

# Contents

<i>Preface</i>	<i>page</i> xix
<i>Acknowledgements</i>	xxiii
<i>Figure reproductions</i>	xxvi
<i>Symbols</i>	xxviii
<b>1 Materials and materials properties</b>	<b>1</b>
<b>1.1 Materials and structure</b>	1
<b>1.2 Organization of the book</b>	3
<b>1.3 About length scales</b>	4
<b>1.4 Wave–particle duality and the de Broglie relationship</b>	7
<b>1.5 What is a material property?</b>	9
1.5.1 Definition of a material property	9
1.5.2 Directional dependence of properties	11
1.5.3 A first encounter with symmetry	14
1.5.4 A second encounter with symmetry	18
<b>1.6 So, what is this book all about?</b>	19
<b>1.7 Historical notes</b>	21
<b>1.8 Problems</b>	22
<b>2 The periodic table of the elements and interatomic bonds</b>	<b>24</b>
<b>2.1 About atoms</b>	24
2.1.1 The electronic structure of the atom	24
2.1.2 The hydrogenic model	25
<b>2.2 The periodic table</b>	27
2.2.1 Layout of the periodic table	32
2.2.2 Trends across the table	34
<b>2.3 Interatomic bonds</b>	38
2.3.1 Quantum chemistry	38
2.3.2 Interactions between atoms	39
2.3.3 The ionic bond	40
2.3.4 The covalent bond	43

2.3.5	The metallic bond	44
2.3.6	The van der Waals bond	45
2.3.7	Mixed bonding	46
2.3.8	Electronic states and symmetry	46
2.3.9	Overview of bond types and material properties	48
<b>2.4</b>	<b>Historical notes</b>	48
<b>2.5</b>	<b>Problems</b>	52
<b>3</b>	<b>What is a crystal structure?</b>	<b>55</b>
<b>3.1</b>	<b>Introduction</b>	55
<b>3.2</b>	<b>The space lattice</b>	58
3.2.1	Basis vectors and translation vectors	58
3.2.2	Some remarks about notation	60
3.2.3	More about lattices	63
<b>3.3</b>	<b>The four 2-D crystal systems</b>	64
<b>3.4</b>	<b>The seven 3-D crystal systems</b>	66
<b>3.5</b>	<b>The five 2-D Bravais nets and fourteen 3-D Bravais lattices</b>	69
<b>3.6</b>	<b>Other ways to define a unit cell</b>	73
<b>3.7</b>	<b>Historical notes</b>	75
<b>3.8</b>	<b>Problems</b>	76
<b>4</b>	<b>Crystallographic computations</b>	<b>79</b>
<b>4.1</b>	<b>Directions in the crystal lattice</b>	79
<b>4.2</b>	<b>Distances and angles in a 3-D lattice</b>	80
4.2.1	Distance between two points	80
4.2.2	The metric tensor	83
4.2.3	The dot-product in a crystallographic reference frame	85
<b>4.3</b>	<b>Worked examples</b>	87
4.3.1	Computation of the length of a vector	87
4.3.2	Computation of the distance between two atoms	87
4.3.3	Computation of the angle between atomic bonds	88
4.3.4	Computation of the angle between lattice directions	89
4.3.5	An alternative method for the computation of angles	90
4.3.6	Further comments	90
<b>4.4</b>	<b>Historical notes</b>	91
<b>4.5</b>	<b>Problems</b>	93
<b>5</b>	<b>Lattice planes</b>	<b>97</b>
<b>5.1</b>	<b>Miller indices</b>	97
<b>5.2</b>	<b>Families of planes and directions</b>	100
<b>5.3</b>	<b>Special case: the hexagonal system</b>	101
<b>5.4</b>	<b>Crystal forms</b>	104
<b>5.5</b>	<b>Historical notes</b>	108
<b>5.6</b>	<b>Problems</b>	109

