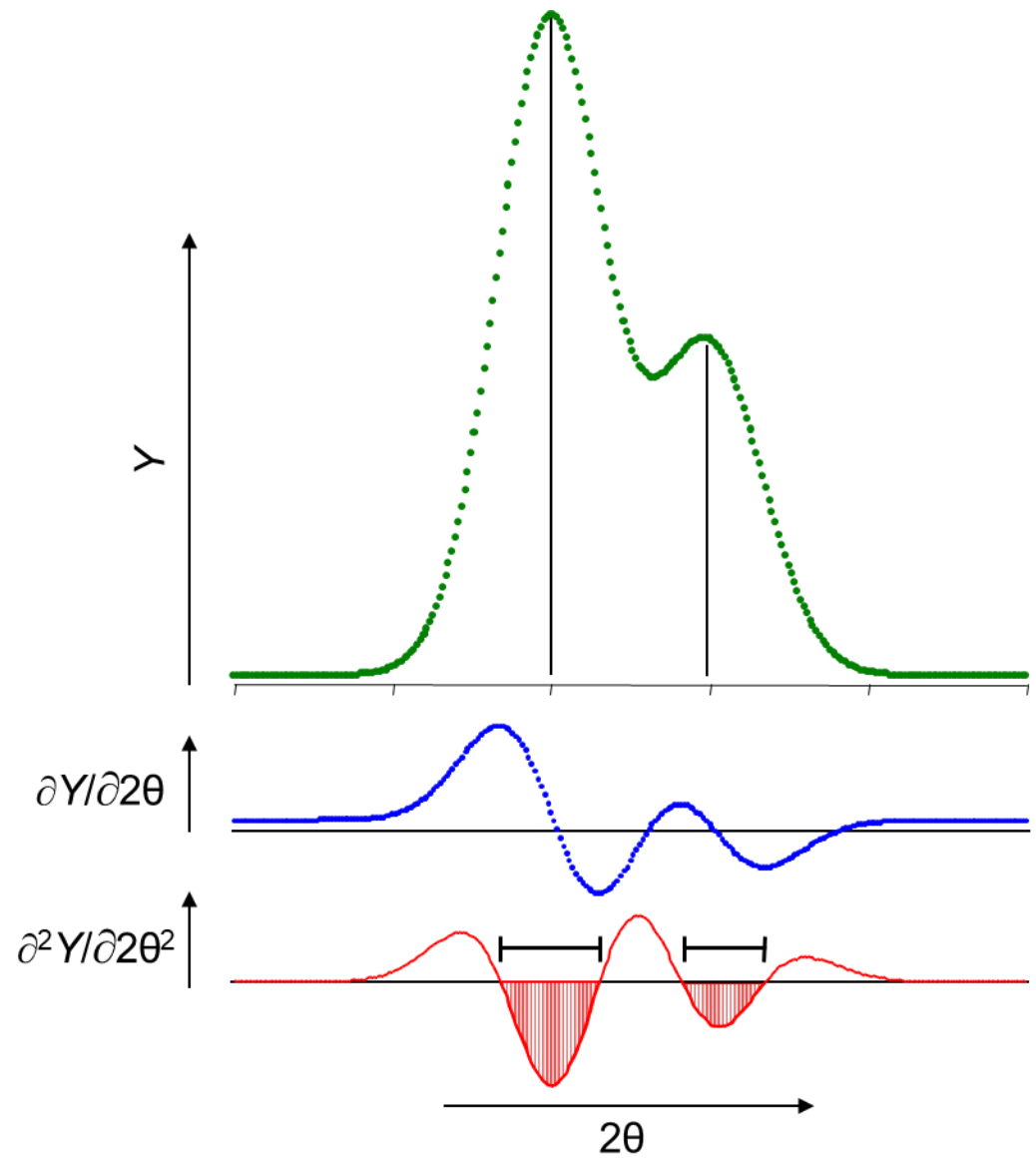
Figure 13.6. An illustration of $\text{K}\alpha_2$ stripping (a). The expanded view of the range between ~ 20 and 40° 2θ highlighting inaccuracies on the high Bragg angle sides of the strongest peaks (b). The expanded view of the same region when the background subtraction and $\text{K}\alpha_2$ stripping was preceded by a 7 point-smoothing (c). Although inaccuracies on high Bragg angle sides are less visible after smoothing, the “improvement” is accompanied by the loss of resolution, which is easily seen from comparison of the two peaks at $\sim 36^\circ$ in (b) and (c).



Eq. 13.10

$$\frac{\partial Y_i}{\partial 2\theta_i} = \frac{Y_{i+1}-Y_i}{s} \quad \text{and} \quad \frac{\partial^2 Y_i}{(\partial 2\theta_i)^2} = \frac{Y_{i+2}-2Y_{i+1}+Y_i}{s^2}$$

Figure 13.7. Intensity distribution in two partially resolved Bragg peaks (*top*) and the corresponding first (*middle*) and second (*bottom*) derivatives. The second derivative forms series of sequential negative regions (*hatched*), which represent both the maximum of each Bragg peak (coinciding with the minimum of the corresponding negative region) and the estimate of peak width near its half maximum (the width of the associated negative sequence).



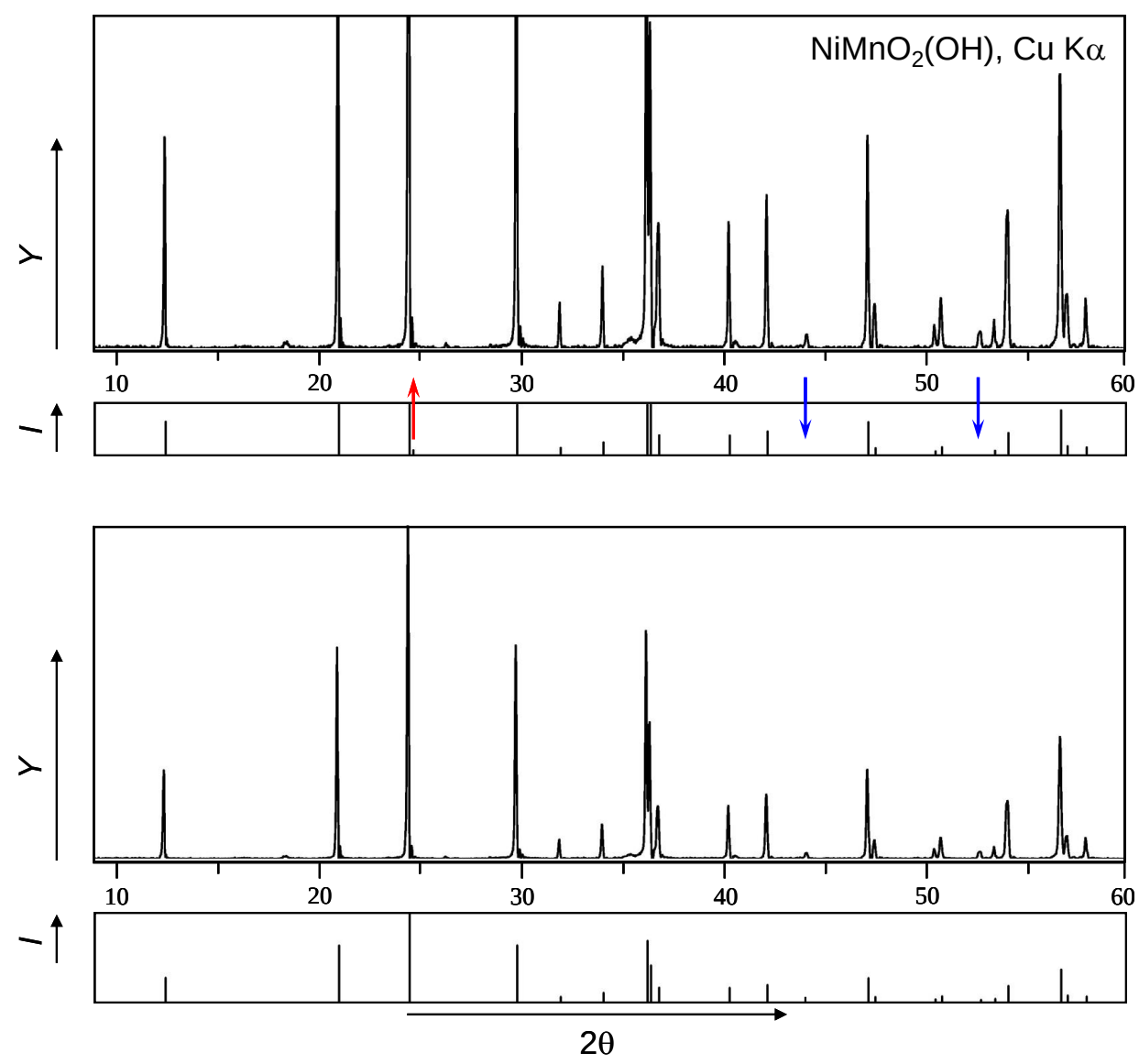
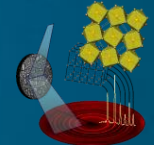


Figure 13.8. Automatic peak search conducted using a second derivative method (*top*) and manually corrected reduced pattern (*bottom*). The red upward arrow placed on the digitized pattern shows a false peak (which was eliminated manually) and the blue downward arrows show the missed peaks (which were added manually).

