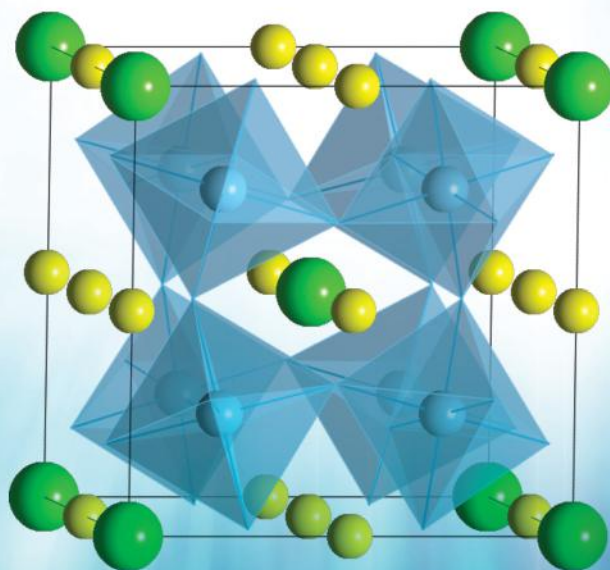


SOLID STATE CHEMISTRY

AND ITS APPLICATIONS

SECOND EDITION STUDENT EDITION



ANTHONY R. WEST

WILEY

IUPAC Periodic Table of the Elements

1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18																																									
1	H	2	He	3	Li	4	Be	5	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																																									
hydrogen	[1.007 1 009]	helium	[4.003]	lithium	[6.938 6 997]	beryllium	[9.012]	boron	[10.81 0 83]	carbon	[12.00 12 02]	nitrogen	[14.00 14 01]	oxygen	[15.99 16 00]	fluorine	[18.99 8 81]	neon	[20.18]	sodium	[22.98 9 10]	magnesium	[24.31]	aluminum	[26.98 0 8]	silicon	[28.08 5 8]	phosphorus	[30.97 3 8]	sulfur	[32.06 5 2]	chlorine	[35.45 3 6]	argon	[39.95]																																								
11	Na	12	Mg	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar	19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr																								
potassium	[39.10]	calcium	[40.08]	scandium	[44.96]	titanium	[47.87]	vanadium	[50.94]	chromium	[52.00]	manganese	[54.94]	iron	[55.85]	cobalt	[58.93]	nickel	[58.69]	copper	[63.55]	zinc	[65.38(2)]	gallium	[69.72]	germanium	[72.63]	arsenic	[74.92]	selenium	[78.96(3)]	bromine	[79.90]	krypton	[83.80]	rubidium	[85.47]	strontium	[87.62]	yttrium	[88.91]	zirconium	[91.22]	niobium	[92.91]	molybdenum	[95.96(2)]	technetium	[98.90]	ruthenium	[101.1]	rhodium	[102.9]	silver	[107.9]	cadmium	[112.4]	indium	[114.8]	tin	[118.7]	antimony	[121.8]	tellurium	[127.6]	iodine	[126.9]	xenon	[131.3]						
87	Fr	88	Ra	89-103	actinoids	89	Y	90	Zr	91	Nb	92	Mo	93	Tc	94	Ru	95	Rh	96	Pd	97	Ag	98	Cd	99	In	100	Hg	101	Tl	102	Pb	103	Bi	104	Po	105	At	106	Rn	107	Fr	108	Ra	109	Ac	110	Th	111	Pa	112	U	113	Np	114	Pu	115	Am	116	Cm	117	Bk	118	Cf	119	Es	120	Fm	121	Md	122	No	123	Lr
francium	[223.0]	radium	[226.0]	actinium	[227.0]	thorium	[232.0]	protactinium	[231.0]	uranium	[238.0]	neptunium	[237.0]	plutonium	[244.0]	americium	[243.0]	curium	[247.0]	berkelium	[247.0]	californium	[251.0]	europium	[152.0]	gadolinium	[157.0]	terbium	[158.9]	erbium	[167.3]	holmium	[164.9]	ytterbium	[173.1]	lutetium	[175.0]	beryllium	[9.012]	boron	[10.81 0 83]	carbon	[12.00 12 02]	nitrogen	[14.00 14 01]	oxygen	[15.99 16 00]	fluorine	[18.99 8 81]	neon	[20.18]	sodium	[22.98 9 10]	magnesium	[24.31]	aluminum	[26.98 0 8]	silicon	[28.08 5 8]	phosphorus	[30.97 3 8]	sulfur	[32.06 5 2]	chlorine	[35.45 3 6]	argon	[39.95]	krypton	[83.80]	xenon	[131.3]	radon	[222.0]		
57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu																																														
lanthanum	[138.9]	cerium	[140.1]	praseodymium	[140.9]	neodymium	[144.2]	promethium	[150.4]	samarium	[150.4]	europium	[152.0]	gadolinium	[157.3]	terbium	[158.9]	dysprosium	[162.5]	holmium	[164.9]	erbium	[167.3]	thulium	[168.9]	ytterbium	[173.1]	lutetium	[175.0]																																														
89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr																																														
actinium	[227.0] <td>thorium</td> <td>[232.0] <td>protactinium</td> <td>[231.0] <td>uranium</td> <td>[238.0] <td>neptunium</td> <td>[237.0] <td>plutonium</td> <td>[244.0] <td>americium</td> <td>[243.0] <td>curium</td> <td>[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td></td></td></td></td></td></td></td>	thorium	[232.0] <td>protactinium</td> <td>[231.0] <td>uranium</td> <td>[238.0] <td>neptunium</td> <td>[237.0] <td>plutonium</td> <td>[244.0] <td>americium</td> <td>[243.0] <td>curium</td> <td>[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td></td></td></td></td></td></td>	protactinium	[231.0] <td>uranium</td> <td>[238.0] <td>neptunium</td> <td>[237.0] <td>plutonium</td> <td>[244.0] <td>americium</td> <td>[243.0] <td>curium</td> <td>[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td></td></td></td></td></td>	uranium	[238.0] <td>neptunium</td> <td>[237.0] <td>plutonium</td> <td>[244.0] <td>americium</td> <td>[243.0] <td>curium</td> <td>[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td></td></td></td></td>	neptunium	[237.0] <td>plutonium</td> <td>[244.0] <td>americium</td> <td>[243.0] <td>curium</td> <td>[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td></td></td></td>	plutonium	[244.0] <td>americium</td> <td>[243.0] <td>curium</td> <td>[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td></td></td>	americium	[243.0] <td>curium</td> <td>[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td></td>	curium	[247.0] <td>berkelium</td> <td>[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td></td>	berkelium	[247.0] <td>californium</td> <td>[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td></td>	californium	[251.0] <td>einsteinium</td> <td>[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td></td>	einsteinium	[252.0] <td>fermium</td> <td>[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td></td>	fermium	[257.0] <td>mendelevium</td> <td>[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td></td>	mendelevium	[258.0] <td>nobelium</td> <td>[259.0] <td>lawrencium</td> <td>[260.0] </td></td>	nobelium	[259.0] <td>lawrencium</td> <td>[260.0] </td>	lawrencium	[260.0]																																														

Key:
 atomic number
 Symbol
 name
 standard atomic weight

Notes

- IUPAC 2009 Standard atomic weights bridged to four significant digits (Table 4 published in *Pure Appl. Chem.* 83, 359-396 (2011); doi: 10.1351/PAC-REP-10-09-14). The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements which lack isotopes with a characteristic isotopic abundance in natural terrestrial samples. See PAC for more details.
 - "Aluminum" and "cesium" are commonly used alternative spellings for "aluminium" and "caesium".
 - Claims for the discovery of all the remaining elements in the last row of the Table, namely elements with atomic numbers 113, 115, 117 and 118, and for which no assignments have yet been made, are being considered by a IUPAC and IUPAP Joint Working Party.
- For updates to this table, see iupac.org/reports/periodic_table/. This version is dated 1 June 2012.
 Copyright © 2012 IUPAC, the International Union of Pure and Applied Chemistry



INTERNATIONAL UNION OF
 PURE AND APPLIED CHEMISTRY

**Solid State Chemistry
and its Applications**

Second Edition

Solid State Chemistry and its Applications

Second Edition

Student Edition

ANTHONY R. WEST

Department of Materials Science and Engineering,
University of Sheffield, UK

WILEY

This edition first published 2014
© 2014 John Wiley & Sons, Ltd

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. It is sold on the understanding that the publisher is not engaged in rendering professional services and neither the publisher nor the author shall be liable for damages arising herefrom. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

Library of Congress Cataloging-in-Publication Data

West, Anthony R.

Solid state chemistry and its applications / Anthony R. West. – Second edition, student edition.

pages cm

Includes index.

ISBN 978-1-119-94294-8 (pbk.)

1. Solid state chemistry. I. Title.

QD478.W47 2014

541'.0421–dc23

2013029528

A catalogue record for this book is available from the British Library.

