

Essentials of CRYSTALLOGRAPHY

M.A. Wahab



Alpha
Science

Essentials of CRYSTALLOGRAPHY

M. A. Wahab



Alpha Science International Ltd.
Oxford, U.K.

**Essentials of
CRYSTALLOGRAPHY**

332 pgs. | 228 figs. | 48 tbls.

M. A. Wahab

Department of Physics

Jamia Millia Islamia (Central University)

New Delhi, India

Copyright © 2009

ALPHA SCIENCE INTERNATIONAL LTD.

7200 The Quorum, Oxford Business Park North
Garsington Road, Oxford OX4 2JZ, U.K.

www.alphasci.com

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the publisher.

ISBN 978-1-84265-392-0

Printed in India

Essentials of
CRYSTALLOGRAPHY

PREFACE

As the name indicates this book contains the essential topics needed to understand the crystals from macroscopic and microscopic point of view and the mode of their growth, structure determination and structural refinements from experimental and theoretical point of view. The aim of the present book is to provide a comprehensive introduction to the subject of crystallography in a simplified manner to the students of M.Sc, M.Phil, and Ph.D of Physical, Chemical, Biological, Materials, Engineering Sciences and Faculties in this field. The subject of crystallography is conceptual and imaginative and the students generally find it relatively difficult. However, the author with all his experience in the field and hard work has successfully made it easy for them to understand.

This book contains a total of fourteen chapters, out of which initial seven chapters deal with the basic aspects of crystallography. They include the development of space lattices, description of macroscopic and microscopic symmetries exhibited by crystalline solids and simplified approach to understand the derivation of point groups and space groups. The chapter number eight particularly deals with the basics of theory and experiments of crystal growth while the chapter number nine deals with the imperfections normally encountered in crystalline solids. The chapter number ten deals with the diffraction methods based on both film and counter techniques and for date collection. The last four chapters deal with topics related to crystal structure analyses they are: factors affecting x-ray intensities, structure factors and fourier synthesis,(where the concepts of structure factor have been developed using optical analogue), and important methods of crystal structure analysis and refinements.

The main features of the book are:

1. Solved examples for a better understanding of the text.
2. Matrix representation of symmetry elements and derivation of point group by simple matrix multiplication.
3. Summary and definitions of important terms at the end of each chapter for quick revision.
4. Problems and exercises.

Although proper care has been taken during the preparation of the manuscript, still some errors are expected to creep in. Any omissions, errors, suggestions brought to the knowledge of the author will be gratefully acknowledged.

First of all I sincerely thank our Vice Chancellor Prof. Musheerul Hasan for providing me the timely needed sabbatical leave. This indeed helped me in completing the MS in time. I sincerely express my sense of gratitude to my Research guide, Prof. G.C. Trigunayat, former Head, Deptt. of

Physics, Delhi University. I also thank colleagues of J.M.I from different departments for their encouragement.

I am indeed grateful to all the authors and publishers of Books and Journals mentioned in the bibliography for freely consulting them and even borrowing some ideas during the preparation of the manuscript. I am also grateful to M/s Narosa Publishing House, New Delhi for timely publication of this book.

My special thanks to the members of my family for their continuous support and encouragement during the preparation of the manuscript. I particularly thank my wife Mrs. Raees Begum for making a fair draft of the entire manuscript.

M.A. Wahab

CONTENTS

<i>Preface</i>	v
1. Bravais Lattice in Two Dimensions	1
1.1 Introduction	1
1.2 Development of One and Two Dimensional Lattices	2
1.3 Basis and the Crystal Structure	3
1.4 Choice of a Unit Cell	4
1.5 Wigner-Seitz Unit Cell	4
1.6 Primitive Lattice Types and Crystal Systems	6
1.7 Centering of Plane Lattices	8
1. Oblique Lattice	8
2. Rectangular Lattice	9
3. Square and Hexagonal Lattices	9
1.8 Two Dimensional Bravais Lattices (Plane Lattices)	10
1.9 Unit Cell Calculations	10
Distance between Two Lattice Points (Oblique System)	10
Linear and Planar Atomic Density	12
Planar Packing Efficiency	13
1.10 Summary	14
1.11 Definitions	14
<i>Review Questions and Problems</i>	15
2. Bravais Lattices in Three Dimensions	16
2.1 Introduction	16
2.2 Development of Three-dimensional Lattices	16
2.3 Choice of Axes and Unit Cells	17
2.4 Derivation of Seven Primitive Lattices/Unit Cells	19
(i) Oblique Lattice	19
(ii) Rectangular Lattice	19