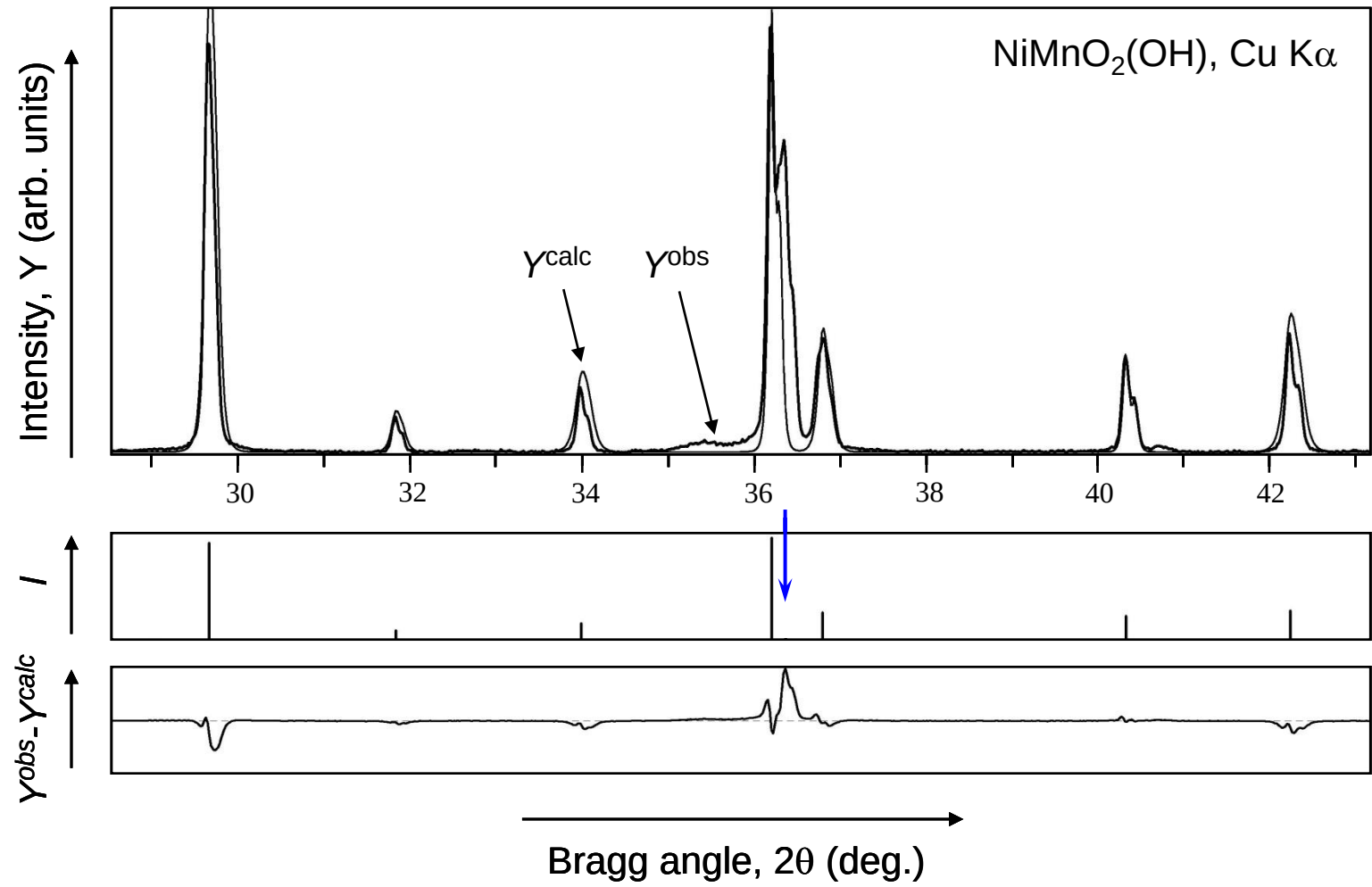
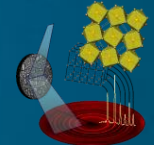


Figure 13.9. Observed (*thick line*) and calculated (*thin line*) intensity profiles in a fragment of the powder diffraction pattern of $\text{NiMnO}_2(\text{OH})$. The position of the missing peak is indicated by a *blue downward facing arrow*. Symmetrical Pearson-VII function with default peak-shape parameters was used in this example.

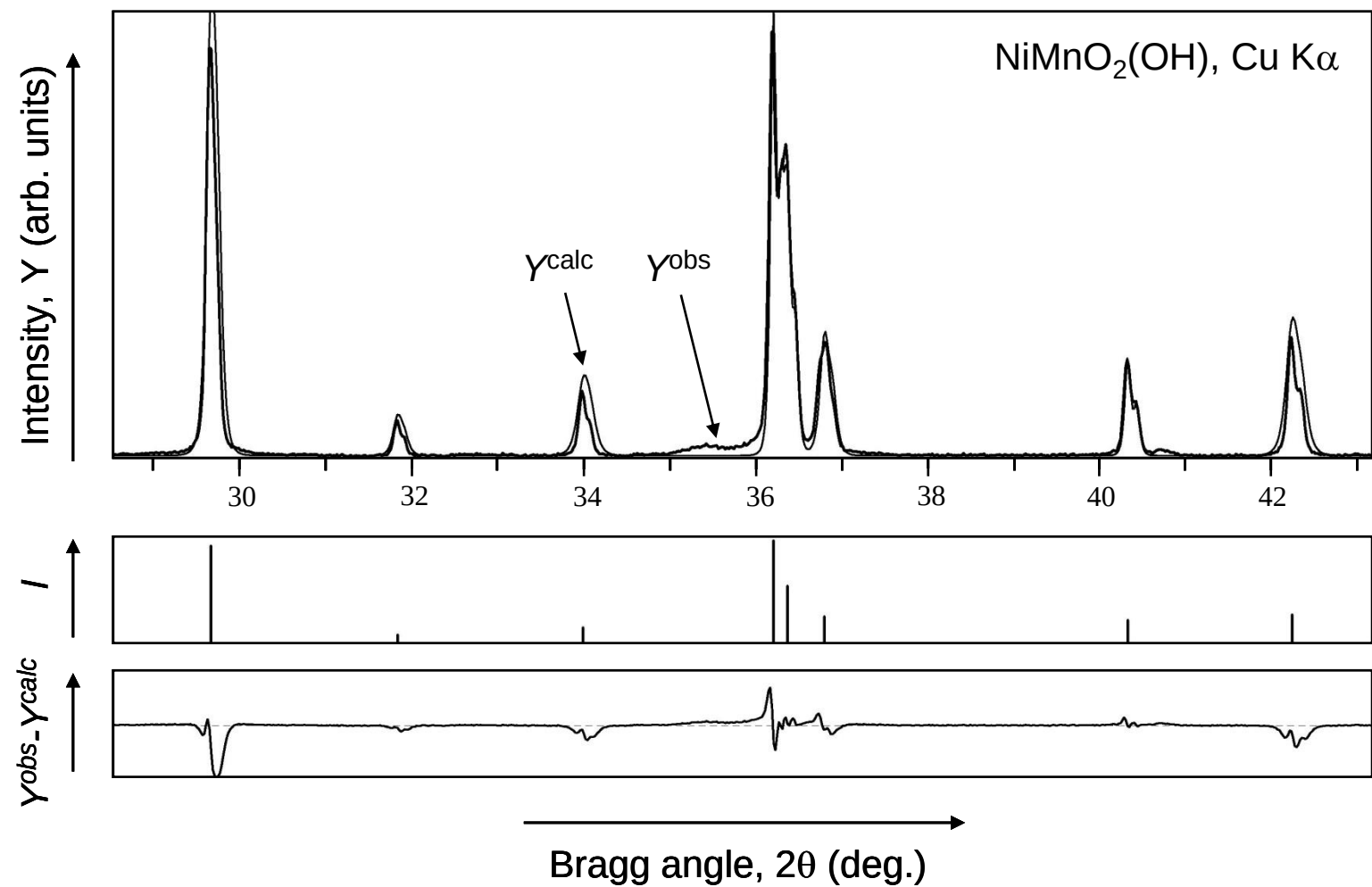
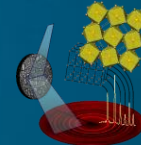


Figure 13.10. Observed and calculated intensity in a fragment of the powder diffraction pattern of NiMnO₂(OH) after adding the missing peak (compare with Figure 13.9).

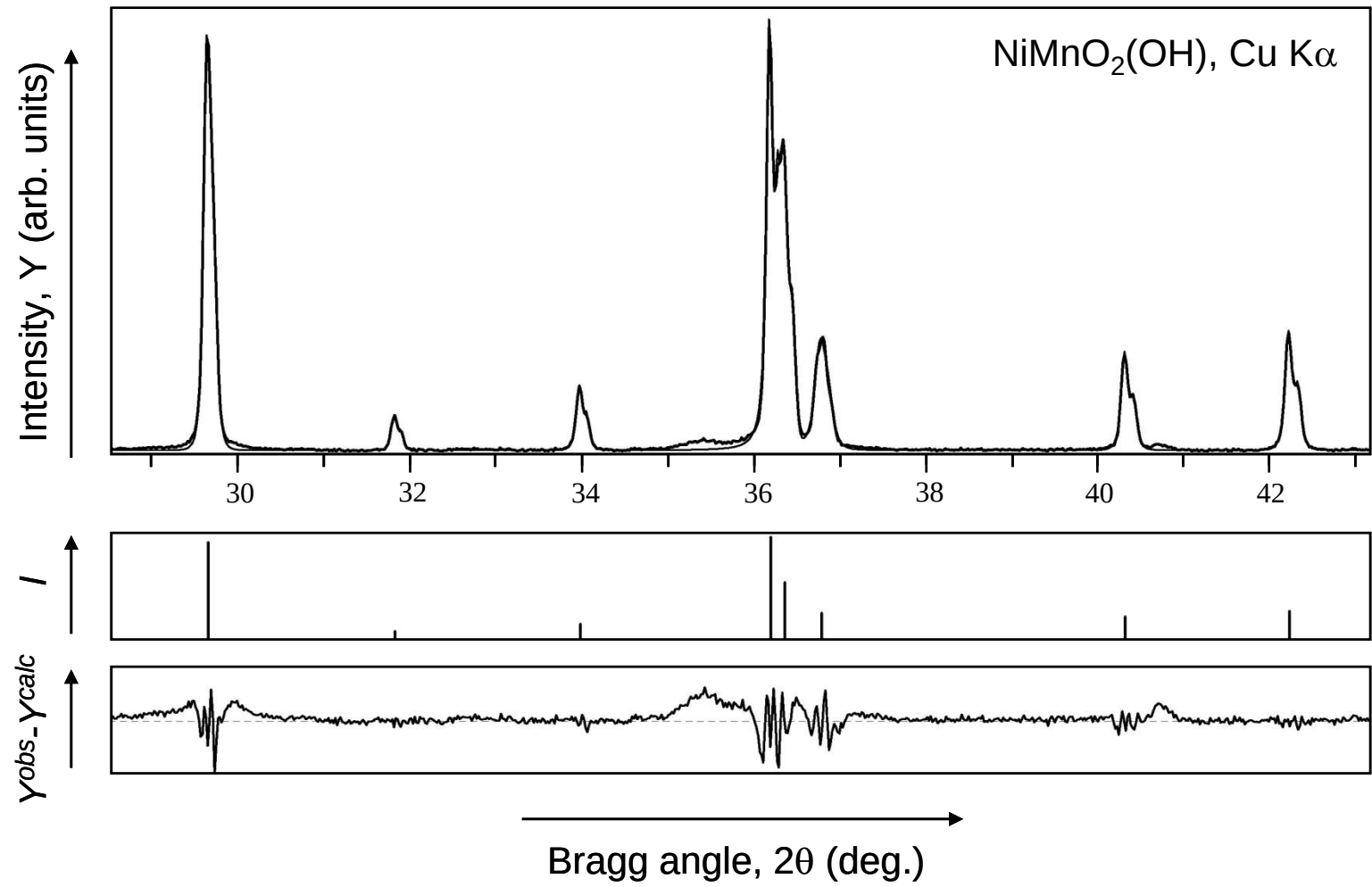
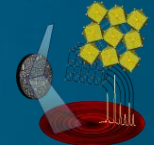


