he role of diffraction methods for the solid-state sciences has been pivotal to determining the (micro)structure of a material. Particularly, the expanding activities in materials science have led to the development of new methods for analysis by diffraction.

This book offers an authoritative overview of the new developments in the field of analysis of matter by (in particular X-ray, electron and neutron) diffraction. It is composed of chapters written by leading experts on "modern diffraction methods". The focus in the various chapters of this book is on the current forefront of research on and applications for diffraction methods. This unique book provides descriptions of the "state of the art" and, at the same time, identifies avenues for future research.

The book assumes only a basic knowledge of solid-state physics and allows the application of the described methods by the readers of the book (either graduate students or mature scientists).

Prof. Mittemeijer and **Dr. Welzel**, who has been a Ph.D. student of Prof. Mittemeijer and a member of his department until shortly, are renowned scientists in the field of analysis of materials by diffraction methods. They have contributed considerably to this scientific discipline, as is shown, for example, by their many widely cited publications. This book presents a comprehensive overview based on their insights into the field, as well as those of the selection of key authors who contributed to this project.



	Preface XV About the Editors XXI List of Contributors XXIII				
	Part I Structure Determination 1				
1	Structure Determination of Single Crystals <i>3</i> Sander van Smaalen				
1.1	Introduction 3				
1.2	The Electron Density 5				
1.3	Diffraction and the Phase Problem 8				
1.4	Fourier Cycling and Difference Fourier Maps 10				
1.5	Statistical Properties of Diffracted Intensities 11				
1.6	The Patterson Function 15				
1.7	Patterson Search Methods 18				
1.8	Direct Methods 19				
1.9	Charge Flipping and Low-Density Elimination 21				
1.10	Outlook and Summary 24				
	References 25				
2	Modern Rietveld Refinement, a Practical Guide 27 Robert Dinnebier and Melanie Müller				
2.1	The Peak Intensity 29				
2.2	The Peak Position 30				
2.3	The Peak Profile 31				
2.4	The Background 38				
2.5	The Mathematical Procedure 39				
2.6	Agreement Factors 39				
2.7	Global Optimization Method of Simulated Annealing 41				
2.8	Rigid Bodies 44				
2.9	Introduction of Penalty Functions 46				
2.10	Parametric Rietveld Refinement 47				

2.10.1	Parameterization of the Scale Factor Depending on Time for Kineti				
	Analysis 49				

- 2.10.2 Parameterization of the Lattice Parameters Depending on Pressure for Determination of the Equations of State 50
- 2.10.3 Parameterization of Symmetry Modes Depending on Temperature for Determination of Order Parameters 53 References 58

3 Structure of Nanoparticles from Total Scattering 61

Katharine L. Page, Thomas Proffen, and Reinhard B. Neder

- 3.1 Introduction 61
- 3.2 Total Scattering Experiments 64
- 3.2.1 Using X-Rays 66
- 3.2.2 Using Neutrons 67
- 3.3 Structure Modeling and Refinement 69
- 3.3.1 Using a Particle Form Factor 69
- 3.3.2 Modeling Finite Nanoparticles 70
- 3.4 Examples 74
- 3.4.1 BaTiO₃ 74
- 3.4.2 CdSe/ZnS Core-Shell Particles 78
- 3.5 Outlook 82

References 83

Part II Analysis of the Microstructure 87

4 Diffraction Line-Profile Analysis

Eric J. Mittemeijer and Udo Welzel

- 4.1 Introduction 89
- 4.2 Instrumental Broadening 90
- 4.2.1 Determination of the Instrumental Profile Using a Reference (Standard) Specimen 92

89

- 4.2.2 Determination of the Instrumental Profile by Calculus 92
- 4.2.3 Subtraction/Incorporation of the Instrumental Broadening 93
- 4.3 Structural, Specimen Broadening 94
- 4.3.1 Measures of Line Broadening; Fourier Series Representation of Diffraction Lines 94
- 4.3.2 Column Length/Crystallite Size and Column-Length/Crystallite-Size Distribution 96
- 4.3.3 Microstrain Broadening 98
- 4.3.3.1 Assumptions in Integral-Breadth Methods 99
- 4.3.3.2 Assumptions in Fourier Methods 100
- 4.3.3.3 Microstrain-Broadening Descriptions Derived from a Microstructural Model 101
- 4.3.4 Anisotropic Size and Microstrain(-Like) Diffraction-Line Broadening 104