(iii) Square Lattice	19
(iv) Rhombic Lattice	21
(v) Hexagonal Lattice	21
2.5 Types of Lattice Centering	21
1. Body Centering (I)	21
2. Face Centering (F)	22
3. Base Centering ($A-$, $B-$, $C-$)	22
4. Rhombohedral Centering	23
2.6 Derivation of Non-primitive (Centered) Lattices	25
Monoclinic System	26
Orthorhombic System	27
Tetragonal System	29
Cubic System	29
2.7 Number of Lattice Points Per Unit Cell	30
2.8 Fractional Coordinates (Oblique System)	30
2.9 Unit Cell Calculations	31
1. Volume of the Unit Cell	31
2. Distance Between Two Lattice Points (Oblique System)	32
3. Linear, Planar and Volume Atomic Density in Crystals	35
4. Volume Packing Efficiency	36
2.10 Interplanar Spacing	37
2.11 Summary	39
2.12 Definitions	39
<i>Review Questions and Problems</i>	39
3. Symmetry Elements in Two Dimensions	41
3.1 Introduction	41
3.2 Symmetry Elements	41
1. Translation	42
2. Proper Rotation	42
3. Reflection (Mirror Line)	43
3.3 Consistent Combinations of Symmetry Operations	43
3.4 Combination of Macroscopic Symmetry Operations	44
(i) Rotation with a Translation t	44
(ii) Rotation and Reflection (Two Reflections)	44
3.5 Point Groups in Two Dimensions	46
3.6 Plane Lattice Consistent with Rotational Symmetry	47
3.7 Plane Lattice Consistent with Mirror Symmetry	54

3.8	Combination of Microscopic Symmetry Operation	55
3.9	Space Group in Two Dimensions (Plane Groups)	55
3.10	Summary	57
3.11	Definitions	58
	<i>Review Questions and Problems</i>	59
4.	Symmetry Elements in Three Dimensions	60
4.1	Introduction	60
4.2	Symmetry Elements	60
4.3	Macroscopic Symmetry Elements	62
4.4	Combinations of Macroscopic Symmetry Operations	62
4.5	Rotation at a Point	62
4.6	Axial Combinations (Two Proper Rotations)	64
4.7	Rotation and Reflection (Rotoreflexion)	67
4.8	Rotation and Inversion (Rotoinversion)	68
4.9	Proper and Improper Rotations	69
	(a) Monoaxial Combinations	70
	(b) Polyaxial Combinations	70
	(c) Coexistence of Proper and Improper Polyaxials	72
4.10	Reflection and Inversion	73
4.11	Classification of Symmetry Operations	76
4.12	Summary	76
4.13	Definitions	77
	<i>Review Questions and Problems</i>	77
5.	Derivation of Point Groups	79
5.1	Introduction	79
5.2	Derivation of Point Groups (Conventional Method)	79
	Rotoreflexion Channel	79
	1. Proper Rotation: X	80
	2. Reflection (Mirror Plane): m	80
	3. Rotoreflexion (\equiv Rotoinversion): \tilde{X}	80
	4. Axial Combinations: XXX	80
	5. Mirror \perp to Rotation Axis: $\frac{X}{m}$	80
	6. Mirror \parallel to Rotation Axis: Xm	81

