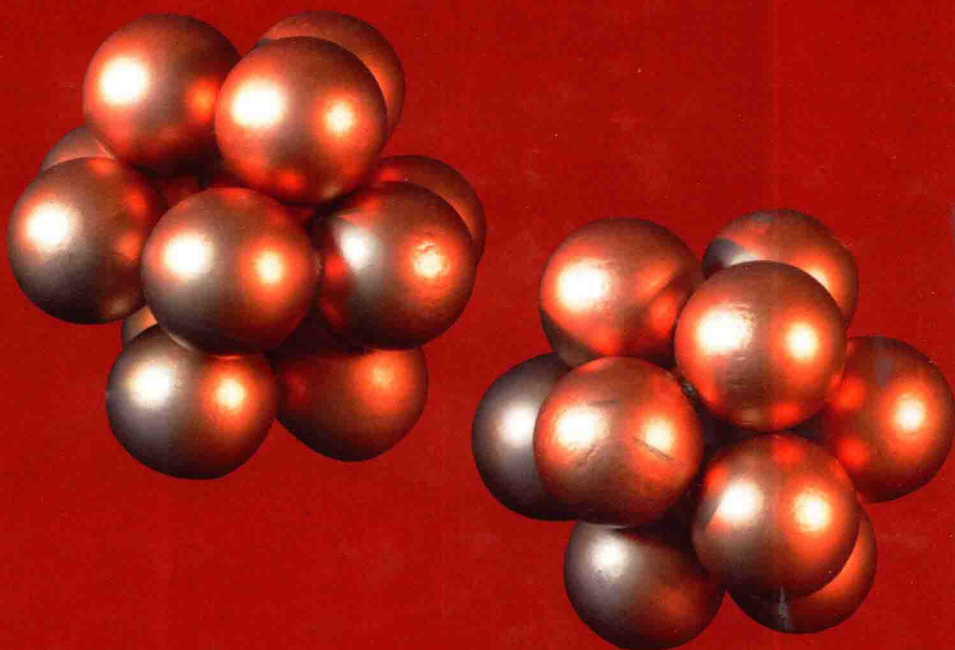


IUCr TEXTS ON CRYSTALLOGRAPHY • 21

# The Basics of Crystallography and Diffraction

Fourth Edition

CHRISTOPHER HAMMOND



INTERNATIONAL UNION OF CRYSTALLOGRAPHY  
OXFORD SCIENCE PUBLICATIONS



# The Basics of Crystallography and Diffraction

## Fourth Edition

---

Christopher Hammond

*University of Leeds*

INTERNATIONAL UNION OF CRYSTALLOGRAPHY

**OXFORD**

UNIVERSITY PRESS

**OXFORD**  
UNIVERSITY PRESS

Great Clarendon Street, Oxford, OX2 6DP,  
United Kingdom

Oxford University Press is a department of the University of Oxford.  
It furthers the University's objective of excellence in research, scholarship,  
and education by publishing worldwide. Oxford is a registered trade mark of  
Oxford University Press in the UK and in certain other countries

© Christopher Hammond 2015

The moral rights of the author have been asserted

First Edition published in 1997  
Second Edition published in 2001  
Third Edition published in 2009  
Fourth Edition published in 2015

Impression: 1

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, without the  
prior permission in writing of Oxford University Press, or as expressly permitted  
by law, by licence or under terms agreed with the appropriate reprographics  
rights organization. Enquiries concerning reproduction outside the scope of the  
above should be sent to the Rights Department, Oxford University Press, at the  
address above

You must not circulate this work in any other form  
and you must impose this same condition on any acquirer

Published in the United States of America by Oxford University Press  
198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data  
Data available

Library of Congress Control Number: 2015930096

ISBN 978-0-19-873867-1 (hbk.)  
ISBN 978-0-19-873868-8 (pbk.)

Printed and bound by  
CPI Group (UK) Ltd, Croydon, CR0 4YY

Links to third party websites are provided by Oxford in good faith and  
for information only. Oxford disclaims any responsibility for the materials  
contained in any third party website referenced in this work.

INTERNATIONAL UNION OF CRYSTALLOGRAPHY  
BOOK SERIES

---

IUCr BOOK SERIES COMMITTEE

Ch. Baerlocher, *Switzerland*  
G. Chapuis, *Switzerland*  
P. Colman, *Australia*  
J. R. Helliwell, *UK*  
K.A. Kantardjieff, *USA*  
T. Mak, *China*  
P. Müller, *USA*  
Y. Ohashi, *Japan*  
A. Pietraszko, *Poland*  
D. Viterbo (*Chairman*), *Italy*

