

# Contents

<b>1</b>	<b>Fundamentals of Crystalline State and Crystal Lattice</b> . . . . .	1
1.1	Crystalline State . . . . .	2
1.2	Crystal Lattice and Unit Cell . . . . .	4
1.3	Shape of the Unit Cell . . . . .	7
1.4	Crystallographic Planes, Directions, and Indices . . . . .	8
1.4.1	Crystallographic Planes . . . . .	8
1.4.2	Crystallographic Directions . . . . .	11
1.5	Reciprocal Lattice . . . . .	11
1.6	Additional Reading . . . . .	14
1.7	Problems . . . . .	14
<b>2</b>	<b>Finite Symmetry Elements and Crystallographic Point Groups</b> . . . . .	17
2.1	Content of the Unit Cell . . . . .	17
2.2	Asymmetric Part of the Unit Cell . . . . .	18
2.3	Symmetry Operations and Symmetry Elements . . . . .	19
2.4	Finite Symmetry Elements . . . . .	22
2.4.1	Onefold Rotation Axis and Center of Inversion . . . . .	25
2.4.2	Twofold Rotation Axis and Mirror Plane . . . . .	26
2.4.3	Threefold Rotation Axis and Threefold Inversion Axis . . . . .	26
2.4.4	Fourfold Rotation Axis and Fourfold Inversion Axis . . . . .	27
2.4.5	Sixfold Rotation Axis and Sixfold Inversion Axis . . . . .	28
2.5	Interaction of Symmetry Elements . . . . .	29
2.5.1	Generalization of Interactions Between Finite Symmetry Elements . . . . .	31
2.5.2	Symmetry Groups . . . . .	32
2.6	Fundamentals of Group Theory . . . . .	33
2.7	Crystal Systems . . . . .	35
2.8	Stereographic Projection . . . . .	36
2.9	Crystallographic Point Groups . . . . .	38
2.10	Laue Classes . . . . .	40
2.11	Selection of a Unit Cell and Bravais Lattices . . . . .	41

2.12	Additional Reading	47
2.13	Problems	47
<b>3</b>	<b>Infinite Symmetry Elements and Crystallographic Space Groups</b>	<b>51</b>
3.1	Glide Planes	51
3.2	Screw Axes	53
3.3	Interaction of Infinite Symmetry Elements	54
3.4	Crystallographic Space Groups	56
3.4.1	Relationships Between Point Groups and Space Groups	57
3.4.2	Full International Symbols of Crystallographic Space Groups	60
3.4.3	Visualization of Space-Group Symmetry in Three Dimensions	62
3.4.4	Space Groups in Nature	63
3.5	International Tables for Crystallography	63
3.6	Equivalent Positions (Sites)	70
3.6.1	General and Special Equivalent Positions	70
3.6.2	Special Sites with Points Located on Mirror Planes	71
3.6.3	Special Sites with Points Located on Rotation and Inversions Axes	72
3.6.4	Special Sites with Points Located on Centers of Inversion	73
3.7	Additional Reading	73
3.8	Problems	73
<b>4</b>	<b>Formalization of Symmetry</b>	<b>77</b>
4.1	Symbolic Representation of Symmetry	77
4.1.1	Finite Symmetry Operations	77
4.1.2	Infinite Symmetry Operations	78
4.2	Algebraic Treatment of Symmetry Operations	79
4.2.1	Transformation of Coordinates of a Point	79
4.2.2	Rotational Transformations of Vectors	83
4.2.3	Translational Transformations of Vectors	84
4.2.4	Combined Symmetrical Transformations of Vectors	85
4.2.5	Augmentation of Matrices	87
4.2.6	Algebraic Representation of Crystallographic Symmetry	88
4.2.7	Interaction of Symmetry Operations	88
4.3	Additional Reading	93
4.4	Problems	94
<b>5</b>	<b>Nonconventional Symmetry</b>	<b>97</b>
5.1	Commensurate Modulation	98
5.2	Incommensurate Modulation	99
5.3	Composite Crystals	100