Figure 13.11. Observed and calculated intensity in a fragment of the powder diffraction pattern of NiMnO₂(OH) after least squares refinement using unit weights (compare with Figure 13.9).

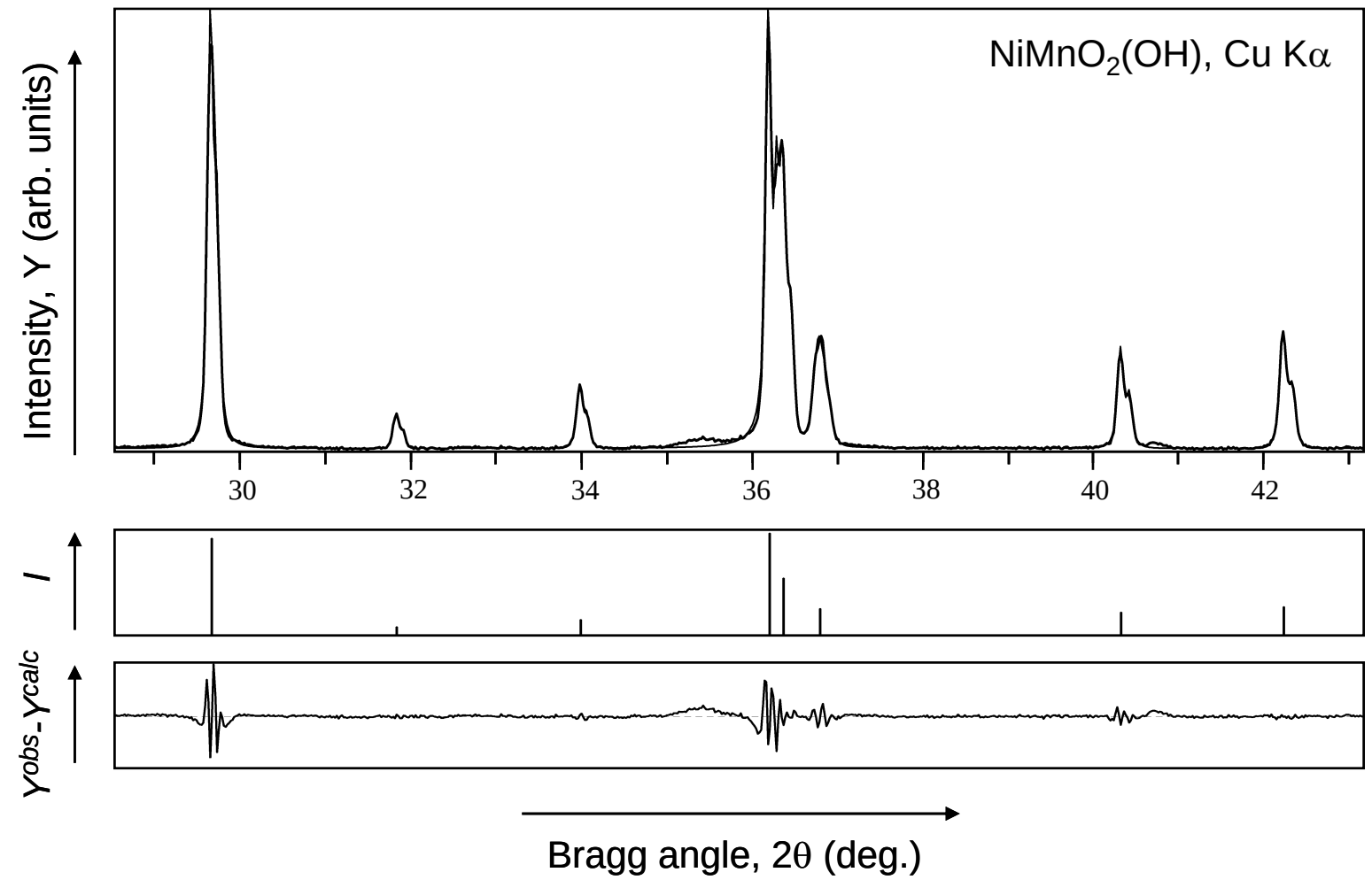
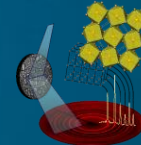


Figure 13.12. Observed and calculated intensity in a fragment of the powder diffraction pattern of NiMnO₂(OH) after least squares refinement using weights inversely proportional to Y_i^{obs} .

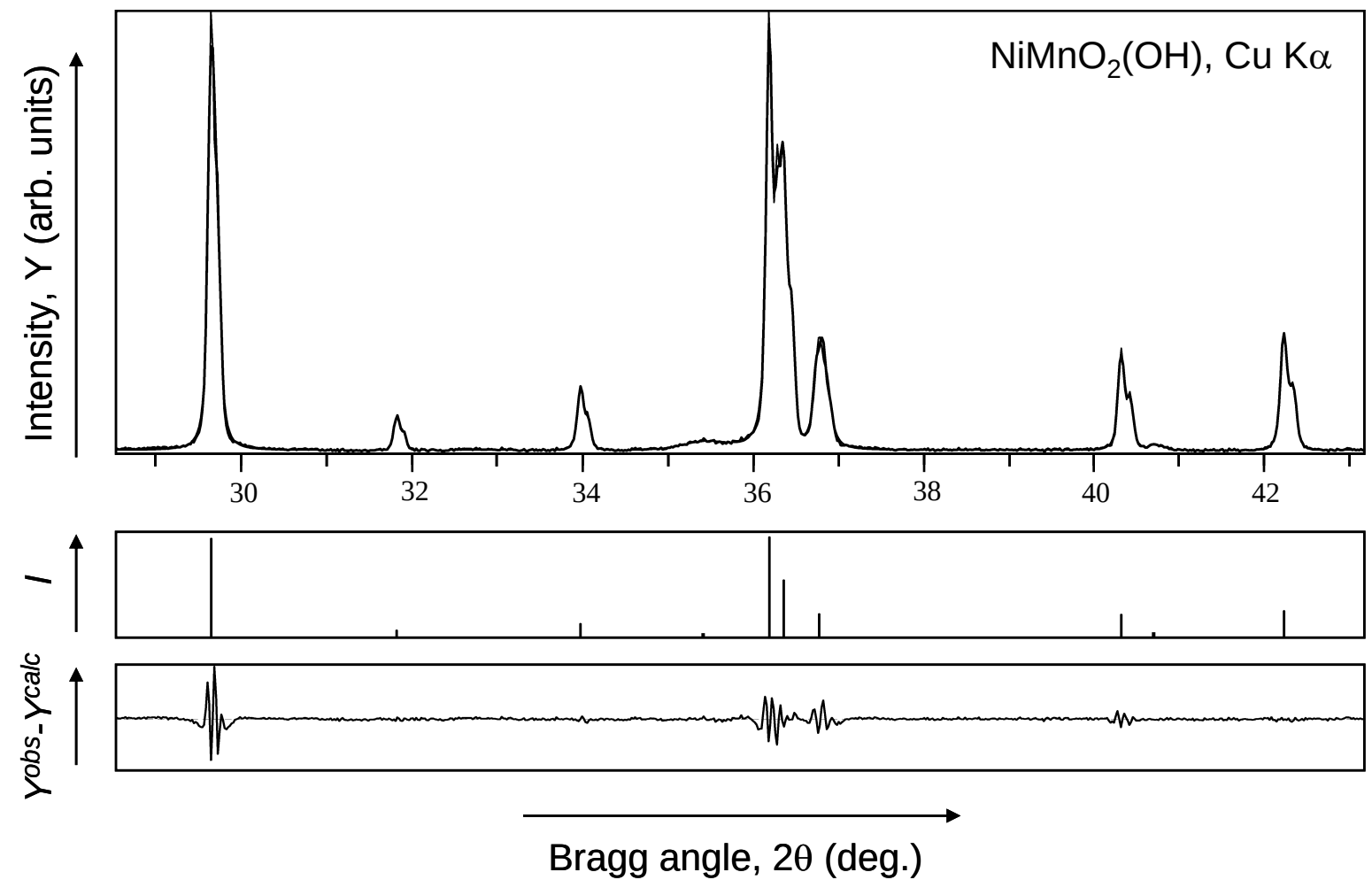
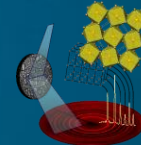


Figure 13.13. Observed and calculated intensity in a fragment of the powder diffraction pattern of $\text{NiMnO}_2(\text{OH})$ after adding two broad peaks at 2θ about 35.4 and 40.8° .