**IUCr Monographs on Crystallography**

- 1 *Accurate molecular structures*  
A. Domenicano, I. Hargittai, editors
- 2 *P.P. Ewald and his dynamical theory of X-ray diffraction*  
D.W.J. Cruickshank, H.J. Juretschke, N. Kato, editors
- 3 *Electron diffraction techniques, Vol. 1*  
J.M. Cowley, editor
- 4 *Electron diffraction techniques, Vol. 2*  
J.M. Cowley, editor
- 5 *The Rietveld method*  
R.A. Young, editor
- 6 *Introduction to crystallographic statistics*  
U. Shmueli, G.H. Weiss
- 7 *Crystallographic instrumentation*  
L.A. Aslanov, G.V. Fetisov, J.A.K. Howard
- 8 *Direct phasing in crystallography*  
C. Giacovazzo
- 9 *The weak hydrogen bond*  
G.R. Desiraju, T. Steiner
- 10 *Defect and microstructure analysis by diffraction*  
R.L. Snyder, J. Fiala and H.J. Bunge
- 11 *Dynamical theory of X-ray diffraction*  
A. Authier
- 12 *The chemical bond in inorganic chemistry*  
I.D. Brown
- 13 *Structure determination from powder diffraction data*  
W.I.F. David, K. Shankland, L.B. McCusker, Ch. Baerlocher, editors
- 14 *Polymorphism in molecular crystals*  
J. Bernstein
- 15 *Crystallography of modular materials*  
G. Ferraris, E. Makovicky, S. Merlino
- 16 *Diffuse X-ray scattering and models of disorder*  
T.R. Welberry

- 17 *Crystallography of the polymethylene chain: an inquiry into the structure of waxes*  
D.L. Dorset
- 18 *Crystalline molecular complexes and compounds: structure and principles*  
F.H. Herstein
- 19 *Molecular aggregation: structure analysis and molecular simulation of crystals and liquids*  
A. Gavezzotti
- 20 *Aperiodic crystals: from modulated phases to quasicrystals*  
T. Janssen, G. Chapuis, M. de Boissieu
- 21 *Incommensurate crystallography*  
S. van Smaalen
- 22 *Structural crystallography of inorganic oxysalts*  
S.V. Krivovichev
- 23 *The nature of the hydrogen bond: outline of a comprehensive hydrogen bond theory*  
G. Gilli, P. Gilli
- 24 *Macromolecular crystallization and crystal perfection*  
N.E. Chayen, J.R. Helliwell, E.H. Snell
- 25 *Neutron protein crystallography: hydrogen, protons, and hydration in bio-macromolecules*  
N. Niimura, A. Podjarny

#### IUCr Texts on Crystallography

- 1 *The solid state*  
A. Guinier, R. Julien
- 4 *X-ray charge densities and chemical bonding*  
P. Coppens
- 8 *Crystal structure refinement: a crystallographer's guide to SHELXL*  
P. Müller, editor
- 9 *Theories and techniques of crystal structure determination*  
U. Shmueli
- 10 *Advanced structural inorganic chemistry*  
Wai-Kee Li, Gong-Du Zhou, Thomas Mak
- 11 *Diffuse scattering and defect structure simulations: a cook book using the program DISCUS*  
R. B. Neder, T. Proffen
- 13 *Crystal structure analysis: principles and practice, second edition*  
W. Clegg, editor
- 14 *Crystal structure analysis: a primer, third edition*  
J.P. Glusker, K.N. Trueblood
- 15 *Fundamentals of crystallography, third edition*  
C. Giacovazzo, editor
- 16 *Electron crystallography: electron microscopy and electron diffraction*  
X. Zou, S. Hovmöller, P. Oleynikov
- 17 *Symmetry in crystallography: understanding the International Tables*  
P.G. Radaelli
- 18 *Symmetry relationships between crystal structures: applications of crystallographic group theory in crystal chemistry*  
U. Müller
- 19 *Small angle X-ray and neutron scattering from solutions of biological macromolecules*  
D.I. Svergun, M.H.J. Koch, P.A. Timmins, R.P. May
- 20 *Phasing in crystallography: a modern perspective*  
C. Giacovazzo
- 21 *The basics of crystallography and diffraction, fourth edition*  
C. Hammond

## Preface to the First Edition (1997)

This book has grown out of my earlier *Introduction to Crystallography* published in the Royal Microscopical Society's Microscopy Handbook Series (Oxford University Press 1990, revised edition 1992). My object then was to show that crystallography is not, as many students suppose, an abstruse and 'difficult' subject, but a subject that is essentially clear and simple and which does not require the assimilation and memorization of a large number of facts. Moreover, a knowledge of crystallography opens the door to a better and clearer understanding of so many other topics in physics and chemistry, earth, materials and textile sciences, and microscopy.

In doing so I tried to show that the ideas of symmetry, structures, lattices and the architecture of crystals should be approached by reference to everyday examples of the things we see around us, and that these ideas were not confined to the pages of textbooks or the models displayed in laboratories.