<b>6 Reciprocal space</b>	<b>111</b>
6.1 Introduction	111
6.2 The reciprocal basis vectors	112
6.3 Reciprocal space and lattice planes	116
6.4 The reciprocal metric tensor	118
6.4.1 Computation of the angle between planes	120
6.4.2 Computation of the length of the reciprocal lattice vectors	120
6.5 Worked examples	124
6.6 Historical notes	126
6.7 Problems	128
<b>7 Additional crystallographic computations</b>	<b>130</b>
7.1 The stereographic projection	130
7.2 About zones and zone axes	133
7.2.1 The vector cross product	134
7.2.2 About zones and the zone equation	139
7.2.3 The reciprocal lattice and zone equation in the hexagonal system	141
7.3 Relations between direct space and reciprocal space	142
7.4 Coordinate transformations	144
7.4.1 Transformation rules	144
7.4.2 Example of a coordinate transformation	147
7.4.3 Converting vector components into Cartesian coordinates	149
7.5 Examples of stereographic projections	153
7.5.1 Stereographic projection of a cubic crystal	153
7.5.2 Stereographic projection of a monoclinic crystal	156
7.6 Historical notes	159
7.7 Problems	161
<b>8 Symmetry in crystallography</b>	<b>163</b>
8.1 Symmetry of an arbitrary object	163
8.2 Symmetry operations	170
8.2.1 Basic isometric transformations	171
8.2.2 Compatibility of rotational symmetries with crystalline translational periodicity	172
8.2.3 Operations of the first kind: pure rotations	174
8.2.4 Operations of the first kind: pure translations	176
8.2.5 Operations of the second kind: pure reflections	179
8.2.6 Operations of the second kind: inversions	180
8.2.7 Symmetry operations that do not pass through the origin	181
8.3 Combinations of symmetry operations	182
8.3.1 Combination of rotations with the inversion center	182
8.3.2 Combination of rotations and mirrors	183
8.3.3 Combination of rotations and translations	185
8.3.4 Combination of mirrors and translations	187

8.3.5 Relationships and differences between operations of first and second type	190
<b>8.4 Point symmetry</b>	<b>191</b>
<b>8.5 Historical notes</b>	<b>194</b>
<b>8.6 Problems</b>	<b>196</b>
<b>9 Point groups</b>	<b>198</b>
<b>9.1 What is a group?</b>	<b>198</b>
9.1.1 A simple example of a group	198
9.1.2 Group axioms	199
9.1.3 Principal properties of groups	201
<b>9.2 Three-dimensional crystallographic point symmetries</b>	<b>203</b>
9.2.1 Step I: the proper rotations	204
9.2.2 Step II: combining proper rotations with two-fold rotations	205
9.2.3 Step IIIa: combining proper rotations with inversion symmetry	207
9.2.4 Step IIIb: combining proper rotations with perpendicular reflection elements	209
9.2.5 Step IV: combining proper rotations with coinciding reflection elements	210
9.2.6 Step Va: combining inversion rotations with coinciding reflection elements	211
9.2.7 Step Vb: combining proper rotations with coinciding and perpendicular reflection elements	212
9.2.8 Step VI: combining proper rotations	212
9.2.9 Step VII: adding reflection elements to Step VI	214
9.2.10 General remarks	214
<b>9.3 Two-dimensional crystallographic point symmetries</b>	<b>226</b>
<b>9.4 Historical notes</b>	<b>227</b>
<b>9.5 Problems</b>	<b>229</b>
<b>10 Plane groups and space groups</b>	<b>230</b>
<b>10.1 Introduction</b>	<b>230</b>
<b>10.2 Plane groups</b>	<b>232</b>
<b>10.3 Space groups</b>	<b>237</b>
<b>10.4 The symmorphic space groups</b>	<b>241</b>
<b>10.5 The non-symmorphic space groups</b>	<b>243</b>
<b>10.6 General remarks</b>	<b>246</b>
<b>10.7 *Space group generators</b>	<b>252</b>
<b>10.8 Historical notes</b>	<b>254</b>
<b>10.9 Problems</b>	<b>256</b>
<b>11 X-ray diffraction: geometry</b>	<b>258</b>
<b>11.1 Introduction</b>	<b>258</b>
<b>11.2 Properties and generation of X-rays</b>	<b>259</b>

