

Contents

1. Diffraction and the X-Ray Powder Diffractometer	1
1.1 Diffraction	1
1.1.1 Introduction to Diffraction	1
1.1.2 Bragg's Law	3
1.1.3 Strain Effects	6
1.1.4 Size Effects	7
1.1.5 A Symmetry Consideration	9
1.1.6 Momentum and Energy	10
1.1.7 Experimental Methods	10
1.2 The Creation of X-Rays	13
1.2.1 Bremsstrahlung	14
1.2.2 Characteristic Radiation	16
1.2.3 Synchrotron Radiation	20
1.3 The X-Ray Powder Diffractometer	23
1.3.1 Practice of X-Ray Generation	23
1.3.2 Goniometer for Powder Diffraction	25
1.3.3 Monochromators, Filters, Mirrors	28
1.4 X-Ray Detectors for XRD and TEM	30
1.4.1 Detector Principles	30
1.4.2 Position-Sensitive Detectors	34
1.4.3 Charge Sensitive Preamplifier	36
1.4.4 Other Electronics	37
1.5 Experimental X-Ray Powder Diffraction Data	38
1.5.1 * Intensities of Powder Diffraction Peaks	38
1.5.2 Phase Fraction Measurement	45
1.5.3 Lattice Parameter Measurement	49
1.5.4 * Refinement Methods for Powder Diffraction Data	52
Further Reading	54
Problems	55
2. The TEM and its Optics	61
2.1 Introduction to the Transmission Electron Microscope	61
2.2 Working with Lenses and Ray Diagrams	66
2.2.1 Single Lenses	66

2.2.2	Multi-Lens Systems	69
2.3	Modes of Operation of a TEM	71
2.3.1	Dark-Field and Bright-Field Imaging	71
2.3.2	Selected Area Diffraction	76
2.3.3	Convergent-Beam Electron Diffraction	79
2.3.4	High-Resolution Imaging	81
2.4	Practical TEM Optics	85
2.4.1	Electron Guns	85
2.4.2	Illumination Lens Systems	87
2.4.3	Imaging Lens Systems	88
2.5	Glass Lenses	91
2.5.1	Interfaces	91
2.5.2	Lenses and Rays	92
2.5.3	Lenses and Phase Shifts	95
2.6	Magnetic Lenses	97
2.6.1	Focusing	97
2.6.2	Image Rotation	99
2.6.3	Pole Piece Gap	100
2.7	Lens Aberrations and Other Defects	102
2.7.1	Spherical Aberration	102
2.7.2	Chromatic Aberration	103
2.7.3	Diffraction	104
2.7.4	Astigmatism	104
2.7.5	Gun Brightness	108
2.8	Resolution	110
	Further Reading	112
	Problems	113
3.	Scattering	119
3.1	Waves and Scattering	119
3.1.1	Wavefunctions	119
3.1.2	Coherent and Incoherent Scattering	122
3.1.3	Elastic and Inelastic Scattering	123
3.1.4	Wave Amplitudes and Cross-Sections	124
3.2	X-Ray Scattering	128
3.2.1	Electrodynamics of X-Ray Scattering	128
3.2.2	* Inelastic Compton Scattering	132
3.2.3	X-Ray Mass Attenuation Coefficients	134
3.3	Coherent Elastic Scattering	136
3.3.1	‡ Born Approximation for Electrons	136
3.3.2	Atomic Form Factors – Physical Picture	141
3.3.3	‡ Scattering of Electrons by Model Potentials	144
3.3.4	‡ * Atomic Form Factors – General Formulation	148
3.4	* Nuclear Scattering	153
3.4.1	Properties of Neutrons	153

