Contents

Preface *page* xvii
Acknowledgments xix

1 Structures of Crystalline Materials 1

1.1 Symmetry 1
1.1.1 Translational Symmetry 2
1.1.2 Rotational Symmetry 3
1.1.3 Crystallographic Point Groups and Crystal Systems 5
1.1.4 Bravais Lattices 5
1.1.5 Introduction to Space Groups 8
1.1.6 Symmetry Elements That Combine Rotation and Translation 9
1.1.7 Space-Group Symbols 11
1.1.8 Description of a Crystal Structure 12
1.2 Databases 13
1.3 Composition 14
1.3.1 Coordination, Stoichiometry, and Connectivity 15
1.3.2 The Generalized 8−N Rule 17
1.4 Structural Principles 18
1.4.1 Packing of Spheres 19
1.4.2 Filling Holes 22
1.4.3 Network Structures 28
1.4.4 Polyhedral Structures 32
1.5 Structures of Selected Materials 38
1.5.1 The Spinel Structure 38
1.5.2 The Garnet Structure 39
1.5.3 Perovskite Structures 40
1.5.4 Silicates 44
1.5.5 Zeolites 46
1.5.6 Zintl Phases 47
1.6 Problems 48
1.7 Further Reading 51
1.8 References 51

2 Defects and More Complex Structures 54

2.1 Point Defects in Crystalline Elemental Solids 54
2.2 Intrinsic Point Defects in Compounds 55
2.3 Thermodynamics of Vacancy Formation 58
2.4 Extrinsic Defects 61
2.5 Solid Solutions and Vegard's Law 63
2.6 Kröger–Vink Notation 65
2.7 Line Defects in Metals 66
2.7.1 Edge Dislocations 66
2.7.2 Screw Dislocations 66
2.8 Planar Defects in Materials 67
2.8.1 Stacking Faults 67
2.8.2 Twinning 68
2.8.3 Antiphase Boundaries 72
2.8.4 Crystallographic Shear Structures 74
2.9 Gross Nonstoichiometry and Defect Ordering 75
2.10 Incommensurate Structures 78
2.11 Infinitely Adaptive Structures 80
2.12 Problems 81
2.13 Further Reading 85
2.14 References 85

3 Defect Chemistry and Nonstoichiometry 87

3.1 Narrow Nonstoichiometry in Oxides 87
3.1.1 Point Defects in a Pure Stoichiometric Oxide 87
3.1.2 Point Defects upon Oxidation/Reduction of the Stoichiometric Oxide 88
3.1.3 Equilibrium Equations for Oxidative and Reductive Nonstoichiometry 89
3.1.4 Defect Equilibria for Schottky-Type Redox Compensation 90
3.1.5 Acceptor-Doped Oxides 93
3.1.6 Donor-Doped Oxides 94
3.1.7 Solid Solubility of Dopants 94
3.1.8 Cautionary Note on Defect Models in Pure Oxides 96
3.2 Wide Nonstoichiometry in Oxides 98
3.3 Point Defects and Diffusion 99
3.3.1 Point-Defect Movements 101
3.3.2 Random Hopping 103
3.3.3 Hopping Under a Driving Force 104

3.3.4 Hopping Under a Concentration Gradient 105
3.3.5 Hopping Under an Electric Field 106
3.3.6 Relationship between Conductivity and Diffusivity 107
3.3.7 Ambipolar Diffusion 108
3.3.8 Temperature Dependence of Diffusivity 111
3.3.9 Diffusivity and Redox Defect Equilibria 111
3.3.10 Outline of Non-Steady-State Diffusion 112
3.3.11 Cautionary Note on Diffusion in Real Materials 114
3.4 Problems 115
3.5 Further Reading 118
3.6 References 118

4 Phase Diagrams and Phase Transitions 120

4.1 Phase Diagrams 120
4.2 Two-Component Phase Diagrams 123
4.2.1 Without Compound Formation 123
4.2.2 With Compound Formation 125
4.2.3 Solid-Solution Formation 128
4.3 Three-Component Phase Diagrams 131
4.4 Structural Phase Transitions 135
4.4.1 Classification of Phase Transitions 136
4.4.2 Symmetry and Order Parameters 137
4.4.3 Introduction to Landau Theory 140
4.4.4 Second-Order Transitions 141
4.4.5 First-Order and Tricritical Transitions 144
4.4.6 Phonons, Soft Modes, and Displacive Transitions 147
4.5 Problems 150
4.6 Further Reading 152
4.7 References 153

