

CRYSTAL STRUCTURES

I. Patterns and Symmetry

M. O'KEEFE

Department of Chemistry
Arizona State University
Tempe AZ 85287

B. G. HYDE

Research School of Chemistry
The Australian National University
Canberra ACT 0200

MINERALOGICAL SOCIETY OF AMERICA
WASHINGTON, D.C.

CRYSTAL STRUCTURES

I. Patterns and Symmetry

Michael O'Keeffe and Bruce G. Hyde

© Copyright 1996

This work is subject to copyright. All rights are reserved by the authors, including those of translation, reprinting, re-use of illustrations, reproducing by photocopying or other means, and storage in data banks.

Printed by
BookCrafters, Inc., Chelsea, Michigan, U.S.A.

ISBN 0-939950-40-5

Published by
MINERALOGICAL SOCIETY OF AMERICA
1015 Eighteenth Street, NW, Suite 601
Washington, DC 20036 USA

Cover: the pattern that results when the twenty faces of an icosahedron are capped by truncated tetrahedra. This occurs as an 84-atom unit of the structure of β -rhombohedral boron. The same pattern is conspicuous in the structure of some intermetallic compounds (see p. 160-163).

MINERALOGICAL SOCIETY OF AMERICA

MONOGRAPH SERIES

FOREWORD

In 1993 the Mineralogical Society of America (MSA) began publishing its Monograph Series with a major work by Frank S. Spear, entitled *Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*. MSA's second monograph was a reprinting of a slightly revised version of the 1971 book, *Crystallography and Crystal Chemistry*, by F. Donald Bloss.

This volume by Michael O'Keeffe and Bruce G. Hyde is the third contribution. As Series Editor, I was responsible for obtaining reviewers. Mike O'Keeffe prepared the entire camera-ready text and the figures which were all drawn specially for the book. As noted in the Preface below, a second volume, *Crystal Structures II. Inorganic Materials* is anticipated in the near future.

Paul H. Ribbe
Blacksburg, Virginia

PREFACE

This book (the first of two volumes) is devoted to the topic of the description of structures, especially periodic structures, and their symmetries. Much of the material is a prerequisite for serious students of solid state chemistry and related sciences (e.g. mineralogy, materials science and solid state physics). Earlier drafts served as part of the lecture notes used for some years for a course in solid state chemistry at Arizona State University; the order of presentation of topics, occasional repetitiveness and the sometimes hectoring tone to some extent reflect this origin.

From a chemist's point of view, probably the most fundamental piece of information about a chemical compound is the way its atoms are arranged in space. For small molecules this information can be fairly readily assimilated, but the task becomes increasingly difficult for macromolecules, as any student of biochemistry can attest. For crystalline solids (which are really "infinite" molecules) the difficulty is equally great, and requires learning the methods appropriate to describing infinite periodic objects. These methods are generally unfamiliar to those who are not professional crystallographers (a fact that greatly hinders

the development of solid state chemistry) and one of the primary aims of this book is to provide a usable introduction to them. This leads inexorably to a discussion of symmetry (translation is a symmetry operation) so we devote the first three chapters to an introduction to point and space symmetry groups using crystallographic conventions.

These three chapters are intended to introduce the language of space groups, and are neither rigorous nor complete. The goal is to enable the reader to be in a position to be able to extract and understand useful information from the crystallographic literature that is the primary source of information about the structure of solids and which contains enormous quantities of buried treasure.

Chapter 4 treats crystal geometry and includes a discussion of transformations of coordinate systems (unit cell transformations). This topic is essential to aspects of crystal chemistry such as describing structural relationships. The chapter also contains a compendium of formulas useful for crystallographic calculations. They are given without proof, but the derivations are, for the most part, elementary and to be found in standard crystallographic texts.

Chapters 5-7 are devoted to the description of simple geometrical patterns that underlie crystal structures. The development proceeds from simple to more complex: polyhedra, clusters of polyhedra, plane patterns, layers of polyhedra, sphere packings, cylinder packings, nets and infinite polyhedra. Many examples are given of the occurrence of these patterns in crystal structures. Most of the more common binary and ternary crystal structures are introduced along the way and, to enhance the value of the book as a self-contained text, we summarize them and their occurrence in chemical compounds in Appendix 5 at the end. (The second volume of this series, which is longer than this one, is devoted to a more complete account of crystal structures.)

Each chapter ends with sections entitled "Notes" and "Exercises." The former are often extended footnotes, somewhat peripheral to the main theme, but considered useful or amusing (or both); they often contain useful reference material or refer to some more-advanced topics. The Exercises are "homework", designed to provide a diagnosis of the understanding of the material in the chapter and also often contain useful results.

The first four appendices are "Notes" that became too long for inclusion in individual chapters. We hope that they will whet the appetites of more-adventuresome readers. The relegation of some material to Notes and Appendices necessitates some cross referencing. This seems to us to be a small price to pay for having a book that can serve both as a textbook for courses and as a general reference. A book with these aspirations has of necessity a split personality. In Chapters 5-7, some sections could well be omitted in a formal course at the instructor's discretion. The same is true of the material in the Notes.

No novelty (except perhaps for the errors) is claimed for the first four chapters, although we hope that even some experienced readers might find one or two items that provide food for thought. The later chapters do (we believe) contain some material of interest that has not been published before.

Although the book has a distinct crystallographic flavor, it is definitely not a textbook on crystallography and we do not discuss, except peripherally, topics such as quasicrystals

and incommensurate crystals that are currently of active concern to inorganic crystallographers and sometimes even the occasion for controversy.

We have spent some years on the study of structures, a delightful pursuit that would not have been possible without the generous support, for which we are indebted, of our respective institutions. M. O'K. also gratefully acknowledges the support of the U.S. National Science Foundation which has funded a program of research in crystal chemistry for a number of years. We came to the study of crystal structures indirectly and in complete ignorance. Over the years we slowly collected a body of information needed to pursue research in the field. We often wished that someone had provided us with this material, and the present text attempts to provide such a package for students who may be in the position we were in 40 years ago.

The text has benefited particularly from the sure touch of Paul Ribbe, who read it in its entirety, identified errors, solecisms, and infelicities, and also made valuable suggestions for improving the presentation. We owe him special thanks.

The book could not have been written without the seemingly infinite patience and forbearance of our wives, Lita O'Keeffe and Marie Hyde, and we dedicate it to them.

Michael O'Keeffe
Tempe

Bruce Hyde
Canberra

A Note to the Reader

Matrices are represented by bold capitals thus: **A**; and often written row-by-row on one line as (a_{11} a_{12} a_{13} / a_{21} a_{22} a_{23} / a_{31} a_{32} a_{33}). **A**^t is the transpose of **A**. Column vectors are lower case **a**: **a**. The corresponding row vector is **a**^t. The magnitude of **a** is *a*. **E** is a unit matrix (with elements $e_{ii} = 1$, $e_{ij} = 0$).

Bold face is also generally used for names of structures. Thus **bcc** refers to the arrangement of points on a body-centered cubic lattice and **NaCl** refers to the structure of NaCl and all iso-structural compounds.

Braces around an atom symbol indicate that reference is being made to its coordination polyhedron. In **quartz** GeO_2 , the coordination of Ge is a {Ge}O₄ tetrahedron, i.e., a Ge-centered O₄ tetrahedron.

Prefixed lower case Roman numeral superscripts in chemical formulas refer to coordination numbers as in ^{iv}Si₂ⁱⁱⁱN₂ⁱⁱO. Upper case Roman numerals in parentheses after chemical symbols refer to oxidation states as in Ag(I)Ag(III)O₂. Arabic numerals in parentheses refer to an arbitrary numbering to distinguish crystallographically-distinct, but chemically-identical, atoms as in B₂O(1)₂O(2).

The notation (*N*×) after interatomic distances or angles means that there are *N* equivalent (symmetry-related) distances or angles of the same magnitude (read "*N* times"). Thus the lengths of the six Ti-O bonds formed by a Ti atom in **rutile** TiO₂ are 1.948 (4×) and 1.980 (2×) Å. (1 Å = 10⁻¹⁰ m.)

We sometimes want to distinguish between compounds with (a) bonds formed between electropositive and electronegative elements (such as metal oxides and halides) (b) bonds between electronegative elements (such as in diamond) and (c) bonds between electropositive elements (as in brass, CuZn). For want of better terms we call these (a) ionic, (b) covalent, and (c) intermetallic. The use of these terms should not be construed to mean that we think that any particular theory of bonding is or is not applicable. Indeed they are merely labels of convenience, and in this book we go to some pains to describe structures and to resist, as far as is humanly possible, the temptation to interpret them. The reader is free from such constraints, of course.

We draw attention to the fact that conventions in crystallography are occasionally subject to change so that readers of the older literature can be misled. For example the short symbols for some cubic point groups and space groups were altered some years ago (see § 3.3.6). The method of describing unit cell transformations requires some care (see § 4.7.5). Our own view on conventions is that it is not so important that they should be logical (which, of course, is desirable), than that their users be consistent, and that changes should be made only for very compelling reasons.

Students of solid state chemistry would be well advised to obtain (or write!) a computer program that calculates distances and angles in crystal structures and another that assists in making drawings. On occasion, structures of lesser interest are simply presented as lists of coordinates—it is often tedious to convert these to drawings or models entirely by hand (although we have done just that for many years). Several good programs that do one or

another of these things are now available commercially. At ASU and ANU we use a program, EUTAX, that will, among other things, do most of the numerical exercises presented herein.¹

Many molecular graphics programs can be "tricked" into accepting fragments of crystal structures as molecules. Usually all coordinates will have to be entered explicitly so we generally give all the coordinates of symmetry-related atoms in crystal structures. For this purpose we use a condensed notation explained in § 3.4. For some comments on drawing structures see § 4.6. All the drawings in this book were made using a Macintosh® computer and Cricket Draw® with, in the case of structure drawings, the help of Cartesian coordinates generated by EUTAX.

At several places we give advice on the construction of models. Our experience is that the best way to learn a structure is to make a model of it (failing that, at least make a drawing or two). One should then look at it repeatedly, especially down principle symmetry axes, until it can be visualized clearly with one's eyes closed. Contrary to a common belief, learning three-dimensional structures is a skill not difficult to acquire but, like that of riding a bicycle, requires some initially frustrating practice. The reward is that, not only will a knowledge of crystal structures be acquired, but also one will learn to appreciate the sometimes stunning beauty of three-dimensional structures.

We entreat the reader working alone not to be discouraged if some material is difficult to understand at first reading. The book is not "bedside" reading but is intended to be read with pencil and paper at hand to verify the statements made. The level of difficulty is not uniform and we include some material (especially in the Notes) in condensed form for future reference if needed. Our advice (we follow it ourselves constantly) to those confronted with a topic that appears incomprehensible, is simply to read it, to read on, and then to return to the topic later. Be aware also that virtually every book (including this one) has *some* errors (M. O'K. would be very grateful if informed of these). If all else fails, get another book! Readers new to the subject who do not have such difficulties have our unstinted admiration.

The Exercises in many instances illustrate important aspects of crystal chemistry. (We call them Exercises to emphasize that a solid state scientist who aspires to obtain some virtuosity needs to exercise constantly, just as does a violinist or a tennis player.) Some of them are cast as statements; one should interpret these as a requirement to demonstrate the validity of the statements made. Yet others simply present interesting structures for the reader to explore. The lazy reader who is unwilling to do this may still find some of the results useful and should at least read them. Some Exercises will be found simple, some are more challenging. Sometimes we give hints and partial answers and some are answered later in the text. We emphasize though, that it is not sufficient to do a problem and obtain the correct answer. One must do a problem, get the correct answer, and *know* that it is the correct answer. After all, this is the situation faced by a practicing scientist (and by us in setting the Exercises).

¹ A Macintosh® version of this program is available from EMLab Software, 16203 S. 26th Place, Phoenix AZ 85048. A Windows® version is planned.