3.4.2	Time-Varying Potentials and Inelastic Neutron Scattering	155
3.4.3	* Coherent Mössbauer Scattering	158
	Further Reading	160
	Problems	160
4.	Inelastic Electron Scattering and Spectroscopy	163
4.1	Inelastic Electron Scattering	163
4.2	Electron Energy-Loss Spectrometry (EELS)	165
4.2.1	Instrumentation	165
4.2.2	General Features of EELS Spectra	167
4.2.3	* Fine Structure	169
4.3	Plasmon Excitations	173
4.3.1	Plasmon Principles	173
4.3.2	* Plasmons and Specimen Thickness	175
4.4	Core Excitations	177
4.4.1	Scattering Angles and Energies – Qualitative	177
4.4.2	‡ Inelastic Form Factor	180
4.4.3	‡ * Double-Differential Cross-Section, $d^2\sigma_{in}/d\phi dE$	184
4.4.4	* Scattering Angles and Energies – Quantitative	186
4.4.5	‡ * Differential Cross-Section, $d\sigma_{in}/dE$	187
4.4.6	‡ Partial and Total Cross-Sections, σ_{in}	189
4.4.7	Quantification of EELS Core Edges	191
4.5	Energy-Filtered TEM Imaging (EFTEM)	193
4.5.1	Spectrum Imaging	193
4.5.2	Energy Filters	193
4.5.3	Chemical Mapping with Energy-Filtered Images	196
4.5.4	Chemical Analysis with High Spatial Resolution	197
4.6	Energy Dispersive X-Ray Spectrometry (EDS)	200
4.6.1	Electron Trajectories Through Materials	200
4.6.2	Fluorescence Yield	203
4.6.3	EDS Instrumentation Considerations	205
4.6.4	Thin-Film Approximation	208
4.6.5	* ZAF Correction	211
4.6.6	Artifacts in EDS Measurements	213
4.6.7	Limits of Microanalysis	215
	Further Reading	217
	Problems	217
5.	Diffraction from Crystals	223
5.1	Sums of Wavelets from Atoms	223
5.1.1	Electron Diffraction from a Material	224
5.1.2	Wave Diffraction from a Material	226
5.2	The Reciprocal Lattice and the Laue Condition	230
5.2.1	Diffraction from a Simple Lattice	230

5.2.2	Reciprocal Lattice	231
5.2.3	Laue Condition	233
5.2.4	Equivalence of the Laue Condition and Bragg's Law . .	233
5.2.5	Reciprocal Lattices of Cubic Crystals	234
5.3	Diffraction from a Lattice with a Basis	235
5.3.1	Structure Factor and Shape Factor	235
5.3.2	Structure Factor Rules	237
5.3.3	Symmetry Operations and Forbidden Diffractions	242
5.3.4	Superlattice Diffractions	243
5.4	Crystal Shape Factor	247
5.4.1	Shape Factor of Rectangular Prism	247
5.4.2	Other Shape Factors	252
5.4.3	Small Particles in a Large Matrix	252
5.5	Deviation Vector (Deviation Parameter)	256
5.6	Ewald Sphere	257
5.6.1	Ewald Sphere Construction	257
5.6.2	Ewald Sphere and Bragg's Law	259
5.6.3	Tilting Specimens and Tilting Electron Beams	259
5.7	Laue Zones	262
5.8	* Effects of Curvature of the Ewald Sphere	262
	Further Reading	266
	Problems	266
6.	Electron Diffraction and Crystallography	273
6.1	Indexing Diffraction Patterns	273
6.1.1	Issues in Indexing	274
6.1.2	Method 1 – Start with Zone Axis	276
6.1.3	Method 2 – Start with Diffraction Spots	279
6.2	Stereographic Projections and Their Manipulation	282
6.2.1	Construction of a Stereographic Projection	282
6.2.2	Relationship Between Stereographic Projections and Electron Diffraction Patterns	284
6.2.3	Manipulations of Stereographic Projections	284
6.3	Kikuchi Lines and Specimen Orientation	290
6.3.1	Origin of Kikuchi Lines	290
6.3.2	Indexing Kikuchi Lines	294
6.3.3	Specimen Orientation and Deviation Parameter	296
6.3.4	The Sign of s	299
6.3.5	Kikuchi Maps	299
6.4	Double Diffraction	302
6.4.1	Occurrence of Forbidden Diffractions	302
6.4.2	Interactions Between Crystallites	303
6.5	* Convergent-Beam Electron Diffraction	304
6.5.1	Convergence Angle of Incident Electron Beam	306
6.5.2	Determination of Sample Thickness	307

