

Contents

1	Theoretical Basis	1
1.1	Matrices, Vectors	1
1.1.1	Introduction	1
1.1.2	Matrices, Determinants, Linear Equations	1
1.1.3	Vector Algebra	10
1.1.4	Linear Independency, Bases, Reciprocal Bases	17
1.1.5	Basis Transformations	25
1.1.6	Lines and Planes	29
1.2	Fundamental Results of Diffraction Theory	40
1.2.1	Fourier Transforms and Convolution Operations	41
1.2.2	Electron Density and Related Functions	45
1.2.3	Diffraction Conditions for Single Crystals	48
2	Preliminary Experiments	52
2.1	Film Methods	52
2.1.1	The Rotation Method	52
2.1.2	Zero Level Weissenberg and Normal Beam Method	56
2.1.3	Upper Level Weissenberg – Equi-Inclination Method	62
2.1.4	Precession and de Jong-Bouman Technique	66
2.2	X-Rays	80
2.2.1	Generation of X-Rays	80
2.2.2	Absorption	85
2.2.3	X-Ray Tubes	91
2.3	Practicing Film Techniques	94
2.3.1	Choice of Experimental Conditions	94
2.3.2	Rotation and Weissenberg Photographs of KAMTRA and SUCROS	99
2.3.3	De Jong-Bouman and Precession Photographs of NITROS and SUCROS	105
3	Crystal Symmetry	111
3.1	Symmetry Operations in a Crystal Lattice	111
3.1.1	Introduction	111
3.1.2	Basic Symmetry Operations	113
3.1.3	Crystal Classes and Related Coordinate Systems	116
3.1.4	Translational Symmetry, Lattice Types and Space Groups	129

3.2	Crystal Symmetry and Related Intensity Symmetry	148
3.2.1	Representation of ρ and F as Fourier Series	148
3.2.2	Intensity Symmetry, Asymmetric Unit	153
3.2.3	Systematic Extinctions	158
3.3	Space Group Determination	160
3.3.1	General Rules	160
3.3.2	Space Group of KAMTRA	163
3.3.3	Space Group of NITROS	168
3.3.4	Space Group of SUCROS	172
4	Diffractometer Measurements	176
4.1	Main Characteristics of a Four-Circle Diffractometer	176
4.1.1	Eulerian Cradle Geometry	178
4.1.2	X-Ray Source, Detector and Controlware	183
4.2	Single Crystal Measurements	188
4.2.1	Choice of Experimental Conditions	188
4.2.2	Precise Determination of Lattice Constants	192
4.2.3	Intensity Measurement	196
5	Solution of the Phase Problem	205
5.1	Preparation of the Intensity Data	205
5.1.1	Data Reduction	206
5.1.2	Normalization	209
5.2	Fourier Methods	216
5.2.1	Interpretation of the Patterson Function	216
5.2.2	Heavy Atom Method, Principle of Difference Electron Density	217
5.2.3	Harker Sections	221
5.2.4	Numerical Calculation of Fourier Syntheses	223
5.2.5	Application of Heavy Atom Method to KAMTRA	227
5.3	Direct Methods	229
5.3.1	Fundamental Formulae	230
5.3.2	Origin Definition, Choice of Starting Set	236
5.3.3	Sign Determination for NITROS – An Example of the Centric Case	253
5.3.4	Phase Determination for SUCROS – An Example of the Acentric Case	262
6	Refinement	267
6.1	Theoretical Aspects	267
6.1.1	F_c -Calculation, Residual Index	267
6.1.2	Theory of Least-Squares Refinement	268
6.2	Practising Least-Squares Methods	275
6.2.1	Aspects of Numerical Calculations	275

3.2 Crystal Symmetry and Related Intensity Symmetry	148
3.2.1 Representation of ρ and F as Fourier Series	148
3.2.2 Intensity Symmetry, Asymmetric Unit	153
3.2.3 Systematic Extinctions	158
3.3 Space Group Determination	160
3.3.1 General Rules	160
3.3.2 Space Group of KAMTRA	163
3.3.3 Space Group of NITROS	168
3.3.4 Space Group of SUCROS	172
4 Diffractometer Measurements	176
4.1 Main Characteristics of a Four-Circle Diffractometer	176
4.1.1 Eulerian Cradle Geometry	178
4.1.2 X-Ray Source, Detector and Controlware	183
4.2 Single Crystal Measurements	188
4.2.1 Choice of Experimental Conditions	188
4.2.2 Precise Determination of Lattice Constants	192
4.2.3 Intensity Measurement	196
5 Solution of the Phase Problem	205
5.1 Preparation of the Intensity Data	205
5.1.1 Data Reduction	206
5.1.2 Normalization	209
5.2 Fourier Methods	216
5.2.1 Interpretation of the Patterson Function	216
5.2.2 Heavy Atom Method, Principle of Difference Electron Density ..	217
5.2.3 Harker Sections	221
5.2.4 Numerical Calculation of Fourier Syntheses	223
5.2.5 Application of Heavy Atom Method to KAMTRA	227
5.3 Direct Methods	229
5.3.1 Fundamental Formulae	230
5.3.2 Origin Definition, Choice of Starting Set	236
5.3.3 Sign Determination for NITROS – An Example of the Centric Case	253
5.3.4 Phase Determination for SUCROS – An Example of the Acentric Case	262
6 Refinement	267
6.1 Theoretical Aspects	267
6.1.1 F_c -Calculation, Residual Index	267
6.1.2 Theory of Least-Squares Refinement	268
6.2 Practising Least-Squares Methods	275
6.2.1 Aspects of Numerical Calculations	275

6.2.2 Execution of a Complete Refinement Process	277
6.2.3 Corrections to be Applied During Refinement	278
6.3 Analysis and Representation of Results	284
6.3.1 Geometrical Data	284
6.3.2 Graphical Representations	288
6.4 Applications to the Test Structures	292
6.4.1 Completion and Refinement of the KAMTRA Structure	292
6.4.2 NITROS Refinement with Extinction Correction	298
6.4.3 SUCROS – Refinement and the Problem of Enantiomorphy	300
1.1.1 Introduction	303
Index	303

The first part of this chapter is concerned with some mathematics which will be used in the later chapters of this book. We assume that the fundamentals of arithmetic and of integral and differential calculus are well-known to the reader, but students of chemistry often have difficulties with the theory of vector and matrix algebra. Since we will make frequent use of these mathematical formalisms, the most important properties of vectors and matrices are briefly discussed.

1.1.2 Matrices, Determinants, Linear Equations

A rectangular array, A , arranged in the form

$$A = \begin{pmatrix} a_{11} & a_{12} & a_{13} & \dots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \dots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \dots & a_{3n} \\ \dots & \dots & \dots & \dots & \dots \\ a_{m1} & a_{m2} & a_{m3} & \dots & a_{mn} \end{pmatrix}$$

is called a matrix. The elements a_{jk} can be arbitrary numbers. If the number of rows is m and the number of columns is n , the matrix is said to be of the order $m \times n$. If $m = n$ the matrix is called a square matrix of order n . The index j of the element a_{jk} indicates its row and the index k the corresponding column. As will be shown in the next chapter, the matrix formalism is a very convenient way to describe vector operations, vector transformations and it provides a very elegant method for solving linear equations.

The introduction of matrices requires a knowledge of matrix algebra. First, we define the basic arithmetic operations of matrices.

The equality of matrices. Two matrices are said to be of equal type if their numbers of rows and columns are equal. Two matrices are equal, if they are of equal type and if all elements in corresponding rows and columns are equal.

Example:

(a) The matrices