5 Chemical Bonding 154

5.1 Ionic Bonding 154
5.1.1 Coulombic Potential Energy 154
5.1.2 Lattice Energy and the Born–Mayer Equation 156
5.1.3 Experimental versus Calculated Lattice-Formation Energies 158
5.2 Atomic Orbitals 161
5.2.1 Energies of Atomic Orbitals 166
5.2.2 Sizes of Atomic Orbitals 168
5.3 Molecular-Orbital Theory 169
5.3.1 Homonuclear Diatomics: H_2^+ and H_2 169
5.3.2 The Heteronuclear Diatomic Case: HHe 173

5.3.3 Orbital Overlap and Symmetry 174
5.3.4 Combination of σ and π Bonding: O_2 175
5.3.5 Symmetry-Adapted Linear Combinations (SALCs) 177
5.3.6 Simple Polyatomic Molecules: BeH_2 and CH_4 179
5.3.7 Conjugated π Bonding: C_6H_6 181
5.3.8 Transition-Metal Complexes: $[CrCl_6]^{3-}$ and $[CoCl_4]^{2-}$ 183
5.3.9 High- and Low-Spin Configurations 186
5.3.10 Jahn–Teller Distortions 188
5.4 Bond Valences 190
5.5 Problems 195
5.6 Further Reading 198
5.7 References 199

6 Electronic Band Structure 200

6.1 The Band Structure of a Hydrogen-Atom Chain 200
6.1.1 The Electronic Structures of Cyclic H_N Molecules 201
6.1.2 Translational Symmetry and the Bloch Function 202
6.1.3 The Quantum Number k 203
6.1.4 Visualizing Crystal Orbitals 204
6.1.5 Band-Structure Diagrams 207
6.1.6 Density-of-States (DOS) Plots 209
6.2 The Band Structure of a Chain of H_2 Molecules 210
6.3 Electrical and Optical Properties 213
6.3.1 Metals, Semiconductors, and Insulators 213
6.3.2 Direct- versus Indirect-Gap Semiconductors 214
6.4 Representing Band Structures in Higher Dimensions 215
6.4.1 Crystal Orbitals in Two Dimensions 215
6.4.2 Crystal Orbitals in Three Dimensions 219
6.5 Band Structures of Two-Dimensional Materials 220
6.5.1 Graphene 221
6.5.2 CuO_2^{2-} Square Lattice 223
6.6 Band Structures of Three-Dimensional Materials 227
6.6.1 α-Polonium 227
6.6.2 Diamond 228
6.6.3 Elemental Semiconductors 230
6.6.4 Rhenium Trioxide 231
6.6.5 Perovskites 233
6.7 Problems 237
6.8 Further Reading 241
6.9 References 242

7 Optical Materials 243
7.1 Light, Color, and Electronic Excitations 243
7.2 Pigments, Dyes, and Gemstones 245
7.3 Transitions between *d* Orbitals (*d*-to-*d* Excitations) 246
7.3.1 Ligand- and Crystal-Field Theory 246
7.3.2 Absorption Spectra and Spectroscopic Terms 248
7.3.3 Correlation Diagrams 252
7.3.4 Selection Rules and Absorption Intensity 255
7.4 Charge-Transfer Excitations 258
7.4.1 Ligand-to-Metal Charge Transfer 259
7.4.2 Metal-to-Metal Charge Transfer 260
7.5 Compound Semiconductors 261
7.5.1 Optical Absorbance, Band Gap, and Color 262
7.5.2 Electronegativity, Orbital Overlap, and Band Gap 263
7.6 Conjugated Organic Molecules 265
7.7 Luminescence 267
7.8 Photoluminescence 268
7.8.1 Components of a Phosphor 268
7.8.2 Radiative Return to the Ground State 270
7.8.3 Thermal Quenching 272
7.8.4 Lanthanoid Activators 274
7.8.5 Non-Lanthanoid Activators 279
7.8.6 Energy Transfer 281
7.8.7 Sensitizers 283
7.8.8 Concentration Quenching and Cross Relaxation 284
7.8.9 Up-Conversion Photoluminescence 285
7.9 Electroluminescence 287
7.9.1 Inorganic Light-Emitting Diodes (LEDs) 287
7.9.2 Organic Light-Emitting Diodes (OLEDs) 289
7.10 Materials for Lighting 291
7.10.1 Fluorescent Lamp Phosphors 292
7.10.2 Phosphor-Converted LEDs for White Light 293
7.11 Problems 294
7.12 Further Reading 298
7.13 References 299

8 Dielectrics and Nonlinear Optical Materials 301
8.1 Dielectric Properties 301
8.1.1 Dielectric Permittivity and Susceptibility 302