6.5.3	Measurements of Unit Cell Parameters	309
6.5.4	‡ Determination of Point Groups	314
6.5.5	‡ Determination of Space Groups	325
6.6	Further Reading	330
	Problems	330
7.	Diffraction Contrast in TEM Images	337
7.1	Contrast in TEM Images	337
7.2	Diffraction from Crystals with Defects	339
7.2.1	Review of the Deviation Parameter, s	339
7.2.2	Atom Displacements, $\delta\mathbf{r}$	340
7.2.3	Shape Factor and t	341
7.2.4	Diffraction Contrast and $\{s, \delta\mathbf{r}, t\}$	342
7.3	Extinction Distance	342
7.4	The Phase-Amplitude Diagram	345
7.5	Fringes from Sample Thickness Variations	347
7.5.1	Thickness and Phase-Amplitude Diagrams	347
7.5.2	Thickness Fringes in TEM Images	348
7.6	Bend Contours in TEM Images	353
7.7	Diffraction Contrast from Strain Fields	357
7.8	Dislocations and Burgers Vector Determination	359
7.8.1	Diffraction Contrast from Dislocation Strain Fields	359
7.8.2	The $\mathbf{g}\cdot\mathbf{b}$ Rule for Null Contrast	362
7.8.3	Image Position and Dislocation Pairs or Loops	368
7.9	Semi-Quantitative Diffraction Contrast from Dislocations	369
7.10	Weak-Beam Dark-Field (WBDF) Imaging of Dislocations	378
7.10.1	Procedure to Make a WBDF Image	378
7.10.2	Diffraction Condition for a WBDF Image	379
7.10.3	Analysis of WBDF Images	380
7.11	Fringes at Interfaces	384
7.11.1	Phase Shifts of Electron Wavelets Across Interfaces	384
7.11.2	Moiré Fringes	387
7.12	Diffraction Contrast from Stacking Faults	391
7.12.1	Kinematical Treatment	391
7.12.2	Results from Dynamical Theory	397
7.12.3	Determination of the Intrinsic or Extrinsic Nature of Stacking Faults	399
7.12.4	Partial Dislocations Bounding the Fault	399
7.12.5	An Example of a Stacking Fault Analysis	400
7.12.6	Sets of Stacking Faults in TEM Images	402
7.12.7	Related Fringe Contrast	403
7.13	Antiphase (π) Boundaries and δ Boundaries	404
7.13.1	Antiphase Boundaries	404
7.13.2	δ Boundaries	405
7.14	Contrast from Precipitates and Other Defects	407

7.14.1	Vacancies	407
7.14.2	Coherent Precipitates	408
7.14.3	Semicoherent and Incoherent Particles	413
	Further Reading	413
	Problems	414
8.	Diffraction Lineshapes	423
8.1	Diffraction Line Broadening and Convolution	423
8.1.1	Crystallite Size Broadening	424
8.1.2	Strain Broadening	426
8.1.3	Instrumental Broadening – Convolution	430
8.2	Fourier Transform Deconvolutions	433
8.2.1	Mathematical Features	433
8.2.2	* Effects of Noise on Fourier Transform Deconvolutions	436
8.3	Simultaneous Strain and Size Broadening	440
8.4	Diffraction Lineshapes from Columns of Crystals	446
8.4.1	Wavelets from Pairs of Unit Cells in One Column	446
8.4.2	A Column Length Distribution	448
8.4.3	‡ Intensity from Column Length Distribution	450
8.5	Comments on Diffraction Lineshapes	451
	Further Reading	454
	Problems	455
9.	Patterson Functions and Diffuse Scattering	457
9.1	The Patterson Function	457
9.1.1	Overview	457
9.1.2	Atom Centers at Points in Space	458
9.1.3	Definition of the Patterson Function	459
9.1.4	Properties of Patterson Functions	461
9.1.5	‡ Perfect Crystals	463
9.1.6	Deviations from Periodicity and Diffuse Scattering	467
9.2	Diffuse Scattering from Atomic Displacements	469
9.2.1	Uncorrelated Displacements – Homogeneous Disorder	469
9.2.2	‡ Temperature	472
9.2.3	* Correlated Displacements – Atomic Size Effects	477
9.3	Diffuse Scattering from Chemical Disorder	481
9.3.1	Uncorrelated Chemical Disorder – Random Alloys	481
9.3.2	‡ * SRO Parameters	485
9.3.3	‡ * Patterson Function for Chemical SRO	487
9.3.4	Short-Range Order Diffuse Intensity	488
9.3.5	‡ * Isotropic Materials	488
9.3.6	* Polycrystalline Average and Single Crystal SRO	490
9.4	* Amorphous Materials	491
9.4.1	‡ One-Dimensional Model	491
9.4.2	‡ Radial Distribution Function	495

9.4.3	‡ Partial Pair Correlation Functions	500
9.5	Small Angle Scattering	502
9.5.1	Concept of Small Angle Scattering	502
9.5.2	* Guinier Approximation (small Δk)	504
9.5.3	* Porod Law (large Δk)	508
9.5.4	‡ * Density-Density Correlations (all Δk)	510
	Further Reading	512
	Problems	513
10.	High-Resolution TEM Imaging	517
10.1	Huygens Principle	518
10.1.1	Wavelets from Points in a Continuum	518
10.1.2	Huygens Principle for a Spherical Wavefront – Fresnel Zones	523
10.1.3	‡ Fresnel Diffraction Near an Edge	527
10.2	Physical Optics of High-Resolution Imaging	532
10.2.1	‡ Wavefronts and Fresnel Propagator	532
10.2.2	‡ Lenses	534
10.2.3	‡ Materials	536
10.3	Experimental High-Resolution Imaging	538
10.3.1	Defocus and Spherical Aberration	538
10.3.2	‡ Lenses and Specimens	543
10.3.3	Lens Characteristics	546
10.4	* Simulations of High-Resolution TEM Images	555
10.4.1	Principles of Simulations	555
10.4.2	Practice of Simulations	561
10.5	Issues and Examples in High-Resolution TEM Imaging	562
10.5.1	Images of Nanostructures	562
10.5.2	Examples of Interfaces	565
10.5.3	* Specimen and Microscope Parameters	568
10.5.4	* Some Practical Issues for HRTEM	576
	Further Reading	580
	Problems	581
11.	High-Resolution STEM Imaging	583
11.1	Characteristics of High-Angle Annular Dark-Field Imaging	583
11.2	Electron Channeling Along Atomic Columns	586
11.2.1	Optical Fiber Analogy	586
11.2.2	‡ Critical Angle	588
11.2.3	* Tunneling Between Columns	589
11.3	Scattering of Channeled Electrons	591
11.3.1	Elastic Scattering of Channeled Electrons	591
11.3.2	* Inelastic Scattering of Channeled Electrons	593
11.4	* Comparison of HAADF and HRTEM Imaging	594
11.5	HAADF Imaging with Atomic Resolution	595