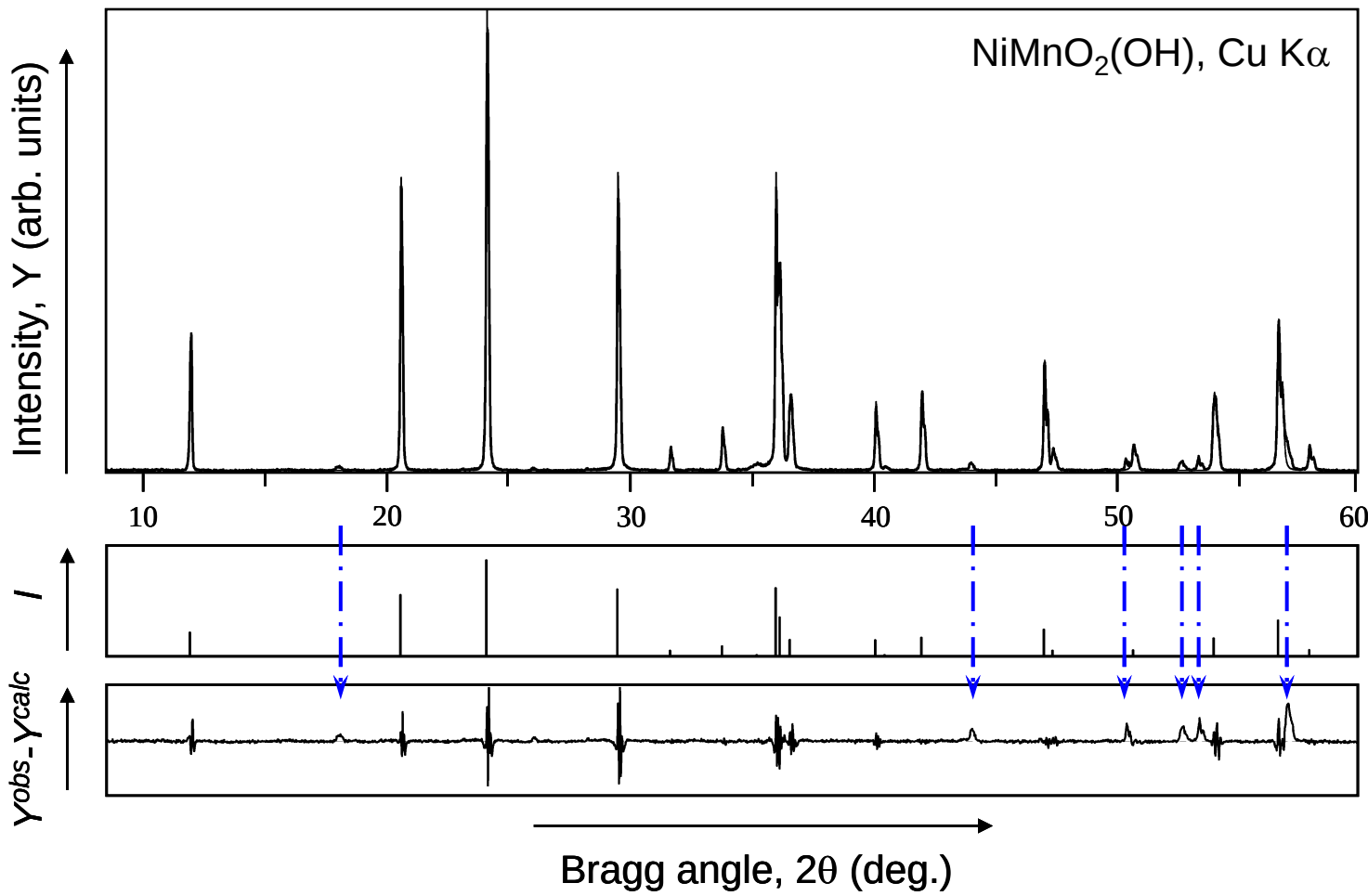
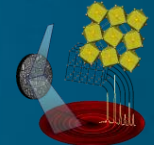


Figure 13.14. Observed and calculated intensity in the powder diffraction pattern of NiMnO₂(OH) after fitting using a Pearson-VII function. Downward facing dash-dotted arrows indicate the positions of six weak Bragg peaks not included in the fit.

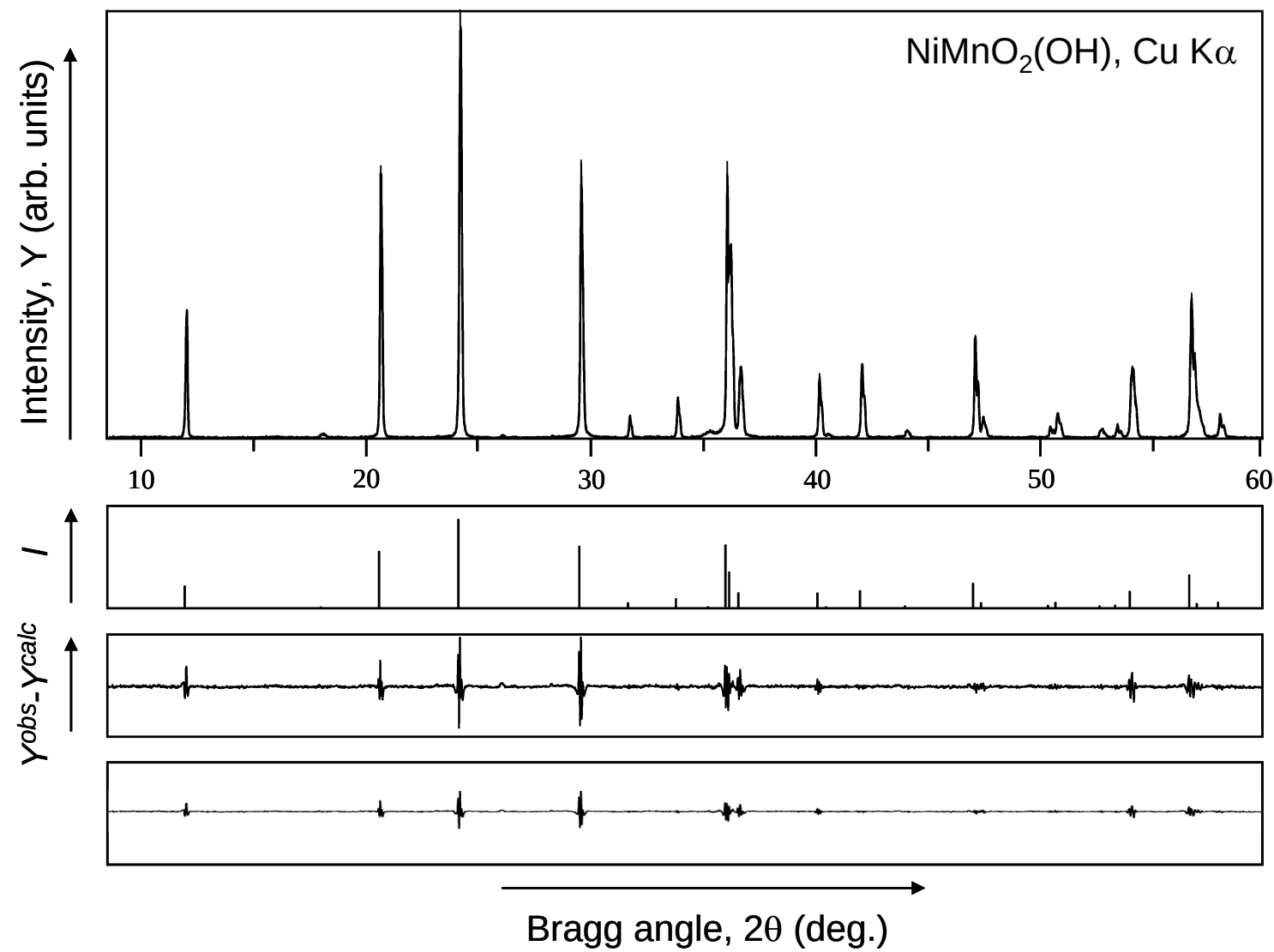
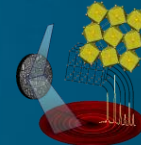


Figure 13.15. Observed and calculated intensity in the powder diffraction pattern of $\text{NiMnO}_2(\text{OH})$ after the completion of profile fitting using the DMSNT algorithm. A symmetrical Pearson-VII function was employed and all present Bragg peaks were included in the fit. The box at the bottom shows the difference between the observed and calculated intensities using the same scale as on the plot of both Y^{obs} and Y^{calc}

