

## Contents of Volume 1

<i>Chapter 1</i>	
<b>Chemical Bonds in Solids</b>	<b>1</b>
J. C. Phillips	
1. Why Solids Are Different from Molecules . . . . .	1
1.1. Quantum Theory of Chemical Bonds . . . . .	5
1.2. The Five Solid Types . . . . .	6
1.3. Bonds and/or Bands? . . . . .	9
2. Crystal Structures and Cohesive Energies of the Elements . . . . .	11
2.1. Valence Groupings . . . . .	11
2.2. Shell Effects . . . . .	12
2.3. Transition Series . . . . .	14
3. Binary Compounds and Alloys . . . . .	17
3.1. Minerals . . . . .	17
3.2. Semiconductors . . . . .	22
3.3. Intermetallic Solutions . . . . .	28
4. Chemical Bonding and Physical Properties . . . . .	30
4.1. Classical Polarizabilities . . . . .	31
4.2. Dispersion . . . . .	32
4.3. Covalent and Ionic Energies . . . . .	34
4.4. Chemical Trends in Physical Properties . . . . .	37
5. Summary . . . . .	39
References . . . . .	40

**Chapter 2**  
**Energy Bands** **43**  
 D. Weaire

1. Introduction ..... 43
  - 1.1. Historical Remarks ..... 43
  - 1.2. The Independent-Electron Approximation ..... 45
2. Energy Bands in General ..... 49
3. The Classical Descriptions of Energy Bands in Periodic Systems ..... 52
  - 3.1. Introduction ..... 52
  - 3.2. Two Classical Limits—Tight Binding and Nearly Free Electron ..... 52
  - 3.3. Tight Binding Theory ..... 53
  - 3.4. Wannier Functions ..... 56
  - 3.5. Nearly-Free-Electron Theory ..... 57
  - 3.6. Pseudopotentials ..... 60
  - 3.7. The Cellular Method ..... 63
  - 3.8. Orthogonalized Plane Wave, Augmented Plane Wave, and Related Methods ..... 63
4. Approximations, Interpolations, Perturbations ..... 66
  - 4.1. Introduction ..... 66
  - 4.2. Moment Methods ..... 67
  - 4.3. Nearly-Free-Electron Perturbation Theory ..... 69
  - 4.4. The  $\mathbf{k} \cdot \mathbf{p}$  Method ..... 70
  - 4.5. Small- $\mathbf{k}$  Expansions for KKR Theory ..... 72
5. Some Relevant Experiments ..... 73
  - 5.1. Introduction ..... 73
  - 5.2. Soft X-Ray Emission and Absorption ..... 75
  - 5.3. Optical Spectroscopy ..... 77
  - 5.4. Fermi Surface Analysis ..... 81
6. Typical Band Structures ..... 83
  - 6.1. Introduction ..... 83
  - 6.2. Simple Metals ..... 84
  - 6.3. Alkali Halides ..... 85
  - 6.4. Group IV Semiconductors ..... 86
  - 6.5. The III–V and II–VI Semiconductors ..... 88
  - 6.6. Silicon Dioxide ..... 90
  - 6.7. Transition Metals ..... 92
  - 6.8. Transition Metal Compounds ..... 92
7. Disordered Solids ..... 94
  - 7.1. Introduction ..... 94
  - 7.2. Definition of Problems ..... 95
  - 7.3. The Density of States in an Alloy ..... 96
  - 7.4. The Anderson Problem ..... 100

- 7.5. Topological Disorder ..... 101
- 7.6. Applications ..... 103
8. Conclusion ..... 106
  - Acknowledgments ..... 106
  - References ..... 107

**Chapter 3**  
**Factors Controlling the Formation and Structure of Phases** **115**  
 W. B. Pearson

1. Introduction ..... 115
2. Practical Prediction of Phase Stability ..... 119
  - 2.1. Metals: Use of Thermodynamic Data ..... 119
  - 2.2. Valence Compounds: Use of Crystal Chemical Knowledge ..... 123
3. General Structural Consequences of Bonding Types ..... 124
  - 3.1. Ionic Crystals ..... 124
  - 3.2. Compounds with Saturated Covalent Bonds ..... 127
  - 3.3. Metallic Phases ..... 128
  - 3.4. *A Priori* Separation of Structure Types ..... 129
4. Atomic Size and Structural Constraint ..... 133
5. Factors Influencing the Stability of Crystal Structures ..... 136
  - 5.1. Electrochemical Factor ..... 136
  - 5.2. Geometric Effects ..... 137
  - 5.3. Energy Band Effects ..... 146
  - 5.4. Environmental Factors ..... 161
6. Distortions of Crystal Structures ..... 164
  - 6.1. Distortions Arising from Cation–Cation Bonds ..... 165
  - 6.2. Jahn–Teller Distortions ..... 168
  - 6.3. Spin–Orbit Coupling Distortions ..... 169
  - 6.4. Magnetic Exchange Energies ..... 170
  - 6.5. Mechanical Instability ..... 170
7. Epilogue ..... 171

Appendix—Structure Diagrams ..... 171  
 Acknowledgments ..... 172  
 References ..... 172