The book contains crystallographic data for two kinds of structure. Data of the first kind are found mainly in Chapters 6 and 7 in which we describe sphere packings and nets. In these cases the coordinates and unit cell parameters given are such as to have unit distance between sphere centers, or between the vertices of nets. These data can easily be recognized because the unit cell parameters are dimensionless. In most instances they have been calculated specially by us and published herein for the first time. On the other hand crystallographic data for real compounds are given throughout the text (specially in Exercises and in Appendix 5). In this second case unit cell edges are invariably given in Å and the data refer to structures published in the open literature. All these data come from one or other of the data bases listed in Section D of the Book List (p. 446); these (or similar sources) should be consulted for references to the original literature. The formula index contains a complete listing of compounds for which crystallographic data are given.

TABLE OF CONTENTS

Preface	iii
A note to the reader	vi
1 SYMMETRY IN TWO DIMENSIONS	
1.1 Point symmetry operations in two dimensions	1
1.2 Coordinate systems and symmetry operations	5
1.3 Translational symmetry: lattices and unit cells	8
1.4 Allowed rotational symmetries of lattices	11
1.5 Unit cell coordinates: describing structures	11
1.6 Glide symmetry	14
1.7 Two-dimensional space groups	14
1.7.1 Oblique system	15
1.7.2 Rectangular system	18
1.7.3 Square system	19
1.7.4 Hexagonal system	19
1.7.5 Synopsis of the two-dimensional space groups	21
1.8 Construction and interpretation of space group symbols	21
1.9 Using the <i>International Tables</i>	22
1.10 Notes	24
1.10.1 Symmetry operations	24
1.10.2 Groups	24
1.10.3 Two-dimensional groups and decoration	25
1.10.4 Matrix manipulations	26
1.11 Exercises	26
2 THREE-DIMENSIONAL POINT GROUPS	
2.1 Point symmetry operations	28
2.1.1 Inversion in a center	29
2.1.2 Rotation plus inversion; axes \bar{N}	30
2.2 Enumeration of the point groups	32
2.2.1 Pure rotation groups: dihedral groups $N2(2)$	32
2.2.2 Groups $Nm(m)$	35
2.2.3 Groups N/m	36
2.2.4 Groups $N/m2/m2/m$	37
2.2.5 Groups $\bar{3}m$, $\bar{4}2m$ and $\bar{6}m2$	38
2.2.6 Summary of the non-cubic crystallographic point groups	40

2.2.7	Cubic and icosahedral rotation groups	40
2.2.8	Cubic and icosahedral groups $m\bar{3}$, $m\bar{3}m$, $\bar{4}3m$ and $m\bar{3}5$	42
2.3	Point groups by system	45
2.4	Coordinate systems and the order of symbols	45
2.5	Notes	47
2.5.1	Rotations	47
2.5.2	Groups of symmetry operations and their orders	48
2.5.3	Derivation of the point groups	49
2.5.4	Curie's law, Friedel's law, Laue classes, optical activity and polarity	50
2.5.5	Cubic and icosahedral groups; generators	51
2.5.6	Non-crystallographic point groups	52
2.5.7	Symmetry and relations between polyhedra	53
2.5.8	Antisymmetry: magnetic or black-and-white groups	54
2.6	Exercises	55
3	THREE-DIMENSIONAL SPACE GROUPS	
3.1	Three-dimensional lattices	58
3.2	Glide and screw axes	62
3.2.1	Glide	62
3.2.2	Screw	63
3.2.3	Comparison of screw and glide	67
3.3	Three-dimensional space groups	67
3.3.1	Triclinic space groups	67
3.3.2	Monoclinic space groups	67
3.3.3	Orthorhombic space groups	70
3.3.4	Tetragonal space groups	73
3.3.5	Trigonal and hexagonal space groups	74
3.3.6	Cubic space groups	74
3.3.7	Space group and crystal class	76
3.4	Using the <i>International Tables</i>	76
3.5	Sub- and super-groups of space groups	80
3.6	Symmetry and the quartz structure—a case study	83
3.7	Notes	88
3.7.1	Additional symmetry elements in the unit cell	88
3.7.2	General and special positions and lattice complexes	88
3.7.3	Matrix representations of symmetry operations	89
3.7.4	Alternative origins and unit cells	91
3.7.5	Standardized descriptions of crystal structures	93
3.7.6	Other symmetry groups with translations	93
3.7.7	The occurrence of symmetry groups	94
3.7.8	Incommensurate crystals, quasicrystals and non-classical symmetries	95
3.8	Exercises	96

4 LATTICE GEOMETRY

4.1	Directions in a crystal	99
4.1.1	General	99
4.1.2	Directions in hexagonal crystals	100
4.2	Planes and Miller indices	101
4.3	Relations between zones (directions) and planes	102
4.4	Unit cell transformations	103
4.4.1	General	103
4.4.2	Rhombohedral to hexagonal and <i>vice versa</i>	104
4.4.3	Cubic to hexagonal	107
4.4.4	Hexagonal to orthohexagonal	108
4.5	Crystallographic calculations	108
4.5.1	Unit cell volume and reciprocal lattice parameters	108
4.5.2	Interatomic distances and the G matrix	110
4.5.3	Angles	111
4.5.4	G matrix and lattice parameters for transformed cells	112
4.5.5	Cartesian coordinates	112
4.5.6	Distances between planes	114
4.6	Drawing crystal structures and using cell transformations	114
4.6.1	Orthographic and clinographic projections	114
4.6.2	Examples of clinographic drawings (ZnS and CaF ₂)	116
4.6.3	Projections using orthohexagonal cells (NaCl, NiAs and TiP)	118
4.6.4	Further examples of projections (ZnS again)	120
4.6.5	Drawing monoclinic structures	122
4.7	Notes	125
4.7.1	Orientation of direct and reciprocal lattices	125
4.7.2	Bragg and Miller indices	125
4.7.3	More equations for triangles and tetrahedra	126
4.7.4	Some matrix expressions written out explicitly	127
4.7.5	Cell transformations in <i>International Tables</i> Vol. A	128
4.8	Exercises	128

5 POLYHEDRA AND TILINGS

5.1	Polyhedra	132
5.1.1	Regular polyhedra	132
5.1.2	Combinations of octahedra and tetrahedra	135
5.1.3	Archimedean polyhedra	136
5.1.4	Prisms, antiprisms and capped prisms	139
5.1.5	Catalan polyhedra: the rhombic dodecahedron, bipyramids and pyramids	141
5.1.6	Deltahedra and the bisdisphenoid	141
5.1.7	Frank-Kasper polyhedra and intergrown polyhedra	143

5.1.8	Relationships between polyhedra with eight vertices	144
5.1.9	Tammes' problem and coordination polyhedra	146
5.1.10	Polyhedra with divalent vertices	147
5.2	Polyhedral clusters	149
5.2.1	Clusters of tetrahedra	150
5.2.2	Clusters of octahedra	152
5.2.3	Octahedra plus tetrahedra: Keggin and spinel units	157
5.2.4	Edge-capped clusters	158
5.2.5	Clusters of truncated tetrahedra and icosahedra	160
5.3	Circle packings and tilings of the plane	163
5.3.1	Regular tilings	164
5.3.2	Archimedean tilings	165
5.3.3	Relationships between tilings	167
5.3.4	Tilings including pentagons and "bronzes"	168
5.3.5	Some 3-connected boron nets: AlB_2 , YCrB_4 , ThMoB_4 and Y_2ReB_6	172
5.3.6	Some boron-carbon nets	173
5.3.7	Polyatomic tilings: self-dual nets	175
5.4	Layers of tetrahedra and/or octahedra: sheet silicates	181
5.4.1	Layers of tetrahedra and octahedra	181
5.4.2	Sheet silicates (phyllosilicates)	184
5.5	Aperiodic tilings and quasicrystals	187
5.6	Notes	190
5.6.1	Relationships between polyhedra and "pseudorotations"	190
5.6.2	Polyhedra, points on a sphere, and related topics	190
5.6.3	Constructing polyhedra	191
5.6.4	Schlegel diagrams and adjacency matrices	191
5.6.5	Coordinates for drawing polyhedra and nets	193
5.6.6	Names of polygons and polyhedra	194
5.6.7	The shapes of crystals	194
5.6.8	$\text{Na}_3\text{Pt}_4\text{Ge}_4$: a structure with stellae quadrangulae	195
5.6.9	Co_9Sg : a structure with stellae octangulae	196
5.6.10	Enumeration of Archimedean polyhedra and tilings	197
5.6.11	Euler's equation applied to plane nets	198
5.6.12	Transformations between patterns: common unit cells	199
5.6.13	Pseudorotations and twinning of nets	202
5.6.14	Symmetries of structures derived by stacking equivalent nets	203
5.6.15	More structures with dual nets: Fe_2P	204
5.7	Exercises	205
6	SPHERE AND CYLINDER PACKINGS	
6.1	The densest packing of spheres	208
6.1.1	Stacking of close-packed layers	209

6.1.2	Hexagonal eutaxy (hcp)	213
6.1.3	Cubic eutaxy (ccp)	213
6.1.4	Other eutactic (cp) arrangements	214
6.1.5	Patterns of filling interstitial sites in cp arrays	217
6.1.6	Stacking incomplete cp layers (honeycomb and kagome)	221
6.1.7	The "size" of interstitial sites	224
6.2	Body-centered cubic (bcc)	225
6.3	Sphere packings and relationships between them	227
6.3.1	11-coordination	228
6.3.2	10-coordination (bct) and a relationship between ccp and bcc	229
6.3.3	Another 10-coordination: C-centered orthorhombic (cco)	231
6.3.4	8-coordination: packing of trigonal prisms	233
6.3.5	Another 8-coordination: the <i>J</i> lattice complex	234
6.3.6	Another 8-coordination: the pyrochlore packing	236
6.3.7	Another 8-coordination: the <i>S</i> lattice complex	237
6.3.8	7-coordination and a relationship between FeSi and NaCl	238
6.3.9	6-coordination: the <i>T</i> lattice complex and crystalite	240
6.3.10	Another 6-coordination: the <i>Y</i> lattice complex	242
6.4	Sphere packings with cube and trigonal prism sites	243
6.4.1	Non-close-packed stackings of 3^6 nets	243
6.4.2	Non-close-packed stackings of 4^4 nets	248
6.4.3	Stacked $3^2.4.3.4$ nets	253
6.5	A summary of sphere packings	255
6.6	Some packings of two kinds of spheres	256
6.6.1	Cu₃Au and Ni₃Sn	256
6.6.2	CuZn (β-brass) and MoSi₂	257
6.6.3	MgCu₂	258
6.6.4	Cr₃Si (<i>A15</i>)	260
6.7	Cylinder (rod) packings	262
6.7.1	Cylinders with parallel axes	262
6.7.2	Cylinders with axes in parallel planes	263
6.7.3	Cubic cylinder packings	265
6.8	Notes	268
6.8.1	Symmetries of arrays of closest packed spheres	268
6.8.2	Neighbors, coordination sequences, and identifying packings	269
6.8.3	Close packing or polyhedron packing? An unsolved problem	270
6.8.4	More on the relationship between bcc and hcp : AuCd	271
6.8.5	More sphere packings	272
6.8.6	Sphere packings with icosahedra: WAl₁₂ and AuZn₃	277
6.8.7	Cubic invariant lattice complexes	281
6.8.8	Common cubic unit cells for arrays	282
6.8.9	Packing of two sizes of sphere: "kissing" numbers	283
6.8.10	The occurrence of cubic cylinder packings	284