The subject of diffraction flows naturally from that of crystallography because by its means—and in most cases only by its means—are the structures of materials revealed. And this applies not only to the interpretation of diffraction patterns but also to the interpretation of images in microscopy. Indeed, diffraction patterns of objects ought to be thought of as being as 'real', and as simply understood, as the objects themselves. One is, to use the mathematical expression, simply the transform of the other. Hence, in discussing diffraction, I have tried to emphasize the common aspects of the phenomena with respect to light, X-rays and electrons.

In Chapter 1 (Crystals and crystal structures) I have concentrated on the simplest examples, emphasizing how they are related in terms of the occupancy of atomic sites and how the structures may be changed by faulting. Chapter 2 (Two-dimensional patterns, lattices and symmetry) has been considerably expanded, partly to provide a firm basis for understanding symmetry and lattices in three dimensions (Chapters 3 and 4) but also to address the interests of students involved in two-dimensional design. Similarly in Chapter 4, in discussing point group symmetry, I have emphasized its practical relevance in terms of the physical and optical properties of crystals.

The reciprocal lattice (Chapter 6) provides the key to our understanding of diffraction, but as a *concept* it stands alone. I have therefore introduced it separately from diffraction and hope that in doing so these topics will be more readily understood. In Chapter 7 (The diffraction of light) I have emphasized the geometrical analogy with electron diffraction and have avoided any quantitative analysis of the amplitudes and intensities of diffracted beams. In my experience the (sometimes lengthy) equations which are required cloud students' perceptions of the basic geometrical conditions for constructive and destructive interference—and which are also of far more practical importance with respect, say, to the resolving power of optical instruments.

Chapter 8 describes the historical development of the geometrical interpretation of X-ray diffraction patterns through the work of Laue, the Braggs and Ewald. The diffraction of X-rays and electrons from single crystals is covered in Chapter 9, but only in the case of X-ray diffraction are the intensities of the diffracted beams discussed.

This is largely because structure factors are important but also because the derivation of the interference conditions between the atoms in the motif can be represented as

nothing more than an extension of Bragg's law. Finally, the important X-ray and electron diffraction techniques from polycrystalline materials are covered in Chapter 10.

The Appendices cover material that, for ease of reference, is not covered in the text. Appendix 1 gives a list of items which are useful in making up crystal models and provides the names and addresses of suppliers. A rapidly increasing number of crystallography programs are becoming available for use in personal computers and in Appendix 2 I have listed those which involve, to a greater or lesser degree, some 'self learning' element. If it is the case that the computer program will replace the book, then one might expect that books on crystallography would be the first to go! That day, however, has yet to arrive. Appendix 3 gives brief biographical details of crystallographers and scientists whose names are asterisked in the text. Appendix 4 lists some useful geometrical relationships.

Throughout the book the mathematical level has been maintained at a very simple level and with few minor exceptions all the equations have been derived from first principles. In my view, students learn nothing from, and are invariably dismayed and perplexed by, phrases such as 'it can be shown that'—without any indication or guidance of *how* it can be shown. Appendix 5 sets out all the mathematics which are needed.

Finally, it is my belief that students appreciate a subject far more if it is presented to them not simply as a given body of knowledge but as one which has been gained by the exertions and insight of men and women perhaps not much older than themselves. This therefore shows that scientific discovery is an activity in which they, now or in the future, can participate. Hence the justification for the historical references, which, to return to my first point, also help to show that science progresses, not by being made more complicated, but by individuals piecing together facts and ideas, and seeing relationships where vagueness and uncertainty existed before.

## Preface to the Fourth Edition (2015)

The successive editions of this book have incorporated a wider range of subject matter, some of which is of a rather more 'advanced' nature. However, I hope that I have adhered throughout to my original objective of showing that crystallography (and diffraction) is not an 'abstruse and difficult subject'. And as the book has expanded I hope that it will serve a further function, namely that of providing a reader with a greater confidence in tackling the more advanced and mathematically sophisticated texts included in Further Reading.

To this end I have used the simplest possible figures (both the drawings and photographs of crystal models) that a student is able to reproduce for himself or herself and which, I hope, will complement and aid an understanding of, the beautiful but invariably more complex computer-generated images of crystal structures that are now so widely available.

Each Chapter and Appendix is largely self-contained, and the Contents and Index have been made sufficiently detailed such that the reader should be able to locate, at a glance, those pages that contain the information which she or he requires.

Finally, there are it seems to me, two 'landmark' X-ray diffraction photographs: Laue's 1912 photograph of zinc blende and Franklin's 1952 photograph of DNA and in view of which I have placed these 'by way of symmetry' at the beginning of this book.

