Contents

1 Electron Sources 1

1.1 Introduction and Definitions of Parameters 2

1.2 Schottky Sources 4

1.2.1 Emission Theory 4

1.2.2 Coulomb Interactions 6

1.2.3 Practical Aspects 7

1.3 Field Emission Sources 8

1.3.1 Emission Theory 8

1.3.2 Practical Aspects 10

1.4 Photo-Emission Sources 10

1.5 Effect of the Electron Source Parameters on Resolution in STEM . . 11

1.5.1 Contributions to the Probe Size 11

1.5.2 Current in a Probe 12

Appendix 14

References 15

2 In situ and Operando 17

2.1 General Principles 18

2.2 Some history 18

2.3 The Possibilities 19

2.3.1 Post-Mortem Characterization 20

2.3.2 Statistics 20

2.4 Time 22

2.4.1 Recording the Data 22

2.4.2 The CCD Camera 22

2.4.3 Direct-Detection Cameras 22

2.4.4 Software and Data Handling 23

2.4.5 Drift Correction 24

2.4.6 Ultrafast Electron Microscopy 25

2.5 The Environment 29

2.5.1 Ultrahigh Vacuum . . . 36
2.5.2 Working in a Gas Cell . . . 37
2.5.3 Working in a Liquid Cell . . . 39
2.6 The Temperature . . . 41
2.6.1 Temperature Measurement . . . 41
2.6.2 Heating . . . 42
2.6.3 Cooling . . . 46
2.7 Other Stimuli . . . 48
2.7.1 Deformation . . . 48
2.7.2 Magnetic Fields . . . 55
2.7.3 Electric Fields . . . 56
2.7.4 Photons . . . 64
2.8 Adding or Removing Material . . . 67
2.8.1 Depositing Layers/Particles . . . 67
2.8.2 Deposition Energy: Electron and Ion Irradiation . . . 68
2.9 The Future . . . 73
Appendix . . . 75
References . . . 76

3 Electron Diffraction and Phase Identification . . . 81
3.1 Introduction . . . 82
3.2 Spinodal Alloys . . . 83
3.2.1 Example: Ordered FeBe Phases and A2 Matrix . . . 83
3.3 Superalloys with Ordered Precipitates . . . 85
3.3.1 Example: γ″ and γ′ Precipitation in Alloy 718 . . . 87
3.3.2 Example: $D0_a$-Ordered δ Precipitation in Alloy 718 . . . 89
3.4 Carbide Precipitation in fcc Alloys . . . 93
3.4.1 Example: $M_{23}C_6$ Precipitation in a Ni–Base Alloy . . . 93
3.4.2 Example: MC Carbides in a Ni–Base Alloy . . . 94
3.5 Ferritic Steels . . . 96
3.5.1 Relationships Between Austenite and Ferrite, Austenite and Martensite (fcc/bcc) . . . 96
3.5.2 Relationship Between Cementite (Orthorhombic Fe_3C or M_3C) and Ferrite/Tempered Martensite . . . 97
3.5.3 Relationships Between Alloy Carbides and Ferrite . . . 97
3.5.4 Precipitation in Ferritic Structures . . . 98
3.6 Epitaxial Oxide on Metal: Presence of Fe_3O_4 on Steel Foils . . . 99
Appendix . . . 101
References . . . 102