ISBN: 9781119942948

Cover images created using CrystalMaker[®] software. CrystalMaker Software Ltd, www.crystallmaker.com

Set in 10/12pt Times by Aptara Inc., New Delhi, India

For Sheena, Isla, Graeme, Jenny and Susie

Contents

Preface	xvii
Chemistry – Solid State Chemistry – Materials Chemistry – Materials Science and Engineering	xix
Companion Website	xxiii
CrystalViewer	xxiii
Crystal Structure Library	xxiv
Biography	xxv
1 Crystal Structures and Crystal Chemistry	1
1.1 Unit Cells and Crystal Systems	1
1.2 Symmetry	3
1.2.1 Rotational Symmetry; Symmetry Elements and Operations	3
1.2.2 Quasicrystals	6
1.2.3 Mirror Symmetry	6
1.2.4 Centre of Symmetry and Inversion Axes	6
1.2.5 Point Symmetry and Space Symmetry	9
1.3 Symmetry and Choice of Unit Cell	10
1.4 Lattice, Bravais Lattice	11
1.5 Lattice Planes and Miller Indices	14
1.6 Indices of Directions	16
1.7 <i>d</i> -Spacing Formulae	17
1.8 Crystal Densities and Unit Cell Contents	17
1.9 Description of Crystal Structures	18
1.10 Close Packed Structures – Cubic and Hexagonal Close Packing	19
1.11 Relationship between Cubic Close Packed and Face Centred Cubic	21
1.12 Hexagonal Unit Cell and Close Packing	21
1.13 Density of Close Packed Structures	22
1.14 Unit Cell Projections and Atomic Coordinates	24
1.15 Materials That Can Be Described as Close Packed	25
1.15.1 Metals	25
1.15.2 Alloys	25
1.15.3 Ionic Structures	26

1.15.3.1	Tetrahedral and Octahedral Sites	26
1.15.3.2	Relative Sizes of Tetrahedral and Octahedral Sites	28
1.15.3.3	Location of Tetrahedral and Octahedral Sites in an <i>fcc</i> Unit Cell; Bond Length Calculations	29
1.15.3.4	Description of Crystal Structures; Fractional Atomic Coordinates	30
1.15.4	Covalent Network Structures	31
1.15.5	Molecular Structures	31
1.15.6	Fullerenes and Fullerides	31
1.16	Structures Built of Space-Filling Polyhedra	33
1.17	Some Important Structure Types	35
1.17.1	Rock Salt (NaCl), Zinc Blende or Sphalerite (ZnS), Fluorite (CaF ₂), Antifluorite (Na ₂ O)	35
1.17.1.1	Rock Salt Structure	37
1.17.1.2	Zinc Blende (Sphalerite) Structure	38
1.17.1.3	Antifluorite/Fluorite Structure	39
1.17.1.4	Bond Length Calculations	41
1.17.2	Diamond	42
1.17.3	Wurtzite (ZnS) and Nickel Arsenide (NiAs)	43
1.17.4	Caesium Chloride (CsCl)	47
1.17.5	Other AX Structures	48
1.17.6	Rutile (TiO ₂), Cadmium Iodide (CdI ₂), Cadmium Chloride (CdCl ₂) and Caesium Oxide (Cs ₂ O)	49
1.17.7	Perovskite (SrTiO ₃)	54
1.17.7.1	Tolerance Factor	57
1.17.7.2	BaTiO ₃	57
1.17.7.3	Tilted Perovskites: Glazer Notation	58
1.17.7.4	CaCu ₃ Ti ₄ O ₁₂ , CCTO	62
1.17.7.5	Anion-Deficient Perovskites	62
1.17.7.6	Stoichiometry–Property Relations	62
1.17.8	Rhenium Trioxide (ReO ₃), Perovskite Tungsten Bronzes, Tetragonal Tungsten Bronzes and Tunnel Structures	63
1.17.9	Spinel	66
1.17.10	Olivine	70
1.17.11	Corundum, Ilmenite and LiNbO ₃	72
1.17.12	Fluorite-Related Structures and Pyrochlore	72
1.17.13	Garnet	75
1.17.14	Perovskite-Rock Salt Intergrowth Structures: K ₂ NiF ₄ , Ruddlesden–Popper Phases and Layered Cuprate Superconductors	76
1.17.15	The Aluminium Diboride Structure (AlB ₂)	80
1.17.16	Silicate Structures – Some Tips to Understanding Them	81
2	Crystal Defects, Non-Stoichiometry and Solid Solutions	83
2.1	Perfect and Imperfect Crystals	83
2.2	Types of Defect: Point Defects	84
2.2.1	Schottky Defect	85
2.2.2	Frenkel Defect	85
2.2.2.1	The Kroger–Vink Notation for Crystal Defects	86
2.2.2.2	Thermodynamics of Schottky and Frenkel Defect Formation	87

2.2.3	Colour Centres	90
2.2.4	Vacancies and Interstitials in Non-Stoichiometric Crystals: Extrinsic and Intrinsic Defects	91
2.2.5	Defect Clusters or Aggregates	92
2.2.6	Interchanged Atoms: Order–Disorder Phenomena	95
2.3	Solid Solutions	95
2.3.1	Substitutional Solid Solutions	96
2.3.2	Interstitial Solid Solutions	98
2.3.3	More Complex Solid Solution Mechanisms: Aliovalent Substitution	99
2.3.3.1	Ionic Compensation Mechanisms	99
2.3.3.2	Electronic Compensation: Metals, Semi- and Superconductors	102
2.3.4	Thermodynamically Stable and Metastable Solid Solutions	104
2.3.5	Experimental Methods for Studying Solid Solutions	104
2.3.5.1	X-ray Powder Diffraction, XRD	104
2.3.5.2	Density Measurements	105
2.3.5.3	Changes in Other Properties – Thermal Activity and DTA/DSC	107
2.4	Extended Defects	108
2.4.1	Crystallographic Shear Structures	108
2.4.2	Stacking Faults	110
2.4.3	Subgrain Boundaries and Antiphase Domains (Boundaries)	110
2.5	Dislocations and Mechanical Properties of Solids	111
2.5.1	Edge Dislocations	112
2.5.2	Screw Dislocations	114
2.5.3	Dislocation Loops	115
2.5.4	Dislocations and Crystal Structure	117
2.5.5	Mechanical Properties of Metals	118
2.5.6	Dislocations, Vacancies and Stacking Faults	120
2.5.7	Dislocations and Grain Boundaries	122
3	Bonding in Solids	125
3.1	Overview: Ionic, Covalent, Metallic, van der Waals and Hydrogen Bonding in Solids	125
3.2	Ionic Bonding	126
3.2.1	Ions and Ionic Radii	126
3.2.2	Ionic Structures – General Principles	130
3.2.3	The Radius Ratio Rules	133
3.2.4	Borderline Radius Ratios and Distorted Structures	135
3.2.5	Lattice Energy of Ionic Crystals	136
3.2.6	Kapustinskii’s Equation	140
3.2.7	The Born–Haber Cycle and Thermochemical Calculations	141
3.2.8	Stabilities of Real and Hypothetical Ionic Compounds	143
3.2.8.1	Inert Gas Compounds	143
3.2.8.2	Lower and Higher Valence Compounds	144
3.2.9	Effect of Partial Covalent Bonding on Crystal Structures	145
3.2.10	Effective Nuclear Charge	147
3.2.11	Electronegativity and Partially Charged Atoms	147
3.2.12	Coordinated Polymeric Structures – Sanderson’s Model	149
3.2.13	Mooser–Pearson Plots and Ionicities	150

3.2.14	Bond Valence and Bond Length	151
3.2.15	Non-Bonding Electron Effects	153
3.2.15.1	d-Electron Effects	153
3.2.15.2	Inert Pair Effect	161
3.3	Covalent Bonding	161
3.3.1	Particle-Wave Duality, Atomic Orbitals, Wavefunctions and Nodes	162
3.3.2	Orbital Overlap, Symmetry and Molecular Orbitals	163
3.3.3	Valence Bond Theory, Electron Pair Repulsion, Hybridisation and Oxidation States	169
3.4	Metallic Bonding and Band Theory	173
3.4.1	Band Structure of Metals	179
3.4.2	Band Structure of Insulators	179
3.4.3	Band Structure of Semiconductors: Silicon	179
3.4.4	Band Structure of Inorganic Solids	181
3.4.4.1	III–V, II–VI and I–VII Compounds	181
3.4.4.2	Transition Metal Compounds	182
3.4.4.3	Fullerenes and Graphite	184
3.5	Bands or Bonds: a Final Comment	185
4	Synthesis, Processing and Fabrication Methods	187
4.1	General Observations	187
4.2	Solid State Reaction or Shake 'n Bake Methods	187
4.2.1	Nucleation and Growth, Epitaxy and Topotaxy	188
4.2.2	Practical Considerations and Some Examples of Solid State Reactions	191
4.2.2.1	Li ₄ SiO ₄	193
4.2.2.2	YBa ₂ Cu ₃ O _{7-δ}	193
4.2.2.3	Na β/β' alumina	193
4.2.3	Combustion Synthesis	194
4.2.4	Mechanosynthesis	195
4.3	Low Temperature or Chimie Douce Methods	196
4.3.1	Alkoxide Sol–Gel Method	196
4.3.1.1	Synthesis of MgAl ₂ O ₄	197
4.3.1.2	Synthesis of Silica Glass	197
4.3.1.3	Spinning of Alumina Fibres	197
4.3.1.4	Preparation of Indium Tin Oxide (ITO) and Other Coatings	198
4.3.1.5	Fabrication of YSZ Ceramics	198
4.3.2	Sol–Gel Method Using Oxyhydroxides and Colloid Chemistry	198
4.3.2.1	Synthesis of Zeolites	199
4.3.2.2	Preparation of Alumina-Based Abrasives and Films	200
4.3.3	Citrate Gel and Pechini Processes	200
4.3.4	Use of Homogeneous, Single-Source Precursors	201
4.3.5	Hydrothermal and Solvothermal Synthesis	202
4.3.6	Microwave Synthesis	204
4.3.7	Intercalation and Deintercalation	205
4.3.7.1	Graphite Intercalation Compounds	207
4.3.7.2	Pillared Clays and Layered Double Hydroxides	208
4.3.7.3	Synthesis of Graphene	209