11.2.1 How do we generate X-rays?	261
11.2.2 Wave length selection	265
<b>11.3 X-rays and crystal lattices</b>	268
11.3.1 Scattering of X-rays by lattice planes	272
11.3.2 Bragg's Law in reciprocal space	275
<b>11.4 Basic experimental X-ray diffraction techniques</b>	280
11.4.1 The X-ray powder diffractometer	281
<b>11.5 Historical notes</b>	290
<b>11.6 Problems</b>	291
<b>12 X-ray diffraction: intensities</b>	<b>294</b>
<b>12.1 Scattering by electrons, atoms, and unit cells</b>	294
12.1.1 Scattering by a single electron	294
12.1.2 Scattering by a single atom	296
12.1.3 Scattering by a single unit cell	301
<b>12.2 The structure factor</b>	303
12.2.1 Lattice centering and the structure factor	303
12.2.2 Symmetry and the structure factor	307
12.2.3 Systematic absences and the International Tables for Crystallography	310
12.2.4 Examples of structure factor calculations	311
<b>12.3 Intensity calculations for diffracted and measured intensities</b>	312
12.3.1 Description of the correction factors	313
12.3.2 Expressions for the total measured intensity	319
<b>12.4 Historical notes</b>	321
<b>12.5 Problems</b>	322
<b>13 Other diffraction techniques</b>	<b>324</b>
<b>13.1 Introduction</b>	324
<b>13.2 *Neutron diffraction</b>	325
13.2.1 Neutrons: generation and properties	327
13.2.2 Neutrons: wave length selection	329
13.2.3 Neutrons: atomic scattering factors	330
13.2.4 Neutrons: scattering geometry	335
13.2.5 Neutrons: example powder pattern	337
<b>13.3 *Electron diffraction</b>	338
13.3.1 The electron as a particle and a wave	338
13.3.2 The geometry of electron diffraction	340
13.3.3 The transmission electron microscope	342
13.3.4 Basic observation modes in the TEM	344
13.3.5 Convergent beam electron diffraction	348
<b>13.4 *Synchrotron X-ray sources for scattering experiments</b>	351
13.4.1 Synchrotron accelerators	352
13.4.2 Synchrotron radiation: experimental examples	354

13.5	Historical notes	356
13.6	Problems	358
<b>14</b>	<b>About crystal structures and diffraction patterns</b>	<b>362</b>
14.1	Crystal structure descriptions	362
14.1.1	Space group description	362
14.1.2	Graphical representation methods	363
14.2	Crystal structures $\leftrightarrow$ powder diffraction patterns	367
14.2.1	The <i>Ni</i> powder pattern, starting from the known structure	367
14.2.2	The <i>NaCl</i> powder pattern, starting from the known structure	371
14.2.3	The <i>Ni</i> structure, starting from the experimental powder diffraction pattern	376
14.2.4	The <i>NaCl</i> structure, starting from the experimental powder diffraction pattern	379
14.2.5	*General comments about crystal structure determination	383
14.3	Historical notes	388
<b>15</b>	<b>Non-crystallographic point groups</b>	<b>403</b>
15.1	Introduction	403
15.2	Example of a non-crystallographic point group symmetry	404
15.3	Molecules with non-crystallographic point group symmetry	405
15.3.1	Fullerene molecular structures	407
15.4	Icosahedral group representations	409
15.5	Other non-crystallographic point groups with five-fold symmetries	414
15.6	Descents in symmetry: decagonal and pentagonal groups	416
15.7	Non-crystallographic point groups with octagonal symmetry	420
15.8	Descents in symmetry: octagonal and dodecagonal groups	420
15.9	Historical notes	424
15.10	Problems	426
<b>16</b>	<b>Periodic and aperiodic tilings</b>	<b>430</b>
16.1	Introduction	430
16.2	2-D plane tilings	431
16.2.1	2-D regular tilings	431
16.2.2	2-D Archimedean tilings	433
16.2.3	<i>k</i> -uniform regular tilings	435
16.2.4	Dual tilings – the Laves tilings	435
16.2.5	Tilings without regular vertices	437
16.3	*Color tilings	438
16.4	*Quasi-periodic tilings	440
16.5	*Regular polyhedra and <i>n</i> -dimensional regular polytopes	441
16.6	Crystals with stacking of $3^6$ tilings	445