4.3.5	Macroscopic Anisotropy 106						
4.3.6	Crystallite Size and Coherency of Diffraction 106						
4.4	Practical Application of Line-Profile Analysis 111						
4.4.1	Line-Profile Decomposition 111						
4.4.1.1	Breadth Methods 111						
4.4.1.2	Fourier Methods 115						
4.4.1.3	Whole Powder-Pattern Fitting 116						
4.4.2	Line-Profile Synthesis 116						
4.4.2.1	General Strain-Field Method 117						
4.4.2.2	Specific Microstructural Models: Whole Powder-Pattern Modeling (WPPM) and Multiple Whole-Profile Modeling/Fitting (MWP) 118						
4.4.2.3	General Atomistic Structure: the Debye Scattering Function 120						
4.5	Conclusions 122						
	References 123						
5	Residual Stress Analysis by X-Ray Diffraction Methods 127 Christoph Genzel, Ingwer A. Denks, and Manuela Klaus						
5.1	Introduction 127						
5.2	Principles of Near-Surface X-Ray Residual Stress Analysis 129						
5.2.1	Fundamental Relations 129						
5.2.2	Concepts of Diffraction Data Acquisition: Angle-Dispersive and						
	Energy-Dispersive Modes 130						
5.2.3	Concepts of Strain Depth Profiling: LAPLACE and Real Space						
	Approach 131						
5.2.3.1	Definition of the Information Depth 131						
5.2.3.2	Depth Profiling in the LAPLACE Space 133						
5.2.3.3	Depth Profiling in Real Space 136						
5.2.3.4	"Fixed" versus "Variable Depth" Methods 139						
5.3	Near-Surface X-Ray Residual Stress Analysis by Advanced and						
	Complementary Methods 141						
5.3.1	Residual Stress Depth Profiling in Multilayered Coating Systems 141						
5.3.1.1	The "Equivalence Thickness" Concept 141						
5.3.1.2	The "Stress Scanning" Method 144						
5.3.2	Residual Stress Gradient Evaluation in Surface-Treated Bulk						
	Samples 147						
5.3.2.1	Fixed Depth Analysis in the Real Space: Direct Access to $\sigma(z)$ 147						
5.3.2.2	Residual Stress Evaluation in the LAPLACE Space: From $\sigma(\tau)$ to						
	σ(z) 149						
5.4	Final Remarks 151						
	References 153						
6	Stress Analysis by Neutron Diffraction 155						
	Lothar Pintschovius and Michael Hofmann						
6.1	Introductory Remarks 155						

6.2	Fundamentals of the Technique 155
6.2.1	The d ₀ -Problem 156
6.2.2	Macrostrains versus Microstrains 157
6.2.3	Strain Tensors 158
6.2.4	Reflection Line Broadenings 158
6.3	Instrumentation 159
6.3.1	Angle-Dispersive Instruments 159
6.3.1.1	Monochromators 159
6.3.1.2	Beam-Defining Optics 160
6.3.1.3	Detectors 161
6.3.1.4	Auxilliaries 162
6.3.2	Time-of-Flight Instruments 162
6.3.3	Special Instruments 164
6.4	Capabilities 164
6.4.1	Types of Materials 164
6.4.2	Spatial Resolution 164
6.4.3	Penetration Depth 165
6.4.4	Accuracy 166
6.4.5	Throughput 166
6.5	Examples 166
6.5.1	Railway Rail 166
6.5.2	Weldments 167
6.5.3	Ceramics 168
6.5.4	Composite Materials 170
	References 170
7	Texture Analysis by Advanced Diffraction Methods 173
	Hans-Rudolf Wenk
7.1	Introduction and Background 173
7.2	Synchrotron X-Rays 177
7.2.1	General Approach 177
7.2.2	Hard Synchrotron X-Rays 178
7.2.3	In situ High-Pressure Experiments 180
7.2.4	From Diffraction Images to Orientation Distribution 183
7.2.5	Opportunities with the Laue Technique 188
7.2.6	Synchrotron Applications 188
7.3	Neutron Diffraction 190
7.3.1	General Comments 190
7.3.2	Monochromatic Neutrons 193
7.3.3	Polychromatic Time-of-Flight (TOF) Neutrons 194
7.3.4	Special Techniques 197
7.3.5	Data Analysis for TOF Neutrons 198
7.3.6	Neutron Applications 202
7.3.6.1	Grain Statistics 202
7.3.6.2	Polymineralic Rocks 202