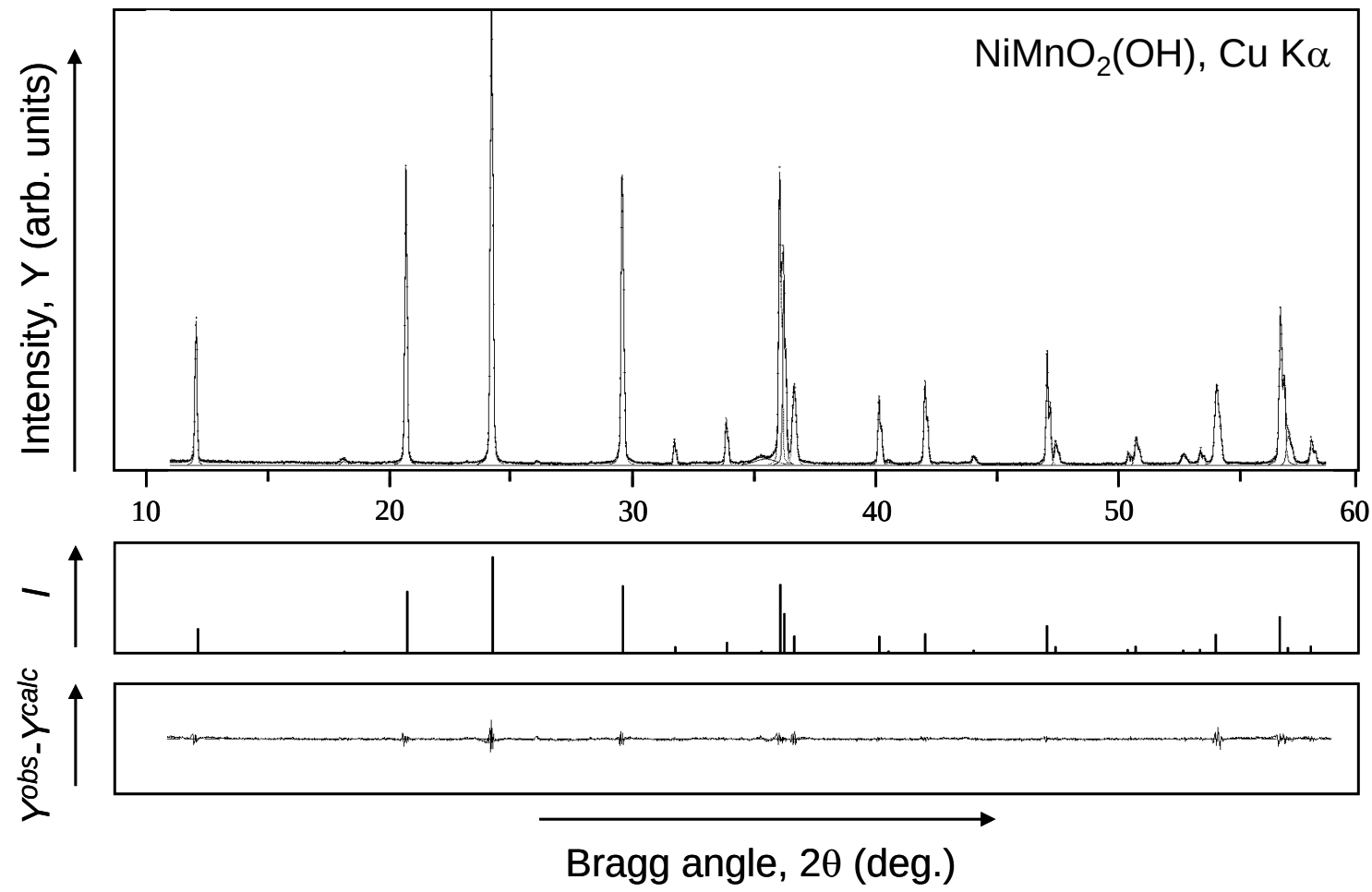
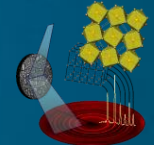


Figure 13.16. Observed and calculated intensity in the powder diffraction pattern of NiMnO₂(OH) after the completion of profile fitting employing the WinCSD algorithm. Pseudo-Voigt function was employed and all present Bragg peaks were included in the fit. The box at the bottom shows the difference between the observed and calculated intensities using the scale identical to that on the plot of both Y^{obs} and Y^{calc}.

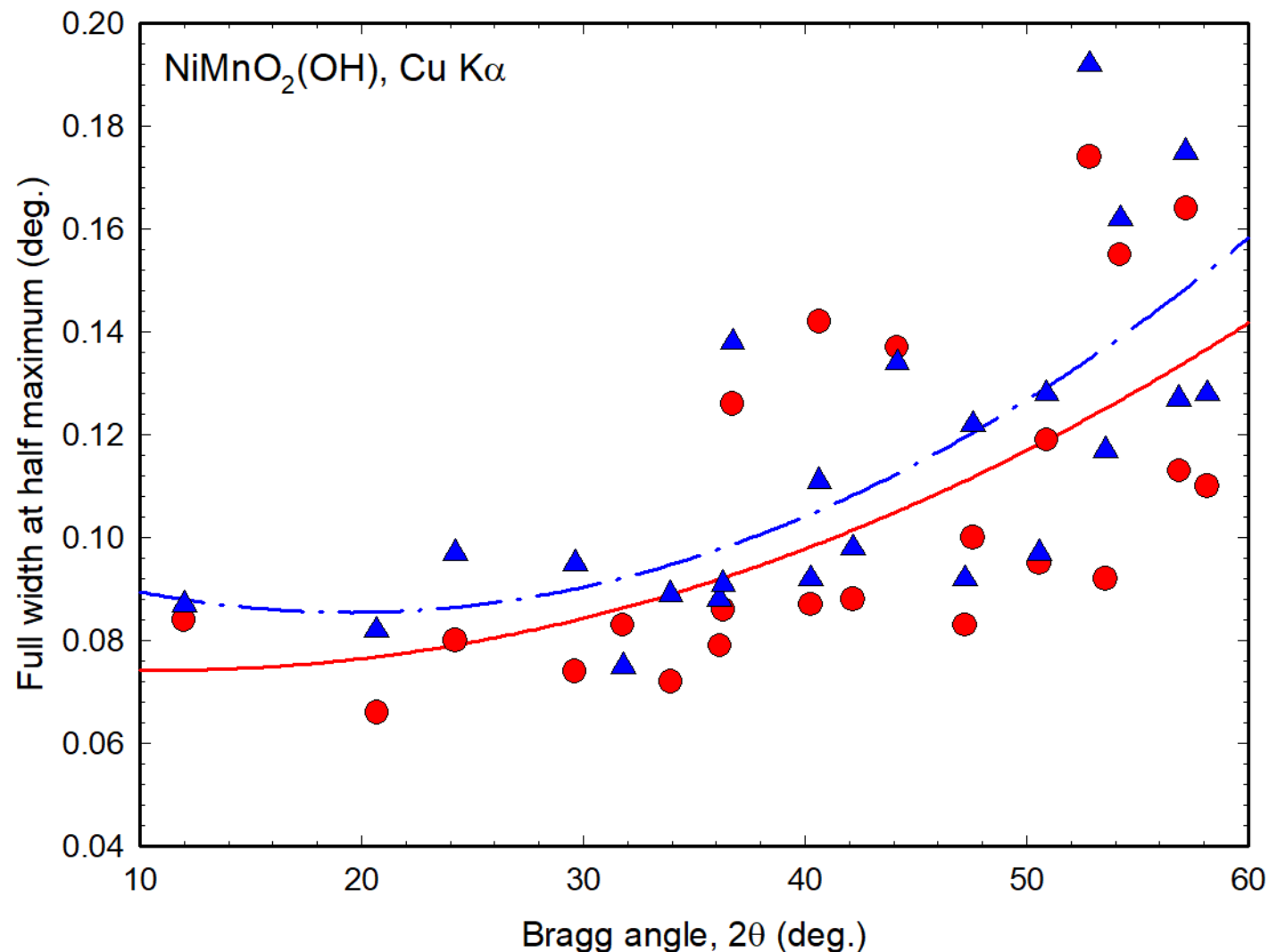
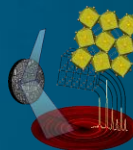


Figure 13.17. The distribution of full widths at half maximum as a function of Bragg angle obtained using DMSNT (red circles, solid line) and WinCSD (blue triangles, dash-dotted line) algorithms. The lines represent parabolic fits of the two sets of data to illustrate the trend.

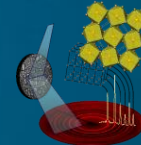


Table 13.2. Major differences in profile fitting algorithms realized in DMSNT and WinCSD.

Property	DMSNT	WinCSD
Peak shape function	Pearson VII or split Pearson VII	pseudo-Voigt
Parameters per peak	4 (Pearson VII) or 6 (split Pearson VII)	3
Common parameters	0	5
Background	Must be subtracted	Refined as a second order polynomial
FWHM	Individual	Individual or common for all peaks
Exponent (β)	Individual	N/A
Mixing parameter (η)	N/A	Common for all peaks
Asymmetry	Individual using split Pearson VII	Common for all peaks

①

48-1152

Quality: Indexed

②

③

Li_{0.6}V_{1.67}O_{3.67} · H₂O
Lithium Vanadium Oxide Hydrate

④

Rad:CuKα1 Lambda:1.54056 Filter:
Cutoff: Int:Diffractionmeter I/Icor:
Ref:Whittingham, M., SUNY at Binghamton, Materials Research Center, NY, USA.Chyrayil, T., Zavalij, P., Whittingham, M., (1992)

⑤

Sys:Tetragonal S.G.:I4/mmm
a:3.7047±0.0003 b:
c:15.804±0.002
α:
β:
γ:
Z:2 mp
Ref2
Dx:2.53 Dm:2.541 SS/FOM: F30=46.5(0.0161,40) Volume[CD]:216.91

⑥

εα:
Ref3
Color:

⑦

Prepared by hydrothermal treatment of tetramethylammonium hydroxide, vanadium pentoxide and Li₂O · H₂O acidified to pH 2-5 for 3 days at 200 °C. Pattern taken at 23(1) °C.

⑧

32 reflections in pattern.

