

# Contents

|   |           |
|---|-----------|
| <b>Preface</b> . . . . .                                      | <b>xi</b> |
| <b>1 Introduction</b> . . . . .                               | <b>1</b>  |
| <b>2 Description of Chemical Structures</b> . . . . .         | <b>2</b>  |
| 2.1 Coordination Numbers and Coordination Polyhedra . . . . . | 3         |
| 2.2 Description of Crystal Structures . . . . .               | 7         |
| 2.3 Atomic Coordinates . . . . .                              | 9         |
| 2.4 Isotypism . . . . .                                       | 10        |
| 2.5 Problems . . . . .  | 11        |
| <b>3 Symmetry</b> . . . . .                                   | <b>12</b> |
| 3.1 Symmetry Operations and Symmetry Elements . . . . .       | 12        |
| 3.2 Point Groups . . . . .                                    | 15        |
| 3.3 Space Groups and Space-Group Types . . . . .              | 20        |
| 3.4 Positions . . . . .                                       | 22        |
| 3.5 Crystal Classes and Crystal Systems . . . . .             | 24        |
| 3.6 Aperiodic Crystals . . . . .                              | 25        |
| 3.7 Disordered Crystals . . . . .                             | 27        |
| 3.8 Problems . . . . .  | 28        |
| <b>4 Polymorphism and Phase Transitions</b> . . . . .         | <b>30</b> |
| 4.1 Thermodynamic Stability . . . . .                         | 30        |
| 4.2 Kinetic Stability . . . . .                               | 30        |
| 4.3 Polymorphism . . . . .                                    | 31        |
| 4.4 Phase Transitions . . . . .                               | 32        |
| 4.5 Phase Diagrams . . . . .                                  | 34        |
| 4.6 Problems . . . . .  | 38        |
| <b>5 Chemical Bonding and Lattice Energy</b> . . . . .        | <b>39</b> |
| 5.1 Chemical Bonding and Structure . . . . .                  | 39        |
| 5.2 Lattice Energy . . . . .                                  | 40        |
| 5.3 Problems . . . . .  | 44        |
| <b>6 The Effective Size of Atoms</b> . . . . .                | <b>45</b> |
| 6.1 Van der Waals Radii . . . . .                             | 46        |
| 6.2 Atomic Radii in Metals . . . . .                          | 46        |
| 6.3 Covalent Radii . . . . .                                  | 47        |
| 6.4 Ionic Radii . . . . .                                     | 48        |
| 6.5 Problems . . . . .  | 51        |

|           |   |            |
|-----------|---|------------|
| <b>7</b>  | <b>Ionic Compounds</b>  | <b>52</b>  |
| 7.1       | Radius Ratios   | 52         |
| 7.2       | Ternary Ionic Compounds   | 55         |
| 7.3       | Compounds with Complex Ions                                     | 56         |
| 7.4       | The Rules of Pauling and Baur                                   | 58         |
| 7.5       | Problems  | 61         |
| <b>8</b>  | <b>Molecular Structures I: Compounds of Main Group Elements</b> | <b>62</b>  |
| 8.1       | Valence Shell Electron-Pair Repulsion                           | 62         |
| 8.2       | Structures with Five Valence Electron Pairs                     | 71         |
| 8.3       | Problems  | 72         |
| <b>9</b>  | <b>Molecular Structures II: Compounds of Transition Metals</b>  | <b>73</b>  |
| 9.1       | Ligand Field Theory   | 73         |
| 9.2       | Ligand Field Stabilization Energy                               | 77         |
| 9.3       | Coordination Polyhedra for Transition Metals                    | 80         |
| 9.4       | Isomerism   | 81         |
| 9.5       | Problems  | 84         |
| <b>10</b> | <b>Molecular Orbital Theory and Chemical Bonding in Solids</b>  | <b>85</b>  |
| 10.1      | Molecular Orbitals  | 85         |
| 10.2      | Hybridization   | 87         |
| 10.3      | The Electron Localization Function                              | 89         |
| 10.4      | Band Theory. The Linear Chain of Hydrogen Atoms                 | 90         |
| 10.5      | The Peierls Distortion  | 93         |
| 10.6      | Crystal Orbital Overlap Population (COOP)                       | 96         |
| 10.7      | Bonds in Two and Three Dimensions                               | 99         |
| 10.8      | Bonding in Metals   | 101        |
| 10.9      | Problems  | 102        |
| <b>11</b> | <b>The Element Structures of the Nonmetals</b>                  | <b>103</b> |
| 11.1      | Hydrogen and the Halogens                                       | 103        |
| 11.2      | Chalcogens  | 105        |
| 11.3      | Elements of the Fifth Main Group                                | 107        |
| 11.4      | Elements of the Fifth and Sixth Main Groups under Pressure      | 111        |
| 11.5      | Carbon  | 113        |
| 11.6      | Boron   | 116        |
| <b>12</b> | <b>Diamond-like Structures</b>                                  | <b>118</b> |
| 12.1      | Cubic and Hexagonal Diamond                                     | 118        |
| 12.2      | Binary Diamond-like Compounds                                   | 118        |
| 12.3      | Diamond-like Compounds under Pressure                           | 120        |
| 12.4      | Polynary Diamond-like Compounds                                 | 123        |
| 12.5      | Widened Diamond Lattices. SiO <sub>2</sub> Structures           | 124        |
| 12.6      | Problems  | 127        |