6.9 Exercises	285
7 NETS AND INFINITE POLYHEDRA	
7.1 Introduction	289
7.1.1 Circuits, rings and Schläfli symbols	290
7.1.2 Schläfli symbols for 4-connected nets	292
7.1.3 Coordination sequences	293
7.1.4 Further definitions	294
7.2 3-connected nets	295
7.3 4-connected nets	298
7.3.1 Diamond, lonsdaleite and their polytypes	299
7.3.2 Two more uniform nets, 6^6	302
7.3.3 Nets derived from 6^3 : CrB₄	303
7.3.4 Two nets related to CrB₄ with zig-zag rods	305
7.3.5 SrAl₂, cancrinite , and related nets with double zig-zags	306
7.3.6 Some nets derived from 4.8^2 with double crankshafts	308
7.3.7 Another net with double crankshafts: gmelinite	310
7.3.8 Alternating "up-down" nets	311
7.3.9 Feldspar and coesite	313
7.3.10 Sodalite	315
7.3.11 NbO and quartz	316
7.3.12 More quasi-regular and/or uniform nets: γ-Si	319
7.3.13 Silica and water nets: keatite and moganite	321
7.4 Nets and infinite polyhedra	323
7.4.1 Linde A : an infinite polyhedron $4^2.6^2$	323
7.4.2 Zeolite rho : infinite polyhedra $4^3.6$ and $4.8.4.8$	324
7.4.3 Zeolite ZK-5 : infinite polyhedron $4^3.8$	325
7.4.4 Faujasite : a second infinite polyhedron $4^3.6$	326
7.4.5 An open structure W*8 , and a related zeolite	327
7.5 Rare and dense 4-connected nets	328
7.5.1 Two dense nets	329
7.5.2 Rare sphere packings	330
7.6 Clathrate hydrates, foams and grains	333
7.7 A summary of the simpler 4-connected nets	337
7.8 Zeolite nets	337
7.8.1 Zig-zag structures	338
7.8.2 Crankshaft structures	341
7.8.3 Saw-tooth structures	343
7.8.4 More up-down structures	346
7.8.5 The "ABC-6" family	347
7.8.6 Pentasils (silicalites), clathrasils and related structures	349
7.8.7 Fibrous zeolites	352

7.8.8 Zeolite net nomenclature and index	353
7.9 5-connected nets	354
7.10 Nets with mixed connectivity	357
7.10.1 (3,4)-connected nets	357
7.10.2 (4,6)-connected nets	360
7.11 Notes	362
7.11.1 More 3-connected nets	362
7.11.2 Model building	364
7.11.3 Identifying nets	365
7.11.4 Diamond and SiC polytypes	365
7.11.5 Two more nets derived from 6^3 : "C" and "D" phases	367
7.11.6 Nets in CdP ₂ and CsAs ₂	368
7.11.7 More on the moganite, quartz , and related nets	369
7.11.8 Stereo pictures of nets: Y* and clathrate hydrates I and II	370
7.11.9 Anion positions and the possibility of open zeolite frameworks	372
7.11.10 References	375
7.12 Exercises	375

APPENDICES

A1 More infinite symmetry groups

A1.1 Layer groups	381
A1.2 Rod groups	383
A1.3 Examples of layers and rods	383
A1.4 One- and two-dimensional "rods" (bands)	384
A1.5 Point groups of infinite order and the symmetry of vectors	386
A1.6 Table of layer and rod group symbols	389

A2 A glimpse into higher dimensions

A2.1 Introduction: polytopes	393
A2.2 Four-dimensional polytopes and honeycombs	394
A2.3 Four- and higher-dimensional lattices	395
A2.4 Symmetry operations in four dimensions	397
A2.5 Numbers of crystallographic symmetry groups	401
A2.6 Generalization of Euler's formula for polyhedra	401
A2.7 References	402

A3 The topology of polyhedra, nets and minimal surfaces

A3.1 Introduction	403
A3.2 Finite polyhedra	403

A3.3 Infinite polyhedra	404
A3.4 Space filling by polyhedra: nets and ring sizes	409
A3.5 Coordination sequences and topological density	411
A3.6 Enumerating and identifying nets	412
A3.7 Curvature and periodic minimal surfaces	413
A3.8 Some conjectures about numbers and sizes of rings	416
A3.9 References	418
A4 Large polyhedra	
A4.1 Introduction	419
A4.2 5-6 polyhedra	419
A4.3 Fullerene polyhedra	421
A4.4 Icosahedral polyhedra	424
A4.5 Space filling packings of 5-6 polyhedra	427
A4.6 Large coordination polyhedra	428
A4.7 Models of large polyhedra	429
A5 Crystal structure data	
A5.1 Introduction	430
A5.2 Elements	430
A5.3 Composition AB (AX)	431
A5.4 Composition AB_2 (AX_2 and A_2X)	432
A5.5 Other binary structure types	433
A5.6 Ternary structure types	434
A5.7 Crystallographic data	435
Tables of 3-dimensional symmetry group symbols	
Crystallographic point groups	440
Monoclinic space group symbols for various settings	441
Orthorhombic space group symbols for various settings	441
Tetragonal and trigonal space groups	443
Hexagonal and cubic space groups	444
Book List	445
Indices	447
Formula index	447
Subject index	449

CHAPTER 1

SYMMETRY IN TWO DIMENSIONS

1.1 Point symmetry operations in two dimensions

The concepts of *symmetry*, *symmetry operations* and *symmetry elements* play essential roles in the description of the structure and properties of matter, and it is very difficult to understand the crystallographic literature without some knowledge of symmetry theory and its jargon. In this and the next two chapters a brief account is given of the symmetries of objects with particular emphasis on the approach and symbolism that has been adopted as standard by crystallographers. No attempt is made to be either rigorous or complete—that would take us too far afield.

For pedagogic reasons we begin with a discussion of the symmetries of two-dimensional objects. In this case it is not too difficult to give an account of the various symmetries that are possible in a way that is plausibly complete. We can then proceed to a discussion of three-dimensional symmetry using the analogy to two dimensions as a prop to understanding. Two-dimensional symmetries are often encountered in practice (the surface of a crystal and the image of a crystal structure observed in an electron microscope are two-dimensional, for example).

A square confined to a plane looks exactly the same if it is rotated 90° around the point at its center—we say that this operation, which leaves the object unchanged in aspect, is a *symmetry operation*. Thus consider the shaded square shown below (Fig. 1.1). Rotating the square about its center point (the small black square) by 90° , 180° ($= 2 \times 90^\circ$) or 270° ($= 3 \times 90^\circ$) leaves it unchanged. Note that the fourfold repetition of rotation by 90° is equivalent to rotation by 360° . Any object is left unchanged after a rotation of 360° about any point and this operation is called the *identity* operation. We generally refer to a symmetry element that entails rotation by $360^\circ/N$ (N is an integer) as N -fold.

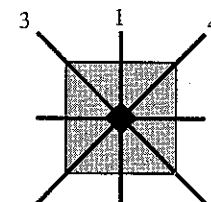


Fig. 1.1. Symmetries of a square.

The point at the center of the square is the location of a *4-fold rotation point* and this one of the *symmetry elements* of the square. Distinguish between the *symmetry element*

and the symmetry operations (in this case repeated rotations by one-fourth of a circle, by convention¹ anticlockwise, about a point). Note also that the application of any symmetry operation on a finite object will always leave at least one point unmoved; for this reason such symmetries are referred to as point operations (or point *isometries*).

The square has other symmetry elements. Reflection of the square in the vertical line (labeled "1" in the figure) going through the center will again leave the square unchanged. The vertical line is a *mirror line*. There is another mirror line (labeled "2") at right angles to this (i.e. horizontal) as the square has 4-fold rotation symmetry.

There is also a second set of mirror lines among the symmetry elements of the square; these (labeled "3" and "4" in the figure) are at 45° to the first set. The reader might try to show that these are *generated* by combinations of 4-fold rotations and one or other of the first set of mirrors. (We will find a simple way to show this later.)²

Repeated application of any point symmetry operation will always eventually result in the identity operation (thus: two successive reflections in the same mirror line or four successive rotations of 90° about the same point). For mathematical reasons it is important to always consider the identity as one of the symmetry elements of any object.

We have identified the entire set of operations of the symmetry elements of the square. It forms a representation of a mathematical group³, and is therefore called the symmetry group—or in this case the *point symmetry group* because at least one point is left invariant by all the symmetry operations.

It is easy to show (we do it below) that in a periodic object (such as a crystal) there is a restriction to point groups that include only 1-, 2-, 3-, 4- or 6-fold rotation symmetry elements. There are ten of these groups in two dimensions; they are called the *crystallographic* point groups. We enumerate them and show patterns with each of the symmetry groups in Fig. 1.2. The patterns are generated by the action of all the symmetry operations of the group on an asymmetric object (in this case a 7).

There are five groups with only rotation points (we include the group that contains only the "one-fold" rotation = identity). A rotation point is symbolized by a number equal to the order of the rotation. For the groups without mirrors, these numbers become also the symbols for the groups which are therefore 1, 2, 3, 4 and 6. These are called the *pure rotation groups*, as the symmetry operations are rotations only. A pattern with pure rotation symmetry will be different from its mirror image and so can be said to have a *hand*. (If the object is left-handed, its mirror image is right-handed and *vice versa*.)

Additional groups are obtained by adding mirror symmetry to the pure rotation groups. The simplest such group is just that obtained by addition of a mirror line (symbol *m*) to group 1 to give group *1m*. This is the symmetry group of a plane object that has but one mirror line. An example is an isosceles triangle or the letter V. Note that group *1m* consists of two operations: reflection in the mirror line and the identity I.

¹This is the convention in crystallography. Many computer graphics programs consider positive rotations to be clockwise.

²For example rotation by 90° anticlockwise followed by reflection in the horizontal mirror is equivalent to reflection in the mirror line running from top left to bottom right.

³The reader unfamiliar with group theory may find the Notes (§ 1.10.2) for this chapter useful.



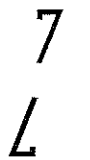


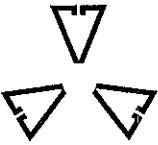

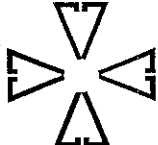
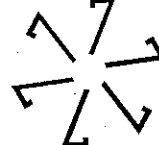
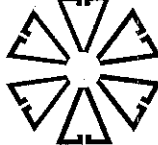
1		1m	
2		2mm	
3		3m	
4		4mm	
6		6mm	

Fig 1.2. Illustrating the 10 two-dimensional crystallographic point groups.

If the symmetry group of an object contains mirror lines, the object is the same as its mirror image and thus will not have a hand. The reader should compare the patterns on the left of Fig. 1.2, which have a hand, to those on the right, which do not.

Next we combine a mirror with a 2-fold rotation (see Fig. 1.2 again). We find in fact that combination of a 2-fold rotation and a mirror results in a second mirror line at right angles to the first, so the group is symbolized $2mm$ to indicate the presence of the two sets of mirror lines (each set consists of one line). Conversely, if we had started with two mirror lines at right angles we would find that we generated a 2-fold rotation point at their intersection.¹ This is the symmetry group of a rectangle or of the letter H.

Proceeding in this way we next generate group $3m$ from a mirror and a 3-fold rotation. This is the symmetry of (for example) an equilateral triangle. Combining a mirror with a 4-fold rotation produces the symmetry group of the square which we have already discussed. The symbol is $4mm$ with two m 's to signify the presence of two sets (of two each) of mirrors. In each set the two mirror lines are related by symmetry. Thus (see Fig. 1.1) a quarter turn takes mirror 1 into mirror 2; mirror lines 3 and 4 are similarly related. On the other hand there is no symmetry operation in the group that converts either mirror 1 or 2 to mirrors 3 or 4—this is why we say there are two *sets* of mirror lines.

Finally we combine a mirror with a 6-fold rotation. Again we get in the symmetry group two sets (now of three each) of mirrors. Accordingly the symbol of the group is $6mm$. A regular plane hexagon has this symmetry. The location of the mirror lines is indicated in Fig. 1.3 below in which the two sets of mirrors are shown as dashed and dotted lines respectively. As in $4mm$, we have a symmetry operation (now rotation by a multiple of a sixth turn) to relate mirror lines in a set, but there is no symmetry operation in the group relating mirrors in one set to any of those in the other set. (Mirror lines of one set are at 30° to those of the other set, i.e. related by a rotation of $360^\circ/12$; but rotation by $1/12$ of a circle is not a symmetry operation of the group).