## Acknowledgements

In the preparation of the successive editions of this book, I have greatly benefited from the advice and encouragement of present and former colleagues in the University of Leeds who have appraised and discussed draft chapters or who have materially assisted in the preparation of the figures. In particular, I wish to mention Dr Andrew Brown, Professor Rik Brydson, Dr Tim Comyn, Dr Andrew Scott, and Mr David Wright (Institute for Materials Research); Dr Jenny Cousens and Professor Michael Hann (School of Design); Dr Peter Evennett (formerly of the Department of Pure and Applied Biology); Dr John Lydon (School of Biological Sciences); Professor Anthony North (Emeritus Professor of Biophysics); the late Dr John Robertson (former Chairman of the IUCr, Book Series Committee), and the late Dr Roy Shuttleworth (formerly of the Department of Metallurgy).

Dr Pam Champness (formerly of the Department of Earth Sciences, University of Manchester) read and advised me on much of the early draft manuscript; Mrs Kate Crennell (formerly Education Officer of the BCA) prepared several of the figures in Chapter 2; Professor István Hargittai (of the Budapest University of Technology and Economics) advised me on the work, and sought out biographical material on A.I. Kitaigorodskii; Professor Amand Lucas (of the University of Namur and Belgian Royal Academy) allowed me to use his optical simulation of the structure of DNA; Dr Keith Rogers (of Cranfield University) advised me on the Rietveld method; Professor Shigeru Ohba (of Keio University, Japan) kindly drew my attention to a number of errors and misprints overlooked in earlier editions; Dr David Watkin (University of Oxford) instructed me on direct and charge-flipping methods and Professor Michael Glazer (Universities of Oxford and Warwick) advised me on space groups and group theory.

Ms Hema Latha of Integra Software Services, Pondicherry, India, Ms Ania Wronski and Dr Sonke Adlung of the Academic Division, Oxford University Press, have guided me in the overall preparation and submission of the manuscript.

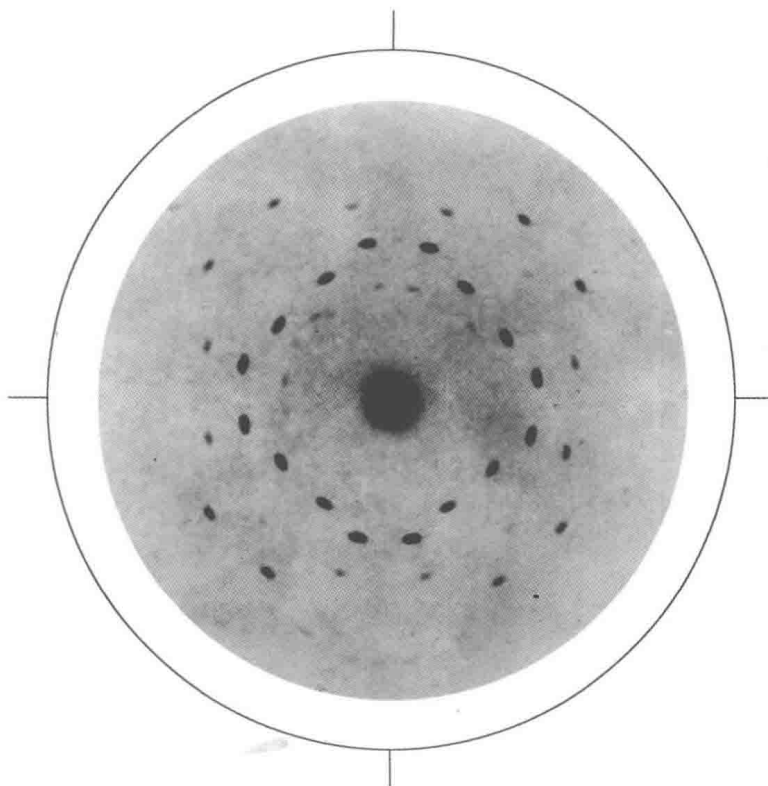
Many other colleagues at Leeds and elsewhere, have permitted me to reproduce figures from their own publications, as have the copyright holders of books and journals. Individual acknowledgements are given in the figure captions.

I would like to thank Miss Susan Toon and Miss Claire McConnell for word processing the manuscript and for attending to my constant modifications to it and to Mr David Horner and Dr Peter Evennett for their careful photographic work.

Finally, I recall with gratitude the great influence of my former teachers, in particular Dr P.M. Kelly and Dr N.F.M. Henry.

C.H.