16.6.1 Simple close-packed structures: <i>ABC</i> stacking	445
16.6.2 Interstitial sites in close-packed structures	447
16.6.3 Representation of close-packed structures	448
16.6.4 Polytypism and properties of SiC semiconductors	450
<b>16.7 3<sup>6</sup> close-packed tilings of polyhedral faces</b>	451
<b>16.8 Historical notes</b>	452
<b>16.9 Problems</b>	455
<b>17 Metallic structures I: simple, derivative, and superlattice structures</b>	<b>459</b>
<b>17.1 Introduction</b>	459
<b>17.2 Classification of structures</b>	460
17.2.1 Strukturbericht symbols	460
17.2.2 Pearson symbols	461
17.2.3 Structure descriptions in this book	462
<b>17.3 Parent structures</b>	463
17.3.1 Geometrical calculations for cubic structures	464
<b>17.4 Atomic sizes, bonding, and alloy structure</b>	466
17.4.1 Hume-Rothery rules	467
17.4.2 Bonding in close-packed rare gas and metallic structures	469
17.4.3 Phase diagrams	474
<b>17.5 Superlattices and sublattices: mathematical definition</b>	475
<b>17.6 Derivative structures and superlattice examples</b>	476
17.6.1 <i>fcc</i> -derived structures and superlattices	476
17.6.2 <i>bcc</i> -derived superlattices	482
17.6.3 Diamond cubic derived superlattices	484
17.6.4 Hexagonal close-packed derived superlattices	486
<b>17.7 Elements with alternative stacking sequences or lower symmetry</b>	489
17.7.1 Elements with alternative stacking sequences	489
17.7.2 Elements with lower symmetry structures	490
<b>17.8 *Natural and artificial superlattices (after Venkataraman <i>et al.</i>, 1989)</b>	494
17.8.1 Superlattice structures based on the L <sub>1</sub> <sub>2</sub> cell	494
17.8.2 Artificial superlattices	497
17.8.3 X-ray scattering from long period multilayered systems	497
17.8.4 Incommensurate superlattices	499
<b>17.9 Interstitial alloys</b>	502
<b>17.10 Historical notes</b>	504
<b>17.11 Problems</b>	506
<b>18 Metallic structures II: topologically close-packed phases</b>	<b>510</b>
<b>18.1 Introduction: electronic states in metals</b>	510
<b>18.2 Topological close packing</b>	513

18.2.1	The Kasper polyhedra	514
18.2.2	Connectivity of Kasper polyhedra	516
18.2.3	Metallic radii	517
<b>18.3</b>	<b>*Frank–Kasper alloy phases</b>	<b>518</b>
18.3.1	A15 phases and related structures	518
18.3.2	The Laves phases and related structures	525
18.3.3	The sigma phase	533
18.3.4	The $\mu$ -phase and the M, P, and R phases	535
<b>18.4</b>	<b>*Quasicrystal approximants</b>	<b>536</b>
18.4.1	$Mg_{32}(Al,Zn)_{49}$ and alpha-Al–Mn–Si crystal structures	537
18.4.2	$Mg_{32}(Al,Zn)_{49}$ and alpha-Al–Mn–Si shell models	538
<b>18.5</b>	<b>Historical notes</b>	<b>541</b>
<b>18.6</b>	<b>Problems</b>	<b>543</b>
<b>19</b>	<b>Metallic structures III: rare earth–transition metal systems</b>	<b>547</b>
<b>19.1</b>	<b>Introduction</b>	<b>547</b>
<b>19.2</b>	<b>RT Laves phases</b>	<b>549</b>
<b>19.3</b>	<b>Cubic <math>UNi_5</math>, <math>Th_6Mn_{23}</math>, and <math>LaCo_{13}</math> phases</b>	<b>550</b>
19.3.1	The $UNi_5$ phase	550
19.3.2	The $Th_6Mn_{23}$ phase	551
19.3.3	The $LaCo_{13}$ phase	553
<b>19.4</b>	<b>*Non-cubic phases</b>	<b>555</b>
19.4.1	$SmCo_3$ and $SmCo_5$ phases	555
19.4.2	Dumbbell substitutions: $\alpha$ - $Sm_2Co_{17}$ and $\beta$ - $Sm_2Co_{17}$ phases	560
19.4.3	Tetragonal phases: $RT_{12}$ and $Nd_2Fe_{14}B$	564
19.4.4	The monoclinic $R_3(Fe,Co)_{29}$ phases	567
<b>19.5</b>	<b>Interstitial modifications</b>	<b>571</b>
<b>19.6</b>	<b>Historical notes</b>	<b>573</b>
<b>19.7</b>	<b>Problems</b>	<b>575</b>
<b>20</b>	<b>Metallic structures IV: quasicrystals</b>	<b>579</b>
<b>20.1</b>	<b>Introduction</b>	<b>579</b>
<b>20.2</b>	<b>The golden mean and pentagonal symmetry</b>	<b>581</b>
<b>20.3</b>	<b>One-dimensional quasicrystals</b>	<b>583</b>
20.3.1	The Fibonacci sequence and Fibonacci lattice derived by recursion	583
20.3.2	Lattice positions in the Fibonacci lattice (following Venkataraman, <i>et al.</i> , 1989)	586
20.3.3	Construction of the Fibonacci lattice by the projection method	587
20.3.4	*The Fourier transform of the Fibonacci lattice (following Venkataraman, <i>et al.</i> , 1989)	590
<b>20.4</b>	<b>*Two-dimensional quasicrystals</b>	<b>591</b>
20.4.1	2-D quasicrystals: Penrose tilings	591
20.4.2	The Penrose tiling derived by projection	597
20.4.3	2-D quasicrystals: other polygonal quasicrystals	598