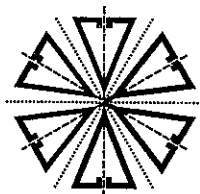


Fig 1.3. Illustrating $6mm$. Dotted and broken lines indicate the location of the two sets of mirrors.

Lifting the restriction to crystallographic symmetry (1-, 2-, 3-, 4-, or 6-fold rotations) we get non-crystallographic point groups. These are rotation groups N with $N = 5$ or > 6 , and the point groups Nm with $N > 3$ and odd (a regular pentagon has symmetry $5m$), and Nmm with $N > 6$ and even (a regular octagon has symmetry $8mm$).

¹The three-dimensional occurrence of this phenomenon is familiar to those who have looked at themselves in two mirrors at right angles. If you have never done this please try!

1.2 Coordinate systems and symmetry operations

Let us consider a Cartesian coordinate system with the x axis pointing down the page and the y axis horizontal as in Fig. 1.4. Further, let the origin be at the 4-fold rotation point of $4mm$. Three of the symmetry elements of that group are indicated: the 4-fold rotation point by a square and two mirror lines by heavy lines.

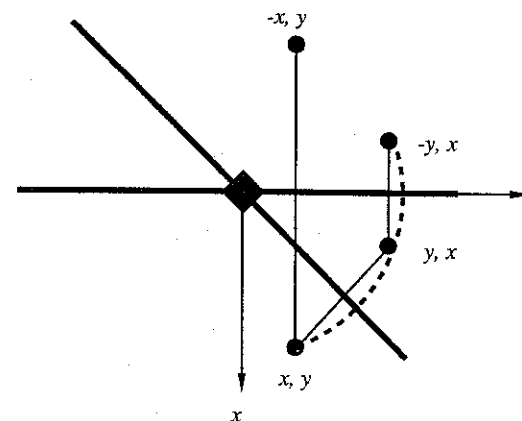


Fig. 1.4. Illustrating the effects of rotations and reflections on a point (see text).

Imagine now the operation of a quarter turn (90° rotation anti-clockwise about the origin) on the point x, y . The point will be translated to a position $-y, x$. This means that the new x coordinate is equal to minus the old y coordinate and the new y coordinate is equal to the old x coordinate; thus if the original point had coordinates $0.2, 0.1$ the new point would have coordinates $-0.1, 0.2$. The transformation can be represented by multiplying the column vector (x/y) (representing the coordinates x, y) by a matrix to give new coordinates x', y' :

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -y \\ x \end{pmatrix}$$

The matrix can be written on one line as $(0 \bar{1} / 1 0)$, with $\bar{1}$ representing -1 , and this is a convenient way of representing the symmetry operation. The matrix corresponding to reflection in the diagonal mirror is $(0 1 / 1 0)$.¹ This transforms the point x, y to y, x as

¹The reader who is not entirely familiar with matrices and their multiplication is well advised to work out the examples given here and subsequently. See the Notes at the end of the chapter (§ 1.10.4) for help with manipulating matrices.

shown in the figure. Finally the operation of reflecting in the horizontal mirror transforms x, y to \bar{x}, y with the corresponding matrix $(\bar{1} \ 0 \ / \ 0 \ 1)$. We may now verify by matrix multiplication that rotation by 90° followed by reflection in the horizontal mirror is equivalent to reflection in the diagonal mirror shown in Fig. 1.4:¹

$$(\bar{1} \ 0 \ / \ 0 \ 1)(0 \ \bar{1} \ / \ 1 \ 0)(x/y) = (0 \ 1 \ / \ 1 \ 0)(x/y) = (y/x)$$

as should be obvious from an inspection of the figure.

Instead of using the matrices to represent the symmetry operations, we could use the transformed coordinates themselves. The resulting coordinates are sometimes known as the Jones symbol. We list in Table 1.1 the matrices and coordinates for all the operations of $4mm$. Reference to Fig 1.2 shows that the original asymmetric object is transformed to eight such objects, so there are eight symmetry operations (eight is the *order* of the group). It is common to symbolize an anticlockwise rotation by a quarter of a circle by 4^1 or 4^+ , rotation by two quarters of a circle (= one half circle) by 4^2 ($= 2^1$) and by three quarters of a circle by 4^3 or 4^- . The last case emphasizes that rotation anticlockwise (the positive sense) by $3/4$ of a circle is equivalent to rotation clockwise (the negative sense) by $1/4$ of a circle.

Table 1.1. Symmetry operations of group $4mm$.

operation	matrix	coordinates
identity = 1	$(1 \ 0 \ / \ 0 \ 1)$	x, y
90° rotation = 4^1	$(0 \ \bar{1} \ / \ 1 \ 0)$	\bar{y}, x
180° rotation = $4^2 = 2^1$	$(\bar{1} \ 0 \ / \ 0 \ \bar{1})$	\bar{x}, \bar{y}
270° rotation = 4^3	$(0 \ 1 \ / \ \bar{1} \ 0)$	y, \bar{x}
reflection in horizontal mirror	$(\bar{1} \ 0 \ / \ 0 \ 1)$	\bar{x}, y
reflection in vertical mirror	$(1 \ 0 \ / \ 0 \ \bar{1})$	x, \bar{y}
reflection in mirror 3 (Fig. 1.1)	$(0 \ 1 \ / \ 1 \ 0)$	y, x
reflection in mirror 4 (Fig. 1.1)	$(0 \ \bar{1} \ / \ \bar{1} \ 0)$	\bar{y}, \bar{x}

In crystallography we do not always use coordinate axes at right angles. In the case of 3-fold or 6-fold symmetry, it is more convenient to take axes inclined at 120° to each other as shown in Fig. 1.5. The figure illustrates the effect of 3-fold rotations on a point x, y from the rotation point taken as origin. The long and short dashed lines have lengths equal to the magnitudes of x and y respectively. Note that to get to the point x, y from the origin, we translate by a distance x parallel to the x axis and then by a distance y parallel to the y axis.

It should be obvious from the figure that after rotation by one-third of a circle (120°) about the origin, the new x coordinate is equal to $-y$, and that the new y coordinate is equal to $x-y$. We therefore write the coordinates of the new point $\bar{y}, x-y$. If the original point were at $x = 0.4$ and $y = 0.1$, the coordinates of the point generated by the rotation of $1/3$ of

a circle (anticlockwise) would be $x = -0.1, y = 0.3$. Repeating this operation takes $\bar{y}, x-y$ to $y-x, \bar{x}$ (i.e. $-0.1, 0.3$ to $-0.3, -0.4$).

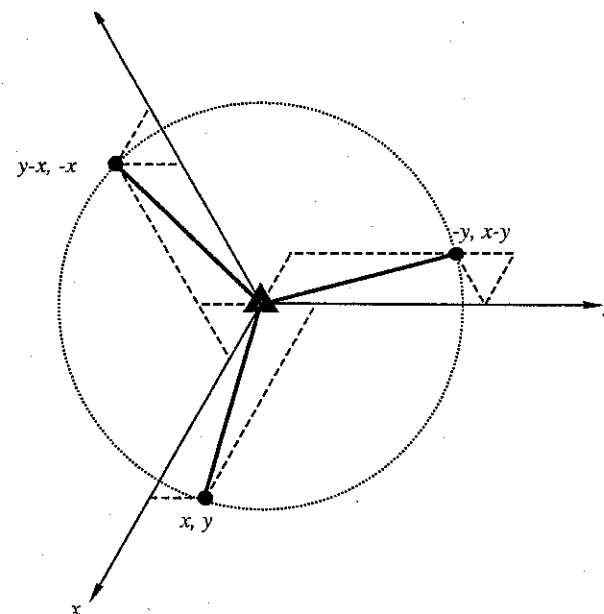


Fig. 1.5. Illustrating a coordinate system with axes (x and y) at 120° .

The symmetry operations of point group 3 can hence be represented as shown in Table 1.2. As there are three symmetry operations, the order of the group is three.

Table 1.2. Representations of the symmetry operations of group 3.

operation	matrix	coordinates
identity = 1	$(1 \ 0 \ / \ 0 \ 1)$	x, y
120° rotation = $3^1 = 3^+$	$(0 \ \bar{1} \ / \ 1 \ \bar{1})$	$\bar{y}, x-y$
240° rotation = $3^2 = 3^-$	$(\bar{1} \ 1 \ / \ \bar{1} \ 0)$	$y-x, \bar{x}$

It is important to note that the matrices and (transformed) coordinates only have the particular form given for the particular *basis* (coordinate system) chosen. A recommended exercise (see Exercise 7 at the end of the chapter) is to find the corresponding matrices and coordinates for a 120° rotation using a Cartesian basis (axes at right angles).

Even with axes at 120° we have to be careful when we consider the point group $3m$.

¹Note that the order of matrix multiplication is important. Reversing the order of the two matrices is equivalent to reversing the order of carrying out the two symmetry operations. (What symmetry operation does one get then?)

There is more than one way we can orient the axes with respect to the mirror lines.¹ There are two ways that prove to be useful in practice as shown in Fig. 1.6. On the left there are mirror lines parallel to the x and y axes; on the right they are perpendicular to the axes. Now it is important to realize that the crystallographer's symbols for symmetry groups not only signify the symmetry elements present, but *also* their orientation with respect to a coordinate system. Accordingly the symbols in the two cases above are different viz. $31m$ and $3m1$. (The full significance of the symbols will be made clear later—for now it is important to note that the two symbols refer to the *same* point group with the coordinate axes in two different orientations with respect to the mirror lines.)

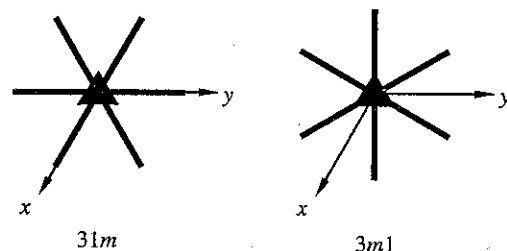


Fig 1.6. Illustrating two orientations of the x and y axes with respect to the symmetry elements (mirror lines) of $3m$.

For the record note that the three mirror reflections operating on x, y give

$$\begin{aligned} \text{for } 31m: & \bar{x}, y, -x; \quad x, -y, \bar{y}; \quad y, x \\ \text{for } 3m1: & x, x-y; \quad y-x, y; \quad \bar{y}, \bar{x} \end{aligned}$$

These, combined with the three points produced by the 3-fold rotation point (given in Table 1.2) produce a total of six points, so the order of the group is six.

1.3 Translational symmetry: lattices and unit cells

We now turn our attention from finite objects to infinite objects with *translational* symmetry. The first important concept that we need is that of a *lattice*. A lattice is an infinite array of points each of which is identically surrounded. In two dimensions a lattice is generated by repeated translations of a point by two non-collinear vectors \mathbf{a} and \mathbf{b} . Thus starting from an arbitrary origin we generate a lattice as the infinite set of points at the end of the vectors $m\mathbf{a} + n\mathbf{b}$ where m, n are positive, negative or zero integers. The lattice is completely determined by the magnitudes, a and b , of the vectors \mathbf{a} and \mathbf{b} and the angle γ

¹In a periodic object (crystal) there is *translational* symmetry and we use axes parallel to translation vectors, so the orientation of the axes is determined by the crystal lattice.

between them.¹

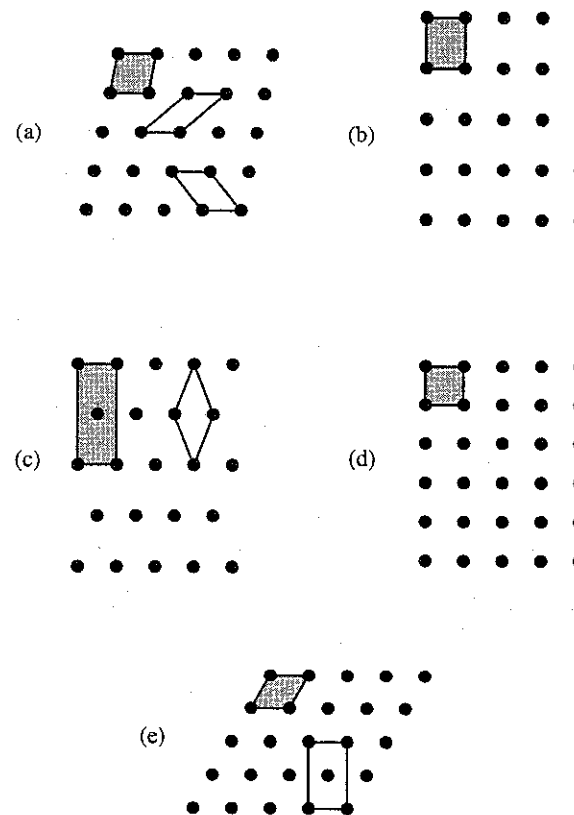


Fig 1.7. The five 2-dimensional Bravais lattices.