2 θ	Int.	h	k	l	2 θ	Int.	h	k	l	2 θ	Int.	h	k	l	2 θ	Int.	h	k	l
11.2026	100	0	0	2	50.5721	8	0	2	2	72.0262	4	2	2	0	83.7228	1	0	1	13
22.4967	19	0	0	4	54.6668	3	0	2	4	73.1843	2	2	2	2	84.1343	1	0	3	5
24.6618	9	0	1	1	55.7443	2	1	2	1	76.5173	1	2	2	4					
29.4652	50	0	1	3	58.0669	3	0	1	9	77.4598	1	0	3	1					
33.9955	1	0	0	6	58.3367	13	1	2	3	79.4091	2	1	2	9					
34.2095	14	1	1	0	58.3367	13	0	0	10	79.6864	4	0	3	3					
36.0710	1	1	1	2	58.4543	4	1	1	8	79.6864	4	0	2	10					
37.3772	4	0	1	5	63.3383	3	1	2	5	81.7407	2	1	1	12					
47.1058	19	0	1	7	69.4008	10	1	1	10	82.1813	2	1	3	0					
49.1443	16	0	2	0	70.4377	7	1	2	7	83.3159	1	1	3	2					

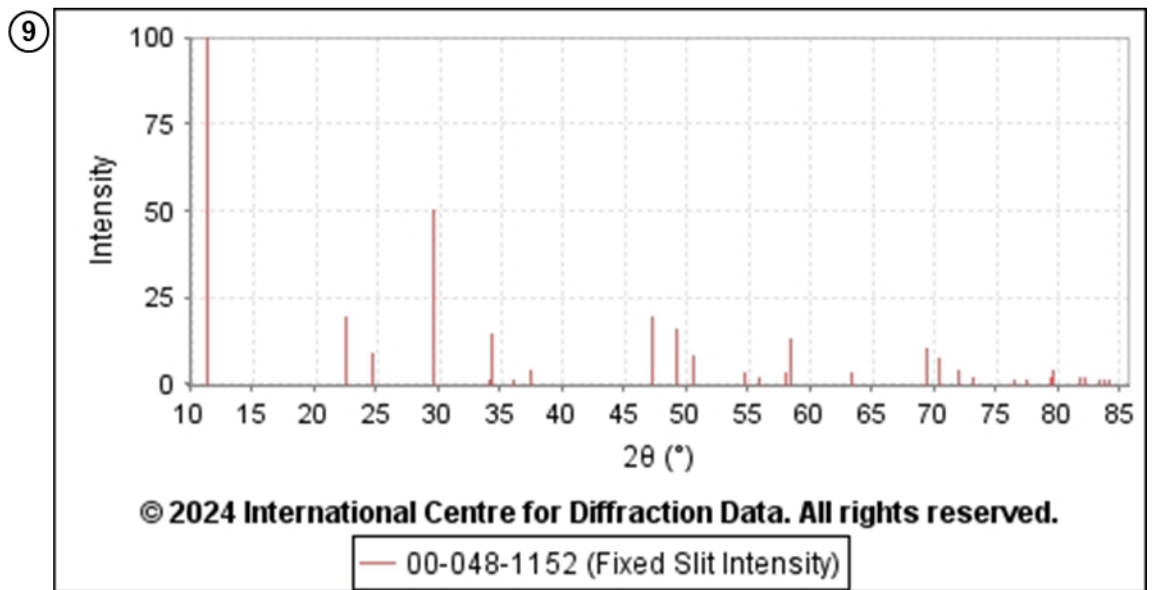


Figure 13.18. An example of a record extracted from the ICDD Powder Diffraction File.

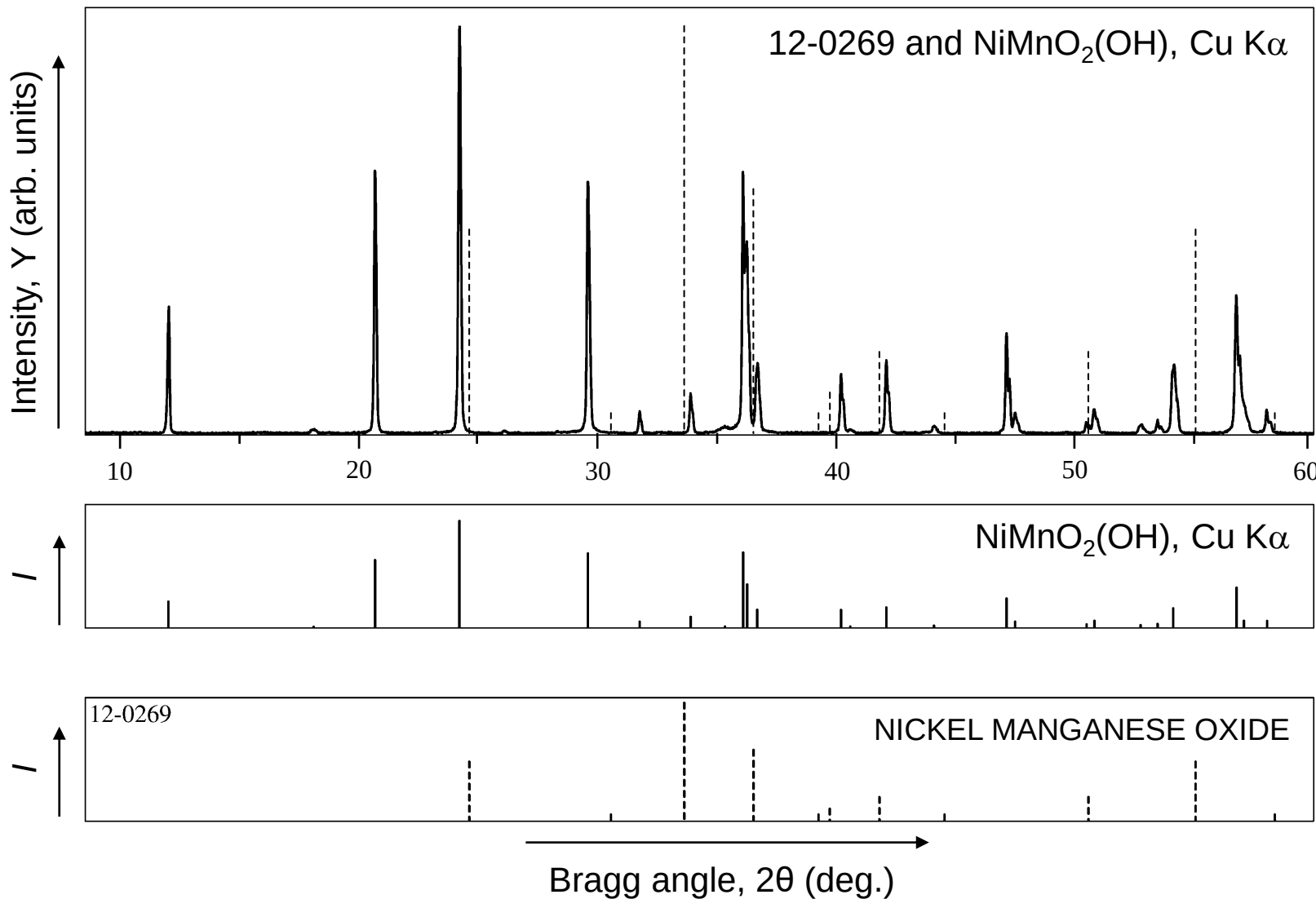
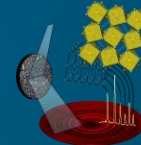


Figure 13.19. Illustration of an incorrect match: Bragg peaks observed in the experimental diffraction pattern of NiMnO₂(OH), shown on top and in the middle (*solid lines*), do not match those present in the nickel manganese oxide, ICDD PDF card No. 12-0269 shown at the bottom and overlapped with the plot on top (*dashed lines*).

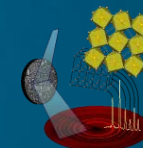


Table 13.3. Selected computer searchable crystallographic databases.

Database	Content/Compounds	No. of entries*
ICDD ^a – Powder Diffraction File	PDF-2, experimental and calculated patterns.	359,400+, 252,600+ with I/Ic
LPF ^b – Pauling File	Inorganic ordered solids. Contains structural, diffraction, phase diagrams, and physical property data.	82,000 crystal structures 55,000 material property 15,000 phase diagrams
ICSD ^c – Inorganic Crystal Structure Data	Inorganic crystal structures, with atomic coordinates, 1913 to date.	299,045+ 10,670 structure types
CSD ^d – Cambridge Structural Database	Crystal structures of organic and metal organic compounds	1.29 million
PDB ^e – Protein Data Bank	Structures of proteins and nucleic acids.	224,201
IZA ^f – Zeolite database	All zeolite structure types: drawings, framework, and simulated patterns	256 framework types
Mineralogy Database ^g	Mineral descriptions, structures and properties, diffraction data (3 lines)	4,714
COD ^h – Crystallography Open Database	Open-access crystal structures of organic, inorganic, minerals	517253