4.3.8	Example of a Difficult Synthesis Made Possible by Chimie Douce Methods: BiFeO ₃	211
4.3.9	Molten Salt Synthesis, MSS	212
4.4	Gas-Phase Methods	213
4.4.1	Vapour-Phase Transport	213
4.4.2	Chemical Vapour Deposition, CVD	216
4.4.2.1	Amorphous Silicon	217
4.4.2.2	Diamond Films	219
4.4.3	Sputtering and Evaporation	221
4.4.4	Atomic Layer Deposition, ALD	222
4.4.5	Aerosol Synthesis and Spray Pyrolysis	223
4.5	High-Pressure Methods	225
4.6	Crystal Growth	226
4.6.1	Czochralski Method	226
4.6.2	Bridgman and Stockbarger Methods	226
4.6.3	Zone Melting	227
4.6.4	Precipitation from Solution or Melt: Flux Method	227
4.6.5	Verneuil Flame Fusion Method	228
5	Crystallography and Diffraction Techniques	229
5.1	General Comments: Molecular and Non-Molecular Solids	229
5.1.1	Identification of Crystalline Solids	229
5.1.2	Structure of Non-Molecular Crystalline Solids	229
5.1.3	Defects, Impurities and Stoichiometry of Crystalline Solids	230
5.2	Characterisation of Solids	231
5.3	X-Ray Diffraction	232
5.3.1	Generation of X-Rays	232
5.3.1.1	Laboratory Sources Utilising Inner Shell Electronic Transitions	232
5.3.1.2	Synchrotron X-ray Sources	235
5.3.2	Interaction of X-Rays with Matter	235
5.3.3	Optical Grating and Diffraction of Light	236
5.3.4	Crystals and Diffraction of X-Rays	238
5.3.4.1	The Laue Equations	238
5.3.4.2	Bragg's Law	239
5.3.5	X-Ray Diffraction Methods	240
5.3.6	The Powder Method – Principles and Uses	240
5.3.6.1	Focusing of X-rays: Theorem of a Circle	243
5.3.6.2	Crystal Monochromators	244
5.3.6.3	Powder Diffractometers	244
5.3.6.4	Guinier Focusing Cameras	245
5.3.6.5	A Powder Pattern of a Crystalline Phase is its 'Fingerprint'	246
5.3.6.6	Powder Patterns and Crystal Structures	247
5.3.7	Intensities	248
5.3.7.1	Scattering of X-rays by an Atom: Atomic Scattering Factors or Form Factors	249
5.3.7.2	Scattering of X-rays by a Crystal – Systematic Absences	250
5.3.7.3	General Equation for Phase Difference, δ	253

5.3.7.4	Intensities and Structure Factors	255
5.3.7.5	Temperature Factors	258
5.3.7.6	R-Factors and Structure Determination	259
5.3.7.7	Structure Refinement from Powder Data: Rietveld Refinement	259
5.3.8	X-Ray Crystallography and Structure Determination – What is Involved?	260
5.3.8.1	The Patterson Method	263
5.3.8.2	Fourier Methods	264
5.3.8.3	Direct Methods	264
5.3.8.4	Electron Density Maps	265
5.4	Electron Diffraction	265
5.5	Neutron Diffraction	266
5.5.1	Crystal Structure Determination	267
5.5.2	Magnetic Structure Analysis	268
5.5.3	Inelastic Scattering, Soft Modes and Phase Transitions	269
6	Other Techniques: Microscopy, Spectroscopy, Thermal Analysis	271
6.1	Diffraction and Microscopic Techniques: What Do They Have in Common?	271
6.2	Optical and Electron Microscopy Techniques	272
6.2.1	Optical Microscopy	272
6.2.1.1	Polarising Microscope	273
6.2.1.2	Reflected Light Microscope	276
6.2.2	Electron Microscopy	276
6.2.2.1	Scanning Electron Microscopy	280
6.2.2.2	Electron Probe Microanalysis, EPMA, and Energy-Dispersive X-ray Spectroscopy, EDS or EDX	281
6.2.2.3	Auger Electron (Emission) Microscopy and Spectroscopy, AES	282
6.2.2.4	Cathodoluminescence, CL	284
6.2.2.5	Transmission Electron Microscopy, TEM, and Scanning Transmission Electron Microscopy, STEM	287
6.2.2.6	Electron Energy Loss Spectroscopy, EELS	288
6.2.2.7	High-Angle Annular Dark Field, HAADF/Z-Contrast STEM	289
6.3	Spectroscopic Techniques	291
6.3.1	Vibrational Spectroscopy: IR and Raman	293
6.3.2	Visible and Ultraviolet (UV) Spectroscopy	296
6.3.3	Nuclear Magnetic Resonance (NMR) Spectroscopy	298
6.3.4	Electron Spin Resonance (ESR) Spectroscopy	301
6.3.5	X-Ray Spectroscopies: XRF, AEFs, EXAFS	303
6.3.5.1	Emission Techniques	303
6.3.5.2	Absorption Techniques	305
6.3.6	Electron Spectroscopies: ESCA, XPS, UPS, AES, EELS	308
6.3.7	Mössbauer Spectroscopy	312
6.4	Thermal Analysis (TA)	314
6.4.1	Thermogravimetry (TG)	315
6.4.2	Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)	315
6.4.3	Applications	317
6.5	Strategy to Identify, Analyse and Characterise ‘Unknown’ Solids	321

7	Phase Diagrams and their Interpretation	325
7.1	The Phase Rule, the Condensed Phase Rule and Some Definitions	325
7.2	One-Component Systems	330
7.2.1	The System H ₂ O	331
7.2.2	The System SiO ₂	332
7.2.3	Condensed One-Component Systems	333
7.3	Two-Component Condensed Systems	333
7.3.1	A Simple Eutectic System	333
7.3.1.1	Liquidus and Solidus	335
7.3.1.2	Eutectic	335
7.3.1.3	Lever Rule	335
7.3.1.4	Eutectic Reaction	336
7.3.1.5	The Liquidus, Saturation Solubilities and Freezing Point Depression	337
7.3.2	Binary Systems with Compounds	337
7.3.2.1	Congruent Melting	337
7.3.2.2	Incongruent Melting, Peritectic Point, Peritectic Reaction	337
7.3.2.3	Non-Equilibrium Effects	339
7.3.2.4	Upper and Lower Limits of Stability	340
7.3.3	Binary Systems with Solid Solutions	340
7.3.3.1	Complete Solid Solution	340
7.3.3.2	Fractional Crystallisation	341
7.3.3.3	Thermal Maxima and Minima	342
7.3.3.4	Partial Solid Solution Systems	342
7.3.4	Binary Systems with Solid–Solid Phase Transitions	344
7.3.5	Binary Systems with Phase Transitions and Solid Solutions: Eutectoids and Peritectoids	345
7.3.6	Binary Systems with Liquid Immiscibility: MgO–SiO ₂	347
7.3.7	Some Technologically Important Phase Diagrams	348
7.3.7.1	The System Fe–C: Iron and Steel Making	348
7.3.7.2	The System CaO–SiO ₂ : Cement Manufacture	349
7.3.7.3	The System Na–S: Na/S Batteries	350
7.3.7.4	The System Na ₂ O–SiO ₂ : Glass Making	351
7.3.7.5	The System Li ₂ O–SiO ₂ : Metastable Phase Separation and Synthetic Opals	352
7.3.7.6	Purification of Semiconducting Si by Zone Refining	353
7.3.7.7	The System ZrO ₂ –Y ₂ O ₃ : Yttria-Stabilised Zirconia, YSZ, Solid Electrolyte	354
7.3.7.8	The System Bi ₂ O ₃ –Fe ₂ O ₃ : Multiferroic BiFeO ₃	354
7.4	Some Tips and Guidelines for Constructing Binary Phase Diagrams	355
8	Electrical Properties	359
8.1	Survey of Electrical Properties and Electrical Materials	359
8.2	Metallic Conductivity	361
8.2.1	Organic Metals: Conjugated Systems	362
8.2.1.1	Polyacetylene	362
8.2.1.2	Poly- <i>p</i> -Phenylene and Polypyrrole	364
8.2.2	Organic Metals: Charge-Transfer Complexes	365

8.3	Superconductivity	366
8.3.1	The Property of Zero Resistance	366
8.3.2	Perfect Diamagnetism; the Meissner Effect	368
8.3.3	Critical Temperature T_c , Critical Field H_c and Critical Current J_c	368
8.3.4	Type I and Type II Superconductors: The Vortex (Mixed) State	370
8.3.5	Survey of Superconducting Materials	371
8.3.6	Crystal Chemistry of Cuprate Perovskites	374
8.3.7	$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, YBCO	376
8.3.7.1	Crystal Structure	376
8.3.7.2	Atom Valences and the Superconducting Mechanism	378
8.3.7.3	Oxygen Content of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	378
8.3.7.4	Determination of Oxygen Content, $7-\delta$	380
8.3.8	Fullerides	381
8.3.9	Applications of Superconductors	381
8.4	Semiconductivity	382
8.4.1	Elemental and Compound Semiconductors with Diamond and Zinc Blende Structures	384
8.4.2	Electrical Properties of Semiconductors	386
8.4.3	Oxide Semiconductors	388
8.4.4	Applications of Semiconductors	389
8.5	Ionic Conductivity	392
8.5.1	Alkali Halides: Vacancy Conduction	393
8.5.1.1	Activation Energy for Ion Hopping: Geometric Considerations	394
8.5.1.2	Ionic Conductivity of NaCl Crystals	396
8.5.1.3	Extrinsic Conductivity in NaCl: Control by Aliovalent Doping	397
8.5.2	Silver Chloride: Interstitial Conduction	399
8.5.3	Alkaline Earth Fluorides	401
8.5.4	Solid Electrolytes (or Fast Ion Conductors, Superionic Conductors)	401
8.5.4.1	General Considerations	401
8.5.4.2	β -Alumina	403
8.5.4.3	Nasicon	409
8.5.4.4	Hollandites and Priderites	409
8.5.4.5	Silver and Copper Ion Conductors	411
8.5.4.6	Fluoride Ion Conductors	413
8.5.4.7	Oxide Ion Conductors	414
8.5.4.8	Li^+ Ion Conductors	418
8.5.4.9	Proton Conductors	421
8.5.4.10	Mixed Ionic/Electronic Conductors	421
8.5.4.11	Applications of Solid Electrolytes and Mixed Conductors	422
8.6	Dielectric Materials	430
8.6.1	From Dielectrics to Conductors	433
8.7	Ferroelectrics	436
8.8	Pyroelectrics	441
8.9	Piezoelectrics	441
8.10	Applications of Ferro-, Pyro- and Piezoelectrics	441

