

Contents

Preface — V

1 Introduction — 1

2 Categorizing and description of crystal structures — 3

- 2.1 Symmetry — 3
- 2.2 Sphere (and rod) packings — 4
- 2.3 Coordination polygons/polyhedra and the five Pauling rules — 5
 - 2.3.1 The five Pauling rules — 6
 - 2.3.2 Effective coordination numbers, linking coordination polyhedra, and Niggli notation — 11
- 2.4 Prototypical compounds – structure types — 12
- 2.5 Networks (nets) — 13

3 Symmetry of crystals — 15

- 3.1 The concept of the unit cell — 16
 - 3.1.1 The metric and the stoichiometry — 16
 - 3.1.2 Lattice points and motifs/bases — 17
 - 3.1.3 The seven crystal systems — 19
- 3.2 The 14 Bravais lattices – centring of unit cells — 20
- 3.3 Crystallographic point groups (crystal classes) – the morphology of crystals — 24
 - 3.3.1 Point symmetry elements — 25
 - 3.3.2 The 32 crystal classes — 30
- 3.4 Further (micro-) translations – glide planes and screw axes — 40
 - 3.4.1 Glide planes — 41
 - 3.4.2 Screw axes — 42
- 3.5 The 230 space groups — 46
 - 3.5.1 Nomenclature of space groups — 46
 - 3.5.2 Deriving point groups from space groups — 47
 - 3.5.3 International tables for crystallography — 47

4 Densest sphere packings — 50

- 4.1 The hexagonal closest packing — 52
- 4.2 The cubic closest packing — 54
- 4.3 Voids in the hcp and ccp packing — 55
- 4.4 Locations of interstitial sites along the packing direction — 57
- 4.5 Stacking variants/polytypes — 58

5 Some important structure types — 60

- 5.1 Metal structures – sphere packings in action — **60**
 - 5.1.1 Cu (ccp or fcc) (*Strukturbericht* type A1) — **60**
 - 5.1.2 Mg (hcp) (*Strukturbericht* type A3) — **62**
 - 5.1.3 Lanthanoids and actinoids – stacking variants — **63**
 - 5.1.4 W (bcc) (*Strukturbericht* type A2) — **65**
 - 5.1.5 α -Polonium — **66**
 - 5.1.6 Special metal structures — **66**
- 5.2 (Ionic) compounds based on densest sphere packings — **69**
- 5.3 Compounds based on a cubic closest packing — **72**
 - 5.3.1 NaCl (*Strukturbericht* type B1) — **72**
 - 5.3.2 CdCl_2 (*Strukturbericht* type C19) — **77**
 - 5.3.3 CrCl_3 , AlCl_3 , and RhBr_3 — **78**
 - 5.3.4 CaF_2 (*Strukturbericht* type C1) — **79**
 - 5.3.5 MgAl_2O_4 (spinel) (*Strukturbericht* type H1₁) — **88**
 - 5.3.6 CaTiO_3 (perovskite, *Strukturbericht* type E2₁) — **91**
- 5.4 Compounds based on a hexagonal closest packing — **102**
 - 5.4.1 NiAs (*Strukturbericht* type B8) — **102**
 - 5.4.2 CdI_2 (*Strukturbericht* type C6) — **105**
 - 5.4.3 $\beta\text{-V}_2\text{N}$ (*Strukturbericht* type L'3₂) — **107**
 - 5.4.4 CaCl_2 (*Strukturbericht* type C35), TiO_2 (rutile) (*Strukturbericht* type C4), and FeS_2 (marcasite) (*Strukturbericht* type C18) — **108**
 - 5.4.5 BiI_3 (*Strukturbericht* type D0₅) — **112**
 - 5.4.6 $\beta\text{-TiCl}_3$ and $\text{MoBr}_3/\text{ZrI}_3/\text{RuBr}_3$ — **113**
 - 5.4.7 $\alpha\text{-Al}_2\text{O}_3$ (corundum, *Strukturbericht* type D5₁) and FeTiO_3 (ilmenite, type E2₂) — **114**
 - 5.4.8 ZnS (wurtzite) (*Strukturbericht* type B4) — **115**
 - 5.4.9 Olivine $(\text{Mg,Mn,Fe})_2\text{SiO}_4$ (*Strukturbericht* type S1₂) — **117**
- 5.5 Other important structure types not based on densest packings — **118**
 - 5.5.1 CsCl (*Strukturbericht* type B2) — **118**
 - 5.5.2 MoS_2 (*Strukturbericht* type C7) — **119**
- Further reading — **120**

6 Defects in solids — 121

- 6.1 Point defects — **122**
 - 6.1.1 Point defects in crystals of elements — **122**
 - 6.1.2 Point defects in ionic compounds — **123**
 - 6.1.3 Kröger-Vink notation for point defects — **125**
 - 6.1.4 Colour centres – a special kind of point defects — **126**
 - 6.1.5 Swapping places – order-disorder phenomena and the relation between superstructures and sublattices — **128**
 - 6.1.6 Non-stoichiometric compounds and defect clusters — **130**