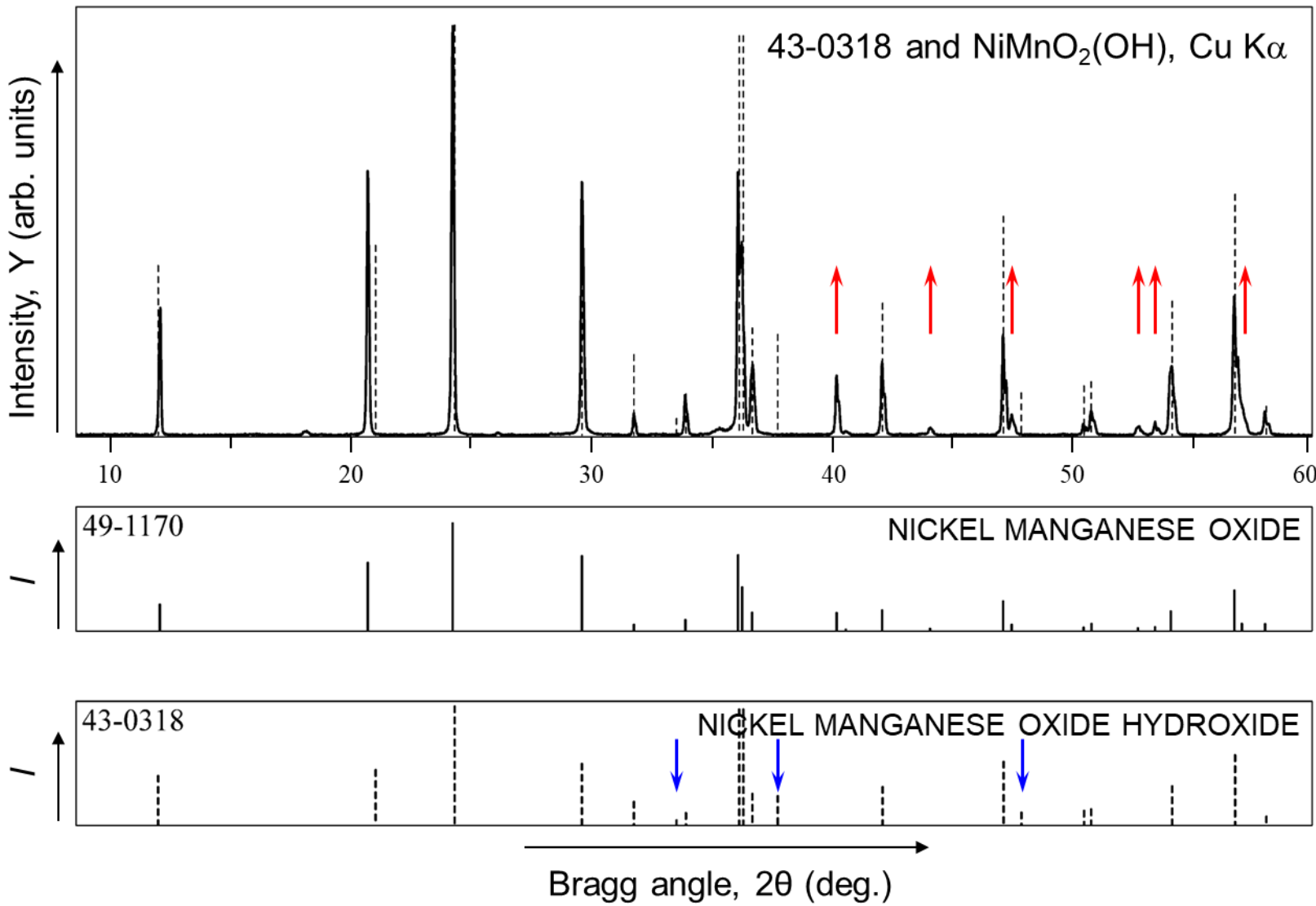
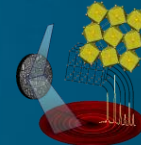


Figure 13.20. Experimental powder diffraction pattern of $\text{NiMnO}_2(\text{OH})$ (*top*) compared with digitized PDF records 49-1170 (*middle, solid lines*) and 43-0318 (*bottom, dashed lines*). Downward *blue arrows* indicate peaks present in the 43-0318 record but absent in the measured pattern. Upward *red arrows* on the experimental pattern indicate observed Bragg peaks that are missing in the 43-0318 record for nickel manganese oxide hydroxide.

43-0318

Quality: Doubtful quality

Ni Mn O2 (O H) Nickel Manganese Oxide Hydroxide																								
Rad:FeKa			Lambda:1.9373			Filter:			d sp:Diffractometer															
Cutoff:			Int:Diffractometer			I/Icor:																		
Ref:Yamamoto, N., 33 48, (1986)																								
Sys:				S.G.:																				
a:		b:		c:		Z:		mp																
α:		β:		γ:																				
Ref2																								
Dx:		Dm:		SS/FOM:		Volume[CD]:0																		
εα:		ηωβ:		εγ:		Sign:		2V:																
Ref3																								
Color:																								
Prepared by hydrothermal treatment at 200-320 C and 100 MPa of an equimolar mixture of \Ni (O H)2\ and SGG-MnOOH in a 1N \N H4 O H\ solution. Chemical analysis (wt.%): Ni 36.0, Mn 34.0, H 0.58, O 29.4. O assigned because unindexed.																								
21 reflections in pattern.																								
2 θ	Int.	h	k	l	2 θ	Int.	h	k	l	2 θ	Int.	h	k	l										
11.9241	41.3				37.8012	24.5				63.4445	12													
21.0048	46.2				42.1740	32.1																		
24.3059	99.9				47.2279	53.3																		
29.6253	51.6				47.9692	10.3																		
31.7969	19.6				50.5841	12																		
33.5754	4				50.8863	13																		
33.9689	10				54.2674	32.6																		
36.1914	97.3				56.8980	58.7																		
36.3582	97.3				58.1954	7																		
36.7434	26.1				61.6166	18.5																		

Figure 13.21. Example of the unindexed PDF card (also see Figure 13.20, *bottom*). In this case, all observed reflections are identified by their Bragg angles and relative intensities but without the Miller indices. As a result, the “Doubtful quality” mark has been assigned to this record. This usually indicates the need for an independent verification before relying on the listed digitized pattern for positive identification of a polycrystalline material. Note that the original experimental data were collected using Fe Kα radiation (see field No. 3). Bragg angles, however, are listed for Cu Kα radiation, and these were recalculated by the search-match utility using the Bragg’s equation.

49-1170			Quality: Quality Data		
Ni Mn O3 Nickel Manganese Oxide					
Rad:CuKa1	Lambda:1.54056	Filter:	d sp:Diffractometer		
Cutoff:	Int:Diffractometer	I/Icor:			
Ref:Whittingham, S., SUNY at Binghamton, MaterialsResearch Center, NY, USA., (1997)					
Sys:Orthorhombic		S.G.:A21am			
a:2.8609±0.0001	b:14.6482±0.0005	c:5.2703±0.0002			
α:	β:	γ:	Z:4	mp	
Ref2					
Dx:4.861	Dm:4.861	SS/FOM: F30=103.1(0.0081,36)		Volume[CD]:220.86	
εα:	ηωβ:	εγ:	Sign:	2V:	
Ref3					
Color:					
Prepared by hydrothermal treatment of tetramethylammonium permanganate, nickel acetate and lithium carbonate for 2 days at 200 C. Pattern taken at 23(1) C.					

55 reflections in pattern.

2 θ	Int.	h	k	l	2 θ	Int.	h	k	l	2 θ	Int.	h	k	l	2 θ	Int.	h	k	l
12.0679	25	0	2	0	47.6194	6	1	5	1	66.2340	1	0	10	1	80.4338	2	1	1	4
20.7417	55	0	2	1	50.6172	3	1	3	2	68.6303	14	1	9	1	80.7356	16	0	12	1
24.2722	100	0	4	0	50.9411	9	0	6	2	69.1962	2	2	2	1	80.7356	16	2	4	2
29.6756	65	0	4	1	52.8898	3	0	8	1	70.6260	5	2	4	0	81.7659	3	1	11	1
31.8434	5	1	1	0	53.6083	3	0	2	3	71.5591	12	0	0	4	83.0093	10	1	3	4
33.9955	10	0	0	2	54.2640	27	1	7	0	72.8763	3	0	2	4	83.2543	6	0	6	4
36.1914	62	0	2	2	56.9133	50	1	5	2	73.2173	4	2	4	1	88.1190	12	1	5	4
36.3735	43	1	3	0	57.2185	12	1	7	1	74.8306	3	0	8	3	88.1190	12	0	12	2
36.7901	23	0	6	0	58.1954	8	0	4	3	75.5715	1	2	0	2	88.6939	6	1	9	3
40.3213	16	1	3	1	61.6257	44	0	8	2	76.3434	3	1	9	2	89.1644	11	1	11	2
40.7014	1	0	6	1	62.2876	6	1	1	3	76.8677	11	2	2	2	93.0153	3	2	4	3
42.2153	22	0	4	2	65.1455	21	2	0	0	77.2366	3	2	6	0	95.6870	10	1	7	4
44.2102	2	1	5	0	65.3921	2	0	6	3	78.4823	4	1	7	3	96.0050	11	2	8	2
47.2644	28	1	1	2	65.6043	1	1	7	2	79.2909	4	1	11	0					

Figure 13.22. Indexed PDF card (also see Figure 13.20, *middle*). Every observed Bragg reflection has been indexed, and the corresponding F_{30} figure of merit (see Sect. 14.4.1) is excellent. Based on these and other established criteria, the quality mark is “Quality Data”, indicating that the included digitized pattern can generally be trusted for positive phase identification.

