

Contents

Foreword	xi
Preface	xiii
Acknowledgements	xvii
1 Crystal Lattices	1
1.1 The Solid State	1
1.2 The Crystal Lattice	5
1.2.1 Two-dimensional Lattices	5
1.2.2 Three-dimensional Lattices	7
1.3 Vectors in Crystallography	10
1.3.1 Geometric Vector Addition and Multiplication	11
1.3.2 Basis Vectors and Coordinates	13
1.3.3 Orthonormal Bases	19
1.3.4 The Scalar Product in an Orthonormal Coordinate System	22
1.3.5 The Vector Product in an Orthonormal Coordinate System	26
1.4 Matrices in Crystallography	28
1.4.1 Matrix Definitions	28
1.4.2 Matrix Operations	30
1.4.3 Matrix Transformations	32
1.4.4 The Determinant of a Matrix	36
1.4.5 The Inverse of a Matrix	41
1.4.6 The Rules of Matrix Algebra	44
1.4.7 The Eigenvectors and Eigenvalues of a Matrix	48
1.5 Coordinate Systems in Crystallography	51
1.5.1 Change of Basis	51
1.5.2 Transformation from the Unit Cell Basis to an Orthonormal Basis	52
1.5.3 Determining Distances and Angles In the Unit Cell	56
1.5.4 Determining the Volume of the Unit Cell	59
1.5.5 Important Identities	62

2	Crystal Symmetry	67
2.1	Symmetry	67
2.2	Symmetry Group Theory	70
2.2.1.	Sets of Symmetry Operations	70
2.2.2.	Symmetry Groups	75
2.3	Point Groups	78
2.3.1.	Molecular Point Symmetry	78
2.3.2.	Matrix Representations of Groups	80
2.3.3.	Character Tables	83
2.3.4.	Lattice and Crystal Point Symmetry. The Hermann-Mauguin Notation.	84
2.3.5.	Stereographic Projections: Crystallographic Point Symmetry Elements.	88
2.3.6.	The 32 Crystallographic Point Groups.	94
2.3.7.	The Symmetry Classification of Crystal Systems.	107
2.4	Space Groups	119
2.4.1.	Translational Symmetry	119
2.4.2.	Crystal Space Symmetry	120
2.4.3.	The Triclinic Space Groups	126
2.4.4.	The Monoclinic Space Groups	128
2.4.5.	The Orthorhombic Space Groups	162
2.4.6.	The Trigonal Space Groups	169
2.4.7.	The Tetragonal Space Groups	175
2.4.8.	The Hexagonal Space Groups	180
2.4.9.	The Cubic Space Groups	184
2.4.10.	General Considerations	189
3	Crystal Diffraction: Theory	195
3.1	Electromagnetic Radiation	195
3.1.1.	The Electric Field.	195
3.1.2.	Waves.	196
3.1.3.	Particles.	199
3.1.4.	Interference.	201
3.2	Diffraction	204
3.2.1.	The Reciprocal Lattice.	209
3.2.2.	X-ray Diffraction: The Diffraction Equation.	225
3.2.3.	X-ray Diffraction: The Electron Density Equation.	238
3.2.4.	X-ray Diffraction: The Spherical Atom Approximation.	249
3.2.5.	Calculating Structure Factors and Electron Density.	257
4	Crystal Diffraction: Experiment	265
4.1	The Sphere of Reflection.	265
4.2	Recording the Diffraction Pattern: Film Methods.	267
4.3	Recording the Diffraction Pattern: Counter Methods.	275
4.3.1.	Serial Detectors	275

4.3.2.	Area Detectors	285
4.4	Determining the Orientation Matrix and Unit Cell.....	289
4.5	Refining the Orientation Matrix and Unit Cell.....	296
4.6	Determining the Bravais Lattice.....	299
4.6.1.	Reduction of the Unit Cell	299
4.6.2.	Searching for Higher Lattice Symmetry.	305
4.6.3.	Symmetry of the Reciprocal Lattice.	309
4.7	The Measurement of Integrated Intensities.....	313
4.7.1.	Reflections	313
4.7.2.	The Integrated Intensity.	315
4.7.3.	Intensities From Serial Detectors	324
4.7.4.	Intensities From Area Detectors	326
4.7.5.	Limits to the Collection of Intensity Data	329
5	Crystal Diffraction: Data	339
5.1	Experimental Error	339
5.1.1.	Random Error	340
5.1.2.	Systematic Error	378
5.2	Scaling the Intensity Data.....	465
5.3	Determining the Space Group.....	471
5.3.1.	Systematic Absences	472
5.3.2.	Intensity Statistics	478
6	Crystal Structure Solution: Experimental	497
6.1	The Patterson Function.....	497
6.1.1.	Patterson Solution: Structures Without Heavy Atoms.	506
6.1.2.	Patterson Solution: Structures With Heavy Atoms.	515
6.1.3.	Patterson Solution: Search Methods.	527
6.2	Other Experimental Methods	537
6.2.1.	The Isomorphous Replacement Method	537
6.2.2.	The Anomalous Dispersion Method	545
6.3	Completion of the Structural Solution: Fourier Methods.....	549
6.3.1.	Electron Density Synthesis	550
6.3.2.	Difference Electron Density Synthesis	557
6.3.3.	The Completion of Macromolecular Structures	565
7	Crystal Structure Solution: Statistical	571
7.1	Direct Methods	571
7.1.1.	Probability Methods: Structure Invariants	573
7.1.2.	Probability Methods: Initial Phases	600
7.1.3.	Probability Methods: Solving the Structure	621
7.2	Other Direct Methods.....	662
7.2.1.	Dual-Space Iteration	663
7.2.2.	Maximum Entropy	664
7.3	Completion of the Structural Solution: Probability Methods.....	665
7.3.1.	Phases from Fourier Structure Factors	666
7.3.2.	Phases from Difference Fourier Structure Factors	669

8	Crystal Structure Refinement	673
	8.1 Linear Least Squares	673
	8.1.1. Weighted Least Squares	678
	8.1.2. Estimation of Parameter Errors	679
	8.1.3. Constrained Least Squares	688
	8.1.4. Restrained Least Squares	692
	8.2 Non-linear Least Squares: Structure Refinement	693
	8.2.1. Weights in Refinement	698
	8.2.2. Estimation of Parameter Errors in Refinement	703
	8.2.3. Refinement Figures of Merit	708
	8.2.4. Constrained Refinement	710
	8.2.5. Restrained Refinement	722
	8.2.6. The Refinement of Twinned Structures	724
	8.2.7. The Refinement of Chiral Structures	726
	8.3 Macromolecular Refinement	729
	8.3.1. Heavy Atom Solutions	729
	8.3.2. Molecular Replacement Solutions	732
	8.3.3. Completion of the Model	734
	8.3.4. Refinement of the Model	737
	 Appendix	
A	A Geometric Derivation of Bragg's Law	747
B	The Fourier Transform: Electron Density & The Structure Factor	749
C	Determination of the Phase Parameter in the Amplitude Reflectivity Ratio	753
D	Reflection From a Single Plane	755
E	A Discussion of Kinematical Models for Extinction	763
F	Probability Integrals: The Modified Bessel Function	767
G	Monte Carlo Optimization – A Simple Example	773
H	Constrained Optimization	777
I	Taylor Series	787
	Bibliography	789
	Index	801