7. Mirror \perp to Axial Combinations: $\frac{XXX}{m}$	81
8. Mirror \parallel to Axial combinations: $XXXm$	81
Rotoinversion Channel	81
5.3 Point Group Notations	83
Schoenflies Notation	85
Hermann-Mauguin (International) Notation	87
5.4 Linear Orthogonal Transformation	88
5.5 Symmetry Operations and Group Theory	90
Group	90
Order of the Group	91
Cyclic Group	92
Generators of a Finite Group	92
Subgroups and Super Groups	92
5.6 Matrix Representation of Symmetry Operations	92
(i) Orthogonal Axes	93
(ii) Crystallographic Axes	96
5.7 Derivation of Point Group (Matrix Method)	97
1. Triclinic Crystal System	97
2. Monoclinic Crystal System	98
3. Orthorhombic Crystal System	99
4. Tetragonal Crystal System	100
5. Trigonal Crystal System	102
6. Hexagonal Crystal System	104
7. Cubic Crystal System	104
5.8 Equivalent Positions in Point Groups	105
5.9 Laue Symmetry	107
5.10 Point Groups, Crystal Classes and Crystal Systems	107
5.11 Summary	108
5.12 Definitions	109
<i>Review Questions and Problems</i>	110
<i>Appendix 1</i>	112
<i>Appendix 2</i>	112
6. Derivation of Space Groups	114
6.1 Introduction	114
6.2 Microscopic Symmetry Elements	114

6.3	Combination of Microscopic Symmetry Operations	114
	Glide Planes	114
	Axial Glide	115
	Diagonal Glide	115
	Diamond Glide	116
	Screw Axes	116
6.4	General Equivalent Positions and Special Positions	117
6.5	Systematic Absences	119
	Systematic Absences Due to Lattice Centering	119
	Systematic Absences Due to Microscopic Symmetries	119
6.6	Space Groups	121
6.7	Classification of Space Groups	121
	The Symmorphic Space Groups	121
	The Non-Symmorphic Space Groups	122
6.8	Derivation of Space Groups	122
	Triclinic Crystal System	123
	Monoclinic Crystal System	123
	Orthorhombic Crystal System	123
	Tetragonal Crystal System	123
	Trigonal Crystal System	125
	Hexagonal Crystal System	125
	Cubic Crystal System	125
6.9	Summary	125
6.10	Definitions	125
	<i>Review Questions and Problems</i>	126
7.	Crystal Planes, Directions and Projections	127
7.1	Crystal Planes and Zones	127
7.2	Crystal Directions and Zone Axes	128
	1. The Zone Law	130
	2. Zone Axis at the Intersection of two Planes	130
	3. Plane parallel to Two Directions	130
	4. The Addition Rule	131
7.3	Miller-Bravais Indices	131
7.4	Transformation of Indices	132
	Transformation of Indices of Crystal Planes (Unit Cell)	133
	(i) Rhombohedral and FCC	133
	(ii) Hexagonal and Orthorhombic	134
	(iii) Rhombohedral and Hexagonal	135

Transformation of Indices of Direction (Zone Axes)	137
Hexagonal (4-index System) and Trigonal (3-index System)	137
7.5 Crystal Projections	138
(i) Projection of Atoms/ions in the Unit Cell	138
(ii) Projection of Crystal Faces (Miller Planes)	139
Spherical Projection	140
Gnomonic Projection	141
Stereographic Projection	141
7.6 The Reciprocal Lattice	142
Some Geometrical Relationships	145
1. The Zone Law	145
2. Zone Axis at the Intersection of Two Planes	146
3. A Plane (hkl) Containing Two Directions $[u_1v_1w_1]$ and $[u_2v_2w_2]$	146
7.7 Summary	147
7.8 Definitions	148
<i>Review Questions and Problems</i>	149
8. Experiment and Theory of Crystal Growth	150
8.1 Introduction	150
8.2 Methods of Crystal Growth	150
8.3 Solution Growth	151
(a) Aqueous Solution Method	152
(b) Flux Method	152
(c) Hydrothermal Method	154
8.4 Melt growth	157
(a) Bridgman–Stockbarger Method	157
(b) Czochralski Method	158
(c) Zone Refining Method	160
(d) Float Zone Method	161
8.5 Nucleation	161
8.6 Energy of Formation of a Nucleus	162
(i) Homogeneous Nucleation	162
(ii) Hetrogeneous Nucleation	167
Cap Shaped Nucleus	167
Disc-shaped (Cylindrical) Nucleus	169
8.7 Velocity of Growth	170
8.8 Theories/Model of Crystal Growth	172