The parallelepiped defined by \mathbf{a} and \mathbf{b} is the basic repeat unit of the lattice and is known as the *unit cell*. As illustrated in Fig. 1.7(a), more than one unit cell (with corresponding lattice vectors \mathbf{a} and \mathbf{b}) can be chosen with lattice points only at the corners. Such unit cells

¹The term "lattice" is widely abused. Crystallographers, in particular, become very upset when *lattice* is used to mean *structure* as in "the diamond lattice" or "the wurtzite lattice" (in neither case do all the atoms fall on lattice points). Such usage is considered a gross solecism. However terms such as *lattice dynamics* and *lattice defects* are in such common usage that one cannot avoid them. The word "lattice" is also used in a quite different sense by mathematicians.

contain one lattice point per cell (each point at each of the four corners is shared by four cells), so no matter how they are chosen each cell has the same area. Usually the shortest pair of vectors with $\gamma \geq 90^\circ$ are chosen as shown by the shaded parallelogram. The quantities a , b and γ are referred to as the *unit cell parameters*.

Lattices are classified by their symmetries. Every point in a general two-dimensional lattice is a site of 2-fold rotation symmetry (remember that a lattice extends to $\pm\infty$ in both directions). For some special relationships of the unit cell parameters, the lattice points are at points of higher symmetry. This is illustrated in Fig. 1.7 which shows the different two-dimensional lattices (known as *Bravais lattices*). The lattices shown in (b) and (c) also have mirror symmetry (the points are at sites of symmetry $2mm$), that shown in (d) has 4-fold rotational symmetry and that shown in (e) has 6-fold rotational symmetry. After we have discussed space group symmetry we will see that the lattices (b) and (c) have different space groups ($p2mm$ and $c2mm$ respectively), and hence are classified as different Bravais lattices. Every two-dimensional lattice has one of only five possible space group symmetries and thus is one of the Bravais lattice types illustrated.

The point symmetry operations that leave a lattice invariant (and one lattice point unmoved) form the point symmetry group of the lattice. As lattice translations leave the lattice invariant (the lattice extends infinitely) the translations are also symmetry elements and the full symmetry group (space group) includes the infinite number of translations.

The constraints on a , b and γ in the five lattices, and names descriptive of the shape of the unit cells are listed in Table 1.3. The table also lists the symmetry at a lattice point.

Table 1.3. Properties of the two-dimensional Bravais lattices.

	constraints	system	point symmetry
(a)	none	oblique	2
(b)	$\gamma = 90^\circ$	rectangular	$2mm$
(c)	$a = b$	rectangular	$2mm$
(d)	$a = b, \gamma = 90^\circ$	square	$4mm$
(e)	$a = b, \gamma = 120^\circ$	hexagonal	$6mm$

It may be objected that the unshaded unit cell in (c) is not rectangular, and that is true, but we can take an alternative unit cell that *is* rectangular (shown shaded in the figure) with lattice points at the corners and one at the center. Most commonly this is done and the constraint for lattice (c) above could have been stated as $\gamma = 90^\circ$ for a cell with lattice points at the corner and in the center.

Note that the unit cells with only one lattice point per unit cell are *primitive*. On the other hand the rectangular unit cell shown in (c) contains two lattice points (one corresponding to the corners, and the one at the center) and is called *centered*. The unit cell parameters for the centered cell in (c) have $a \neq b$, $\gamma = 90^\circ$ as in (b) but, as noted above, the two lattices have different space group symmetries. Two-dimensional lattices represented by a primitive cell are symbolized by p and that conventionally represented by a centered cell is symbolized by c .

The terms *oblique*, *rectangular*, *square*, and *hexagonal* refer to the crystal system. Clearly there are four crystal systems in two dimensions.

1.4 Allowed rotational symmetries of lattices

We pause now to prove the assertion that the only rotational symmetries allowed in periodic structures are 1-, 2-, 3-, 4- and 6-fold rotations. Certainly one or more of the lattices (a)-(e) of the previous section have one or more of these symmetries (note that e.g. a 6-fold symmetry includes 1-, 2- and 3-fold).

A proof, which is very old, proceeds as follows. We take an arbitrary lattice and identify the shortest lattice vector \mathbf{a} . Now consider two lattice points A and B separated by \mathbf{a} (see Fig. 1.8). Let there be N -fold rotation points at A and B . Let B' be the image of B after rotation by $360^\circ/N$ about A , and A' the image of A after rotation by $-360^\circ/N$ about B . A' and B' must also be lattice points. The distance $B'A'$ is equal to $a[1 - 2\cos(360^\circ/N)]$ and must be equal to 0, a or $>a$ (if $B'A' < a$ then \mathbf{a} was not the shortest lattice vector). We consider each of these possibilities in turn:

$$B'A' = 0: \quad 1 - 2\cos(360^\circ/N) = 0 \quad N = 6$$

$$B'A' = a: \quad 1 - 2\cos(360^\circ/N) = 1 \quad N = 4$$

$$B'A' > a: \quad 1 - 2\cos(360^\circ/N) > 1 \quad N < 4 \text{ (i.e. 3, 2 or 1)}$$

Thus the only possible values of N are 1, 2, 3, 4 or 6. *Q.E.D.*¹

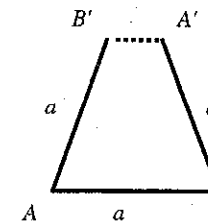


Fig. 1.8. Illustrating the proof that only 1-, 2-, 3-, 4- or 6-fold rotations are allowed rotational symmetries of lattices.

1.5 Unit cell coordinates: describing structures

For a periodic structure we now know how to specify the unit cell. To completely define the structure the next thing we have to do is to specify what is in the unit cell.

¹The unconvinced reader is invited to consider the case of $N = 5$.

The reference coordinate system is always taken with the x axis parallel to a and the y axis parallel to b . Usually the y axis is drawn horizontal and the x axis down the page so that the origin of coordinates is at the top left corner of the unit cell. The scale of x is in units of a (the magnitude of the vector a) and the scale of y is in units of b . In these terms the coordinates of the unit cell corners are $0,0$; $0,1$; $1,0$ and $1,1$. Note that x and y are dimensionless; for example the distance from the origin at $0,0$ to a point $x,0$ is xa and a has dimensions of length.

Any point in the unit cell will be specified by x,y where x and y will be in the range 0 to <1 . It is important to note that coordinates equal to, or greater than, 1 are not used. This is because (for example) the existence of a point at $0,y$ implies a point at $1,y$. Both these points are shared with two unit cells so we would be counting points twice if we gave the coordinates of both points. Likewise $x,0$ implies $x,1$ and $0,0$ implies $0,1$ and $1,0$ and $1,1$.

Sometimes crystallographers use negative coordinates such as \bar{x} or \bar{y} . These should be interpreted as $1-x$ and $1-y$ respectively. It should be clear that adding (or subtracting) an integer to either x or y will always produce an identical point in another unit cell (remember that we have translational symmetry). The point in the reference cell will always have $0 \leq x,y < 1$. It should be noted, however, that when illustrating unit cells of structures it is conventional to show points (if there are any) on all edges and corners.

We now consider some examples: A certain pattern has a rectangular unit cell with $a = 1.73$ (actually $\sqrt{3}$) and $b = 2.0$. There are three points per unit cell with coordinates A: $0,0.5$; B: $0.5,0.25$; C: $0.5,0.75$. Fig. 1.9 shows (on the left) a unit cell with the points plotted as circles (note that the point at $1,0.5$ corresponding to A is also shown). In the center is part of the pattern obtained by repeating the unit cell. To make the pattern clearer, on the right the points nearest to each other have been joined together and the outline of the unit cell omitted. This pattern is observed in layers of atoms in some crystal structures. This example illustrates what is generally the case—although the pattern is completely specified by the shape and content of the unit cell, it can only be fully appreciated by drawing a number of unit cells.

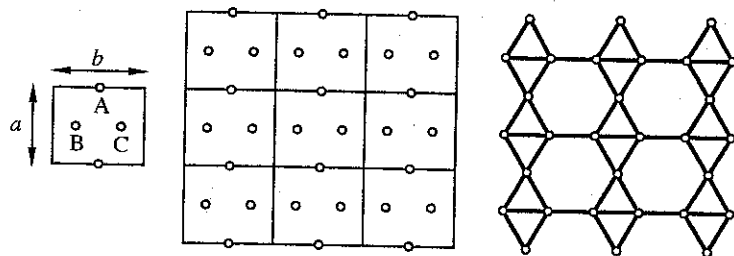


Fig. 1.9. Left: a unit cell of a pattern. Middle: nine unit cells. Right: the same pattern with nearest neighbors joined by lines.

A second example involves a hexagonal cell. Now $b = a$ and $\gamma = 120^\circ$. Points are at $0,0.5$; $0.5,0$ and $0.5,0.5$. Fig 1.10 shows (on the left) a unit cell, in the center nine unit

cells and on the right, the pattern outlined by joining nearest neighbors in the same way as in Fig. 1.9. This pattern is one that is encountered repeatedly in crystal chemistry. It is often called the *kagome* pattern after the Japanese word for bamboo weaves used in basket making. It is also very frequently encountered in ornamental designs.

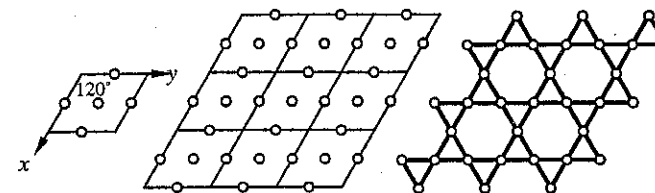


Fig. 1.10. Left: a (hexagonal) unit cell of a pattern. Middle: nine unit cells. Right: the kagome pattern 3.6.3.6.

Note that in the kagome pattern every point has the same surroundings in the sense that the polygons *in sequence* meeting at the vertex are hexagon, triangle, hexagon, triangle. By contrast in the pattern of Fig. 1.9 there are two kinds of point; at one kind (A) the sequence is the same as in kagome (hexagon, triangle, hexagon, triangle) but at the other kind (B and C) it is hexagon, hexagon, triangle, triangle. Both patterns are examples of *tilings* or *tessellations* of the plane by a combination of regular polygons.

A digression on tilings: If the plane is covered completely by just one kind of regular polygon, we have a *regular* tiling. It is not difficult to prove that there are just the three of these. The first, in which six triangles (3-gons) meet at a point, is often symbolized 3^6 ; the second, in which four squares (4-gons) meet at a point, is symbolized 4^4 ; the third in which three hexagons (6-gons) meet at a point is symbolized 6^3 . (This last is also known as the *honeycomb* pattern, for an obvious reason.) The symbols 3^6 , 4^4 and 6^6 are known as *Schläfli* symbols.¹

If the plane is similarly covered by more than one kind of regular polygon, and all points at which three or more polygons meet are of the same kind (related by symmetry), we have the *semiregular* or *Archimedean* tilings of the plane. The kagome pattern (Fig. 1.10) is of this type and is symbolized 3.6.3.6 as the polygons in cyclic order around each point are 3-gon, 6-gon, 3-gon, 6-gon. There are eight different semi-regular tilings; we describe them later (Chapter 5). It is also convenient to refer to them by their Schläfli symbols. End of digression.