11.5.1	* Effect of Defocus	595
11.5.2	Experimental Examples	597
11.6	* Lens Aberrations and Their Corrections	599
11.6.1	C_s Correction with Magnetic Hexapoles	599
11.6.2	‡ Higher-Order Aberrations and Instabilities	602
11.7	Examples of C_s -Corrected Images	604
11.7.1	Three-Dimensional Imaging	605
11.7.2	High Resolution EELS	606
	Further Reading	607
	Problems	608
12.	Dynamical Theory	611
12.1	Chapter Overview	611
12.2	‡ * Mathematical Features of High-Energy Electrons in a Periodic Potential	613
12.2.1	‡ * The Schrödinger Equation	613
12.2.2	‡ Kinematical and Dynamical Theory	619
12.2.3	* The Crystal as a Phase Grating	621
12.3	First Approach to Dynamical Theory – Beam Propagation	623
12.4	‡ Second Approach to Dynamical Theory – Bloch Waves and Dispersion Surfaces	627
12.4.1	Diffracted Beams, $\{\Phi_{\mathbf{g}}\}$, are Beats of Bloch Waves, $\{\psi^{(j)}\}$	627
12.4.2	Crystal Periodicity and Dispersion Surfaces	633
12.4.3	Energies of Bloch Waves in a Periodic Potential	637
12.4.4	General Two-Beam Dynamical Theory	640
12.5	Essential Difference Between Kinematical and Dynamical Theories	646
12.6	‡ Diffraction Error, $s_{\mathbf{g}}$, in Two-Beam Dynamical Theory	651
12.6.1	Bloch Wave Amplitudes and Diffraction Error	651
12.6.2	Dispersion Surface Construction	653
12.7	Dynamical Diffraction Contrast from Crystal Defects	655
12.7.1	Dynamical Diffraction Contrast Without Absorption	655
12.7.2	‡ * Two-Beam Dynamical Theory of Stacking Fault Contrast	660
12.7.3	Dynamical Diffraction Contrast with Absorption	664
12.8	‡ * Multi-Beam Dynamical Theories of Electron Diffraction	669
	Further Reading	672
	Problems	672
Bibliography	677
Further Reading	677
References and Figures	682

A. Appendix	691
A.1 Indexed Powder Diffraction Patterns	691
A.2 Mass Attenuation Coefficients for Characteristic $K\bar{\alpha}$ X-Rays .	692
A.3 Atomic Form Factors for X-Rays	693
A.4 X-Ray Dispersion Corrections for Anomalous Scattering	697
A.5 Atomic Form Factors for 200 keV Electrons and Procedure for Conversion to Other Voltages	698
A.6 Indexed Single Crystal Diffraction Patterns: fcc, bcc, dc, hcp .	703
A.7 Stereographic Projections	713
A.8 Examples of Fourier Transforms	717
A.9 Debye–Waller Factor from Wave Amplitude	720
A.10 Review of Dislocations	721
A.11 TEM Laboratory Exercises	728
A.11.1 Preliminary – JEOL 2000FX Daily Operation	728
A.11.2 Laboratory 1 – Microscope Procedures and Calibration with Au and MoO_3	732
A.11.3 Laboratory 2 – Diffraction Analysis of θ' Precipitates .	735
A.11.4 Laboratory 3 – Chemical Analysis of θ' Precipitates ..	739
A.11.5 Laboratory 4 – Contrast Analysis of Defects	740
A.12 Fundamental and Derived Constants	742
 Index	 745

In section titles, the asterisk, “*,” denotes a more specialized topic. The double dagger, “‡,” warns of a higher level of mathematics, physics, or crystallography.