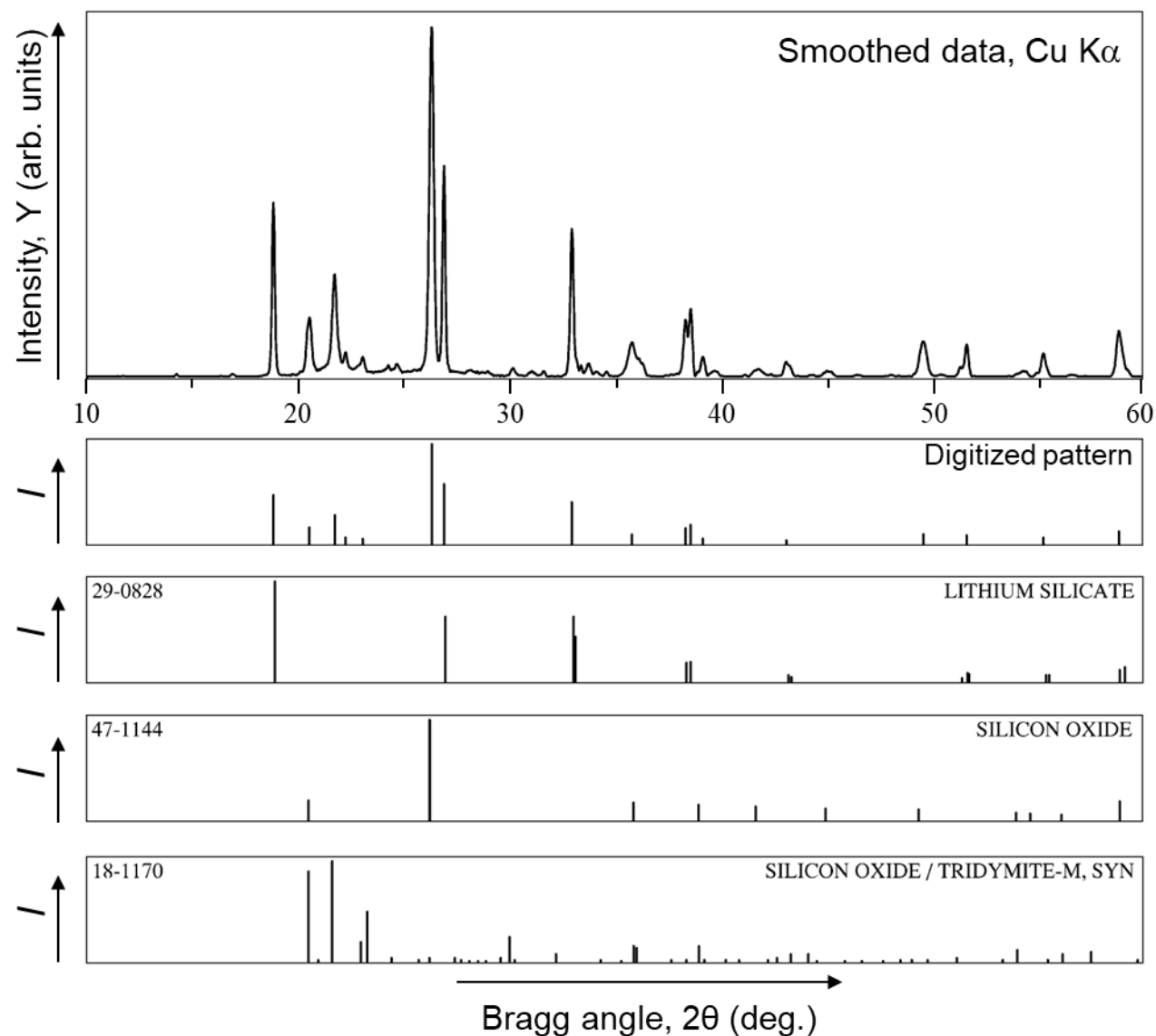
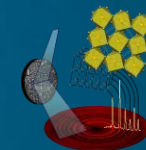
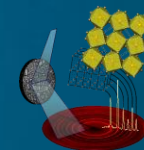


Figure 13.23. The results of a qualitative analysis of a multiple phase sample. Three crystalline phases are clearly identifiable: lithium silicate – Li_2SiO_3 , silicon oxide – SiO_2 (quartz), and a different polymorph of silicon oxide – tridymite. A low quality diffraction pattern collected during a fast experiment was employed in this example. The data shown on top were smoothed, the background was subtracted, and the $\text{K}\alpha_2$ components were stripped before the digitized pattern (shown below the smoothed profile) was obtained using an automatic peak search. Note that many weak Bragg reflections were missed in the peak search.



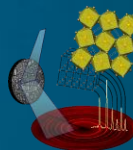
1. The absorption-diffraction method:

Klug's equation:

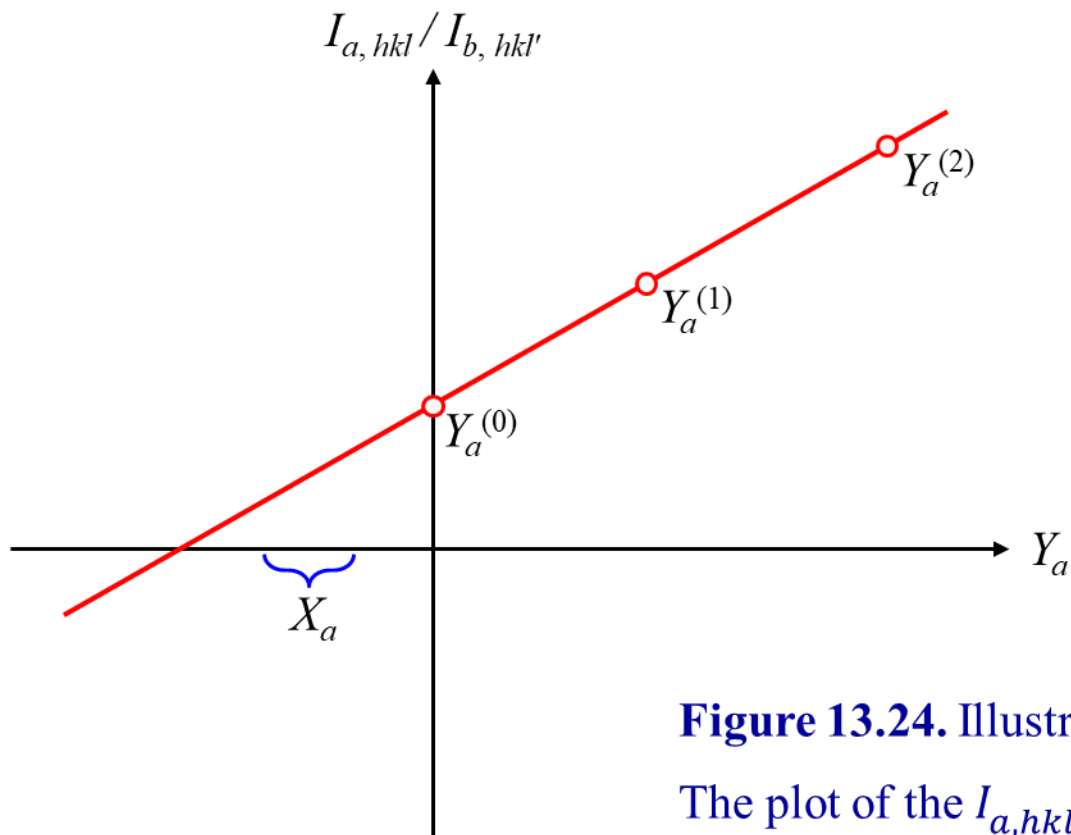
$$X_a = \frac{(I_{a,hkl}/I_{a,hkl}^0)(\mu/\rho)_b}{(\mu/\rho)_a - (I_{a,hkl}/I_{a,hkl}^0)[(\mu/\rho)_a - (\mu/\rho)_b]}$$

Eq. 13.14

- X_a is the mass fraction of phase a in the mixture,
- $I_{a,hkl}$ and $I_{a,hkl}^0$ are intensities of the selected Bragg reflection, hkl , for phase a in the mixture and in the pure state, respectively,
- $(\mu/\rho)_{a,b}$ are the mass absorption coefficients for phases a and b , respectively



2. Method of standard additions or spiking method:



The intensity ratio:

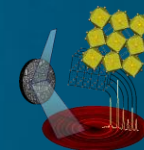
$$\frac{I_{a,(hkl)}}{I_{b,(hkl)'}} = K' \frac{X_a + Y_a}{X_b} \quad \text{Eq. 13.15}$$

Or assuming a constant mass of phase b :

$$\frac{I_{a,(hkl)}}{I_{b,(hkl)'}} = K(X_a + Y_a) \quad \text{Eq. 13.16}$$

Figure 13.24. Illustration of the standard addition method for quantitative analysis.

The plot of the $I_{a,hkl}/I_{b,hkl'}$ intensity ratio as a function of the known amount (Y_a) of added phase a . The point marked $Y_a^{(0)}$ corresponds to the original two-phase mixture. The unknown amount of phase a in the original sample is X_a .



3. *Internal standard method:*

likely the most commonly used approach in a quantitative phase analysis.

$$\frac{I_{a,(hkl)}}{I_{b,(hkl)'}} = K \frac{X_a}{Y_b} \quad \text{Eq. 13.17}$$

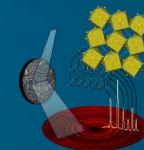
4. *The reference intensity ratio method:*

is based on the experimentally established intensity ratio between the strongest Bragg peaks in the examined phase and in a standard reference material.

5. *Full pattern decomposition*

using Le Bail's or Pawley's techniques.

$$w_i = s_i \prod_{j \neq i}^N \mu_j / \sum_{j=1}^N \left(s_j \prod_{k \neq j}^N \mu_k \right) \quad \text{Eq. 13.18}$$

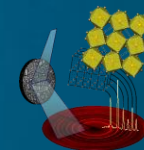


13.3.4 Phase Contents from Rietveld Refinement

Weight fraction, w' : $w' \approx K \cdot ZMV$ **Eq. 13.19**

Normalized weigh fraction: $w_i = w'_i / \sum_j w'_j = (KZMV)_i / \sum_j (KZMV)_j$ **Eq. 13.20**

Volume (v) fraction: $v_i = (KV^2)_i / \sum_j (KV^2)_j$ **Eq. 13.21**



13.3.5 Determination of Amorphous Content or Degree of Crystallinity

External standard for determining absolute phase composition:

$$w_i = \frac{K_i(ZMV)_i}{K_S(ZMV)_S} w_S^c \frac{(\mu/\rho)_m}{(\mu/\rho)_S} \quad \text{Eq. 13.22}$$

$$w_A = 1 - \sum_{i=1}^N w_i \quad \text{Eq. 13.23}$$

Internal standard for absolute phase composition using Rietveld refinement:

$$w_i = w_i^r \frac{w_S'}{w_S^r} \quad \text{Eq. 13.24}$$

$$w_A = \frac{1 - w_S'/w_S^r}{1 - w_S} \quad \text{Eq. 13.25}$$

Microabsorption effect by Brindley:

$$\tau_i = \frac{1}{V_i} \int_0^{V_i} \exp[-(\mu_i - \mu_S)l] dv \quad \text{Eq. 13.26}$$

$$w_i^c = \frac{w_i}{\tau_i} / \sum_{j=1}^N \frac{w_j}{\tau_j} \quad \text{Eq. 13.27}$$