We have noted that the pattern in Fig. 1.9 contains two kinds of point. The kagome pattern in Fig. 1.10 contains only one kind of point, as in this pattern the points are related by symmetry. Thus starting from one point we can generate two more by rotating about a 3-fold point (there are 3-fold rotation points in the centers of all the triangles) and get an equilateral triangle of points. Repeating the pattern of three points by the translation vectors

¹After the great Swiss mathematician, Ludwig Schläfli (1814-1895). Mathematicians write 3^6 (for example) as (3,6) as this allows easier extension to higher dimensions (as in Schläfli's pioneering work).

a and **b** recovers the pattern of points. This array of points however is *not* a lattice (this is an important point)—a lattice is generated by translations alone.¹

1.6 Glide symmetry

We have identified three kinds of symmetry operation: rotation, reflection and translation. It transpires that we can combine two of these operations to give a new symmetry operation: translation + reflection = *glide*. The translation direction and the mirror line must be parallel to each other and to one of the lattice translation vectors. The symmetry operation is the compound one of first reflection in a line (a *glide line*) and then translation parallel to the line by a distance d .² Repetition of this operation will produce a pattern that is periodic with a period $2d$. The vector of length $2d$ must therefore be a lattice vector. Fig. 1.11 illustrates nine successive glides of a triangle initially on the left: the glide line is shown in the conventional representation as a dashed line. The symbol for a glide line is g (compare with m for a mirror line). If you walk in a straight line, and with a uniform step, along a beach, your footprints will be related by glide symmetry.



Fig. 1.11. Illustrating glide. The glide line is shown as a broken line.

1.7 Two-dimensional space groups

We are now in a position to enumerate the symmetry groups that are obtained in two dimensions by combining the point operations with those that involve translation. We will find that there are 17 such two-dimensional space groups. We first combine the point group operations of rotation and reflection with translation and then consider the cases where reflection lines are replaced by glide lines. Groups obtained by the combination of point operations with translations are called *symmorphic*. Additional *non-symmorphic* groups are obtained by replacing (where appropriate) mirror lines by glide lines. The diligent reader will work through each example by letting the symmetry operations act on an asymmetric object; Exercise 8 shows how to proceed. If this is done, patterns similar to those shown in the different parts of Fig. 1.12 (below) will be obtained.

¹Note that points (or atoms *etc.*) related by lattice translations are often referred to as *identical* (a lattice is an infinite array of *identical* points). Points that are related by symmetry operations other than pure translations are sometimes called *equivalent*.

²Actually in this case the order in which these operations is carried out is unimportant; one could translate and *then* reflect.

1.7.1 Oblique system

We start with the simplest case in which there is translational symmetry only with an oblique lattice. This is the symmetry of the pattern obtained from periodic translations of an asymmetric object in two dimensions. The symbol for the symmetry group is $p1$. The p symbolizes the lattice (primitive) and the 1 the associated point group.

As already noted, an oblique lattice by itself has 2-fold rotation symmetry at the lattice points, so it is also compatible with the pattern obtained by repeating an object (which may be *e.g.* a collection of points) with 2-fold rotation symmetry by oblique lattice vectors. The symmetry group consisting of the combination of the translations with 2-fold rotations is symbolized $p2$.

No other symmetries are possible with an oblique lattice so we have found the two possible space groups in the oblique system: $p1$ and $p2$. Patterns with these symmetries are shown in Fig. 1.12 (a). Note that in the parts of Fig. 1.12, the patterns are generated by the symmetry operations operating on a single asymmetric object (a scalene triangle) and the number of such triangles per primitive unit cell is the same as the order of the point group from which the space group is derived.¹

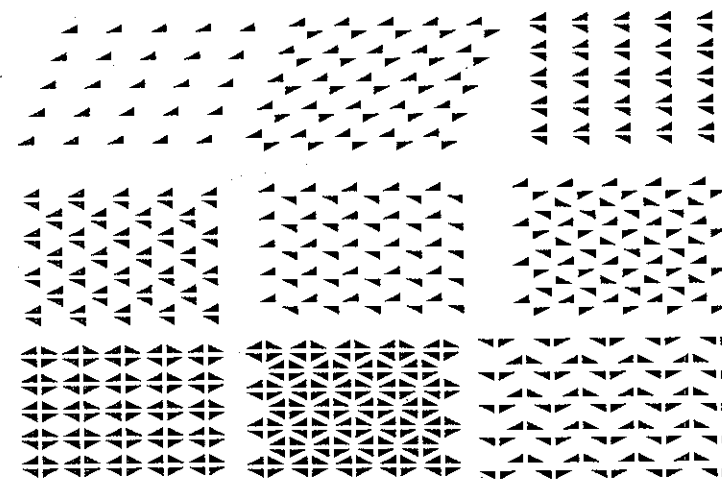


Fig. 1.12 (a). Illustrating the oblique and rectangular two-dimensional space groups. Each pattern has different symmetry (which should be identified).

¹The device of using a scalene triangle as an asymmetric object is old [see *e.g.* L. Weber, *Zeits. Kristallogr.* 70, 309 (1929)] and patterns similar to those in the various parts of Fig. 1.12 are to be found for example in *Elementary Crystallography* by M. J. Buerger [Wiley, New York (1963)]. The space groups are deliberately left unidentified in the figure. The reader should provide the labels. This is an easy exercise, but it should be done.

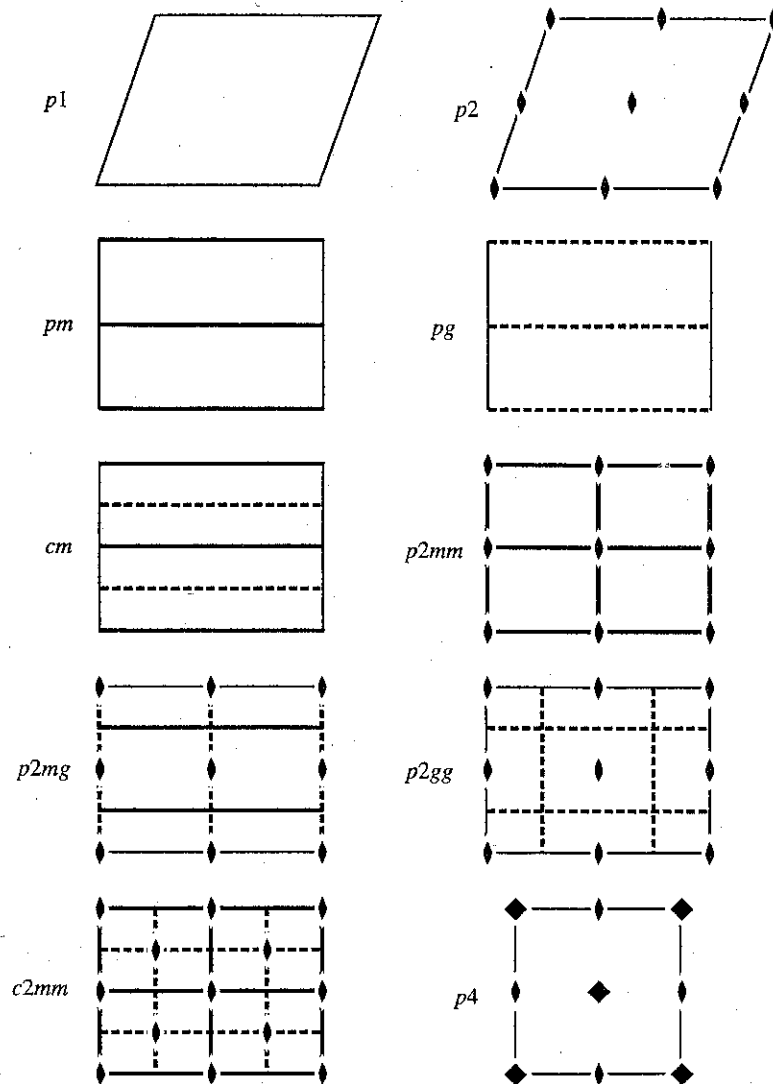


Fig. 1.13. This figure is continued on the next page (see the caption there).

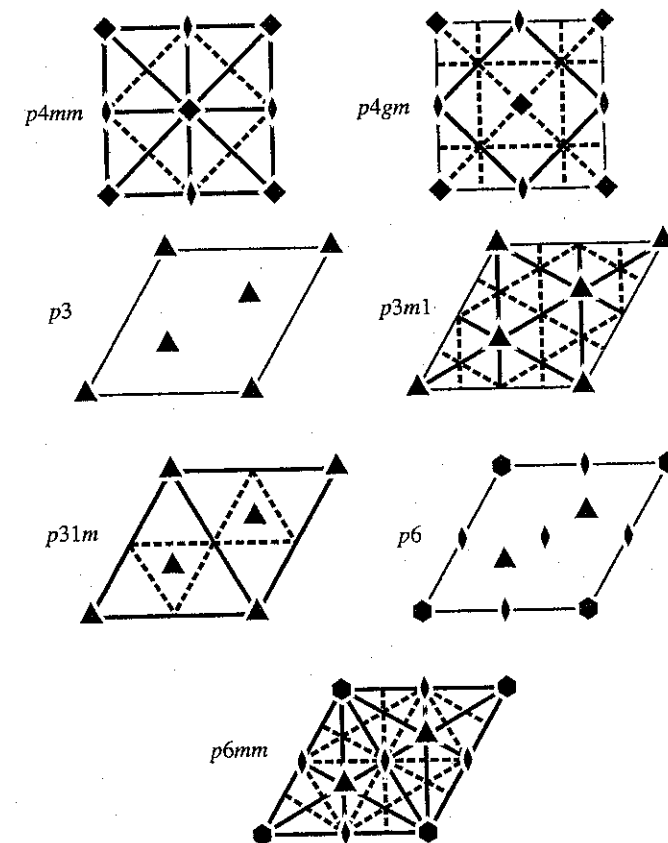


Fig. 1.13. The symmetry elements of the two-dimensional space groups. Light lines outline a unit cell. Heavy solid lines indicate the location of mirror lines and broken lines indicate the positions of glide lines. 2-, 3-, 4- and 6-fold rotation points are represented by "lenses", triangles, squares and hexagons respectively.

Figure 1.13 shows the location of the symmetry elements in one unit cell for the space groups. In $p1$, there are only translations, but in $p2$, in addition to the 2-fold rotation points at the corners of the cell, there are also 2-fold rotation points (whose locations are indicated by the two-pointed symbols) in the middle of the edges and the center of the unit cell. Note that *all* the symmetry elements of $p2$ are obtained by combining one rotation point with translations.¹

1.7.2 Rectangular system

The rectangular lattice p has mirror symmetry and the lattice translations can be combined with point group $1m$ to give a symmetry group $p1m1$ (often abbreviated to pm).² The symmetry elements of this group consist of orthogonal lattice translations and a family of mirror lines parallel to one of the axes. The spacing between the mirror lines is one-half of the lattice repeat.

We can also combine the elements of $1m$ with the translations of the centered rectangular lattice c to get space group $c1m1$ (abbreviated symbol cm). Note in Fig. 1.13 that the space group also contains glide lines interleaved with the mirror lines. These should be identified in the appropriate part of Fig. 1.12.

Point symmetry group $2mm$ is also compatible with a rectangular lattice, so we have space groups $p2mm$ and $c2mm$ (often abbreviated to pmm and cmm respectively). These are the space groups of the primitive and centered rectangular lattices respectively. Note that they are different symmetries and in particular $c2mm$ contains glide lines that are absent in $p2mm$ (Fig. 1.13 again).

Now that we have mirror lines in the space groups, we must consider the possibilities that arise when mirror lines are replaced by glide lines. Thus the mirror line in the symmorphic group $p1m1$ can be replaced by a glide line to give the non-symmorphic group $p1g1$ (often abbreviated pg). Again the symmetry elements should be identified in Figs. 1.12 (a) and 1.13.