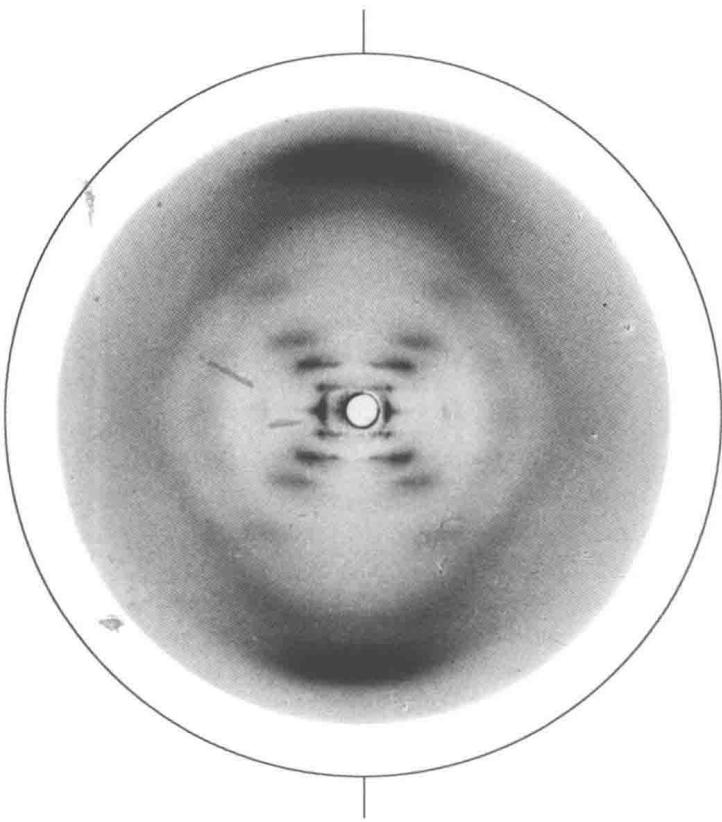
*Institute for Materials Research  
University of Leeds  
Leeds, LS2 9JT  
July 2014*



*X-ray photograph of zinc blende*

One of the eleven 'Laue Diagrams' in the paper submitted by Walter Friedrich, Paul Knipping and Max von Laue to the Bavarian Academy of Sciences and presented at its Meeting held on June 8th 1912—the paper which demonstrated the existence of internal atomic regularity in crystals and its relationship to the external symmetry.

The X-ray beam (central black spot) is incident along one of the cubic crystal axes of the (face-centred cubic) ZnS structure and consequently the diffraction spots show the four-fold symmetry of the atomic arrangement about the axis. But notice also that the spots are not circular in shape—they are elliptical; the short axes of the ellipses all lying in radial directions. William Lawrence Bragg realized the great importance of this seemingly small observation: he had noticed that slightly divergent beams of light (of circular cross-section) reflected from mirrors also gave reflected spots of just these elliptical shapes. Hence he went on to formulate the Law of Reflection of X-Ray Beams which unlocked the door to the structural analysis of crystals.



*X-ray photograph of deoxyribonucleic acid*

The photograph of the 'B' form of DNA taken by Rosalind Franklin and Raymond Gosling in May 1952 and published, together with the two papers by J. D. Watson and F. H. C. Crick and M. H. F. Wilkins, A. R. Stokes and H. R. Wilson, in the 25 April issue of *Nature*, 1953, under the heading 'Molecular Structure of Nucleic Acids'.

The specimen is a fibre (axis vertical) containing millions of DNA strands roughly aligned parallel to the fibre axis and separated by the high water content of the fibre; this is the form adopted by the DNA in living cells. The X-ray beam is normal to the fibre and the diffraction pattern is characterised by four lozenges or diamond-shapes outlined by fuzzy diffraction haloes and separated by two rows or arms of spots radiating outwards from the centre. These two arms are characteristic of helical structures and the angle between them is a measure of the ratio between the width of the molecule and the repeat-distance of the helix. But notice also the sequence of spots along each arm; there is a void where the fourth spot should be and this 'missing fourth spot' not only indicates that there are two helices intertwined but also the separation of the helices along the chain. Finally, notice that there are faint diffraction spots in the two side lozenges, but not in those above and below, an observation which shows that the sugar-phosphate 'backbones' are on the outside, and the bases on the inside, of the molecule.

This photograph provided the crucial experimental evidence for the correctness of Watson and Crick's structural model of DNA—a model not just of a crystal structure but one which shows its inbuilt power of replication and which thus unlocked the door to an understanding of the mechanism of transmission of the gene and of the evolution of life itself.

# Contents

<i>X-ray photograph of zinc blende</i> (Friedrich, Knipping, and von Laue, 1912)	xvi
<i>X-ray photograph of deoxyribonucleic acid</i> (Franklin and Gosling, 1952)	xvii