5.4	Symmetry of Modulated Structures . . . . .	101
5.5	Quasicrystals . . . . .	103
5.6	Additional Reading . . . . .	105
5.7	Problems . . . . .	105
<b>6</b>	<b>Properties, Sources, and Detection of Radiation . . . . .</b>	<b>107</b>
6.1	Nature of X-Rays . . . . .	109
6.2	Production of X-Rays . . . . .	110
6.2.1	Conventional Sealed X-Ray Sources . . . . .	111
6.2.2	Continuous and Characteristic X-Ray Spectra . . . . .	113
6.2.3	Rotating Anode X-Ray Sources . . . . .	116
6.2.4	Synchrotron Radiation Sources . . . . .	117
6.3	Other Types of Radiation . . . . .	119
6.4	Detection of X-Rays . . . . .	121
6.4.1	Detector Efficiency, Linearity, Proportionality and Resolution . . . . .	121
6.4.2	Classification of Detectors . . . . .	123
6.4.3	Point Detectors . . . . .	125
6.4.4	Line and Area Detectors . . . . .	128
6.5	Additional Reading . . . . .	131
6.6	Problems . . . . .	131
<b>7</b>	<b>Fundamentals of Diffraction . . . . .</b>	<b>133</b>
7.1	Scattering by Electrons, Atoms and Lattices . . . . .	134
7.1.1	Scattering by Electrons . . . . .	136
7.1.2	Scattering by Atoms and Atomic Scattering Factor . . . . .	138
7.1.3	Scattering by Lattices . . . . .	140
7.2	Geometry of Diffraction by Lattices . . . . .	142
7.2.1	Laue Equations . . . . .	142
7.2.2	Braggs' Law . . . . .	142
7.2.3	Reciprocal Lattice and Ewald's Sphere . . . . .	144
7.3	Additional Reading . . . . .	148
7.4	Problems . . . . .	148
<b>8</b>	<b>The Powder Diffraction Pattern . . . . .</b>	<b>151</b>
8.1	Origin of the Powder Diffraction Pattern . . . . .	152
8.2	Representation of Powder Diffraction Patterns . . . . .	157
8.3	Understanding of Powder Diffraction Patterns . . . . .	159
8.4	Positions of Powder Diffraction Peaks . . . . .	162
8.4.1	Peak Positions as a Function of Unit Cell Dimensions . . . . .	163
8.4.2	Other Factors Affecting Peak Positions . . . . .	165
8.5	Shapes of Powder Diffraction Peaks . . . . .	168
8.5.1	Peak-Shape Functions . . . . .	170
8.5.2	Peak Asymmetry . . . . .	179
8.6	Intensity of Powder Diffraction Peaks . . . . .	182

8.6.1	Integrated Intensity . . . . .	182
8.6.2	Scale Factor . . . . .	185
8.6.3	Multiplicity Factor . . . . .	186
8.6.4	Lorentz-Polarization Factor . . . . .	187
8.6.5	Absorption Factor . . . . .	188
8.6.6	Preferred Orientation . . . . .	194
8.6.7	Extinction Factor . . . . .	199
8.7	Additional Reading . . . . .	201
8.8	Problems . . . . .	201
<b>9</b>	<b>Structure Factor . . . . .</b>	<b>203</b>
9.1	Structure Amplitude . . . . .	203
9.1.1	Population Factor . . . . .	204
9.1.2	Temperature Factor (Atomic Displacement Factor) . . . . .	206
9.1.3	Atomic Scattering Factor . . . . .	211
9.1.4	Phase Angle . . . . .	215
9.2	Effects of Symmetry on the Structure Amplitude . . . . .	217
9.2.1	Friedel Pairs and Friedel's Law . . . . .	218
9.2.2	Friedel's Law and Multiplicity Factor . . . . .	220
9.3	Systematic Absences . . . . .	220
9.3.1	Lattice Centering . . . . .	221
9.3.2	Glide Planes . . . . .	222
9.3.3	Screw Axes . . . . .	223
9.4	Space Groups and Systematic Absences . . . . .	225
9.5	Additional Reading . . . . .	235
9.6	Problems . . . . .	236
<b>10</b>	<b>Solving the Crystal Structure . . . . .</b>	<b>239</b>
10.1	Fourier Transformation . . . . .	239
10.2	Phase Problem . . . . .	245
10.2.1	Patterson Technique . . . . .	246
10.2.2	Direct Methods . . . . .	250
10.2.3	Structure Solution from Powder Diffraction Data . . . . .	253
10.3	Total Scattering Analysis Using Pair Distribution Function . . . . .	255
10.4	Additional Reading . . . . .	261
10.5	Problems . . . . .	262
<b>11</b>	<b>Powder Diffractometry . . . . .</b>	<b>263</b>
11.1	Brief History of the Powder Diffraction Method . . . . .	264
11.2	Beam Conditioning in Powder Diffractometry . . . . .	269
11.2.1	Collimation . . . . .	271
11.2.2	Monochromatization . . . . .	274
11.3	Principles of Goniometer Design in Powder Diffractometry . . . . .	280
11.3.1	Goniostats with Strip and Point Detectors . . . . .	283
11.3.2	Goniostats with Area Detectors . . . . .	287