9	Magnetic Properties	445
9.1	Physical Properties	445
9.1.1	Behaviour of Substances in a Magnetic Field	446
9.1.2	Effects of Temperature: Curie and Curie–Weiss Laws	448
9.1.3	Magnetic Moments	449
9.1.4	Mechanisms of Ferro- and Antiferromagnetic Ordering: Superexchange	452
9.1.5	Some More Definitions	453
9.2	Magnetic Materials, their Structures and Properties	455
9.2.1	Metals and Alloys	455
9.2.2	Transition Metal Monoxides	458
9.2.3	Transition Metal Dioxides	459
9.2.4	Spinels	459
9.2.5	Garnets	462
9.2.6	Ilmenites and Perovskites	464
9.2.7	Magnetoplumbites	464
9.3	Applications: Structure–Property Relations	464
9.3.1	Transformer Cores	464
9.3.2	Permanent Magnets	466
9.3.3	Magnetic Information Storage	466
9.4	Recent Developments	467
9.4.1	Magnetoresistance: Giant and Colossal	467
9.4.2	Multiferroics	469
10	Optical Properties: Luminescence and Lasers	473
10.1	Visible Light and the Electromagnetic Spectrum	473
10.2	Sources of Light, Thermal Sources, Black Body Radiation and Electronic Transitions	473
10.3	Scattering Processes: Reflection, Diffraction and Interference	476
10.4	Luminescence and Phosphors	476
10.5	Configurational Coordinate Model	478
10.6	Some Phosphor Materials	480
10.7	Anti-Stokes Phosphors	481
10.8	Stimulated Emission, Amplification of Light and Lasers	482
10.8.1	The Ruby Laser	484
10.8.2	Neodymium Lasers	485
10.8.3	Semiconductor Lasers and the Light-Emitting Diode, LED	486
10.9	Photodetectors	488
10.10	Fibre-Optics	490
10.11	Solar Cells	492
	Further Reading	493
	Appendix A: Interplanar Spacings and Unit Cell Volumes	505
	Appendix B: Model Building	507
	Appendix C: Geometrical Considerations in Crystal Chemistry	511

Appendix D: How to Recognise Close Packed (Eutactic) Structures	515
Appendix E: Positive and Negative Atomic Coordinates	517
Appendix F: The Elements and Some of Their Properties	519
Questions	525
Index	537

Preface

This book is a slimmed down, student edition of ‘Solid State Chemistry and its Applications’ whose second edition is scheduled for publication in 2015/6. It is modelled on the authors’ ‘Basic Solid State Chemistry’, but has been completely rewritten with about 40% new material added and all the diagrams drawn professionally, in full colour. The nine chapters in ‘Basic’ have become ten in this new edition since ‘Magnetic and Optical Properties’ is split into separate chapters.

In the period since the second edition of ‘Basic’ was published in 1999, we have witnessed many major new discoveries and developments in the solid state chemistry of inorganic materials with topics such as colossal magnetoresistance, multiferroics, light emitting diodes and graphene. New materials synthesis techniques have evolved such as mechanosynthesis, microwave-hydrothermal synthesis and atomic layer deposition and of course, there have been many improvements in the techniques used to characterise solids including use of synchrotrons for diffraction and spectroscopy as well as high resolution scanning transmission electron microscopy permitting atomic-level identification and structural imaging. It was felt that an updated version of both ‘Basic’ and ‘Solid State Chemistry and its Applications’ was long overdue, therefore.

A major feature of this new edition is the extensive coverage of the crystal structures of important families of inorganic solids. Purchasers of the book will be able to download, free, a bespoke and easy-to-use CrystalMaker[®] viewer program. The CrystalViewer software is accompanied by more than 100 crystal structure models which users will be able to view on their computers with the facility to rotate the structures, view them from different orientations and either highlight or hide different structural features. CrystalViewer and the accompanying structure files can be downloaded from the companion website at <http://www.wiley.com/go/west/solidstatechemistrystudent>.

Many people have helped and encouraged me in preparing this new edition. Special thanks are due to: John McCallum who produced many of the crystal structure drawings and files, Frances Kirk who prepared the whole manuscript, in electronic format, and Wiley staff Sarah Hall and Sarah Tilley for their enthusiastic encouragement and involvement: in particular, Sarah Hall was instrumental in making the CrystalMaker[®] arrangements and Sarah Tilley oversaw all the artwork preparations.

Anthony R. West
Sheffield
July 2013

Chemistry – Solid State Chemistry – Materials Chemistry – Materials Science and Engineering

Chemistry is an evolving subject! Traditionally, there have been three branches of chemistry: organic, physical and inorganic, with some arguments in favour of including analytical as a fourth branch. An alternative, fairly new classification (favoured by the author!) divides chemistry into two broad areas: molecular (which includes liquids and gases) and non-molecular (or solid state). The ways in which we think about, make, analyse and use molecular and non-molecular substances are completely different, as shown by a comparison of one ‘simple’ substance in each category, toluene and aluminium oxide:

Comparison of the chemistries of molecular and non-molecular materials

Characteristic	Toluene	Aluminium oxide
Formula	Fixed, $C_6H_5CH_3$	Usually fixed, Al_2O_3 , but for other oxides may be variable, e.g. $Fe_{1-x}O$
Are defects present?	Not allowed: missing or mis-placed atoms give rise to different molecules	Unavoidable: small concentration of vacancies, interstitials and dislocations are always present
Doping possibilities	Not possible without producing a different molecule	Doping or solid solution formation allows control and optimisation of properties, e.g. ruby is Cr-doped Al_2O_3
Structure and its determination	Molecular structure can be determined spectroscopically: NMR/Mass Spec/IR. Determine packing arrangement, bond lengths and angles, by single crystal X-ray diffraction. Usually, structural information is then complete.	Full characterisation of a solid requires structural and compositional information across the length scales from local, to unit cell, nano and microscales. Many diffraction, spectroscopic and microscopic techniques are needed for full characterisation.
Properties and applications	Controlled by molecular formula and configuration; cannot be modified by doping. Some properties (e.g. pharmaceutical activity) may depend on molecular packing arrangements in crystals.	Properties/applications depend on crystal structure, defects, dopants, surface structure, particle size and whether the material is a powder, single crystal, film, etc. Consider the diverse applications of Al_2O_3 : films and ceramics used as insulators; powders used as abrasive; with Cr^{3+} dopants, ruby is used for lasers; porous solids used as catalyst supports.

Thus, for toluene, once its formula and molecular structure had been determined there were few remaining issues to be resolved other than, perhaps, the detailed packing arrangement of molecules in crystalline toluene at low temperatures or the possible discovery and evaluation, even today, of as-yet unknown chemical, biological or pharmaceutical properties of pure toluene.

Alumina, by contrast, is a highly complex material; its properties, and therefore potential applications, depend on different aspects of its structure (bulk, defect, surface, nano), the methods needed to fabricate it in different forms and shapes, the possibility of doping to modify its properties and the characterisation or determination of its structure (and its composition, whether homogeneous or heterogeneous, if doped) across all length scales. This is solid state chemistry!

The biggest contrast between molecular and non-molecular materials is that the latter can be doped, allowing modification and control of properties such as magnetism, superconductivity and colour/optical band gap. By contrast, attempts to dope molecules are inevitably frustrated since replacing one atom in the molecule by another, or creating defects such as missing atoms, lead to entirely different molecules.

In recent decades, *materials chemistry* has emerged as a distinct branch of chemistry which covers both non-molecular, solid state materials (oxides, halides, etc.) and many molecular materials (especially, functional polymers and organic solids with potentially useful physical properties). Materials chemistry cuts across the traditional disciplines of chemistry but also includes something extra which is an interest in the physical properties of compounds and materials. In the past, solid state physics and materials science have been the usual ‘home’ for physical properties; but now, they are an intrinsic part of solid state and materials chemistry.

The distinction between *materials chemistry* and *materials science* is often unclear but can be summarised broadly as follows:

Materials chemistry

Synthesis – structure determination – physical properties – new materials

Materials science

Processing and fabrication – characterisation – optimisation of properties and testing – improved/new materials for engineering applications in products or devices.

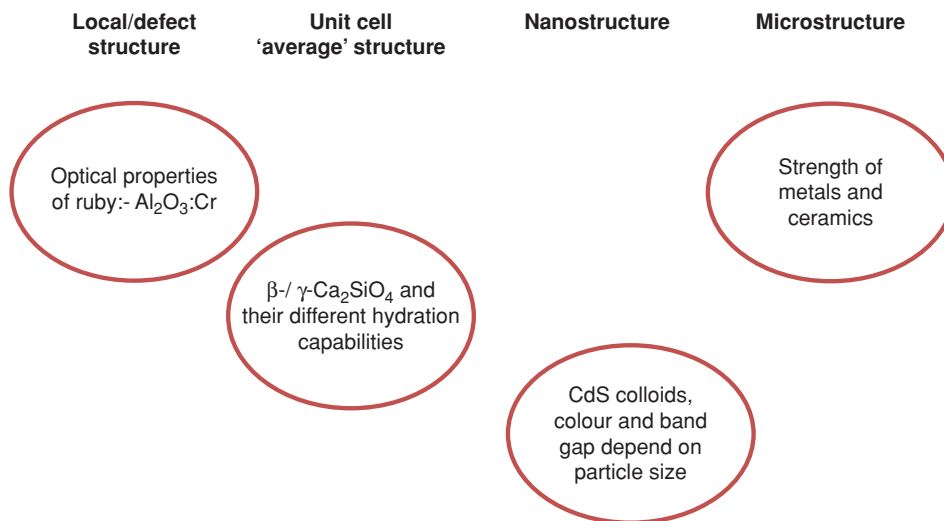
Materials science focuses on materials that are already known to be useful or have the potential to be developed for applications, either by compositional control to optimise properties or by fabrication into desired forms, shapes or products. Materials science therefore includes whatever aspects of chemistry, physics and engineering that are necessary to achieve the desired aims.