We remarked that the symmorphic group $c1m1$ already contains glide lines so there is *not* a new group " $c1g1$ " to be obtained by replacing the mirrors of $c1m1$ by glide.³

From the symmorphic group $p2mm$ we get the non-symmorphic groups $p2mg$ and $p2gg$ (often abbreviated pmg and pgg) as illustrated in Fig. 1.13.

As explained below, the symbol $p2mg$ refers to the space group in which there are mirror lines perpendicular to **a** and glide lines perpendicular to **b**. The group $p2gm$ is the same symmetry group but now the axis perpendicular to the mirror lines is **b** and the axis perpendicular to the glide lines is **a**. Thus $p2mg$ and $p2gm$ are two different *settings* of the

¹A reminder that here, and throughout the rest of § 1.7, the reader who is unfamiliar with the material will: (a) Verify that the patterns in Fig. 1.12 are indeed generated by the basic point group operations plus translations. (b) Verify the existence of the symmetry elements shown in Fig. 1.13 from the patterns of Fig. 1.12.

²The significance of the "1"s in the symbol is explained below. The novice may well wish to reread this section after reading § 1.8.

³The skeptical reader should nevertheless do the experiment. It will be found that replacing the mirror lines in $c1m1$ by glide lines will produce mirror lines where the old glide lines were.

same space group with the first arbitrarily chosen as the *standard setting*. This illustrates that symbols for space groups can change with relabeling of the axes. This is not much of a problem in two dimensions, but we will need to devote careful attention to the analogous question in three dimensions.

It is important to recall that glide lines *already* exist in cm and $c2mm$ so there are no new groups cg , $c2mg$ or $c2gg$. We have therefore identified all the rectangular space groups.

1.7.3 Square system

In the square system, we can combine the translations of the square lattice with the point symmetries that include a 4-fold rotation, i.e. 4 and $4mm$, getting space groups $p4$ and $p4mm$ (short symbol $p4m$). It should be seen in Fig. 1.13 that the combination of lattice translations and a 4-fold point at the origin generates a second 4-fold point at the center of the cell and 2-fold points in the middle of the cell edges. The pattern of symmetry $p4mm$ should be identified in Fig. 1.12 (b) and the glide lines parallel to the unit cell diagonals (shown in Fig. 1.13) identified.

The existence of one set of glide lines parallel to the second set of mirrors (symbolized by the second "m") in $p4mm$ means that although there is a new space group $p4gm$ (short symbol $p4g$) there are not new groups $p4mg$ or $p4gg$. Again identify the space groups in Fig. 1.12 (b) and locate the symmetry elements. We have now identified all the square space groups.

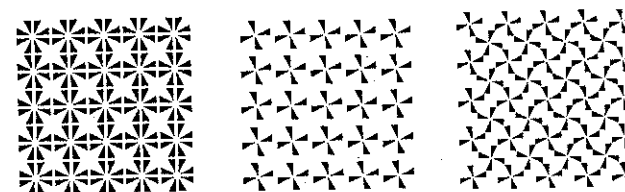


Fig. 1.12 (b). Illustrating the square two-dimensional space groups. Each pattern has different symmetry.

1.7.4 Hexagonal system

In the hexagonal system we can combine the translations of the hexagonal lattice with the point symmetries 3, $3m$, 6, and $6mm$.

As already explained (see Fig. 1.6) $3m$ can be oriented in two ways with respect to the coordinate axes (which are parallel to the lattice translations) to give two *distinct* space groups $p3m1$ and $p31m$. Patterns with these two symmetries are shown in Fig. 1.12 (c). To determine which is which (a) outline a unit cell, (b) identify the mirror lines. $p3m1$ is the one that has mirror lines normal to the cell edges (compare Fig. 1.13).

The other symmorphic space groups are $p3$, $p6$ and $p6mm$ (sometimes abbreviated to $p6m$). Note again in Fig. 1.13 the presence of additional symmetry elements, in particular in the hexagonal system we always have 3-fold points at $1/3, 2/3$ and $2/3, 1/3$.

The groups $p3m1$ and $p31m$ both already have glide lines so there are no new groups to be derived by replacing mirrors by glides in these instances. Finally there are glide lines parallel to both sets of mirrors in $p6mm$ so again there are no new groups to be obtained by replacing the mirrors by glides.¹ We have therefore concluded the enumeration all the two-dimensional space groups.

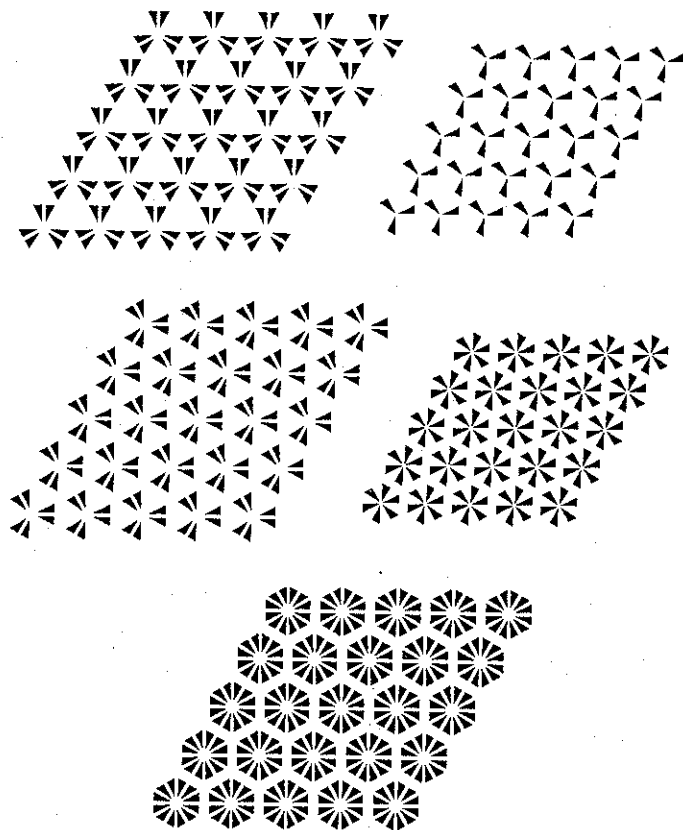


Fig. 1.12 (c). Illustrating the hexagonal two-dimensional space groups.

¹In the centered rectangular lattice mirror lines and glide lines are interleaved throughout space. The hexagonal lattice may be considered as a special case of a centered rectangular lattice (see Table 1.3, p. 10 and Exercise 2, p. 26).

1.7.5 Synopsis of the two-dimensional space groups

Table 1.4 below summarizes the two-dimensional space groups. The final column lists first the symmorphic groups and secondly the non-symmorphic groups obtained when mirror lines are replaced by glide lines. Note that the *system* is determined by the shape of the conventional unit cell, or equivalently by the point symmetry at a point of the lattice (Table 1.3). The point group from which a space group is derived is the *class*.

Table 1.4. Synopsis of the two-dimensional space groups (short symbols in parentheses)

system	point group (class)	space group symmorphic $m \rightarrow g$	
oblique	1	$p1$	
	2	$p2$	
rectangular	1m	$p1m1$ (pm)	$p1g1$ (pg)
	2mm	$c1m1$ (cm)	
		$p2mm$ (pmm)	$p2mg$ (pmg)
		$c2mm$ (cmm)	$p2gg$ (pgg)
square	4	$p4$	
	4mm	$p4mm$ (p4m)	$p4gm$ (p4g)
hexagonal	3	$p3$	
	3m	$p3m1$	
		$p31m$	
	6	$p6$	
	6mm	$p6mm$ (p6m)	

1.8 Construction and interpretation of space group symbols

We now summarize the rules for constructing and interpreting space group symbols. It is emphasized that the space group symbol both identifies the space group and specifies the orientation of the reference axes with respect to the symmetry elements. In specifying the direction of mirror or glide lines we actually specify the directions of the normals to them (for reasons that will become apparent in Chapter 3). Note that in interpreting the space group symbol, we have first to identify the system (oblique, rectangular, square or hexagonal).

The first letter of a space group symbol refers to the lattice type and must be "p" or "c."

In the **oblique** system we have either $p1$ or $p2$ as space group symbol.

In the **rectangular** system there are (in the long, or full, symbol) three places after the lattice symbol. The first of these three places has a symbol which refers to the nature of the rotation point and is either "1" or "2." The next symbol refers to the nature of the symmetry line ("m" or "g") normal to **a** (the normal to the mirror or glide line is parallel to **a**). The last symbol refers to the nature of the symmetry element normal to **b** and is either "1", "m" or "g." Note the use of "1" as a *place marker* to avoid ambiguity when no symmetry element is present. The standard setting for pm is with the mirror planes normal to **a** hence the long symbol $p1m1$; if for some reason we wished to label the axis normal to the mirror plane **b**, the space group symbol would now be written $p11m$.

In the **square** system the first position of the space group symbol is for the lattice (must be p). The second is for the rotational symmetry (must be 4) the third (if present) is for symmetry elements along x and y (i.e. parallel to **a** and **b**—because of the 4-fold symmetry these symmetry elements must be the same) and the fourth position (in the full symbol) signifies the presence of symmetry elements at 45° to x and y (i.e. along the directions $a \pm b$).

In the **hexagonal** system the first position of the space group symbol is again p . The second indicates the rotational symmetry (3 or 6). The third position signifies symmetry elements along the x and y directions (which are at 120°), i.e. parallel to **a** and **b** and to the third equivalent direction which is parallel to $-(a+b)$. The fourth positions refer to symmetry elements at 90° to x and y . Recall that the orientations of mirror lines are specified by the directions of their normals and note again the use of 1 as a place marker in $p3m1$ and $p31m$. Accordingly in $p3m1$ the normals to the mirrors are parallel to **a** and **b** [the mirror lines are normal to **a** and **b** and $-(a+b)$]; in $p31m$ the normal to the mirrors are at right angles to **a** and **b** [the mirror lines are parallel to **a** and **b** and $-(a+b)$].

1.9 Using the International Tables

Volume A of the *International Tables for Crystallography* (see the Book List) is the standard (and indispensable) source of information about space groups.¹ Fig. 1.13 closely follows the diagrams in that book which we often refer to just as the *International Tables*.

The *International Tables* also gives the coordinates of the points in one unit cell obtained by the operation of the symmetry operations of the space group on an arbitrary point x, y . These are the coordinates of the *general* positions. The number of general positions will equal the order of the point group multiplied by the number of lattice points per unit cell (1 for p and 2 for c).

¹Two points to note here about the *Tables*: (a) The two-dimensional space groups are there called "plane groups". (b) The short symbols (which are widely used elsewhere) are not used for these groups (see p. 16 of the *Tables* for more on this point).

There are also *special* positions in the unit cell. These correspond to points that are either at rotation points or on mirror lines. Thus consider the group $p6mm$ (see Fig. 1.13, p. 17). The point at the origin is on a 6-fold rotation point and operation of the 6-fold rotation will not generate any new points. Likewise the same point is also on the mirror planes so the mirror planes produce no new points. In fact the symmetry operations produce no new points at all. This may be verified by substituting $x = 0$ and $y = 0$ in the coordinates of the general positions listed below.

Other special positions of $p6mm$ are on the 3-fold points at $1/3, 2/3$ and $2/3, 1/3$. The symmetry operations acting on one of these points will produce only the other as may be verified by substituting $x = 1/3$ and $y = 2/3$ in the coordinates of the general positions.¹

In Table 1.5 below we give for $p6mm$ (short symbol $p6m$): first the number of positions of a given kind, then the *Wyckoff* notation (a, b , etc.) and then the coordinates of the positions. Refer to Fig. 1.13 to see that the positions 6 e correspond to points constrained to lie on one set of mirror lines and thus at sites of symmetry m . The positions 6 d are likewise arbitrary points on the second set of mirror lines and again at sites of symmetry m . Positions 3 c are points on 2-fold rotation points and at the intersection of two mirrors, and so are at sites with point symmetry $2mm$. Positions 2 b are on 3-fold rotation points at the intersection of three mirror lines so they are at sites with symmetry $3m$. Point 1 a (at the origin) has symmetry $6mm$. The letters a, b , etc. have no special significance except to serve as (universally accepted!) labels. Each space group will have special and general positions labeled from a (for the highest symmetry points), alphabetically to whatever letter is necessary for the general positions. The last entry in the table below is the point symmetry at each kind of site.