11.4	Nonambient Powder Diffractometry	292
11.4.1	Variable Temperature Powder Diffractometry	292
11.4.2	Principles of Variable Pressure Powder Diffractometry	294
11.4.3	Powder Diffractometry in High Magnetic Fields	296
11.5	Additional Reading	299
11.6	Problems	299
<b>12</b>	<b>Collecting Quality Powder Diffraction Data</b>	<b>301</b>
12.1	Sample Preparation	301
12.1.1	Powder Requirements and Powder Preparation	301
12.1.2	Powder Mounting	304
12.1.3	Sample Size	310
12.1.4	Sample Thickness and Uniformity	311
12.1.5	Sample Positioning	313
12.1.6	Effects of Sample Preparation on Powder Diffraction Data	314
12.2	Data Acquisition	318
12.2.1	Wavelength	318
12.2.2	Monochromatization	320
12.2.3	Incident Beam Aperture	322
12.2.4	Diffracted Beam Aperture	325
12.2.5	Variable Aperture	329
12.2.6	Power Settings	330
12.2.7	Classification of Powder Diffraction Experiments	331
12.2.8	Step Scan	331
12.2.9	Continuous Scan	334
12.2.10	Scan Range	336
12.3	Quality of Experimental Data	338
12.3.1	Quality of Intensity Measurements	339
12.3.2	Factors Affecting Resolution	342
12.4	Additional Reading	343
12.5	Problems	344
<b>13</b>	<b>Preliminary Data Processing and Phase Analysis</b>	<b>347</b>
13.1	Interpretation of Powder Diffraction Data	348
13.2	Preliminary Data Processing	353
13.2.1	Background	355
13.2.2	Smoothing	359
13.2.3	$K\alpha_2$ Stripping	361
13.2.4	Peak Search	363
13.2.5	Profile Fitting	366
13.3	Phase Identification and Quantitative Analysis	377
13.3.1	Crystallographic Databases	377
13.3.2	Phase Identification	382
13.3.3	Quantitative Analysis	390

13.3.4	Phase Contents from Rietveld Refinement . . . . .	394
13.3.5	Determination of Amorphous Content or Degree of Crystallinity . . . . .	395
13.4	Additional Reading . . . . .	399
13.5	Problems . . . . .	400
<b>14</b>	<b>Determination and Refinement of the Unit Cell . . . . .</b>	<b>407</b>
14.1	The Indexing Problem . . . . .	407
14.2	Known Versus Unknown Unit Cell Dimensions . . . . .	410
14.3	Indexing: Known Unit Cell . . . . .	412
14.3.1	High Symmetry Indexing Example . . . . .	414
14.3.2	Other Crystal Systems . . . . .	420
14.4	Reliability of Indexing . . . . .	421
14.4.1	The $F_N$ Figure of Merit . . . . .	424
14.4.2	The $M_{20}(M_N)$ Figure of Merit . . . . .	425
14.5	Introduction to Ab Initio Indexing . . . . .	426
14.6	Cubic Crystal System . . . . .	428
14.6.1	Primitive Cubic Unit Cell: $\text{LaB}_6$ . . . . .	430
14.6.2	Body-Centered Cubic Unit Cell: $\text{U}_3\text{Ni}_6\text{Si}_2$ . . . . .	432
14.7	Tetragonal and Hexagonal Crystal Systems . . . . .	434
14.7.1	Indexing Example: $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ . . . . .	437
14.8	Automatic Ab Initio Indexing Algorithms . . . . .	440
14.8.1	Indexing in Direct Space . . . . .	441
14.8.2	Indexing in Reciprocal Space . . . . .	444
14.9	Unit Cell Reduction Algorithms . . . . .	447
14.9.1	Delaunay–Ito Transformation . . . . .	448
14.9.2	Niggli Reduction . . . . .	449
14.10	Automatic Ab Initio Indexing: Computer Codes . . . . .	450
14.10.1	TREOR . . . . .	451
14.10.2	DICVOL . . . . .	453
14.10.3	ITO . . . . .	454
14.10.4	Selecting a Solution . . . . .	455
14.11	Ab Initio Indexing Examples . . . . .	457
14.11.1	Hexagonal Indexing: $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ . . . . .	457
14.11.2	Monoclinic Indexing: $(\text{CH}_3\text{NH}_3)_2\text{Mo}_7\text{O}_{22}$ . . . . .	462
14.11.3	Triclinic Indexing: $\text{Fe}_7(\text{PO}_4)_6$ . . . . .	466
14.11.4	Pseudo-Hexagonal Indexing: $\text{LiB}(\text{C}_2\text{O}_4)_2$ . . . . .	470
14.12	Precise Lattice Parameters and Linear Least Squares . . . . .	473
14.12.1	Linear Least Squares . . . . .	475
14.12.2	Precise Lattice Parameters from Linear Least Squares . . . . .	477
14.13	Concluding Remarks . . . . .	485
14.14	Additional Reading . . . . .	485
14.15	Problems . . . . .	486