**Chapter 4**  
**Structure and Composition in Relation to Properties** **175**  
 J. H. Wernick

1. Magnetic Behavior ..... 176
  - 1.1. Introduction ..... 176
  - 1.2. The 3*d* Transition Elements ..... 180

1.3. Rare Earth Metals.....	182
1.4. Role of Local Atomic Environment Regarding Development of Atomic Moments and Long-Range Order.....	187
1.5. Directional Ordering and Magnetic Anisotropy.....	194
1.6. Magnetic Oxides.....	199
1.7. Magnetic Semiconductors.....	205
1.8. Linear and Two-Dimensional Magnetic Behavior.....	214
1.9. Amorphous Magnetic Materials.....	217
1.10. Summary.....	218
2. Superconducting Behavior.....	219
2.1. Introduction.....	219
2.2. The Cr <sub>3</sub> Si ( $\beta$ -W) and Transition Metal Nitride and Carbide Phases. Electron Concentration and Lattice Instability...	225
2.3. Role of Stoichiometry and Atomic Order.....	234
2.4. Metastable Superconducting Phases.....	236
2.5. Paramagnetic Impurities in Superconductors.....	237
2.6. Ternary Superconducting Chalcogenides.....	238
2.7. Superconductivity of Degenerate Semiconductors.....	239
2.8. Summary.....	240
3. Dielectric Materials.....	240
3.1. Ferroelectrics.....	240
3.2. Piezoelectrics.....	247
3.3. Nonlinear Optical Materials.....	249
3.4. Electrooptic and Pyroelectric Materials.....	257
3.5. Summary.....	258
4. Mechanical Behavior.....	259
4.1. Introduction.....	259
4.2. Elastic Behavior.....	260
4.3. Plastic Behavior.....	267
4.4. Summary.....	271
Acknowledgments.....	272
References.....	272

Chapter 5

**Introduction to Chemical and Structural Defects in Crystalline Solids** 283  
Morris E. Fine

1. Introduction.....	283
2. Point Defects.....	287
3. Dislocations.....	291
4. Planar Defects.....	310
5. Volumetric Defects.....	322
Acknowledgments.....	329
References.....	330

Chapter 6

**Defect Equilibria in Solids** 335

George G. Libowitz

1. Introduction.....	335
1.1. Native Defects.....	335
1.2. Law of Mass Action and Point Defects.....	337
1.3. Electronic Defects.....	338
1.4. Energetics of Defect Formation.....	339
2. Native Defects.....	339
2.1. Defect Equilibria in Elemental Crystals.....	339
2.2. Defect Equilibria in Binary Compounds.....	341
2.3. Nonstoichiometry—Equilibria with External Phases.....	345
2.4. Ionization of Defects.....	351
2.5. Relationship between Mass Action Law and Statistical Thermodynamics.....	361
2.6. Defect Interactions.....	367
3. Multicomponent Systems.....	371
3.1. Equilibria Involving Foreign Atoms.....	371
3.2. Multicomponent Compounds.....	378
4. Extended Defects.....	380
Acknowledgment.....	383
References.....	383

Chapter 7

**Characterization of Solids—Chemical Composition** 387

W. Wayne Meinke

1. Introduction.....	387
2. Current Capability for Determination of Chemical Composition.....	388
2.1. Introduction.....	388
2.2. General Overview.....	389
2.3. Analytical Techniques: Present Status.....	391
2.4. Precision and Sensitivity of Analytical Techniques.....	408
3. Application of Current Techniques to Characterization of Materials.....	408
3.1. Characterization of Major Phase.....	408
3.2. Characterization of Minor Phases and Impurities.....	413
3.3. Characterization of Surfaces.....	415
4. Utilization of Existing Techniques.....	416
4.1. Literature Examples.....	416
4.2. Factors Determining Use.....	416
Acknowledgments.....	426
References.....	426

*Chapter 8*  
**Structural Characterization of Solids** **437**  
 R. E. Newnham and Rustum Roy

1. Introduction ..... 437
2. Structural Characterization by Optical Techniques ..... 439
  - 2.1. Morphology ..... 439
  - 2.2. Bulk Optical Properties..... 441
  - 2.3. Scattering Studies ..... 444
  - 2.4. Surface Characterization ..... 444
  - 2.5. Particle Size and Shape..... 448
3. Structural Characterization by X-Ray Diffraction ..... 451
  - 3.1. X-Ray Powder Methods..... 451
  - 3.2. Single-Crystal X-Ray Methods ..... 458
  - 3.3. Temperature and Pressure Experiments..... 467
  - 3.4. X-Ray Topography and Interferometry..... 474
4. Electron Methods for Materials Characterization..... 476
  - 4.1. Electron Microscopy..... 476
  - 4.2. Electron Diffraction ..... 480
  - 4.3. Scanning Electron Microscopy ..... 484
5. Neutron Scattering from Solids..... 487
  - 5.1. Neutron Sources ..... 487
  - 5.2. Interactions with Matter..... 489
  - 5.3. Structure Analysis with Neutrons ..... 490
  - 5.4. Magnetic Structure Analysis ..... 491
  - 5.5. Lattice and Spin Dynamics ..... 493
6. Spectroscopy and Local Symmetry ..... 496
  - 6.1. Absorption Spectra in the Visible Range ..... 497
  - 6.2. Infrared Absorption Spectroscopy ..... 499
  - 6.3. Raman Spectra..... 501
  - 6.4. Soft X-Ray Spectra ..... 501
  - 6.5. Electron Spin Resonance ..... 503
  - 6.6. Nuclear Magnetic Resonance ..... 506
  - 6.7. Mössbauer Effect..... 510
  - 6.8. Electron Spectroscopy..... 513
  - 6.9. Acoustic Spectroscopy ..... 514
7. Physical Properties as Characterization Tools..... 515
  - 7.1. Introduction..... 515
  - 7.2. Some Crystal Physical Generalizations..... 516
  - 7.3. Dielectric Measurements ..... 518
  - 7.4. Electrical Characterization of Solids..... 519
  - 7.5. Magnetic Measurements..... 521
  - 7.6. Calorimetric Measurements..... 527

Acknowledgment ..... 529  
 References..... 529

**Index** ..... **535**