Materials chemistry is much more than just a subset of materials science, however, since it is freed from the constraint of a focus on specific applications; materials chemists love to synthesise new materials and measure their properties, some of which may turn out to be useful and contribute to the development of new industries, but they do this within an overarching interest in new chemistry, new structures and improved understanding of structure – composition – property relationships.

A curious fact is that, in the early days of chemistry, inorganic chemistry had as its main focus, the elements of the periodic table and their naturally occurring or easy-to-make compounds such as oxides and halides. Inorganic chemistry subsequently diversified to include organometallic chemistry and coordination chemistry but interestingly, many traditional inorganic materials have returned to centre-stage and are now at the heart of solid state materials science. Examples include: Cr-doped Al_2O_3 for lasers; doped Si semiconductors

for microelectronics; doped ZrO_2 as the solid electrolyte in solid oxide fuel cells; BaTiO_3 as the basis of the capacitor industry with a total annual production worldwide exceeding 10^{12} units; copper oxide-based materials for superconductor applications; and many, many more. The scope for developing new solid state materials/applications is infinite, judging by the ‘simple’ example of Al_2O_3 described above. Most such materials tend not to suffer from problems such as volatilisation, degradation and atmospheric attack, which are often a drawback of molecular materials, and can be used safely in the environment.

It is important to recognise also that physical properties of inorganic solids often depend on structure at different length scales, as shown by the following examples:



Thus in the case of ruby, which is a natural gemstone and was the first material in which LASER action – light amplification by stimulated emission of radiation – was demonstrated, two structural aspects are important. One is the host crystal structure of corundum, α - Al_2O_3 and the other is the Cr^{3+} dopant which substitutes at random for about 1% of the Al^{3+} ions in the corundum lattice: the Cr-O bond lengths and the octahedral site symmetry are controlled by the host structure; the two together combine to give the red ruby colour by means of d-d transitions within the Cr chromophore and the possibility of accessing the long-lived excited states that are necessary for LASER action.

A remarkable example of the effect of crystal structure details at the unit cell scale on properties is shown by dicalcium silicate, Ca_2SiO_4 which is readily prepared in two polymorphic forms at room temperature. One, the β -polymorph, reacts with water to give a semicrystalline calcium silicate hydrate which sets rock-solid and is a main constituent of concrete; the other polymorph, γ - Ca_2SiO_4 , does not react with water. Just think, the entire construction industry rests on the detailed polymorphism of dicalcium silicate! It is not sufficient that one of the key components of cement has the right composition, Ca_2SiO_4 ; in addition, the precise manner in which ions are packed together in the solid state is critical to its hydration properties and whether or not it turns into concrete.

At the nanoscale, crystalline particles may contain many hundreds of unit cells but often their properties are different from powders, ceramics or single crystals of the same material with larger-sized grains simply because of the influence of surface energies. In small nanoparticles, surface free energies and structures

increasingly dominate the total free energy of a material, as shown by the colour, and associated band gap, of CdS nanoparticles (or colloids in older terminology) which can be fine-tuned by controlling the particle size.

Some properties are determined by structure at the micron ($1\ \mu\text{m} = 10^3\ \text{nm} = 10^4\ \text{\AA} = 10^{-3}\ \text{mm}$) scale and this is the reason why ‘microstructure’ features strongly in the characterisation of metals and ceramics, primarily using optical and electron microscopy techniques. Frequently, impurities/dopants may precipitate at grain boundaries and surfaces and these can have a dramatic influence on for instance, the mechanical properties.

These examples illustrate the awesome challenges that must be met before an inorganic solid can be regarded as fully characterised across the length scales. This, coupled with the enormous number of inorganic crystal structures that are known, and the possibility to introduce dopants which modify properties, underlines why solid state chemistry is a central subject to many areas of physical science, engineering and technology.

This book concerns solid state chemistry and focuses on inorganic solids: their crystal structures, defect structures and bonding; the methods used to synthesise them and determine their structures; their physical properties and applications. Organic and other molecular materials are included in the coverage if their properties in the solid state complement, or relate to, those of inorganic solids. Physical properties are an intrinsic part of solid state chemistry since the whole area of structure–property relations requires the insights and input of chemistry to synthesise and characterise materials, as well as a good understanding of physical properties and the factors that control them.

Companion Website

This textbook is supported by a website which contains a variety of supplementary resources:

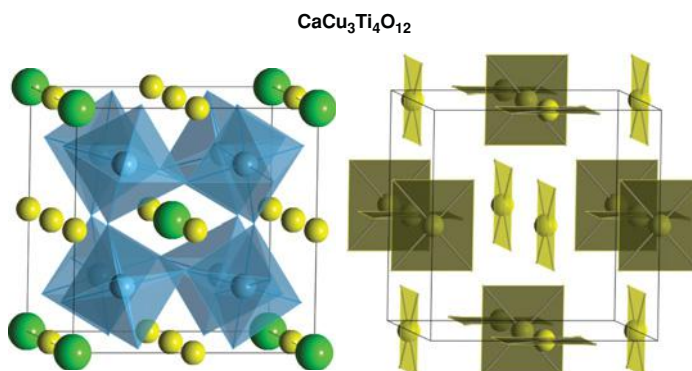
<http://www.wiley.com/go/west/solidstatechemistrystudent>

Online you will find PowerPoint slides of all figures from the book, as well as solutions to the set of questions. The website also gives you access to a CrystalMaker[®] viewer program. The CrystalViewer software is available for Windows and Mac, and is accompanied by a broad array of crystal structures for you to view and manipulate.

CrystalViewer

CrystalViewer is a visualisation program for displaying and manipulating crystal structures. The CrystalViewer software facilitates the exploration of crystal structures from the book in three dimensions, allowing users to view the structures in different orientations, and highlight/hide different structural features so as to aid the interpretation of complex crystal structures. The CrystalViewer program is accompanied by over 100 crystal structure files; many of these structures relate directly to illustrations from the book, identified by their figure numbers, and a variety of additional structures are provided to complement the concepts and applications discussed in the text.

The CrystalViewer software and accompanying structure files can be downloaded from the companion website at <http://www.wiley.com/go/west/solidstatechemistrystudent>



CrystalMaker[®] CrystalMaker Software Ltd. www.crystalmaker.com

An example of how a crystal structure can appear very different, depending on which aspects are emphasised, is shown here for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, in which the two diagrams highlight either the TiO_6 octahedra or the CuO_4 square planar units.

Crystal Structure Library

A Crystal Structure Library is available on the companion website containing >100 structures which can be examined in detail using the CrystalViewer Software. The structures which correspond directly to figures in the book are listed below, with the relevant figure number noted in parentheses. Many more crystal structures are available online, including minerals and other inorganic structures. Further structures may be added from time to time.

Major Inorganic Structure Types (and relevant book diagrams)

β -alumina, NaAl ₁₁ O ₁₇ (8.23 and 8.24)	Li ₃ N (8.32)
BaTiO ₃ (8.40)	LiCoO ₂ / α -NaFeO ₂ (8.35)
<i>bcc</i> metal (2.12)	LiNbO ₃ (1.46)
Brass, ZnCu (2.11)	Magnetoplumbite (9.14)
Brownmillerite, Ca ₂ (Fe,Al) ₂ O ₅ (1.42)	MgB ₂ (1.51)
CaC ₂ (1.10)	Nasicon, NaZr ₂ (PO ₄) ₃ (8.27)
CaCu ₃ Ti ₄ O ₁₂ (1.42)	Nickel arsenide, NiAs (1.35)
CdCl ₂ (1.40)	Olivine, LiFePO ₄ (1.45)
CdI ₂ (1.39)	PbFCl, matlockite (8.6)
Chevreil Phase, BaMo ₆ S ₈ (8.6)	PbO (3.14)
Corundum, α -Al ₂ O ₃ (1.46)	Perovskite, SrTiO ₃ (1.41)
CsCl (1.36)	Pyrochlore (1.48)
Diamond (1.33)	Rock salt, NaCl (1.2, 1.29 and 1.31)
<i>fcc</i> metal (1.20)	Rutile, TiO ₂ (1.37)
Fluorite/antifluorite, CaF ₂ (1.29, 1.30 and 1.34)	Spinel (1.44)
Garnet, Y ₃ Fe ₅ O ₁₂ (1.49)	Tetragonal tungsten bronze (1.43)
GdFeO ₃ (1.41)	Wurtzite, ZnS (1.35)
<i>hcp</i> metal (1.21)	YBa ₂ Cu ₃ O ₆ (8.8)
Hollandite (8.27)	YBa ₂ Cu ₃ O ₇ (8.8)
Ilmenite, FeTiO ₃ (1.46)	Zinc blende/sphalerite, ZnS (1.29 and 1.33)
K ₂ NiF ₄ (1.50)	ZrCuSiAs (8.6)
Layered double hydroxides (4.11)	

Biography

Tony West obtained his BSc degree in Chemistry at University College Swansea and his PhD at the University of Aberdeen, where he worked with Professor F. P. Glasser on silicate chemistry. He was appointed as a Lecturer in Aberdeen in 1971 and developed a lifetime interest in the then-emerging field of solid state chemistry with special interest in the synthesis of new oxide materials, their crystal structures and electrical properties. He was awarded a DSc from Aberdeen in 1984 and rose through the ranks to become Professor of Chemistry in 1989 before moving to the University of Sheffield, Department of Materials Science and Engineering, as Head of Department in 1999, a post he held until 2007.

Tony was founding editor of the *Journal of Materials Chemistry* and subsequently established the Materials Chemistry Forum, which has now become the Materials Chemistry Division of the Royal Society of Chemistry. He organised the First International Conference on Materials Chemistry, MCI, in Aberdeen, 1993, and co-organised the first Materials Discussion, MDI, in Bordeaux, 1998. He also served as President of the Inorganic Chemistry Division of IUPAC, 2004–2007.