<b>15 Solving Crystal Structure from Powder Diffraction Data</b> . . . . .	497
15.1 Ab Initio Methods of Structure Solution . . . . .	497
15.1.1 Conventional Reciprocal Space Methods . . . . .	498
15.1.2 Conventional Direct Space Modeling . . . . .	499
15.1.3 Unconventional Direct, Reciprocal, and Dual Space Methods . . . . .	500
15.1.4 Validation and Completion of the Model . . . . .	505
15.2 The Content of the Unit Cell . . . . .	506
15.3 Pearson's Classification . . . . .	509
15.4 Finding Structure Factors from Powder Diffraction Data . . . . .	510
15.5 Nonlinear Least Squares . . . . .	513
15.6 Quality of Profile Fitting . . . . .	517
15.6.1 Visual Assessment of the Quality of Profile Fitting . . . . .	518
15.6.2 Figures of Merit . . . . .	521
15.7 The Rietveld Method . . . . .	524
15.7.1 Fundamentals of the Rietveld Method . . . . .	527
15.7.2 Classes of Rietveld Refinement Parameters . . . . .	529
15.7.3 Restraints, Constraints, and Rigid-Bodies . . . . .	531
15.7.4 Figures of Merit and Quality of Rietveld Refinement . . . . .	538
15.7.5 Common Problems and How to Deal with Them . . . . .	539
15.7.6 Termination of Rietveld Refinement . . . . .	542
15.8 Concluding Remarks . . . . .	543
15.9 Additional Reading . . . . .	544
<b>16 Crystal Structure of LaNi<sub>4.85</sub>Sn<sub>0.15</sub></b> . . . . .	547
16.1 Full Pattern Decomposition . . . . .	549
16.2 Solving the Crystal Structure . . . . .	556
16.3 Rietveld Refinement Using Cu K $\alpha$ <sub>1,2</sub> Radiation . . . . .	560
16.3.1 Scale Factor and Profile Parameters . . . . .	561
16.3.2 Overall Atomic Displacement Parameter . . . . .	563
16.3.3 Individual Parameters, Free and Constrained Variables . . . . .	564
16.3.4 Anisotropic Atomic Displacement Parameters . . . . .	567
16.3.5 Multiple Phase Refinement . . . . .	567
16.3.6 Refinement Results . . . . .	568
16.4 Rietveld Refinement Using Mo K $\alpha$ <sub>1,2</sub> Radiation . . . . .	569
16.5 Combined Refinement Using Different Sets of Diffraction Data . . . . .	573
<b>17 Crystal Structure of CeRhGe<sub>3</sub></b> . . . . .	579
17.1 Full Pattern Decomposition . . . . .	579
17.2 Solving the Crystal Structure from X-Ray Data . . . . .	583
17.2.1 Highest Symmetry Attempt . . . . .	584
17.2.2 Low-Symmetry Model . . . . .	586
17.3 Solving the Crystal Structure from Neutron Data . . . . .	589
17.4 Rietveld Refinement . . . . .	595
17.4.1 X-Ray Data, Correct Low Symmetry Model . . . . .	595