1	Crystals and crystal structures	1
1.1	The nature of the crystalline state	1
1.2	Constructing crystals from close-packed hexagonal layers of atoms	5
1.3	Unit cells of the hcp and ccp structures	6
1.4	Constructing crystals from square layers of atoms	9
1.5	Constructing body-centred cubic crystals	9
1.6	Interstitial structures	11
1.7	Some simple ionic and covalent structures	18
1.8	Representing crystals in projection: crystal plans	20
1.9	Stacking faults and twins	20
1.10	The crystal chemistry of inorganic compounds	27
1.10.1	<i>Bonding in inorganic crystals</i>	28
1.10.2	<i>Representing crystals in terms of coordination polyhedra</i>	30
1.11	Introduction to some more complex crystal structures	32
1.11.1	<i>Perovskite (<math>\text{CaTiO}_3</math>), barium titanate (<math>\text{BaTiO}_3</math>) and related structures</i>	32
1.11.2	<i>Tetrahedral and octahedral structures—silicon carbide and alumina</i>	34
1.11.3	<i>The oxides and oxy-hydroxides of iron</i>	36
1.11.4	<i>Silicate structures</i>	38
1.11.5	<i>The structures of silica, ice and water</i>	44
1.11.6	<i>The structures of carbon</i>	48
	Exercises	54

2	Two-dimensional patterns, lattices and symmetry	56
2.1	Approaches to the study of crystal structures	56
2.2	Two-dimensional patterns and lattices	57
2.3	Two-dimensional symmetry elements	59
2.4	The five plane lattices	62
2.5	The seventeen plane groups	65
2.6	One-dimensional symmetry: border or frieze patterns	66
2.7	Symmetry in art and design: counterchange patterns	66
2.8	Layer (two-sided) symmetry and examples in woven textiles	74
2.9	Non-periodic patterns and tilings	78
	Exercises	83

3	Bravais lattices and crystal systems	86
3.1	Introduction	86
3.2	The fourteen space (Bravais) lattices	86
3.3	The symmetry of the fourteen Bravais lattices: crystal systems	90
3.4	The coordination or environments of Bravais lattice points: space-filling polyhedra	92
	Exercises	97
4	Crystal symmetry: point groups, space groups, symmetry-related properties and quasiperiodic crystals	99
4.1	Symmetry and crystal habit	99
4.2	The thirty-two crystal classes	101
4.3	Centres and inversion axes of symmetry	102
4.4	Crystal symmetry and properties	106
4.5	Translational symmetry elements	110
4.6	Space groups	113
4.7	Bravais lattices, space groups and crystal structures	120
4.8	The crystal structures and space groups of organic compounds	123
	4.8.1 <i>The close packing of organic molecules</i>	124
	4.8.2 <i>Long-chain polymer molecules</i>	127
4.9	Quasicrystals (quasiperiodic crystals or crystalloids)	129
	Exercises	134
5	Describing lattice planes and directions in crystals: Miller indices and zone axis symbols	135
5.1	Introduction	135
5.2	Indexing lattice directions—zone axis symbols	136
5.3	Indexing lattice planes—Miller indices	137
5.4	Miller indices and zone axis symbols in cubic crystals	140
5.5	Lattice plane spacings, Miller indices and Laue indices	141
5.6	Zones, zone axes and the zone law, the addition rule	143
	5.6.1 <i>The Weiss zone law or zone equation</i>	143
	5.6.2 <i>Zone axis at the intersection of two planes</i>	143
	5.6.3 <i>Plane parallel to two directions</i>	144
	5.6.4 <i>The addition rule</i>	144
5.7	Indexing in the trigonal and hexagonal systems: Weber symbols and Miller-Bravais indices	145
5.8	Transforming Miller indices and zone axis symbols	148
5.9	Transformation matrices for trigonal crystals with rhombohedral lattices	151
5.10	A simple method for inverting a $3 \times 3$ matrix	152
	Exercises	153

6	The reciprocal lattice	155
6.1	Introduction	155
6.2	Reciprocal lattice vectors	155
6.3	Reciprocal lattice unit cells	157
6.4	Reciprocal lattice cells for cubic crystals	161
6.5	Proofs of some geometrical relationships using reciprocal lattice vectors	163
6.5.1	<i>Relationships between <math>\mathbf{a}</math>, <math>\mathbf{b}</math>, <math>\mathbf{c}</math> and <math>\mathbf{a}^*</math>, <math>\mathbf{b}^*</math>, <math>\mathbf{c}^*</math></i>	163
6.5.2	<i>The addition rule</i>	164
6.5.3	<i>The Weiss zone law or zone equation</i>	164
6.5.4	<i>d-spacing of lattice planes (<math>hkl</math>)</i>	165
6.5.5	<i>Angle <math>\rho</math> between plane normals (<math>h_1k_1l_1</math>) and (<math>h_2k_2l_2</math>)</i>	165
6.5.6	<i>Definition of <math>\mathbf{a}^*</math>, <math>\mathbf{b}^*</math>, <math>\mathbf{c}^*</math> in terms of <math>\mathbf{a}</math>, <math>\mathbf{b}</math>, <math>\mathbf{c}</math></i>	166
6.5.7	<i>Zone axis at intersection of planes (<math>h_1k_1l_1</math>) and (<math>h_2k_2l_2</math>)</i>	166
6.5.8	<i>A plane containing two directions <math>[u_1v_1w_1]</math> and <math>[u_2v_2w_2]</math></i>	166
6.6	Lattice planes and reciprocal lattice planes	166
6.7	Summary	169
	Exercises	169
7	The diffraction of light	170
7.1	Introduction	170
7.2	Simple observations of the diffraction of light	172
7.3	The nature of light: coherence, scattering and interference	177
7.4	Analysis of the geometry of diffraction patterns from gratings and nets	180
7.5	The resolving power of optical instruments: the telescope, camera, microscope and the eye	187
	Exercises	197
8	X-ray diffraction: the contributions of Max von Laue, W. H. and W. L. Bragg and P. P. Ewald	198
8.1	Introduction	198
8.2	Laue's analysis of X-ray diffraction: the three Laue equations	199
8.3	Bragg's analysis of X-ray diffraction: Bragg's law	202
8.4	Ewald's synthesis: the reflecting sphere construction	204
	Exercises	209
9	The diffraction of X-rays	210
9.1	Introduction	210
9.2	The intensities of X-ray diffracted beams: the structure factor equation and its applications	214