8.9	Theories Based on Atomic Model	172
1.	Kossel's Theory	172
2.	Screw Dislocation Theory	174
8.10	Theories Based on Thermodynamics Considerations	175
1.	The Diffusion Theory	175
2.	Bulk Diffusion Model	178
3.	BCF Bulk Diffusion Model	179
(i)	Hemi-Spherical Force Field	180
(ii)	Semi-Cylindrical Force Field	181
(iii)	Plane Force Field	182
8.11	Concentration of Kinks and Mobility of Adsorbed Molecules	184
8.12	Summary	185
8.13	Definitions	186
	<i>Review Questions and Problems</i>	186
9.	Crystal Imperfections	188
9.1	Introduction	188
9.2	Concentration of Point Imperfections	188
	Schottky Imperfection (Monoatomic Solid)	188
	Frenkel Imperfection (Monoatomic Solid)	190
	Schottky Imperfection (Ionic solid)	191
9.3	The Geometry of Dislocations	192
9.4	Burgers Vector and Burgers Circuit	193
9.5	Energy of A Dislocation	194
9.6	Slip Planes and Slip Directions	196
9.7	Dislocation Reactions	196
9.8	Density of Dislocations	199
9.9	Observation of Dislocations	200
(a)	Method Based on Growth Spirals	200
(b)	Method Based on Etch Pits	200
(c)	Optical and Electron-Optical Methods	201
(d)	Decoration Method	201
(e)	X-ray Diffraction Topography	201
9.10	Surface Imperfections	203
	Grain Boundary	203
	Tilt and Twist Boundary	203
	Stacking Faults	205
(i)	Stacking Faults in FCC Crystals	205
(ii)	Stacking Faults in HCP Crystals	206

9.11	Summary	208
9.12	Definitions	208
	<i>Review Questions and Problems</i>	210
10.	Diffraction Methods	212
10.1	Introduction	212
10.2	Production of <i>X</i> -rays	212
10.3	<i>X</i> -ray Diffraction	215
	Bragg's Law	215
	The Laue Equations	217
10.4	Diffraction Condition and Bragg's Law	220
10.5	The <i>X</i> -ray Diffraction Experiments	222
10.6	The Powder Method	222
	Indexing of Powder Lines	223
10.7	The Laue Method	227
	Indexing of Laue Photographs	228
10.8	The Rotation/Oscillation Method	230
	Interpretation of Rotation/Oscillation Photographs (Formation of Layer Lines)	231
	Indexing of Rotation/Oscillation Photographs	233
10.9	The Weissenberg Method	236
	Equi-inclination Setting	241
	Indexing of Weissenberg Photographs	242
10.10	The Precession Method	246
10.11	<i>X</i> -ray Diffractometers	247
	Powder <i>X</i> -ray Diffractometer	248
	Single Crystal <i>X</i> -ray Diffractometer	248
10.12	Other Diffraction Methods	250
	Neutron Diffraction	250
	Electron Diffraction	252
10.13	Summary	253
10.14	Definitions	255
	<i>Review Questions and Problems</i>	255
11.	Factors Affecting <i>X</i>-ray Intensities	258
11.1	Introduction	258
11.2	The Structure Factor	258
11.3	The Lorentz Factor	260
11.4	The Polarization Factor	262