17.4.2	X-Ray Data, Wrong High-Symmetry Model . . . . .	598
17.4.3	Neutron Data . . . . .	599
<b>18</b>	<b>Crystal Structure of Nd<sub>5</sub>Si<sub>4</sub></b> . . . . .	<b>603</b>
18.1	Full Pattern Decomposition . . . . .	603
18.2	Solving the Crystal Structure . . . . .	604
18.3	Rietveld Refinement . . . . .	607
<b>19</b>	<b>Empirical Methods of Solving Crystal Structures</b> . . . . .	<b>611</b>
19.1	Crystal Structure of Gd <sub>5</sub> Ge <sub>4</sub> . . . . .	612
19.2	Crystal Structure of Gd <sub>5</sub> Si <sub>4</sub> . . . . .	615
19.3	Crystal Structure of Gd <sub>5</sub> Si <sub>2</sub> Ge <sub>2</sub> . . . . .	616
19.4	Rietveld Refinement of Gd <sub>5</sub> Ge <sub>4</sub> , Gd <sub>5</sub> Si <sub>4</sub> , and Gd <sub>5</sub> Si <sub>2</sub> Ge <sub>2</sub> . . . . .	620
19.4.1	Gd <sub>5</sub> Ge <sub>4</sub> . . . . .	620
19.4.2	Gd <sub>5</sub> Si <sub>4</sub> . . . . .	623
19.4.3	Gd <sub>5</sub> Si <sub>2</sub> Ge <sub>2</sub> . . . . .	627
19.5	Structure–Property Relationships . . . . .	630
<b>20</b>	<b>Crystal Structure of NiMnO<sub>2</sub>(OH)</b> . . . . .	<b>633</b>
20.1	Observed Structure Factors from Experimental Data . . . . .	633
20.2	Solving the Crystal Structure . . . . .	636
20.3	A Few Notes About Using GSAS . . . . .	640
20.4	Completion of the Model and Rietveld Refinement . . . . .	643
20.4.1	Initial Refinement Steps . . . . .	643
20.4.2	Where Is Mn and Where Is Ni? . . . . .	647
20.4.3	Finalizing the Refinement of the Model Without Hydrogen . . . . .	648
20.4.4	Locating Hydrogen . . . . .	648
20.4.5	Combined Rietveld Refinement . . . . .	650
<b>21</b>	<b>Crystal Structure of <i>tma</i>V<sub>3</sub>O<sub>7</sub></b> . . . . .	<b>655</b>
21.1	Observed Structure Factors . . . . .	656
21.2	Solving the Crystal Structure . . . . .	658
21.3	Completion of the Model and Rietveld Refinement . . . . .	661
21.3.1	Unrestrained Rietveld Refinement . . . . .	662
21.3.2	Rietveld Refinement with Restraints . . . . .	665
<b>22</b>	<b>Crystal Structure of <i>ma</i><sub>2</sub>Mo<sub>7</sub>O<sub>22</sub></b> . . . . .	<b>669</b>
22.1	Possible Model of the Crystal Structure . . . . .	669
22.2	Rietveld Refinement and Completion of the Model . . . . .	672
<b>23</b>	<b>Crystal Structure of Mn<sub>7</sub>(OH)<sub>3</sub>(VO<sub>4</sub>)<sub>4</sub></b> . . . . .	<b>679</b>
23.1	Solving the Crystal Structure . . . . .	680
23.2	Rietveld Refinement . . . . .	682
23.3	Determining Chemical Composition . . . . .	685



<b>24</b>	<b>Crystal Structure of FePO<sub>4</sub></b> .....	691
24.1	Building and Optimizing the Model of the Crystal Structure .....	692
24.2	Rietveld Refinement .....	696
<b>25</b>	<b>Crystal Structure of Acetaminophen, C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub></b> .....	703
25.1	Ab Initio Indexing and Le Bail Fitting .....	705
25.2	Solving the Crystal Structure .....	709
25.2.1	Creating a Model .....	709
25.2.2	Optimizing the Model (Solving the Structure) .....	713
25.3	Restrained Rietveld Refinement .....	717
25.4	Chapters 15–25: Additional Reading .....	721
25.5	Chapters 15–25: Problems .....	723
<b>Index</b>	.....	729



<http://www.springer.com/978-0-387-09578-3>

Fundamentals of Powder Diffraction and Structural  
Characterization of Materials, Second Edition

Pecharsky, V.; Zavalij, P.

2009, XXIV, 744 p., Softcover

ISBN: 978-0-387-09578-3