- 7.3.6.3 In situ Experiments and Phase Transformations 203
- 7.3.6.4 Magnetic Textures 204

7.4 Electron Diffraction 204

- 7.4.1 Transmission Electron Microscope 204
- 7.4.2 Scanning Electron Microscope (SEM) 205
- 7.4.3 EBSD Applications 209
- 7.4.3.1 Misorientations 209
- 7.4.3.2 In situ Heating 209
- 7.4.3.3 In situ Deformation 210
- 7.4.3.4 3D Mapping 211
- 7.4.3.5 Residual Strain Analysis 211
- 7.5 Comparison of Methods 212
- 7.6 Conclusions 213
 - Acknowledgments 214
 - References 214

8 Surface-Sensitive X-Ray Diffraction Methods 221

- Andreas Stierle and Elias Vlieg
- 8.1 Introduction 221
- 8.1.1 Structure Determination by X-Ray Diffraction 223
- 8.2 X-Ray Reflectivity 224
- 8.3 Bragg Scattering in Reduced Dimensions (Crystal Truncation Rod Scattering) 227
- 8.3.1 Thin-Film Diffraction 227
- 8.3.2 Surface Diffraction from Half-Infinite Systems 230
- 8.3.2.1 Surface Relaxations 232
- 8.3.2.2 Surface Reconstructions and Fourier Methods 234
- 8.3.2.3 Surface Roughness 237
- 8.3.2.4 Vicinal Surfaces 239
- 8.3.2.5 Two-Layer Roughness Model for Growth Studies 240
- 8.3.2.6 Interface Diffraction 245
- 8.3.2.7 The Specular Rod 247
- 8.4 Grazing Incidence X-Ray Diffraction 249
- 8.5 Experimental Geometries 252
- 8.6 Trends 254
 - Acknowledgments 255
 - References 255
- 9The Micro- and Nanostructure of Imperfect Oxide Epitaxial Films259Alexandre Boulle, Florine Conchon, and René Guinebretière9.19.1Diffracted Amplitude and Intensity2609.1.1Diffracted Amplitude2609.1.2Diffracted Intensity261
- 9.2 The Correlation Volume 262
- 9.2.1 Crystallite Size and Shape 262

9.2.2	Crystallite Size Fluctuations 265	
9.2.3	Crystallite Shape Fluctuations 267	
9.3	Lattice Strain 269	
9.3.1	Statistical Properties 269	
9.3.2	Spatial Properties 272	
9.4	Example 274	
9.5	Strain Gradients 277	
9.5.1	Background 277	
9.5.2	Strain Profile Retrieval 277	
9.5.3	Example 278	
9.6	Conclusions 279	
	References 281	
	Part III Phase Analysis and Phase Transformations 283	
10	Quantitative Phase Analysis Using the Rietveld Method 285	
	Ian C. Madsen, Nicola V.Y. Scarlett, Daniel P. Riley,	
	and Mark D. Raven	
10.1	Introduction 285	
10.2	Mathematical Basis 286	
10.2.1	Rietveld-Based Methods 286	
10.2.2	Improving Accuracy 290	
10.2.3	Correlation with Thermal Parameters 292	
10.3	Applications in Minerals and Materials Research 295	
10.3.1	Crystallization from Hydrothermal Solutions 295	
10.3.2	Energy-Dispersive Diffraction 298	
10.3.2.1	Application of EDD to the Study of Inert Anodes for Light Metal Production 301	5.5.6.
10.3.3	Quantitative Phase Analysis in Mineral Exploration 304	
10.3.3.1	Particle Statistics 306	
10.3.3.2	Preferred Orientation 306	
10.3.3.3	Microabsorption 306	
10.3.3.4	Identification of Mineral Types and Polytypes 307	
10.3.3.5	Element Substitution and Solid Solution 307	
10.3.3.6	Severe Peak Overlap 308	
10.3.3.7	Poorly Crystalline Components 309	
10.3.3.8	Clay and Disordered Structures 309	
10.3.4	The Reynolds Cup 310	
10.3.5	Use of QPA-Derived Kinetics in the Design of Novel	
-	Materials 312	
10.3.5.1	Methodologies for Synthesis Optimization Using OPA 312	
10.3.5.2	Design and Synthesis Optimization of Novel Materials: $M_{n+1}AX$ Phases 312	n
10.3.5.3	In situ Differential Thermal Analysis (DTA) Using OPA 316	
10.4	Summary 318	