4 Convergent-Beam Electron Diffraction: Symmetry and Large-Angle Patterns . . . 103
4.1 Symmetry . . . 104
4.2 Point-Group Determination . . . 104
4.3 Space-Group Determination . . . 109
4.3.1 Forbidden Reflections . . . 109
4.3.2 Black Crosses . . . 111
4.3.3 Complete Procedure for Space-Group Determination . . . 113
4.4 Ni_3Mo – A Worked Example . . . 114
4.4.1 Ni_3Mo – a Worked Example, Part I: Point Group . . . 114
4.4.2 Qualifications . . . 118
4.4.3 Ni_3Mo – a Worked Example, Part II: Space Group . . . 119
4.5 Additional and Alternative Symmetry Methods . . . 120
4.5.1 Symmetry Determination from Off-Axis Patterns . . . 120
4.5.2 Symmetry from Precession Patterns . . . 122
4.6 More on Glide Planes . . . 123
4.6.1 GM Lines in HOLZ Reflections . . . 124
4.6.2 Glide Planes Normal to the Beam . . . 124
4.7 Beyond Symmetry . . . 124
4.7.1 Enantiomorphous Pairs: Handedness . . . 126
4.7.2 Polarity . . . 126
4.7.3 Coherent Convergent-Beam Diffraction . . . 127
4.8 Tanaka Methods . . . 127
4.9 LACBED . . . 127
4.9.1 The Nature of LACBED Patterns . . . 129
4.9.2 Obtaining LACBED Patterns in Practice . . . 130
4.9.3 Choosing the Parameters . . . 131
4.10 Spherical Aberration and LACBED . . . 132
4.11 Crystal Defects in LACBED Patterns: Dislocations . . . 132
4.12 Crystal Defects in LACBED Patterns: Stacking Faults and Antiphase Boundaries . . . 134
4.13 Other Tanaka Methods . . . 134
4.13.1 Bright- and Dark-Field LACBED . . . 134
4.13.2 Convergent-Beam Imaging (CBIM) . . . 136
4.13.3 Rastering Techniques . . . 137
Appendix . . . 141
References . . . 142