11.5	The Temperature Factor	264
11.6	The Multiplicity Factor	264
11.7	The Absorption Factor	265
11.8	Extinction	266
11.9	The <i>R</i> -Factor	268
11.10	Summary	268
11.11	Definitions	269
	<i>Review Questions and Problems</i>	270
12.	Structure Factors and Fourier Synthesis	272
12.1	Introduction	272
12.2	Waves Motion	272
12.3	Superposition of Waves	273
12.4	Phase of a Wave in Three Dimensions (Unit Cell)	275
12.5	The Structure Factor of a Crystal	276
12.6	The Fourier Synthesis	277
12.7	Special Structure Factors Due to Symmetry	279
	Case I: Center of Symmetry	280
	Case II: 2-fold Rotation (<i>z</i> -axis)	280
	Case III: $m \perp z$ -axis	280
	Case IV: 2-fold Screw Axis Along [001], 2_1	281
	Case V: <i>a</i> -glide Oriented Along [010]	281
12.8	Special Structure Factors Due to Lattice Centering	282
	Case I: Body Centering in a Cubic Lattice	282
	Case II: Face Centering in a Cubic Lattice	283
12.9	Anomalous Scattering	284
12.10	Summary	285
12.11	Definitions	286
	<i>Review Questions and Problems</i>	287
13.	Crystal Structure Analysis	289
13.1	Introduction	289
13.2	Trial and Error Method	289
13.3	The Patterson Function	290
13.4	The Heavy Atom Method	292
13.5	Isomorphous Replacement	293
13.6	Superposition Method	294
13.7	Direct Methods	294
	Inequality Relationship	295

Case I. Center of Symmetry	296
Case II. 2-fold Axis (\parallel to z)	297
Statistical Method	297
13.8 Summary	299
13.9 Definitions	299
<i>Review Questions and Problems</i>	300
14. Crystal Structure Refinements	301
14.1 Introduction	301
14.2 Successive Fourier Syntheses	301
14.3 Difference Fourier Synthesis	302
(i) Position Error	303
(ii) Missing Atoms	303
(iii) Errors in the Thermal Parameters	304
14.4 Least-Squares Refinement	305
14.5 Constrained Least-Squares Refinement	307
14.6 Automation of Structure Analysis	307
14.7 Summary	309
14.8 Definitions	309
<i>Review Questions and Problems</i>	310
<i>Bibliography</i>	311
<i>Subject Index</i>	313

BRAVAIS LATTICE IN TWO DIMENSIONS

1.1 INTRODUCTION

From our everyday experience, we are familiar with a one dimensional iron chain and two dimensional periodic patterns as in wall papers (Fig. 1.1) and fabrics etc. We find a large variety in design by changing both the forms of the basic motif (or unit of pattern) and the spacing of its periodic repetition. To analyse the nature of the given pattern, a single motif is selected such that the pattern could be obtained by two periodic transformations in two non collinear directions. Thus the essential features of the given pattern are specified by two non parallel translation vectors. Replacing each motif in the pattern with a point, a periodic pattern of points defined by the same translation

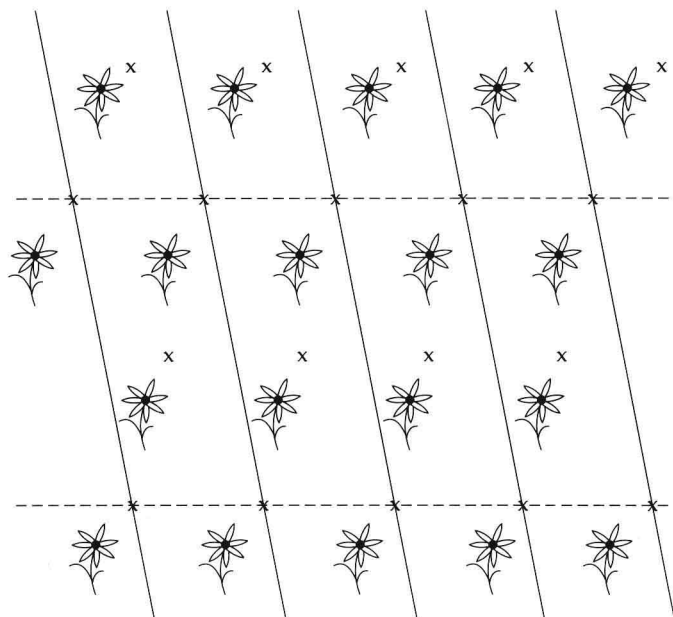


Fig. 1.1 A two dimensional periodic pattern