Acknowledgments 318 References 318 Kinetics of Phase Transformations and of Other Time-Dependent 11 Processes in Solids Analyzed by Powder Diffraction 321 Andreas Leineweber and Eric J. Mittemeijer 11.1 Introduction 321 11.2 Kinetic Concepts 323 11.2.1 Process Rates 323 The Temperature Dependence of the Process Rate 327 11.2.2 Arrhenius-Type Temperature Dependence of the Rate Constant 11.2.2.1 k(T) 327Non-Arrhenius-Type Process Kinetics 328 11.2.2.2 Rate Laws for Isothermally Conducted Processes 330 11.2.3 mth-Order Kinetics of Homogeneous Processes 330 11.2.3.1 Johnson-Mehl-Avrami-Kolmogorov Kinetics of Heterogeneous Phase 11.2.3.2 Transformations 331 Grain Growth and Ostwald Ripening 332 11.2.3.3 11.2.3.4 Volume-Diffusion-Controlled Processes 333 11.2.3.5 Order-Disorder-Related Processes 333 Rate Laws for Nonisothermally Conducted Processes 336 11.2.4 Tracing the Process Kinetics by Powder Diffraction 337 11.3 Mode of Measurement: In Situ versus Ex Situ Methods 339 11.4 11.5 Types of Kinetic Processes and Examples 342 11.5.1 Local Composition in Solid is Retained 342 Reconstructive, Polymorphic Transformations $\alpha \rightarrow \beta$ 11.5.1.1 342 11.5.1.2 Polymorphic Transformations of Order-Disorder Character and Related Processes 346 Polymorphic Transformations of Polytypic Character 347 11.5.1.3 11.5.1.4 Grain Growth 349 Local Concentration Variations within Isolated Solid Systems 11.5.2 350 11.5.2.1 Precipitation Processes 350 Solid-State Reaction between Different Phases 351 11.5.2.2 Composition Changes in Solids by Reaction with Fluid Matter 11.5.3 352 11.6 Concluding Remarks 354 References 354 Part IV Diffraction Methods and Instrumentation 359

12 Laboratory Instrumentation for X-Ray Powder Diffraction: Developments and Examples 361

Udo Welzel and Eric J. Mittemeijer

12.1 Introduction: Historical Sketch 361

12.2 Laboratory X-Ray Powder Diffraction: Instrumentation 365

12.2.1 Overview 365

12.2.2	Laboratory	X-Ray	Sources;	Monochromatization	365
--------	------------	-------	----------	--------------------	-----

- 12.2.2.1 X-Ray Sources 365
- 12.2.2.2 Monochromatization/Filtering 368
- 12.2.3 Debye–Scherrer (–Hull) Geometry 370
- 12.2.4 Monochromatic Pinhole Techniques 371
- 12.2.5 (Para-)Focusing Geometries 371
- 12.2.5.1 Seemann–Bohlin Geometry 372
- 12.2.5.2 Bragg–Brentano Geometry 373
- 12.2.6 Instrumental Aberrations of (Para-)Focusing Geometries 376
- 12.2.7 Parallel-Beam Geometry 377
- 12.2.7.1 Polycapillary Collimators 378
- 12.2.7.2 X-Ray Mirrors 379
- 12.2.7.3 X-Ray Mirrors versus X-Ray Lenses; Comparative Discussion 381
- 12.2.7.4 Instrumental Aberrations of Parallel-Beam Geometry 383
- 12.2.8 Further, Recent Developments 384
- 12.2.8.1 Two-Dimensional Detectors 384
- 12.2.8.2 Microdiffraction 387
- 12.2.8.3 Energy-Dispersive Diffraction 388
- 12.3 Examples 388
- 12.3.1 Parallel-Beam Diffraction Methods 388
- 12.3.1.1 High Brilliance, Parallel-Beam Laboratory X-Ray Source 388
- 12.3.1.2 Applications 389
- 12.3.2 Two-Dimensional Diffraction Methods 391 Acknowledgments 394 References 394
- 13 The Calibration of Laboratory X-Ray Diffraction Equipment Using NIST Standard Reference Materials 399
 - James P. Cline, David Black, Donald Windover, and Albert Henins Introduction 399
- 13.2 The Instrument Profile Function 400
- 13.3 SRMs, Instrumentation, and Data Collection Procedures 411
- 13.4 Data Analysis Methods 418
- 13.5 Instrument Qualification and Validation 423
- 13.6 Conclusions 436