5 Electron Crystallography, Charge-Density Mapping, and Nanodiffraction 145

5.1 Can We Quantify Electron Diffraction Data? 146

5.2 Quantitative CBED for Charge-Density Mapping 147

5.3 Strain Mapping, High Voltage, Lattice Parameters Measured by QCBED 153

5.4 Spot Patterns – Solving Crystal Structures 155

5.5 The Precession Method 157

5.6 Diffuse Scattering, Defects, Phonons, and Phase Transitions 158

5.7 Diffractive Imaging, Ptychography, STEM Holography, Ronchigrams, and All That 159

5.8 Equipment for Quantitative Electron Diffraction 162

Appendix 163

References 164

6 DigitalMicrograph 167

6.1 Introduction 168

6.1.1 What Is DigitalMicrograph? 168

6.1.2 Installing DigitalMicrograph Offline 168

6.1.3 A (Very) Quick Overview 168

6.2 Understanding Data 170

6.2.1 What is an Image? 170

6.2.2 Image Display 171

6.2.3 Number Formats 173

6.2.4 Image Calibration and Image Tags 178

6.2.5 Some Simple Tools 180

6.2.6 Extracting Subsets of Data 181

6.3 Digital Image Processing 183

6.3.1 Image 'Filters' 185

6.3.2 Fourier Transformation in Images 187

6.3.3 Fourier Filtering 189

6.3.4 Coordinate Transformations 192

6.4 Scripting and Plugins 193

Appendix 195

References 195

7 Electron Waves, Interference, and Coherence 197

7.1 Introduction 198

7.2 Description of Waves 198

7.2.1 Plane Wave 199

7.2.2 Spherical Wave 199

7.2.3 Modulated Wave 199

7.3 Interference 200

7.4 Modulation of a Wave by an Object 201

7.5 Propagation of Waves 201

7.5.1 Fresnel Approximation in the Near-Field of the Object 202

7.5.2 Fraunhofer Approximation in the Far-Field of the Object 202

7.6 Imaging: Formation of the Image Wave 203

7.6.1 Fourier Transform of the Object Exit Wave 203

7.6.2 Building the Image Wave by Inverse Fourier Transform of the Fourier Spectrum 203

7.7 Electron Wave Function 204

7.8 Electron Interference 205

7.9 Findings 206

7.10 Interpretation 207

7.11 Coherence 207

7.11.1 Spatial Coherence 208

7.11.2 Coherent Current 210

7.11.3 Temporal Coherence 211

7.11.4 Total Degree of Coherence 211

7.11.5 A Generalization 211

7.11.6 Coherence at Inelastic Interaction 211

Appendix 213

References 213

8 Electron Holography 215

8.1 Big Problem with TEM: Phase Contrast 216

8.2 Wave Modulation and Conventional Imaging 216

8.2.1 Amplitude Modulation 216

8.2.2 Phase Modulation 217

8.2.3 What Do We See in an Electron Image? 218

8.3 Principle of Image-Plane Off-Axis Holography 219

8.3.1 Recording a Hologram 219

8.3.2 Reconstructing the Object Exit-Wave 220

8.3.3 What Have We Achieved so Far? 223

8.4 Properties of the Reconstructed Object Exit-Wave 223

8.5 Requirements of Holography 224

8.6 Quality Criteria 224

8.7 Application to Electric Potentials on Nanometer Scale 225
8.7.1 Phase Shift Due to Electrostatic Potentials 225
8.7.2 Experimental Considerations 226
8.7.3 Application Example: p–n Junctions 227
8.8 Further Derivatives of Electron Holography 227
8.8.1 Holographic Tomography 227
8.8.2 Dark-Field Holography 228
Appendix 230
References 230
9 Focal-Series Reconstruction 233
9.1 Motivation: Why the Effort? 234
9.2 Quick Walk Through Electron Diffraction 235
9.3 From the Wavefunction to the Image 237
9.3.1 Imaging with a 'Neutral' Microscope 238
9.3.2 Linear Imaging with a Constant-Phase-Shift Microscope . . 240
9.3.3 Linear Imaging with a Real Microscope 241
9.3.4 From Oscillations to Windings: an Integral View on Linear Imaging 247
9.4 From the Images to the Wavefunction 249
9.4.1 Tomographic Interpretation of Focal Series 249
9.4.2 Fundamental Properties of Focal Series 250
9.4.3 An Explicit Solution to the Linear Inversion Problem 253
9.4.4 Nonlinear Reconstruction 255
9.4.5 Numerical Correction of Residual Aberrations 256
9.5 Application Examples 257
9.5.1 Twin Boundaries in $BaTiO_3$ 258
9.5.2 Stacking Fault in GaAs 260
Appendix 263
References 264
10 Direct Methods for Image Interpretation 267
10.1 Introduction 268
10.2 Basics of Image Formation 268
10.2.1 Real imaging 268
10.2.2 Successive Imaging Steps 269
10.2.3 Coherent Imaging 269
10.2.4 High-Resolution Imaging in the TEM 270
10.3 Focal-Series Reconstruction of the Exit Wave 271

10.4 Interpretation of the Reconstructed Exit Wave 271
10.4.1 Electron Channeling 272
10.4.2 Argand Plot 273
10.5 Quantitative Structure Refinement 274
10.5.1 Precision Versus Resolution 276
10.5.2 Quantitative Model-Based Structure Determination 276
Appendix 280
References 280
11 Imaging in STEM 283
11.1 Z-Contrast STEM: an Introduction 284
11.1.1 Independent Scatterers 284
11.1.2 An Array of Scatterers 284
11.1.3 As the Crystal Thickens 284
11.1.4 Inside and Outside 286
11.1.5 The Effect of Defects 287
11.1.6 Quasicrystals 288
11.2 An Electron's Eye View of STEM 288
11.2.1 Plane Waves and Probes 291
11.2.2 Rayleigh, Airy and Resolution 292
11.3 Lens Aberrations for STEM 293
11.3.1 The Benefits of Aberration Correction 295
11.3.2 Resolution in the Third Dimension – Depth Resolution . . . 300
11.4 Spatial and Temporal Incoherence 305
11.4.1 Spatial Incoherence 305
11.4.2 Temporal Incoherence 306
11.4.3 "How Do I Know if I Have a Coherent Probe?" The Ronchigram 306
11.5 Coherent or Incoherent Imaging 310
11.5.1 A Point Detector; Coherent Imaging 311
11.5.2 An Infinite Detector: Incoherent Imaging 312
11.5.3 An Annular Detector: Incoherent Dark-Field or Bright-Field Imaging 314
11.5.4 Atoms Are Smaller in HAADF STEM 315
11.5.5 Transverse Coherence 316
11.5.6 The Origin of Contrast in the Scanned Image 317
11.5.7 Transfer Function and Damping Function 318
11.5.8 Longitudinal Coherence 319