Table 1.5. Special and general positions of $p6mm$

wyckoff notation	coordinates	symmetry
12 f	$x, y; \bar{y}, x-y; y-x, \bar{x}; y, x; \bar{x}, y-x; x-y, \bar{y}$ $\bar{x}, \bar{y}; y, y-x; x-y, x; \bar{y}, \bar{x}; x, x-y; y-x, y$	1
6 e	$x, \bar{x}; x, 2x; 2\bar{x}, \bar{x}; \bar{x}, x; \bar{x}, 2\bar{x}; 2x, x$	m
6 d	$x, 0; 0, x; \bar{x}, \bar{x}; \bar{x}, 0; 0, \bar{x}; x, x$	m
3 c	$1/2, 0; 0, 1/2; 1/2, 1/2$	$2mm$
2 b	$1/3, 2/3; 2/3, 1/3$	$3m$
1 a	$0, 0$	$6mm$

Having available the coordinates of the general and special positions allows a considerable economy in specifying structure. Thus only the coordinates of one of a set of general positions need to be given. In some cases no coordinates need be given explicitly. Thus to completely specify the positions of the points in the kagome pattern (3.6.3.6) described above, it is sufficient to give the space group ($p6mm$), the magnitude of the unit cell parameter (a) and to state that points are at positions c . The points of the honeycomb pattern (6³) are at b (make a quick sketch). Another example using this space group is

¹Remember that $x = -1/3$ is equivalent to $x = 2/3$ etc.

given in Exercise 3 at the end of the chapter.

In a space group with a centered lattice the existence of a point x, y implies the existence of an identical point at $1/2+x, 1/2+y$ because translation by $1/2, 1/2$ is a symmetry operation. In the *International Tables* the positions of *cm* are given as shown in table 1.6.

Table 1.6. Special and general positions of *cm*.

		$(0,0; 1/2, 1/2) +$
4 b	$x, y; \bar{x}, y$	
2 a	$0, y$	

Thus the coordinates of the general positions are $x, y; \bar{x}, y; 1/2+x, 1/2+y; 1/2-x, 1/2+y$ and the coordinates of the special positions *a* are $0, y; 1/2, 1/2+y$ (i.e. on the mirror lines at $x = 0$ and $x = 1/2$).

1.10 Notes

1.10.1 Symmetry operations

The symmetry operations we have discussed are special cases of general geometrical transformations or mappings. They are those which preserve distances and angles and hence the term *isometry*. There are many mappings in which there is a one-to-one correspondence between the object before and after the transformation. A *similarity* transformation is one in which angles, but not distances are conserved. It may be considered as the result of an isometry followed by an expansion or contraction in scale. Another transformation of interest is inversion or reflection in a circle. For examples of the remarkable patterns that can arise from repeated reflections in a system of circles see R. Courant & H. Robbins, *What is Mathematics?*, Oxford University Press, Oxford (1941) p. 162.

1.10.2 Groups

Introductions to symmetry group theory¹ are F. A. Cotton, *Chemical Applications of Group Theory*, 3rd Edition, Wiley, New York (1990) and Boisen & Gibbs (Book List).

A group is a set of (at least one) things with the following properties.

• There is defined a *binary operation* symbolized by $*$ such that $\alpha*\beta = \gamma$, where α, β and γ are all members of the group. In the case of symmetry operations, $\alpha*\beta$ means operation β followed by operation α , and γ is also a symmetry operation. Note that in general $\alpha*\beta$ and $\beta*\alpha$ are not equal (but may be). If for every pair of elements in the group $\alpha*\beta = \beta*\alpha$ the group is said to be *commutative* or *abelian*.

¹Note that in this chapter we haven't done any group theory (nor shall we in subsequent chapters). All we have done is to *enumerate* certain kinds of symmetry group.

• $\alpha*(\beta*\gamma) = (\alpha*\beta)*\gamma$ (this is the *associative rule*).

• There exists an element ϵ in the group such that $\epsilon*\alpha = \alpha*\epsilon = \alpha$ for α equal to any member of the group. In symmetry groups ϵ corresponds to the identity operation.

• For any element α in the group there is another β (the *inverse* of α) such that $\alpha*\beta = \beta*\alpha = \epsilon$. α and β may be the same (for example two reflections in the same mirror result in the identity) or different [rotation by one-third of a circle ($3^1 = 3^+$) followed by rotation by two-thirds of a circle ($3^2 = 3^-$), or *vice versa*, again results in the identity ($3^1*3^2 = 3^2*3^1 = 1$)].

The number of distinct elements in the group is the *order* of the group. The simplest possible group (of order 1) contains only ϵ .

An example of a finite group (of order three) is the numbers 0, 1 and 2 if the group operation $*$ is defined as "addition modulo 3", i.e. $\alpha*\beta \equiv (\alpha+\beta) \pmod{3}$. Thus we have:

$0*0 = 0$	$1*0 = 1$	$2*0 = 2$
$0*1 = 1$	$1*1 = 2$	$2*1 = 0$
$0*2 = 2$	$1*2 = 0$	$2*2 = 1$

Here 0 corresponds to ϵ , and 1 and 2 are the inverses of each other. We can write out the above relationships as a "multiplication" table. "Multiplication" refers to the group operation, in this case "addition modulo 3."

	0	1	2
0	0	1	2
1	1	2	0
2	2	0	1

This group has the same structure as (is *isomorphic* with) the point symmetry group 3 whose elements are the identity and rotations by one-third and by two-thirds of a circle. These two sets of things with their appropriate group operation ($*$) form two different representations of the same abstract group.

The matrices that we derived for symmetry operations (see e.g. the case of *4mm* Table 1.1) form a representation of the same abstract group as do the symmetry operations themselves if the group operation now is identified as matrix multiplication.

1.10.3 Two-dimensional space groups and decoration

The occurrence of periodic patterns in decoration is familiar and dates from antiquity. A most striking source of periodic patterns is the XIV century designs in the Alhambra of Granada in Spain. More recently, the Dutch artist M. C. Escher was inspired by the Alhambra to produce some remarkable periodic designs which have been used as an aid to teaching crystallography [C. H. MacGillavry, *Symmetry Aspects of M. C. Escher's Periodic Drawings*, Oosthoek, Utrecht (1965)]. Escher's art also provides some beautiful

examples of repeated similarity transforms.

The Moors did not use all the two-dimensional space groups in the decoration of the Alhambra. It is interesting that the explicit enumeration of the 17 two-dimensional groups was only done *after* the 230 three-dimensional space groups were enumerated. The symmetry groups of three-dimensional objects with translations in only two dimensions are the 80 *layer groups* which are sometimes of use in crystal chemistry. We refer to these again in Chapter 3 (see also Appendix A1).

1.10.4 Matrix manipulations

The reader entirely unfamiliar with matrix manipulations will have to consult one of the very many elementary mathematics texts that deal with such matters. In this chapter we use only 2×2 matrices such as $A = (a_{11} \ a_{12} / a_{21} \ a_{22})$ and 2×1 matrices (2 rows and 1 column; also known as column vectors) such as $x = (x_1 / x_2)$.

Multiplication of a 2×1 matrix by a 2×2 matrix give a new 2×1 matrix as in $Ax = y$, where $y = (a_{11}x_1 + a_{12}x_2 / a_{21}x_1 + a_{22}x_2)$.

Multiplication of a 2×2 matrix by a 2×2 matrix gives a new 2×2 matrix as in $AB = C$, where $C = (a_{11}b_{11} + a_{12}b_{21} \ a_{11}b_{12} + a_{12}b_{22} / a_{21}b_{11} + a_{22}b_{21} \ a_{21}b_{12} + a_{22}b_{22})$. Note that the order of multiplication is important and in general $AB \neq BA$ (recall that the order in which symmetry operations are carried out *may* be important).

1.11 Exercises

1. Circles of unit diameter are packed as closely as possible on a plane. A fraction $\pi/\sqrt{12}$ of the area of the plane is covered. The symmetry is $p6mm$ and the centers of the circles are on the points of a hexagonal lattice. (Do this by packing coins of one kind on a table top.)

2. A hexagonal lattice can be described by a centered rectangular cell with $b/a = \sqrt{3}$. (The centered cell is sometimes called *orthohexagonal*).

3. A pattern often encountered in crystal chemistry and in ornament is the Archimedean tiling 3.4.6.4 which has symmetry $p6mm$. If the edges of the polygons are equal to 1, the unit cell parameter is $a = 1 + \sqrt{3}$ and the points are in 6 e (Table 1.5) with $x = 1/(3 + \sqrt{3})$. Verify by plotting the pattern. [Hint: if you have difficulty plotting with hexagonal axes see Fig. 4.10, p. 121.]

4. The symmetry of the face of a conventional brick wall is $c2mm$.

5. A pair of parallel mirror lines separated by a distance d produces an infinite set of mirror lines with spacing d and translational symmetry with period $2d$ (the barber shop phenomenon).

6. Use the matrices given in Table 1.1 to construct a multiplication table for $4mm$.

7. Referred to Cartesian coordinates (axes at 90°), rotation by 120° about the origin of a point x, y gives a new point at $-x/2 - \sqrt{3}y/2, \sqrt{3}x/2 - y/2$. The trace (sum of diagonal terms) of the matrix generating the new coordinates from the old is -1 , and is independent of the choice of coordinate system (compare the matrix given in Table 1.2 for axes at 120°).

8. In Fig. 1.14 (below) the broken lines represent two glide lines at right angles; the light rectangle represents a unit cell of edges a and b . Start with an asymmetric object (7) in the upper left corner of the cell and use the glide reflections and translations (a and b) to generate images of the original object. This process has been begun in the figure in which straight arrows represent translations and the bent ones represent glide reflections. In this way we will generate all the symmetry elements of pgg ($p2gg$). Identify all the symmetry elements in the unit cell (objects of every pair must be related by a symmetry operation). Compare with Fig. 1.13 (in which the unit cell origin is taken at a different point).

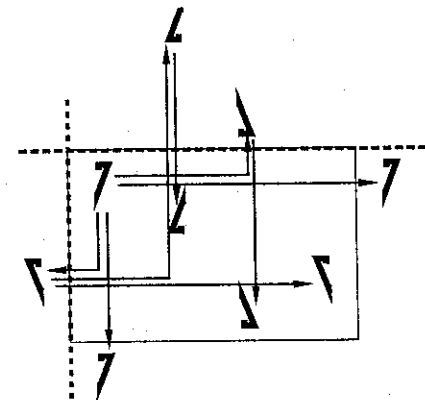


Fig. 1.14. See Exercise 8.

9. The orders of the point symmetry groups can be found by counting the numbers of replicas of the asymmetric object that are in the patterns of Fig. 1.2. The number of asymmetric objects (scalene triangles) in a unit cell of the patterns of Fig. 1.12 will be the same as the order of the point group of the space group if the cell is primitive, and twice that if the cell is centered. Verify for each space group.

10. Many examples of two-dimensional patterns (tilings) appear in Chapter 5. Identify the symmetry elements and verify their space groups.

Then there is the story of the crystallographer who was asked for the next letter in the sequence A, B, C, D, E... His response naturally was K as this is the next letter in the alphabet with symmetry m (not *exactly* in the font used here!). What are the symmetries of F, G, H, I, J, S, +, #, *, ★, 916? (Answers: 1, 1, $2mm$, $2mm$, 1, 2, $4mm$, 2, $8mm$, $5m$, 2.)