<b>20.5 *Three-dimensional quasicrystals</b>	601
20.5.1 3-D Penrose tilings	602
20.5.2 Indexing icosahedral quasicrystal diffraction patterns	603
20.5.3 Icosahedral quasicrystal diffraction patterns and quasilattice constants	606
20.5.4 3-D Penrose tiles: stacking, decoration and quasilattice constants	607
20.5.5 3-D Penrose tiles: projection method	609
<b>20.6 *Multiple twinning and icosahedral glass models</b>	610
<b>20.7 *Microscopic observations of quasicrystal morphologies</b>	612
<b>20.8 Historical notes</b>	613
<b>20.9 Problems</b>	615
<b>21 Metallic structures V: amorphous metals</b>	<b>619</b>
<b>21.1 Introduction</b>	619
<b>21.2 Order in amorphous and nanocrystalline alloys</b>	620
<b>21.3 Atomic positions in amorphous alloys</b>	623
<b>21.4 Atomic volume, packing, and bonding in amorphous solids</b>	624
21.4.1 DRPHS model	626
21.4.2 Binding in clusters: crystalline and icosahedral short range order	627
21.4.3 Icosahedral short range order models	628
<b>21.5 Amorphous metal synthesis</b>	629
<b>21.6 Thermodynamic and kinetic criteria for glass formation</b>	630
<b>21.7 Examples of amorphous metal alloy systems</b>	632
21.7.1 Metal–metalloid systems	633
21.7.2 Rare earth–transition metal systems	635
21.7.3 Early transition metal – late transition metal systems	635
21.7.4 Multicomponent systems for magnetic applications	637
21.7.5 Multicomponent systems for non-magnetic applications	639
<b>21.8 *X-ray scattering in amorphous materials</b>	640
<b>21.9 *Extended X-ray absorption fine structure (EXAFS)</b>	645
<b>21.10 Mössbauer spectroscopy</b>	648
<b>21.11 Historical notes</b>	649
<b>21.12 Problems</b>	651
<b>22 Ceramic structures I</b>	<b>654</b>
<b>22.1 Introduction</b>	654
<b>22.2 Ionic radii</b>	655
<b>22.3 Bonding energetics in ionic structures</b>	658
<b>22.4 Rules for packing and connectivity in ionic crystals</b>	660
22.4.1 Pauling's rules for ionic structures	660
22.4.2 Radius ratio rules for ionic compounds	661
<b>22.5 Halide salt structures: CsCl, NaCl, and CaF<sub>2</sub></b>	664
<b>22.6 Close packed sulfide and oxide structures: ZnS and Al<sub>2</sub>O<sub>3</sub></b>	668