11.6 Dynamical Diffraction . . . 323
11.7 Other Sources of Image Contrast . . . 326
11.8 Image Processing . . . 329
11.9 Image Simulation . . . 332
11.9.1 Bloch Waves . . . 333
11.9.2 Multislice . . . 333
11.9.3 Bloch Waves with Absorption . . . 333
11.9.4 There Is No Stobb's Factor in HAADF . . . 334
11.10 Future Directions . . . 335
Appendix . . . 337
References . . . 338
12 Electron Tomography . . . 343
12.1 Theory of Projection . . . 344
12.2 Back-Projection . . . 346
12.3 Constrained Reconstruction . . . 347
12.3.1 Constraint by Projection Consistency . . . 347
12.3.2 Constraint by Discrete Methods . . . 348
12.3.3 Constraint by Symmetry . . . 348
12.3.4 Metric-Based Constraint . . . 348
12.4 Other Reconstruction Approaches . . . 350
12.5 Meeting the Projection Requirement . . . 350
12.6 STEM Tomography . . . 351
12.7 Element-Selected Tomography . . . 354
12.8 Dark-Field TEM Tomography . . . 356
12.9 Holographic Tomography . . . 358
12.10 Atomistic Tomography . . . 359
12.11 Experimental Limitations . . . 360
12.12 Beam Damage and Contamination . . . 364
12.13 Automated Acquisition . . . 365
12.14 Tilt-Series Alignment . . . 366
12.15 Visualization of Three-Dimensional Datasets . . . 368
12.16 Segmentation . . . 369
12.17 Quantitative Analysis of Volumetric Data . . . 371
Appendix . . . 373
References . . . 373
13 EFTEM . . . 377
13.1 Introduction . . . 378
13.2 Why Use EFTEM? . . . 378

13.3 Instrumentation for EFTEM . . . 379
13.3.1 General TEM Considerations . . . 379
13.3.2 The Imaging Filter . . . 379
13.3.3 Detector Considerations . . . 380
13.4 Limitations and Artefacts . . . 381
13.4.1 Spatial Resolution in EFTEM Images . . . 381
13.4.2 Non-Isochromaticity . . . 383
13.4.3 Sample Drift . . . 383
13.4.4 Diffraction Contrast . . . 384
13.4.5 Illumination Convergence . . . 384
13.5 Application of EFTEM . . . 385
13.5.1 Zero-Loss Imaging and Diffraction . . . 385
13.5.2 Measuring Relative Thickness (t/λ Mapping) . . . 386
13.6 Core-Loss Elemental Mapping . . . 387
13.6.1 Elemental Mapping (Three-Window Method) . . . 387
13.6.2 Jump-Ratio Mapping (Two-Window Method) . . . 388
13.7 EFTEM Spectrum-Imaging . . . 389
13.8 Low-Loss Imaging . . . 392
13.9 Alternative Imaging Techniques for Biological Specimens . . . 393
13.10 Quantitative Elemental Mapping . . . 394
13.11 Chemical State Mapping Using ELNES . . . 396
13.12 Hybrid EFTEM Modes (ω-q, Line Spectrum EFTEM) . . . 397
13.13 EFTEM Tomography . . . 398
Appendix . . . 401
References . . . 401
14 Calculating EELS . . . 405
14.1 Introduction . . . 406
14.2 Density Functional Theory (DFT) . . . 407
14.2.1 Introduction to DFT . . . 407
14.2.2 The Exchange Correlation Potential . . . 409
14.2.3 Approximations to the Potential . . . 409
14.2.4 Basis Sets . . . 410
14.2.5 The Korringa–Kohn–Rostoker (KKR) Method . . . 412
14.3 Calculations of the ELNES . . . 412
14.3.1 ELNES Theory . . . 412
14.3.2 The Core Hole . . . 414
14.3.3 Multiplet Theory . . . 415
14.3.4 Multiple Scattering (MS) Methods . . . 416