6.1.7	Substitutional and interstitial solid solutions —	132
6.2	Line defects – dislocations —	138
6.2.1	Edge dislocations —	138
6.2.2	Screw dislocations —	140
6.2.3	Movement of dislocations – plastic deformation —	141
6.2.4	Crystallographic shear planes —	144
6.3	Planar defects —	146
6.3.1	Stacking faults, turbostratification, and interstratification —	146
6.3.2	Internal boundaries in single crystals – mosaicity —	148
6.3.3	Grain boundaries —	149
6.3.4	Twin boundaries —	150
6.4	Volume defects —	150
	Conclusion and further reading —	153
7	Phase diagrams —	154
7.1	One-component systems —	154
7.2	Two-component systems —	155
7.2.1	Complete miscibility – solid solutions —	156
7.2.2	Singly eutectic systems —	157
7.2.3	Systems with compound formation that melt congruently —	159
7.2.4	Systems with compound formation but incongruent melting —	160
7.2.5	Systems with compound formation with an upper or lower limit of stability —	161
	Further reading —	162
8	Electronic structure of solid-state compounds —	163
8.1	Bloch functions, Bloch's theorem, the quantum number k , and crystal orbitals —	166
8.2	Bandwidth, density of states, and the Fermi level —	172
8.3	The Peierls distortion —	174
8.4	Band structures in two- and three-dimensional systems —	178
8.5	Examples of real band structures —	178
8.5.1	ReO_3 – a d^1 compound with metallic properties —	180
8.5.2	MoS_2 – a d^2 semiconductor with an indirect band gap —	181
8.6	Direct and indirect band gaps —	183
	Further reading —	184
9	Magnetic properties of solid-state compounds —	185
9.1	Diamagnetism and paramagnetism —	185
9.1.1	Quantifying the magnetic moments of paramagnetic substances —	188
9.1.2	Pauli paramagnetism —	191
9.2	Cooperative magnetic phenomena —	193

9.2.1	Ferromagnetism —	199
9.2.2	Antiferromagnetism and superexchange interactions —	203
9.2.3	Ferrimagnetism and double exchange —	205
9.3	Some magnetic materials —	208
9.3.1	Cubic spinel ferrites —	208
9.3.2	Garnets —	208
9.3.3	Hexagonal ferrites – magnetoplumbites —	209
	Further reading —	211
10	Phosphors, lamps, lasers, and LEDs —	212
10.1	Phosphors —	212
10.1.1	Fluorescent lamps —	215
10.1.2	Phosphors for CRTs of TVs and computer screens —	217
10.2	(Solid-state) lasers —	218
10.2.1	Operation conditions —	219
10.2.2	The ruby and the He-Ne laser —	220
10.2.3	Classification of lasers —	222
10.3	LEDs —	224
	Further reading —	226
11	Superconductivity —	227
11.1	From the metallic to the superconducting state —	227
11.1.1	The Meissner-Ochsenfeld effect and type I and type II superconductors —	228
11.1.2	The BCS theory —	230
11.2	Superconducting materials —	232
11.2.1	The elements —	232
11.2.2	Binary compounds, alloys, and intermetallics —	232
11.2.3	Oxo cuprates – the high-temperature superconducting revolution —	234
11.2.4	Further superconducting compounds —	236
	Further reading —	241
12	Ceramics —	242
12.1	Definition and classification of ceramics and the ceramic method —	242
12.2	(Alumo)silicate ceramics (traditional ceramics) —	245
12.3	Binary oxide ceramics —	247
12.3.1	α - Al_2O_3 —	247
12.3.2	ZrO_2 —	247
12.3.3	TiO_2 , MgO , and BeO —	249
12.4	Mixed oxide ceramics —	249
12.4.1	Aluminium titanate —	249
12.4.2	Barium titanate and lead zirconate titanate —	250

12.5	Boride ceramics —	253
12.6	Carbide ceramics —	253
12.6.1	Boron carbide —	254
12.6.2	Silicon carbide —	254
12.7	Silicide ceramics —	256
12.8	Nitride ceramics —	257
12.8.1	Boron nitride —	258
12.8.2	Aluminium nitride —	259
12.8.3	Silicon nitride and SiALONs —	260
12.8.4	Aluminium oxynitride —	262
12.9	Glass-ceramics —	263
	Further reading —	264
13	Intermetallic phases —	265
13.1	Classification scheme —	266
13.2	Ordered solid solutions – superstructures —	268
13.2.1	Superstructures of the bcc packing —	269
13.2.2	Superstructures derived from densest packings (ccp or hcp) —	270
13.3	Hume-Rothery phases —	273
13.3.1	The γ -brass structure —	275
13.4	Zintl phases —	277
13.5	Packing-dominated phases (Frank-Kasper and Laves phases) —	279
13.5.1	The geometrical principles in FK phases and the FK coordination polyhedra —	280
13.5.2	Laves phases —	281
13.5.3	Variants of Laves phases —	285
13.5.4	σ -, μ -, M, P, and R phases —	288
13.5.5	The Cr_3Si structure (<i>Strukturbericht</i> type A15) —	290
14	Porous crystals, reticular chemistry, and the net approach —	295
14.1	Zeolites and zeotypes —	295
14.1.1	Structural chemistry and building units of zeolites —	297
14.1.2	Technically important zeolites —	303
14.2	Metal-organic frameworks —	310
14.2.1	Carbon capture and sequestration —	315
14.2.2	Hydrogen storage —	316
14.2.3	Methane storage —	318
14.2.4	Water harvesting from air —	320
14.2.5	Other (potential) applications —	322
14.3	Networks and topology —	322
14.3.1	Graphs and nets —	323
14.3.2	Turning crystal structures into their underlying nets —	324

XII — Contents

- 14.3.3 Topology and net descriptors — **325**
- 14.3.4 Characterizing and identifying nets — **328**
 - Further reading — **331**

Appendix A

***Strukturbericht* designations and Pearson symbols — 333**

References — 345

Subject index — 351

Formula index — 363