Tony is a Fellow of the Royal Society of Chemistry, the Institute of Physics, the Institute of Materials, Minerals and Mining (IOM³), and the Royal Society of Edinburgh. Over the years he has received several awards, including an Industrial Award in Solid State Chemistry from the RSC (1996), the Griffiths Medal and Prize from the IOM³ (2008), the Epsilon de Oro Award from the Spanish Society of Glass and Ceramics (2007) and the Chemical Record Lectureship from the Chemical Societies of Japan (2007). He has been awarded the 2013 John B. Goodenough Award in Materials Chemistry by the RSC, a lifetime award which recognises exceptional and sustained contributions to the field of materials chemistry.

1

Crystal Structures and Crystal Chemistry

Solid state chemistry is concerned mainly with crystalline inorganic materials, their synthesis, structures, properties and applications. A good place to begin is with *crystal structures* and *crystal chemistry*. All necessary crystal structure information is contained in data on unit cells, their dimensions and the positions or atomic coordinates of atoms inside the unit cell. Crystal chemistry combines this basic structural information with information about the elements, their principal oxidation states, ionic radii, coordination requirements and preferences for ionic/covalent/metallic bonding. A working knowledge of the Periodic Table and the properties of elements is, of course, invaluable to be able appreciate crystal chemistry, but conversely, knowledge of crystal structures and especially crystal chemistry provides a very useful way to gain increased understanding of the elements and their compounds.

Many of the properties and applications of crystalline inorganic materials revolve around a surprisingly small number of structure types. In this chapter, the main families of inorganic structures are reviewed, especially those which have interesting properties; more details of the vast array of structures may be found in the encyclopaedic text by Wells and also in the Wyckoff *Crystal Structures* book series. First, however, we must consider some basic concepts of crystallography.

1.1 Unit Cells and Crystal Systems

Crystals are built up of regular arrangements of atoms in three dimensions; these arrangements can be represented by a repeat unit or motif called the *unit cell*. The unit cell is defined as *the smallest repeating unit which shows the full symmetry of the crystal structure*. Let us see exactly what this means, first in two dimensions. A section through the NaCl structure is shown in Fig. 1.1(a); possible repeat units are given in (b) to (e). In each, the repeat unit is a square and adjacent squares share edges and corners. Adjacent squares are identical, as they must be by definition; thus, all the squares in (b) have Cl⁻ ions at their corners and centres. The repeat units in (b), (c) and (d) are all of the same size and, in fact, differ only in their relative position. The choice of origin of the repeat unit is to some extent a matter of personal taste, even though its size, shape and orientation are fixed. The repeat unit of NaCl is usually chosen as (b) or (c) rather than (d) because it is easier to draw and visualise the structure as a whole if the repeat unit contains atoms or ions at special positions such as corners and edge centres. Another guideline is that usually the origin is chosen so that the symmetry of the structure is evident (next section).

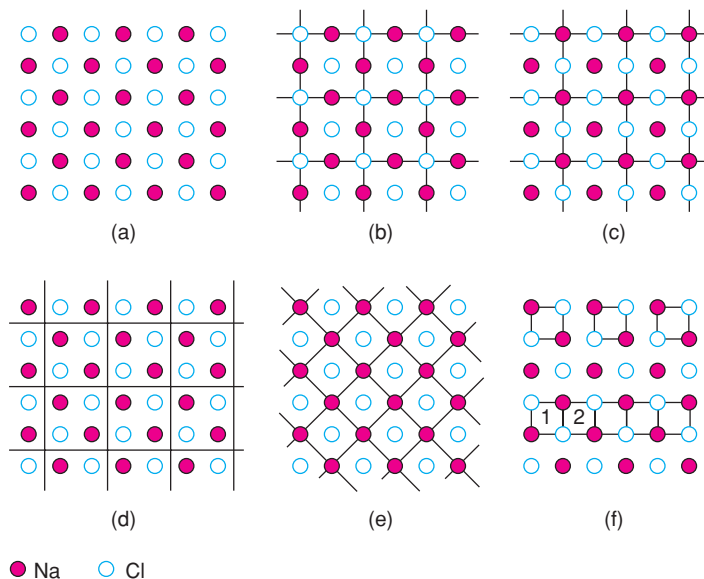


Figure 1.1 (a) Section through the NaCl structure, showing (b) to (e) possible repeat units and (f) incorrect units.

In the hypothetical case that two-dimensional (2D) crystals of NaCl could form, the repeat unit shown in (e), or its equivalent with Cl at the corners and Na in the middle, would be the correct unit. Comparing (e) and, for example, (c), both repeat units are square and show the 2D symmetry of the structure; as the units in (e) are half the size of those in (c), (e) would be preferred according to the above definition of the unit cell. In three dimensions, however, the unit cell of NaCl is based on (b) or (c), rather than (e) because only they show the cubic symmetry of the structure (see later).

In (f) are shown two examples of what is *not* a repeat unit. The top part of the diagram contains isolated squares whose area is one-quarter of the squares in (c). It is true that each square in (f) is identical but it is not permissible to isolate unit cells or areas from each other, as happens here. The bottom part of the diagram contains units that are not identical; thus square 1 has Na in its top right corner whereas 2 has Cl in this position.

The unit cell of NaCl in three dimensions is shown in Fig. 1.2; it contains Na at the corner and face centre positions with Cl at the edge centres and body centre. Each face of the unit cell looks like the unit area shown

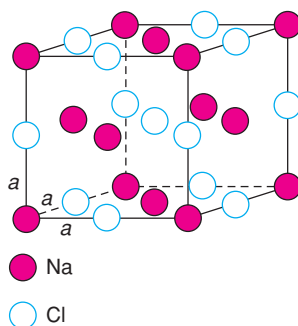


Figure 1.2 Cubic unit cell of NaCl, $a = b = c$.

Table 1.1 The seven crystal systems

Crystal system	Unit cell shape ^b	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	One threefold axis	R
Monoclinic ^a	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	None	P

^aTwo settings of the monoclinic cell are used in the literature, the most commonly used one given here, with b as the unique axis and the other with c defined as the unique axis: $a \neq b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$.

^bThe symbol \neq means 'not necessarily equal to'. Sometimes, crystals possess *pseudo-symmetry*. For example, a unit cell may be geometrically cubic but not possess the essential symmetry elements for cubic symmetry; the true symmetry is then lower, perhaps tetragonal.

in Fig. 1.1(c). As in the 2D case, the choice of origin is arbitrary; an equally valid unit cell could be chosen in which Na and Cl are interchanged. The unit cell of NaCl is *cubic*. The three edges: a , b and c are equal in length. The three angles: α (between b and c), β (between a and c) and γ (between a and b) are all 90° . A cubic unit cell also possesses certain symmetry elements, and these, together with the shape define the cubic unit cell.

The seven *crystal systems* listed in Table 1.1 and shown in Fig. 1.3 are the seven independent unit cell shapes that are possible in three-dimensional (3D) crystal structures. Six of these unit cell shapes are closely inter-related and are either cubic or can be derived by distorting a cube in various ways, as shown in Fig. 1.3(b).

Thus, if one axis, c , is of different length to the others, the shape is *tetragonal*; if all three axes are different, the shape is *orthorhombic*. If, now, one of the angles, β , is not 90° , the shape is *monoclinic*, whereas if all three angles differ from 90° , the shape is *triclinic*. Finally, if the cube is stretched, or compressed, along a body diagonal so that all three angles remain equal, but different from 90° , the shape is *trigonal*.

The remaining unit cell shape is *hexagonal*. A hexagonal-shaped box is shown in Fig. 1.3 and discussed later with reference to Fig. 1.21, but the true unit cell is only one-third of this size, as shown.

Although it is common practice to describe unit cells by their shapes, it is more correct to describe them by the presence or absence of symmetry. Thus, for example, if a unit cell has four intersecting threefold axes, it must be cubic in shape; the reverse does not necessarily apply and the unit cell could be fortuitously cubic but not have the threefold symmetries in the atomic arrangements. The essential symmetry for each crystal system is given in the third column of Table 1.1. Let us deal next with symmetry.

1.2 Symmetry

1.2.1 Rotational symmetry; symmetry elements and operations

Symmetry is most easily defined using examples. Consider the silicate tetrahedron shown in Fig. 1.4(a). If it is rotated about an axis passing along the vertical Si–O bond, then every 120° the tetrahedron finds itself in an identical position. Effectively, the three basal oxygens change position with each other every 120° . During a complete 360° rotation, the tetrahedron passes through three such identical positions. The fact that different (i.e. >1) identical orientations are possible means that the SiO_4 tetrahedron possesses symmetry. The axis