9.3	The broadening of diffracted beams: reciprocal lattice points and nodes	223
9.3.1	<i>The Scherrer equation: reciprocal lattice points and nodes</i>	223
9.3.2	<i>Integrated intensity and its importance</i>	227
9.3.3	<i>Crystal size and perfection: mosaic structure and coherence length</i>	227
9.4	Fixed $\theta$ , varying $\lambda$ X-ray techniques: the Laue method	228
9.5	Fixed $\lambda$ , varying $\theta$ X-ray techniques: oscillation, rotation and precession methods	231
9.5.1	<i>The oscillation method</i>	232
9.5.2	<i>The rotation method</i>	234
9.5.3	<i>The precession method</i>	235
9.6	X-ray diffraction from single crystal thin films and multilayers	239
9.7	X-ray (and neutron) diffraction from ordered crystals	243
9.8	Practical considerations: X-ray sources and recording techniques	246
9.8.1	<i>The generation of X-rays in X-ray tubes</i>	247
9.8.2	<i>Synchrotron X-ray generation</i>	248
9.8.3	<i>X-ray recording techniques</i>	249
	Exercises	249
10	X-ray diffraction of polycrystalline materials	252
10.1	Introduction	252
10.2	The geometrical basis of polycrystalline (powder) X-ray diffraction techniques	253
10.2.1	<i>Intensity measurement in the X-ray diffractometer</i>	258
10.2.2	<i>Back reflection and Debye-Scherrer powder techniques</i>	260
10.3	Some applications of X-ray diffraction techniques in polycrystalline materials	262
10.3.1	<i>Accurate lattice parameter measurements</i>	262
10.3.2	<i>Identification of unknown phases</i>	263
10.3.3	<i>Measurement of crystal (grain) size</i>	266
10.3.4	<i>Measurement of internal elastic strains</i>	266
10.4	Preferred orientation (texture, fabric) and its measurement	267
10.4.1	<i>Fibre textures</i>	268
10.4.2	<i>Sheet textures</i>	269
10.5	X-ray diffraction of DNA: simulation by light diffraction	272
10.6	The Rietveld method for structure refinement	277
	Exercises	280
11	Electron diffraction and its applications	283
11.1	Introduction	283
11.2	The Ewald reflecting sphere construction for electron diffraction	284
11.3	The analysis of electron diffraction patterns	288

11.4	Applications of electron diffraction	290
11.4.1	<i>Determining orientation relationships between crystals</i>	290
11.4.2	<i>Identification of polycrystalline materials</i>	292
11.4.3	<i>Identification of quasiperiodic crystals (quasicrystals)</i>	292
11.5	Kikuchi and electron backscattered diffraction (EBSD) patterns	294
11.5.1	<i>Kikuchi patterns in the TEM</i>	294
11.5.2	<i>Electron backscattered diffraction (EBSD) patterns in the SEM</i>	298
11.6	Image formation and resolution in the TEM	300
	Exercises	304
12	The stereographic projection and its uses	308
12.1	Introduction	308
12.2	Construction of the stereographic projection of a cubic crystal	311
12.3	Manipulation of the stereographic projection: use of the Wulff net	314
12.4	Stereographic projections of non-cubic crystals	317
12.5	Applications of the stereographic projection	320
12.5.1	<i>Representation of point group symmetry</i>	320
12.5.2	<i>Representation of orientation relationships</i>	322
12.5.3	<i>Representation of preferred orientation (texture or fabric)</i>	323
12.5.4	<i>Trace analysis</i>	325
	Exercises	328
13	Fourier analysis in diffraction and image formation	329
13.1	Introduction—Fourier series and Fourier transforms	329
13.2	Fourier analysis in crystallography	332
13.2.1	<i>X-ray resolution of a crystal structure</i>	337
13.3	The structural analysis of crystals and molecules	338
13.3.1	<i>Trial and error methods</i>	339
13.3.2	<i>The Patterson function: Patterson or vector maps</i>	340
13.3.3	<i>Interpretation of Patterson maps: heavy atom and isomorphous replacement techniques</i>	346
13.3.4	<i>Direct methods</i>	348
13.3.5	<i>Charge flipping</i>	349
13.4	Analysis of the Fraunhofer diffraction pattern from a grating	350
13.5	Abbe theory of image formation	356
14	The physical properties of crystals and their description by tensors	362
14.1	Introduction	362
14.2	Second rank tensor properties	363