14.4 Calculating Low-Loss EELS . . . 417
Appendix . . . 421
References . . . 422
15 Diffraction & X-ray Excitation . . . 425
15.1 Introduction . . . 426
15.2 ALCHEMI . . . 426
15.3 Gedanken ALCHEMI . . . 426
15.4 Two Examples . . . 428
15.4.1 Dilute Solution/Partition Coefficient Analysis . . . 428
15.4.2 Concentrated Solution/OTL Analysis . . . 430
15.5 Delocalization and Axial Channeling . . . 431
15.6 Optimizing ALCHEMI: 'Statistical' ALCHEMI . . . 432
15.7 Incoherent Channeling Patterns . . . 432
15.8 Vacancies and Interstitials . . . 432
15.9 Chemistry . . . 434
Appendix . . . 435
References . . . 436
16 X-ray and EELS Imaging . . . 439
16.1 What Are Spectral Images and Why Should We Collect Them? . . . 440
16.2 Some History . . . 441
16.3 Acquisition and Analysis of Spectral Images . . . 442
16.3.1 Sampling and the Effect of Probe Versus Pixel Size (STEM-XEDS/EELS) or Magnification (EFTEM) . . . 442
16.3.2 Signal: Count Rate, Dwell Time, Spectral Image Size, and Acquisition Time . . . 443
16.3.3 Drift Correction and Beam Damage . . . 446
16.3.4 Conventional Data Analysis Methods . . . 446
16.4 Multivariate Statistical Analysis Methods . . . 451
16.4.1 Principal Components Analysis (PCA) . . . 454
16.4.2 Factor Rotations . . . 455
16.4.3 Multivariate Curve Resolution (MCR) . . . 456
16.4.4 Quantification . . . 457
16.5 Example of X-ray and Electron Energy-Loss Spectral Image Acquisition and Analysis . . . 458
16.5.1 Fe-Ni Spectral Image Acquisition and Quantification . . . 458
16.5.2 Mn-Doped $SrTiO_3$ Grain Boundary Spectral Image Acquisition and Quantification . . . 459
16.5.3 Plasmon Mapping of AG Nanorods: EELS Spectral Image Analysis . . . 462

Appendix . . . 464
References . . . 464
17 Practical Aspects and Advanced Applications of XEDS . . . 467
17.1 Performance Parameters of XEDS Detectors . . . 468
17.1.1 Detector, Fundamental Parameters . . . 468
17.1.2 Monitoring Detector Contamination . . . 470
17.1.3 Software to Determine Detector Parameters . . . 471
17.2 X-ray Spectrum Simulation – a Tutorial and Applications of DTSA 472
17.2.1 What Is DTSA? . . . 473
17.2.2 A Brief Tutorial of X-ray Spectrum Simulation for a Thin Specimen Using DTSA . . . 475
17.2.3 Details of X-ray Simulation in DTSA . . . 477
17.2.4 Application 1: Confirmation of Peak Overlap . . . 481
17.2.5 Application 2: Evaluation of X-ray Absorption into a Thin Specimen . . . 482
17.2.6 Application 3: Evaluation of the AEM-XEDS Interface . . . 483
17.2.7 Application 4: Estimation of the Detectability Limits . . . 483
17.3 The ζ-factor Method: a New Approach for Quantitative X-ray Analysis of Thin Specimens . . . 486
17.3.1 Why Bother with Quantification? . . . 486
17.3.2 What Is the ζ-factor? . . . 487
17.3.3 Quantification Procedure in the ζ-factor Method . . . 488
17.3.4 Determination of ζ factors . . . 489
17.3.5 Applications of ζ-factor Method . . . 490
17.4 Contemporary Aplications of X-ray Analysis . . . 492
17.4.1 Renaissance of X-ray Analysis . . . 493
17.4.2 XEDS Tomography for 3D Elemental Distribution . . . 494
17.4.3 Atomic Resolution X-ray Mapping . . . 495
Appendix . . . 500
References . . . 501
Figure and Table Credits . . . 505
Index . . . 515