13.1

References 437

14Synchrotron Diffraction: Capabilities, Instrumentation, and
Examples 439

Gene E. Ice

- 14.1 Introduction 439
- 14.2 The Underlying Physics of Synchrotron Sources 441
- 14.2.1 Storage Ring Sources 441
- 14.2.2 Free-Electron Lasers and Other Emerging X-Ray Sources 445
- 14.3 Diffraction Applications Exploiting High Source Brilliance 445

- 14.3.1 Microdiffraction 446
- 14.3.1.1 Microdiffraction Example 1: Stress-Driven Sn Whisker Growth 449
- 14.3.1.2 Microdiffraction Example 2: Damage in Ion-Implanted Si 451
- 14.3.1.3 Other Microdiffraction Applications 452
- 14.3.2 Surface and Interface Diffraction 452
- 14.3.2.1 Surface Diffraction Example 1: Truncation Rod Scattering (TRS) 453
- 14.3.2.2 Surface Diffraction Example 2: Surface Studies of Phase Transformations in Langmuir–Blodgett Films 455
- 14.4 High Q-Resolution Measurements 456
- 14.5 Applications of Tunability: Resonant Scattering 456
- 14.5.1 Resonant Scattering Example 1: Multiple Anomalous Diffraction, MAD 458
- 14.5.2Resonant Scattering Example 2: 3λ Determination of Local
Short-Range Correlation in Binary Alloys461
- 14.5.3 Resonant Scattering Example 3: Determination of Magnetic Structure and Correlation Lengths 464
- 14.6 Future: Ultrafast Science and Coherence 465
- 14.6.1 Coherent Diffraction 466
- 14.6.2 Ultrafast Diffraction 466 References 467

15 High-Energy Electron Diffraction: Capabilities, Instrumentation, and Examples 469

- Christoph T. Koch
- 15.1 Introduction 469
- 15.2 Instrumentation 470
- 15.2.1 Fundamentals 470
- 15.2.2 Diffraction Modes in a TEM 472
- 15.2.3 Femtosecond Electron Diffraction 474
- 15.3 Electron Diffraction Methods in the TEM 474
- 15.3.1 Precession Electron Diffraction (PED) 474
- 15.3.2 Quantitative Convergent-Beam Electron Diffraction (QCBED) 476
- 15.3.3 Large-Angle Convergent-Beam Electron Diffraction (LACBED) 477
- 15.3.4 Large-Angle Rocking-Beam Electron Diffraction (LARBED) 478
- 15.3.5 Diffraction Tomography 482
- 15.3.6 Real-Space Crystallography 482
- 15.3.7 Coherent Diffractive Imaging (CDI) with Electrons 483
- 15.3.8 Mapping Strain by Electron Diffraction 485
- 15.4 Summary and Outlook 486
 - Acknowledgment 486

References 486

- 16 In Situ Diffraction Measurements: Challenges, Instrumentation, and Examples 491 Helmut Ehrenberg, Anatoliy Senyshyn, Manuel Hinterstein, and Hartmut Fuess
- 16.1 Introduction 491
- 16.2 Instrumentation and Experimental Challenges 492
- 16.2.1 General Considerations 492
- 16.2.2 Absorption 493
- 16.2.3 Detection Challenges 494
- 16.3 Examples 497
- 16.3.1 Electrochemical *In Situ* Studies of Electrode Materials and *In Operando* Investigations of Li-Ion Batteries 497
- 16.3.2 *In situ* Studies of Piezoceramics in Electric Fields 502 Acknowledgment 515 References 515

Index 519