8.1.2 Polarization and the Clausius–Mossotti Equation 303
8.1.3 Microscopic Mechanisms of Polarizability 305
8.1.4 Frequency Dependence of the Dielectric Response 306
8.1.5 Dielectric Loss 308
8.2 Dielectric Polarizabilities and the Additivity Rule 309
8.3 Crystallographic Symmetry and Dielectric Properties 313
8.4 Pyroelectricity and Ferroelectricity 314
8.4.1 Ferroelectricity in $BaTiO_3$ 314
8.4.2 Antiferroelectricity 319
8.5 Piezoelectricity 321
8.6 Local Bonding Considerations in Non-Centrosymmetric Materials 324
8.6.1 Second-Order Jahn–Teller Distortions with d^0 Cations 325
8.6.2 Second-Order Jahn–Teller Distortions with s^2p^0 Cations 327
8.7 Nonlinear Optical Materials 330
8.8 Nonlinear Susceptibility and Phase Matching 331
8.9 Important SHG Materials 334
8.9.1 KH_2PO_4 336
8.9.2 $KTiOPO_4$ 336
8.9.3 Niobates and Tantalates 338
8.9.4 Organic and Polymer NLO Materials 339
8.9.5 Borates 340
8.10 Problems 343
8.11 Further Reading 346
8.12 References 346

9 Magnetic Materials 349

9.1 Magnetic Materials and Their Applications 349
9.2 Physics of Magnetism 349
9.2.1 Bar Magnets and Atomic Magnets 349
9.2.2 Magnetic Intensity, Induction, Energy, Susceptibility, and Permeability 352
9.2.3 Unit Systems in Magnetism 355
9.3 Types of Magnetic Materials 356
9.4 Atomic Origins of Magnetism 357
9.4.1 Electron Movements Contributing to Magnetism and Their Quantization 357
9.4.2 Atomic Magnetic Moments 359
9.4.3 Magnetic Moments for 3*d* Ions in Compounds 363
9.4.4 Magnetic Moments for 4*f* Ions in Compounds 366
9.4.5 Note on Magnetic Moments of 4*d* and 5*d* Metals in Compounds 366

9.5 Diamagnetism 367
9.6 Paramagnetism 367
9.6.1 Curie and Curie–Weiss Paramagnetism 368
9.6.2 Pauli Paramagnetism 371
9.7 Antiferromagnetism 372
9.8 Superexchange Interactions 374
9.9 Ferromagnetism 377
9.9.1 Ferromagnetic Insulators and Half-Metals 381
9.9.2 Ferromagnetic Metals 382
9.9.3 Superferromagnets 384
9.10 Ferrimagnetism 385
9.11 Frustrated Systems and Spin Glasses 387
9.12 Magnetoelectric Multiferroics 388
9.13 Molecular and Organic Magnets 389
9.14 Problems 391
9.15 Further Reading 394
9.16 References 394

10 Conducting Materials 396

10.1 Conducting Materials 396
10.2 Metals 398
10.2.1 Drude Model 398
10.2.2 Free-Electron Model 402
10.2.3 Fermi–Dirac Distribution 403
10.2.4 Carrier Concentration 405
10.2.5 Carrier Mobility and Effective Mass 406
10.2.6 Fermi Velocity 407
10.2.7 Scattering Mechanisms 409
10.2.8 Band Structure and Conductivity of Aluminum 411
10.2.9 Band Structures and Conductivity of Transition Metals 412
10.3 Semiconductors 414
10.3.1 Carrier Concentrations in Intrinsic Semiconductors 414
10.3.2 Doping 416
10.3.3 Carrier Concentrations and Fermi Energies in Doped Semiconductors 419
10.3.4 Conductivity 421
10.3.5 p–n Junctions 422
10.3.6 Light-Emitting Diodes and Photovoltaic Cells 425
10.3.7 Transistors 426

10.4 Transition-Metal Compounds 428
10.4.1 Electron Repulsion: The Hubbard Model 428
10.4.2 Transition-Metal Compounds with the NaCl-Type Structure 431
10.4.3 Transition-Metal Compounds with the Perovskite Structure 434
10.5 Organic Conductors 437
10.5.1 Conducting Polymers 438
10.5.2 Polycyclic Aromatic Hydrocarbons 441
10.5.3 Charge-Transfer Salts 443
10.6 Carbon 445
10.6.1 Graphene 445
10.6.2 Carbon Nanotubes 447
10.7 Problems 451
10.8 Further Reading 454
10.9 References 455

11 Magnetotransport Materials 457

11.1 Magnetotransport and Its Applications 457
11.2 Charge, Orbital, and Spin Ordering in Iron Oxides 458
11.2.1 The Verwey Transition in Magnetite, Fe_3O_4 458
11.2.2 Double-Cell Perovskite, $YBaFe_2O_5$ 460
11.2.3 $CaFeO_3$ and $SrFeO_3$ 462
11.3 Charge and Orbital Ordering in Perovskite-Type Manganites 465
11.3.1 Spin and Orbital Ordering in $CaMnO_3$ and $LaMnO_3$ 465
11.3.2 The $La_{1-x}Ca_xMnO_3$ Phase Diagram 468
11.3.3 Tuning the Colossal Magnetoresistance 470
11.4 Half-Metals and Spin-Polarized Transport 472
11.4.1 Magnetoresistant Properties of Half-Metals 472
11.4.2 CrO_2 476
11.4.3 Heusler Alloys 477
11.4.4 Half-Metals with Valence-Mixing Itinerant Electrons 480
11.5 Problems 481
11.6 Further Reading 483
11.7 References 483