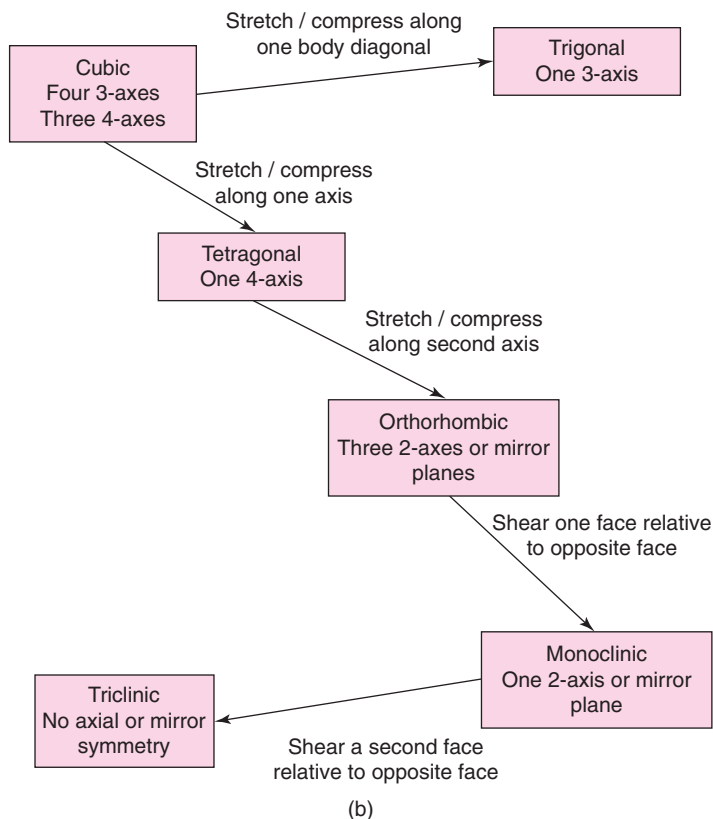
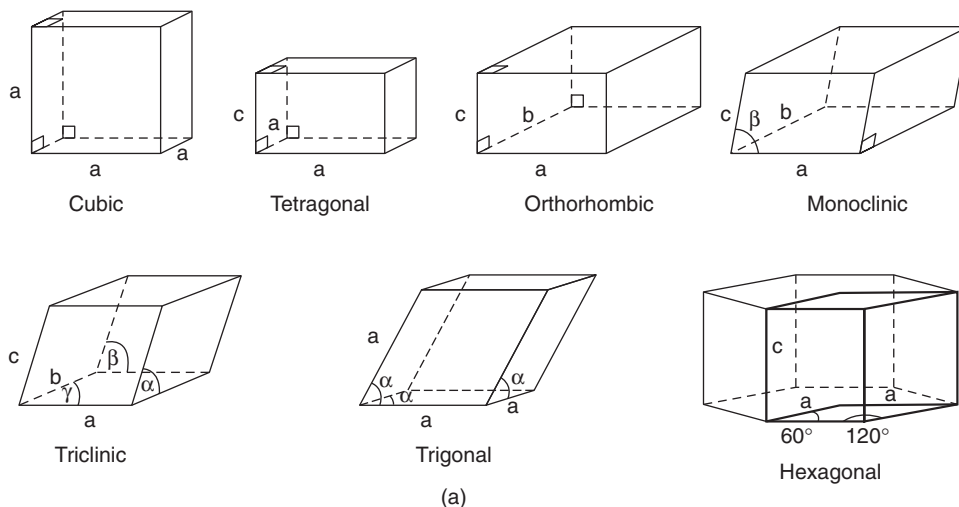


Figure 1.3 (a) The seven crystal systems and their unit cell shapes; (b) five of the seven crystal systems can be derived from cubic by structural distortions.

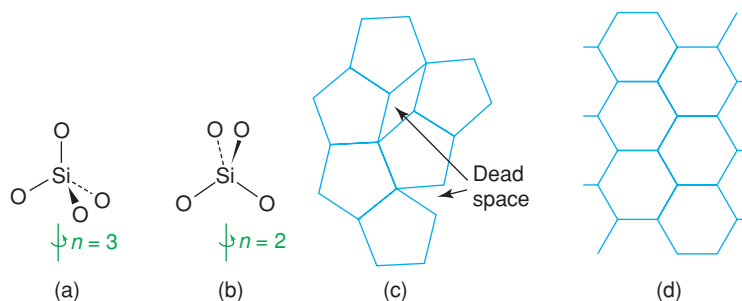


Figure 1.4 (a) Threefold and (b) twofold rotation axes; (c) the impossibility of forming a complete layer of pentagons; (d) a complete layer of hexagons.

about which the tetrahedron may be rotated is called a *rotation axis*; it is an example of a *symmetry element*. The process of rotation is an example of a *symmetry operation*.

The symmetry elements that are important in crystallography are listed in Table 1.2. There are two nomenclatures for labelling them, the Hermann–Mauguin system used in crystallography and the Schönflies system used in spectroscopy. Ideally, there would be only one system which everybody uses, but this is unlikely to come about since (a) both systems are very well established, (b) crystallographers require elements of *space symmetry* that spectroscopists do not, and vice versa, (c) spectroscopists use a more extensive range of *point symmetry* elements than crystallographers.

The symmetry element described above for the silicate tetrahedron is a rotation axis, with symbol n . Rotation about this axis by $360/n$ degrees gives an identical orientation and the operation is repeated n times before the original configuration is regained. In this case, $n = 3$ and the axis is a *threefold rotation axis*. The SiO_4 tetrahedron possesses four threefold rotation axes, one in the direction of each Si–O bond.

When viewed from another angle, SiO_4 tetrahedra possess *twofold rotation axes* [Fig. 1.4(b)] which pass through the central Si and bisect the O–Si–O bonds. Rotation by 180° leads to indistinguishable orientations of the tetrahedra. The SiO_4 tetrahedron possesses three of these twofold axes.

Crystals may display rotational symmetries 2, 3, 4 and 6. Others, such as $n = 5, 7$, are never observed in 3D crystal structures based on a regular periodic repetition of the unit cell and its contents. This is shown in Fig. 1.4(c), where a fruitless attempt has been made to pack pentagons to form a complete layer; thus, individual pentagons have fivefold symmetry but the array of pentagons does not. For hexagons with sixfold

Table 1.2 Symmetry elements

	Symmetry element	Hermann–Mauguin symbols (crystallography)	Schönflies symbols (spectroscopy)
Point symmetry	Mirror plane	m	σ_v, σ_h
	Rotation axis	$n = 2, 3, 4, 6$	C_n (C_2, C_3 , etc.)
	Inversion axis	\bar{n} ($= \bar{1}, \bar{2}$, etc.)	–
	Alternating axis ^a	–	S_n (S_1, S_2 , etc.)
	Centre of symmetry	$\bar{1}$	i
Space symmetry	Glide plane	a, b, c, d, n	–
	Screw axis	$2_1, 3_1$, etc.	–

^aThe *alternating axis* is a combination of rotation (n -fold) and reflection perpendicular to the rotation axis. It is little used in crystallography.

rotation axes (d), a complete layer is easily produced; both the individual hexagons and the overall array exhibit sixfold symmetry. This is not to say that molecules which have pentagonal symmetry, $n = 5$, cannot exist in the crystalline state. They can, of course, but their fivefold symmetry cannot be exhibited by the crystal as a whole.

1.2.2 Quasicrystals

The discovery of a new state of matter, the *quasicrystalline state*, by Schechtman and colleagues in 1982 (and which led to the Nobel Prize in Chemistry in 2011) appeared at first sight to violate the rules concerning allowable rotational symmetries in crystal lattices. From their single-crystal diffraction patterns, rotational symmetries such as $n = 5$ but also $n = 10$ and 12 were observed whereas, as shown in Fig. 1.4(c), a regular crystal lattice exhibiting fivefold rotational symmetry cannot exist. The answer to this conundrum is that quasicrystals do not have regularly repeating crystal structures based on a single unit cell motif. Instead, they have fully ordered but non-periodic arrays constructed from more than one motif or building block.

Elegant examples of quasisymmetry are found in so-called Penrose tiling, as shown in Fig. 1.5. In this example, space is filled completely by a combination of red and blue diamonds; such a tiling pattern has many local areas of fivefold symmetry but the structure as a whole is not periodic, does not exhibit fivefold symmetry and a regular repeat unit cannot be identified. Quasicrystals have since been discovered in a wide range of alloy systems and also in organic polymer and liquid crystal systems; they have been discovered in Nature in an Al–Cu–Fe alloy named icosahedrite that was believed to have been part of a meteorite and had existed on Earth for billions of years. It is probably just a matter of time before they are discovered also in inorganic oxide materials, natural or synthetic.

In the early days of work on quasicrystals, an alternative explanation for possible fivefold symmetry was based on *twinning*, as shown schematically in Fig. 1.6. Five identical crystalline segments are shown, each of which has twofold rotational symmetry in projection. Pairs of crystal segments meet at a coherent interface or *twin plane* in which the structures on either side of the twin plane are mirror images of each other. The five crystal segments meet at a central point which exhibits fivefold symmetry as a macroscopic element of point symmetry but the individual crystal segments clearly do not exhibit any fivefold symmetry. Schechtman showed conclusively that twinning such as shown in Fig. 1.6 could not explain the quasicrystalline state.

1.2.3 Mirror symmetry

A *mirror plane*, m , exists when two halves of, for instance, a molecule can be interconverted by carrying out the imaginary process of reflection across the mirror plane. The silicate tetrahedron possesses six mirror planes, one of which, running vertically and perpendicular to the plane of the paper, is shown in Fig. 1.7(a). The silicon and two oxygens, 1 and 2, lie on the mirror plane and are unaffected by reflection. The other two oxygens, 3 and 4, are interchanged on reflection. A second mirror plane lies in the plane of the paper; for this, Si and oxygens 3, 4 lie on the mirror but oxygen 2, in front of the mirror, is the image of oxygen 1, behind the mirror.

1.2.4 Centre of symmetry and inversion axes

A *centre of symmetry*, $\bar{1}$, exists when any part of a structure can be reflected through this centre of symmetry, which is a point, and an identical arrangement found on the other side. An AlO_6 octahedron has a centre of symmetry, Fig. 1.7(b), located on the Al atom. If a line is drawn from any oxygen, e.g. 1, through the centre and extended an equal distance on the other side, it terminates at another oxygen, 2. A tetrahedron, e.g. SiO_4 , does not have a centre of symmetry (a).