|  |            |
|--|------------|
| <b>13 Polyanionic and Polycationic Compounds, Zintl Phases</b>                           | <b>128</b> |
| 13.1 The Generalized $8 - N$ Rule  | 128        |
| 13.2 Polyanionic Compounds, Zintl Phases   | 130        |
| 13.3 Polycationic Compounds  | 137        |
| 13.4 Cluster Compounds   | 138        |
| 13.5 Problems  | 149        |
| <b>14 Packings of Spheres. Metal Structures</b>  | <b>150</b> |
| 14.1 Closest-packings of Spheres   | 150        |
| 14.2 Body-centered Cubic Packing of Spheres  | 153        |
| 14.3 Other Metal Structures  | 154        |
| 14.4 Problems  | 155        |
| <b>15 The Sphere-packing Principle for Compounds</b>                                     | <b>157</b> |
| 15.1 Ordered and Disordered Alloys   | 157        |
| 15.2 Compounds with Close-packed Atoms   | 158        |
| 15.3 Structures Derived of Body-centered Cubic Packing (CsCl Type)                       | 160        |
| 15.4 Hume–Rothery Phases   | 161        |
| 15.5 Laves Phases  | 162        |
| 15.6 Problems  | 165        |
| <b>16 Linked Polyhedra</b>   | <b>166</b> |
| 16.1 Vertex-sharing Octahedra  | 168        |
| 16.2 Edge-sharing Octahedra  | 173        |
| 16.3 Face-sharing Octahedra  | 175        |
| 16.4 Octahedra Sharing Vertices and Edges  | 176        |
| 16.5 Octahedra Sharing Edges and Faces   | 179        |
| 16.6 Linked Trigonal Prisms  | 180        |
| 16.7 Vertex-sharing Tetrahedra. Silicates  | 180        |
| 16.8 Edge-sharing Tetrahedra   | 188        |
| 16.9 Problems  | 189        |
| <b>17 Packings of Spheres with Occupied Interstices</b>                                  | <b>190</b> |
| 17.1 The Interstices in Closest-packings of Spheres                                      | 190        |
| 17.2 Interstitial Compounds  | 194        |
| 17.3 Structure Types with Occupied Octahedral Interstices in Closest-packings of Spheres | 195        |
| 17.4 Perovskites   | 202        |
| 17.5 Occupation of Tetrahedral Interstices in Closest-packings of Spheres                | 206        |
| 17.6 Spinel  | 208        |
| 17.7 Problems  | 211        |
| <b>18 Symmetry as the Organizing Principle for Crystal Structures</b>                    | <b>212</b> |
| 18.1 Crystallographic Group–Subgroup Relations   | 212        |
| 18.2 The Symmetry Principle in Crystal Chemistry   | 214        |
| 18.3 Structural Relationships by Group–Subgroup Relations                                | 215        |
| 18.4 Symmetry Relations at Phase Transitions. Twinned Crystals                           | 221        |
| 18.5 Problems  | 225        |

|   |            |
|---|------------|
| <b>19 Physical Properties of Solids</b>         | <b>226</b> |
| 19.1 Mechanical Properties                      | 226        |
| 19.2 Piezoelectric and Ferroelectric Properties | 227        |
| 19.3 Magnetic Properties                        | 231        |
| <b>20 Nanostructures</b>                        | <b>241</b> |
| <b>21 Pitfalls and Linguistic Aberrations</b>   | <b>246</b> |
| <b>References</b>                               | <b>249</b> |
| <b>Answers to the Problems</b>                  | <b>256</b> |
| <b>Index</b>                                    | <b>259</b> |