12 Superconductivity 486

12.1 Overview of Superconductivity 486
12.2 Properties of Superconductors 488
12.3 Origins of Superconductivity and BCS Theory 492
12.4 C_{60}-Derived Superconductors 500
12.5 Molecular Superconductors 505

12.6 $BaBiO_3$ Perovskite Superconductors 509
12.7 Cuprate Superconductors 511
12.7.1 La_2CuO_4 "214" Materials 512
12.7.2 $YBa_2Cu_3O_{7-\delta}$ "YBCO" or "123" Materials 513
12.7.3 Other Cuprates 516
12.7.4 Electronic Properties of Cuprates 517
12.8 Iron Pnictides and Related Superconductors 521
12.9 Problems 523
12.10 Further Reading 526
12.11 References 526

13 Energy Materials: Ionic Conductors, Mixed Conductors, and Intercalation Chemistry 529
13.1 Electrochemical Cells and Batteries 529
13.2 Fuel Cells 532
13.3 Conductivity in Ionic Compounds 533
13.4 Superionic Conductors 536
13.4.1 AgI: A Cation Superionic Conductor 536
13.4.2 PbF_2: An Anionic Superionic Conductor 539
13.5 Cation Conductors 540
13.5.1 Sodium β-alumina 540
13.5.2 Other Ceramic Cation Conductors 542
13.5.3 Polymeric Cation Conductors 543
13.6 Proton Conductors 545
13.6.1 Water-Containing Proton Conductors 546
13.6.2 Acid Salts 547
13.6.3 Perovskite Proton Conductors 548
13.7 Oxide-Ion Conductors 549
13.7.1 Fluorite-Type Oxide-Ion Conductors 552
13.7.2 Perovskite, Aurivillius, Brownmillerite, and Other Oxide Conductors 553
13.7.3 SOFC Electrode Materials and Mixed Conductors 555
13.8 Intercalation Chemistry and Its Applications 555
13.8.1 Graphite Intercalation Chemistry 556
13.8.2 Lithium Intercalation Chemistry and Battery Electrodes 559
13.8.3 Lithium-Ion Batteries with Oxide Cathodes 561
13.8.4 Electrochemical Characteristics of Lithium Batteries 568
13.8.5 Other Lithium Battery Electrode Materials 569
13.9 Problems 573
13.10 Further Reading 576
13.11 References 576

14 Zeolites and Other Porous Materials 579

14.1 Zeolites 579
14.1.1 Representative Structures of Zeolites 581
14.1.2 Roles of Template Molecules in Zeolite Synthesis 586
14.1.3 Zeolites in Catalysis 588
14.1.4 Ion-Exchange Properties 593
14.1.5 Drying Agents, Molecular Sieving, and Sorption 595
14.1.6 AlPOs and Related Materials 596
14.2 Mesoporous Aluminosilicates 597
14.3 Other Porous Oxide Materials 600
14.4 Metal–Organic Frameworks (MOFs) 605
14.4.1 MOF Structures 605
14.4.2 Some Applications of MOFs 608
14.5 Problems 612
14.6 Further Reading 615
14.7 References 616

15 Amorphous and Disordered Materials 619

15.1 The Atomic Structure of Glasses 620
15.2 Topology and the Structure of Glasses 622
15.3 Oxide Glasses 625
15.4 Optical Properties and Refractive Index 625
15.5 Optical Fibers 631
15.6 Nucleation and Growth 633
15.7 The Glass Transition 634
15.8 Strong and Fragile Behavior of Liquids and Melts 639
15.9 Low-Temperature Dynamics of Amorphous Materials 642
15.10 Electronic Properties: Anderson Localization 644
15.11 Metallic Glasses 647
15.12 Problems 651
15.13 Further Reading 652
15.14 References 652

Appendix A: Crystallographic Point Groups in Schönflies Symbolism 655
Appendix B: International Tables for Crystallography 656
Appendix C: Nomenclature of Silicates 661
Appendix D: Bond-Valence Parameters in Solids 662
Appendix E: The Effect of a Magnetic Field on a Moving Charge 663
Appendix F: Coupling *j–j* 664

Appendix G: The Langevin Function 665
Appendix H: The Brillouin Function 666
Appendix I: Measuring and Analyzing Magnetic Properties 670
Appendix J: Fundamental Constants of Exact Value 672
References for Appendices 673
Index 674