<b>22.7 Perovskite and spinel structures</b>	671
22.7.1 Perovskites: $ABO_3$	671
22.7.2 Spinel: $AB_2O_4$	675
<b>22.8 Non-cubic close-packed structures: NiAs, <math>CdI_2</math>, and <math>TiO_2</math></b>	679
<b>22.9 *Layered structures</b>	681
22.9.1 Magnetoplumbite phases	681
22.9.2 Aurivillius phases	682
22.9.3 Ruddelston–Popper phases	683
22.9.4 Tungsten bronzes	685
22.9.5 Titanium carbosulfide	686
<b>22.10 Additional remarks</b>	687
<b>22.11 *Point defects in ceramics</b>	687
<b>22.12 Historical notes</b>	690
<b>22.13 Problems</b>	692
<b>23 Ceramic structures II: high temperature superconductors</b>	<b>695</b>
<b>23.1 Introduction: superconductivity</b>	695
<b>23.2 High temperature superconductors: nomenclature</b>	697
<b>23.3 *Perovskite-based high temperature superconductors</b>	697
23.3.1 Single layer perovskite high temperature superconductors	697
23.3.2 Triple-layer perovskite-based high temperature superconductors	701
<b>23.4 *BSCCO, TBCCO, HBCCO, and ACBCCO HTSC layered structures</b>	707
23.4.1 The BSCCO double-layer high temperature superconductors	708
23.4.2 The TBCCO double-layer high temperature superconductors	711
23.4.3 The TBCCO single-layer high temperature superconductors	713
23.4.4 The HBCCO high temperature superconductors	716
23.4.5 The ACBCCO high temperature superconductors	717
23.4.6 Rutheno-cuprate high temperature superconductors	718
23.4.7 Infinite-layer high temperature superconductors	719
<b>23.5 *Structure–properties relationships in HTSC superconductors</b>	720
23.5.1 Type I and Type II superconductors	720
23.5.2 The flux lattice and flux pinning in Type II superconductors	721
<b>23.6 Historical notes</b>	724
<b>23.7 Problems</b>	726
<b>24 Ceramic structures III: silicates and aluminates</b>	<b>730</b>
<b>24.1 Introduction</b>	730
<b>24.2 Orthosilicates (nesosilicates)</b>	734
24.2.1 Olivine minerals and gemstones	735
24.2.2 Garnets	736
24.2.3 Other orthosilicate minerals	738
<b>24.3 Pyrosilicates (sorosilicates)</b>	739
<b>24.4 Chains of tetrahedra, metasilicates (inosilicates)</b>	740

<b>24.5 Double chains of tetrahedra</b>	744
<b>24.6 Sheets of tetrahedra, phyllosilicates</b>	744
24.6.1 Mica	745
24.6.2 Kaolinite	746
<b>24.7 Networks of tetrahedra, tectosilicates</b>	747
24.7.1 Quartz	747
24.7.2 Cage structures in the tectosilicates	749
<b>24.8 Random networks of tetrahedra: silicate glasses</b>	752
<b>24.9 Mesoporous silicates</b>	753
<b>24.10 Sol-gel synthesis of silicate nanostructures</b>	754
<b>24.11 Historical notes</b>	756
<b>24.12 Problems</b>	757
<b>25 Molecular solids</b>	<b>760</b>
<b>25.1 Introduction</b>	760
<b>25.2 Simple molecular crystals: ice, dry ice, benzene, the clathrates, and self-assembled structures</b>	761
25.2.1 Solid H <sub>2</sub> O: ice	761
25.2.2 Solid CO <sub>2</sub> : dry ice	763
25.2.3 Hydrocarbon crystals	764
25.2.4 Clathrates	765
25.2.5 Amphiphiles and micelles	767
<b>25.3 Polymers</b>	768
25.3.1 Polymer classification	769
25.3.2 Polymerization reactions and products	770
25.3.3 Polymer chains: spatial configurations	773
25.3.4 Copolymers and self-assembly	774
25.3.5 Conducting and superconducting polymers	777
25.3.6 Polymeric derivatives of fullerenes	778
<b>25.4 Biological macromolecules</b>	779
25.4.1 DNA and RNA	779
25.4.2 Virus structures	782
<b>25.5 Fullerene-based molecular solids</b>	786
25.5.1 Fullerites	788
25.5.2 Fullerides	790
25.5.3 Carbon nanotubes	790
<b>25.6 Historical notes</b>	794
<b>25.7 Problems</b>	796
References	799
Index	824