

Contents

1	Introduction	1
2	Crystal Lattices	3
2.1	The Lattice	3
2.1.1	The Unit Cell	4
2.1.2	Atom Parameters	5
2.1.3	The Seven Crystal Systems	6
2.2	The Fourteen Bravais Lattices	7
2.2.1	The Hexagonal, Trigonal and Rhombohedral Systems	8
2.2.2	The Reduced Cell	9
3	The Geometry of X-Ray Diffraction	13
3.1	X-Rays	13
3.2	Interference by a One-Dimensional Lattice	16
3.3	The Laue Equations	18
3.4	Lattice Planes and hkl -Indices	20
3.5	The Bragg Equation	22
3.6	Higher Orders of Diffraction	23
3.7	The Quadratic Form of the Bragg Equation	23
4	The Reciprocal Lattice	27
4.1	From the Direct to the Reciprocal Lattice	27
4.2	The Ewald Construction	30
5	Structure Factors	33
5.1	Atom Formfactors	33
5.2	Atom Displacement Factors	35
5.3	Structure Factors	37
6	Crystal Symmetry	41
6.1	Simple Symmetry Elements	41
6.1.1	Coupling of Symmetry Elements	42
6.1.2	Combination of Symmetry Elements	44
6.2	Symmetry Directions	44

6.3	Symmetry Elements Involving Translation	46
6.3.1	Combination of Translation with Other Symmetry Elements	46
6.3.2	Coupling of Translation with Other Symmetry Elements	46
6.4	The 230 Space Groups	52
6.4.1	Space-group Notation in International Tables for Crystallography	52
6.4.2	Centrosymmetric Crystal Structures	55
6.4.3	The Asymmetric Unit	56
6.4.4	Space Group Types	57
6.4.5	Group-Subgroup Relationships	57
6.5	Visible Effects of Symmetry	58
6.5.1	Microscopic Structure	58
6.5.2	Macroscopic Properties and Crystal Classes	59
6.5.3	Symmetry of the Lattice	59
6.5.4	Symmetry of the Diffraction Pattern — The Laue Groups	59
6.6	Determination of the Space Group	61
6.6.1	Determination of the Laue Group	61
6.6.2	Systematic Absences	62
6.7	Transformations	65
7	Experimental Methods	67
7.1	Growth, Choice and Mounting of a Single Crystal	67
7.2	Measuring the Diffraction Pattern of Single Crystals	71
7.2.1	Film Methods	71
7.2.2	The Four-circle (serial) Diffractometer	74
7.2.3	Reflection profile and scan type	78
7.3	Area Detector Systems	81
7.4	Data Reduction	86
7.4.1	<i>Lp</i> correction	86
7.4.2	Standard Uncertainty	87
7.4.3	Absorption Correction	89
7.5	Other Diffraction Methods	91
7.5.1	Neutron Scattering	91
7.5.2	Electron Scattering	92
8	Structure Solution	93
8.1	Fourier Transforms	93
8.2	Patterson Methods	95
8.2.1	Symmetry in Patterson Space	97
8.2.2	Structure Solution Using Harker Peaks	97
8.2.3	Patterson shift methods	99
8.3	Direct Methods	100
8.3.1	Harker-Kasper Inequalities	100
8.3.2	Normalized Structure Factors	101
8.3.3	The Sayre Equation	102

8.3.4	The Triplet Relationship	103
8.3.5	Origin Fixation	105
8.3.6	Strategies of Phase Determination	106
9	Structure Refinement	111
9.1	The Method of Least Squares	111
9.1.1	Refinement Based on F_0 or F_0^2 Data	115
9.2	Weights	116
9.3	Crystallographic <i>R</i> -Values	118
9.4	Refinement Techniques	119
9.4.1	Location and Treatment of Hydrogen Atoms	120
9.4.2	Restricted Refinement	121
9.4.3	Damping	122
9.4.4	Symmetry Restrictions	122
9.4.5	Residual Electron Density	123
9.5	Rietveld Refinement	124
10	Additional Topics	127
10.1	Disorder	127
10.1.1	Site Occupancy Disorder	127
10.1.2	Positional and Orientational Disorder	128
10.1.3	One- and Two-Dimensional Disorder	130
10.1.4	Modulated Structures	131
10.1.5	Quasicrystals	131
10.2	Anomalous Dispersion and “Absolute Structure”	132
10.2.1	Chiral and Polar Space Groups	137
10.3	Extinction	139
10.4	The Renninger Effect	141
10.5	The $\lambda/2$ -Effect	142
10.6	Thermal Diffuse Scattering (TDS)	143
11	Errors and Pitfalls	145
11.1	Wrong Atom-Types	145
11.2	Twinning	146
11.2.1	Classification by the Twin-Element	147
11.2.2	Classification According to Macroscopic Appearance	147
11.2.3	Classification According to Origin	148
11.2.4	Diffraction Patterns of Twinned Crystals and their Interpretation	149
11.2.5	Twinning or Disorder?	155
11.3	False Unit Cells	155
11.4	Space Group Errors	156
11.5	Misplaced Origins	158
11.6	Poor Atom Displacement Parameters	159

12 Interpretation and Presentation of Results	161
12.1 Bond Lengths and Bond Angles	161
12.2 Best Planes and Torsion Angles	162
12.3 Structural Geometry and Symmetry	163
12.4 Structural Diagrams	165
12.5 Electron Density	169
13 Crystallographic Databases	171
13.1 The Inorganic Crystal Structure Database (ICSD)	171
13.2 The Cambridge Structural Database (CSD)	171
13.3 The Metals Crystallographic Data File (CRYST-MET)	175
13.4 Other Collections of Crystal Structure Data	175
13.5 Deposition of Structural Data in Data Bases	175
13.6 Crystallography on the Internet	176
14 Outline of a Crystal Structure Determination	177
15 Worked Example of a Structure Determination	181
Bibliography	199
Index	205