14.2.1	<i>General expression for a second rank tensor relating two vectors</i>	363
14.2.2	<i>Simplification of second rank tensor equations: principal axes</i>	366
14.2.3	<i>Representation of second rank tensor properties: the representation quadric</i>	366
14.3	Neumann's principle	368
14.3.1	<i>Pyroelectricity and ferroelectricity</i>	369
14.4	Second rank tensors that describe stress and strain	369
14.4.1	<i>The stress tensor: principal axes (eigenvectors) and principal values (eigenvalues)</i>	369
14.4.2	<i>The strain tensor, Neumann's principle, and thermal expansion</i>	372
14.4.3	<i>Atomic displacement parameters (ADPs)</i>	374
14.5	The optical properties of crystals	374
14.6	Third rank tensors: piezoelectricity	379
14.7	Fourth rank tensor properties: elasticity	380
	Exercises	382
Appendix 1	Computer programs, models and model-building in crystallography	385
Appendix 2	Polyhedra in crystallography	393
Appendix 3	Biographical notes on crystallographers and scientists mentioned in the text	403
Appendix 4	Some useful crystallographic relationships	449
Appendix 5	A simple introduction to vectors and complex numbers and their use in crystallography	452
Appendix 6	Systematic absences (extinctions) in X-ray diffraction and double diffraction in electron diffraction patterns	459
Appendix 7	Group theory in crystallography	469
	Answers to exercises	481
	Further Reading	497
	Index	507

# Crystals and crystal structures

## 1.1 The nature of the crystalline state

The beautiful hexagonal patterns of snowflakes, the plane faces and hard faceted shapes of minerals and the bright cleavage fracture surfaces of brittle iron have long been recognized as external evidence of an internal order—evidence, that is, of the patterns or arrangements of the underlying building blocks. However, the nature of this internal order, or the form and scale of the building blocks, was unknown.

The first attempt to relate the external form or shape of a crystal to its underlying structure was made by Johannes Kepler\* who, in 1611, wrote perhaps the first treatise on geometrical crystallography, with the delightful title, 'A New Year's Gift or the Six-Cornered Snowflake' (*Strena Seu de Nive Sexangula*).<sup>1</sup> In this he speculates on the question as to why snowflakes always have six corners, never five or seven. He suggests that snowflakes are composed of tiny spheres or globules of ice and shows, in consequence, how the close-packing of these spheres gives rise to a six-sided figure. It is indeed a simple experiment that children now do with pennies at school. Kepler was not able to solve the problem as to why the six corners extend and branch to give many patterns (a problem not fully resolved to this day), nor did he extend his ideas to other crystals. The first to do so, and to consider the structure of crystals as a general problem, was Robert Hooke\* who, with remarkable insight, suggested that the different shapes of crystals which occur—rhombs, trapezia, hexagons, etc.—could arise from the packing together of spheres or globules. Figure 1.1 is 'Scheme VII' from his book *Micrographia*, first published in 1665. The upper part (Fig. 1) is his drawing, from the microscope, of 'Crystalline or Adamantine bodies' occurring on the surface of a cavity in a piece of broken flint and the lower part (Fig. 2) is of 'sand or gravel' crystallized out of urine, which consist of 'Slats or such-like plated Stones... their sides shaped into **Rhombs, Rhomboids** and sometimes into **Rectangles and Squares**'. He goes on to show how these various shapes can arise from the packing together of 'a company of bullets' as shown in the inset sketches A–L, which represent pictures of crystal structures which have been repeated in innumerable books, with very little variation, ever since. Also implicit in Hooke's sketches is the *Law of the Constancy of Interfacial Angles*; notice that the solid lines which outline the crystal faces are (except for the last sketch, L) all at 60° or 120° angles which clearly arise from the close-packing of the spheres. This law was first stated by Nicolaus Steno,\* a near contemporary of Robert

\* Denotes biographical notes available in Appendix 3.

<sup>1</sup> *The Six-Cornered Snowflake*, reprinted with English translation and commentary. Classic Texts in the Physical Science Oxford University Press, Oxford, 2014.