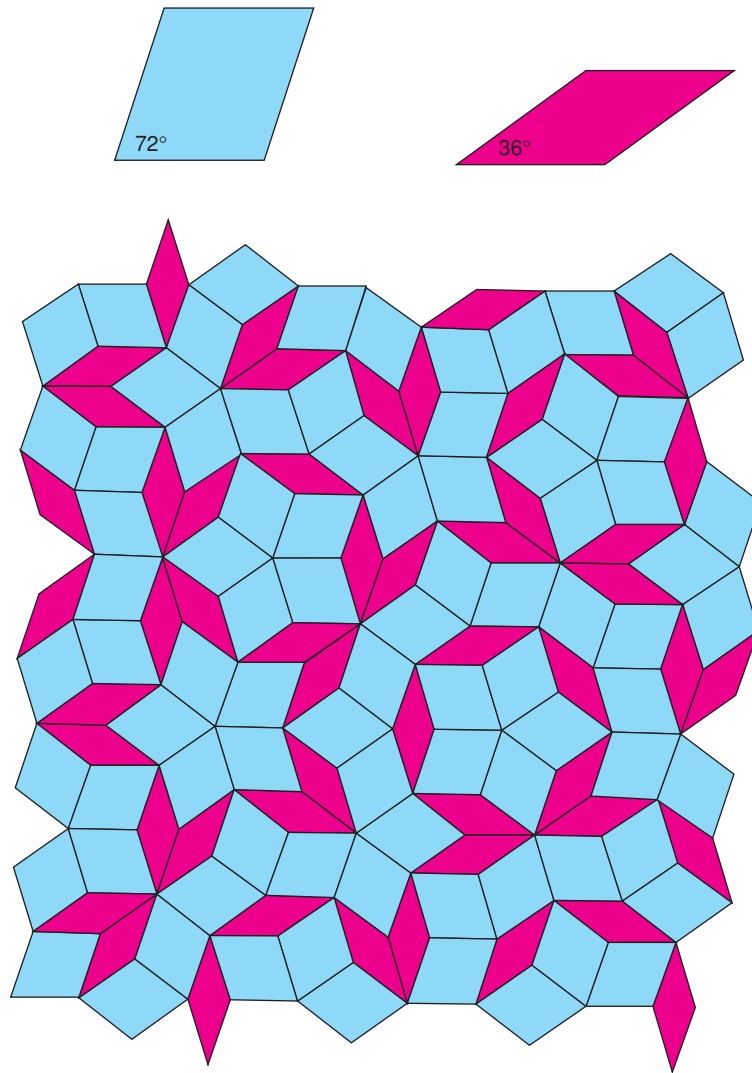


Figure 1.5 Two-dimensional Penrose tiling constructed by packing together two different sets of parallelograms. Adapted with permission from C. Janot, *Quasicrystals*, © 1997 Oxford University Press.

The *inversion axis*, \bar{n} , is a combined symmetry operation involving rotation (according to n) and inversion through the centre. A $\bar{4}$ (*fourfold inversion*) axis is shown in (c). The first stage involves rotation by $360/4 = 90^\circ$ and takes, for example, oxygen 2 to position 2'. This is followed by inversion through the centre, at Si, and leads to position 3. Oxygens 2 and 3 are therefore related by a $\bar{4}$ axis. Possible inversion axes in crystals are limited to $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$ for the same reason that only certain pure rotation axes are allowed. The onefold inversion axis is not a separate symmetry element, but is simply equivalent to the centre of symmetry; also, the twofold inversion axis is the same as a mirror plane perpendicular to that axis.

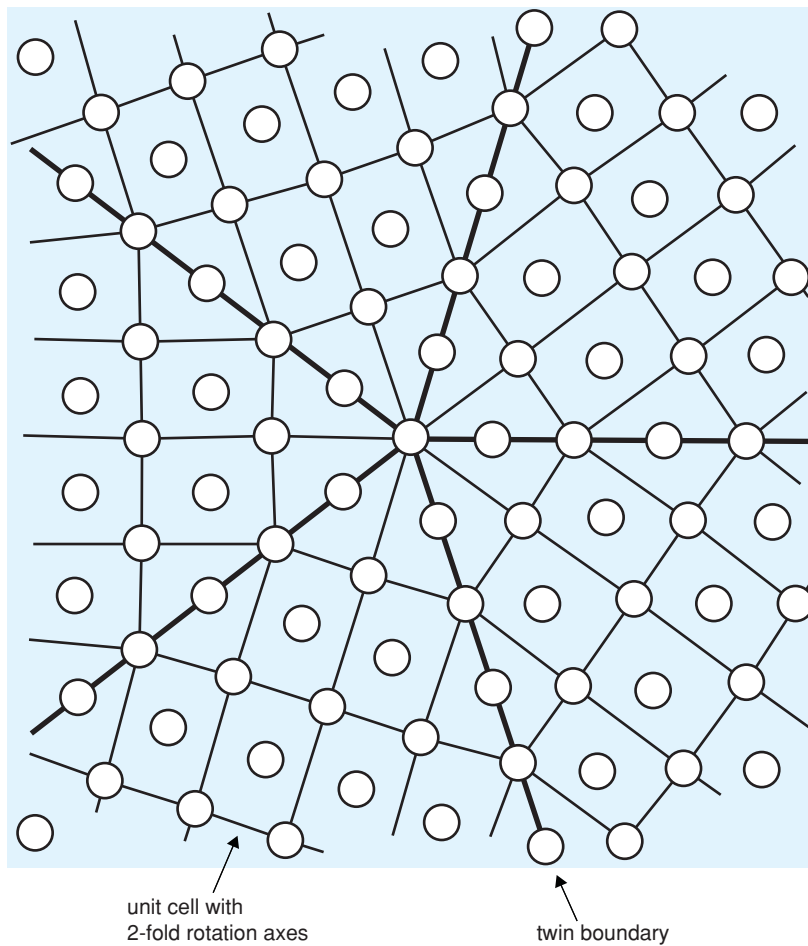


Figure 1.6 Hypothetical twinned structure showing fivefold symmetry. Adapted with permission from J. M. Dubois, *Useful Quasicrystals*, pg 10, © 2005 World Scientific Publishing Company.

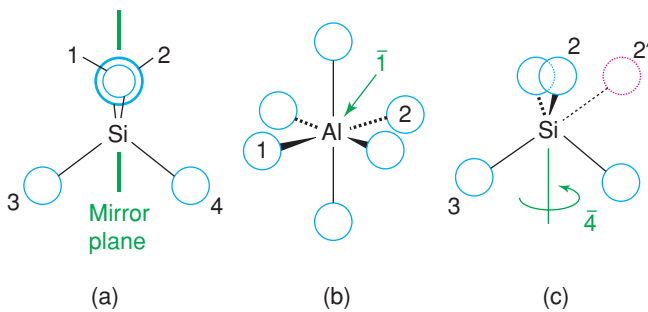


Figure 1.7 Symmetry elements: (a) mirror plane; (b) centre of symmetry; (c) fourfold inversion axis.

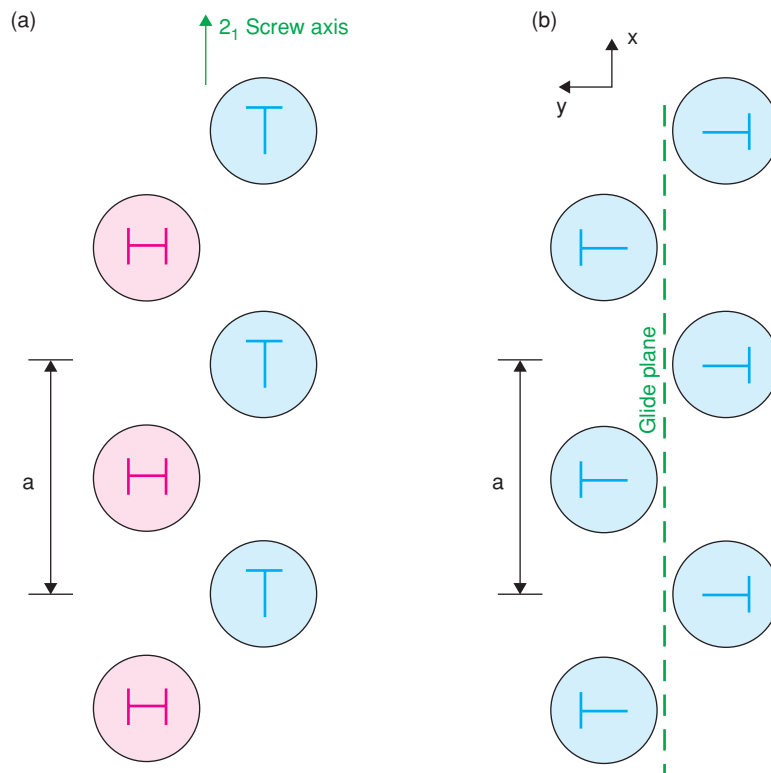


Figure 1.8 Arrangement of coins with heads (H) and tails (T) illustrating (a) a 2_1 screw axis parallel to a and (b) an a glide plane perpendicular to b ; in each case, translation between symmetry-related objects is by $a/2$.

1.2.5 Point symmetry and space symmetry

The symmetry elements discussed so far are elements of *point symmetry*. For each, at least one point stays unchanged during the symmetry operation, i.e. an atom lying on a centre of symmetry, rotation axis or mirror plane does not move during the respective symmetry operations. Finite-sized molecules can only possess point symmetry elements, whereas crystals may have extra symmetries that include translation steps as part of the symmetry operation. These are elements of *space symmetry*, of which there are two types.

The *screw axis* combines translation and rotation; the atoms or ions in a crystal which possesses screw axes appear to lie on spirals about these axes. A schematic example is shown in Fig. 1.8(a). All you need to demonstrate a screw axis is a handful of coins which can be arranged on a flat surface with either their heads (H) or tails (T) facing upwards. The symbol for a screw axis, X_Y , indicates translation by the fraction Y/X of the unit cell edge in the direction of the screw axis together with simultaneous rotation by $360/X^\circ$ about the screw axis. Thus, a 4_2 axis parallel to a involves translation by $a/2$ and rotation by 90° ; this process is repeated twice along a for every unit cell.

The *glide plane* combines translation and reflection, as shown schematically in Fig. 1.8(b). Translation may be parallel to any of the unit cell axes (a , b , c), to a face diagonal (n) or to a body diagonal (d). The a , b , c and n glide planes all have a translation step of half the unit cell in that direction; by definition, the d glide plane has a translation step which is $1/4$ of the body diagonal. For the *axial glide planes* a , b and c , it is important