Contents

1. Introduction 1
1.1 Why This Book Was Written and What It Contains 1
1.2 The Thermodynamic Origin of Phase Diagrams 4
1.2.1 First-Order Transitions Without Compositional Change – The pT Phase Diagram 5
1.2.2 First-Order Transitions with Compositional Change – The Alloy Phase Diagram 6
1.2.3 Second-Order Transitions 8
1.3 Adiabatic Decoupling of the Ionic and Electronic Degrees of Freedom 9
1.4 The One-Electron Approximation 10
1.5 Tightly-Bound and Nearly-Free Electrons; Potentials and Pseudopotentials 13
1.6 Response Theory and Interatomic Interactions 18
1.7 The Statistical Mechanics of a Vibrating Lattice 20
1.8 Periodic, Aperiodic and Quasi-Periodic Structures 22
1.9 Elementary Excitations in Aperiodic Structures 24
1.9.1 Effective Medium Approximations 24
1.9.2 The Recursion Method and Related Techniques 27
1.10 Configurational Thermodynamics of Solids and Liquids 28
1.10.1 Order-Disorder Transitions 29
1.10.2 From the Interatomic Force Law to the Structure of a Liquid 30
1.10.3 Order-Parameter Approach to Freezing and Melting 31

2. Interatomic Forces in Metals and Alloys 34
2.1 Pseudopotentials 34
2.1.1 The Operator Approach 35
2.1.2 The Scattering Approach 37
2.1.3 Model Potentials 39
2.2 Response Theory 40
2.2.1 Nonlocality 45
2.2.2 Screening Beyond the Random Phase Approximation 46
2.3 Effective Pair Potentials in Pure Metals 48

2.4 Effective Pair Potentials in Binary Alloys 54
2.4.1 Chemical Compression 58
2.4.2 Chemical Ordering 59
2.5 Interatomic Forces in Non-Simple Metals and Alloys 63
2.6 Beyond Perturbation Theory 65

3. Phase Stability of Crystalline Metals 67
3.1 Simple-Metal Cohesion 67
3.1.1 An Excursion into Transition-Metal Cohesion 72
3.2 Structural Stability 77
3.3 Trends in Crystal Structures 79
3.3.1 A Brief Remark on Transition Metal Structures 82
3.3.2 The Crystal Structures of the Lanthanides 84
3.3.3 Charge-Density Analysis of Bonding 85
3.4 Pressure-Induced Phase Changes 88
3.5 Thermodynamics of Crystalline Metals 90
3.5.1 Harmonic Lattice Dynamics 90
3.5.2 Anharmonicity 94
3.5.3 Variational Method for Calculating Thermodynamic Properties (Gibbs-Bogoljubov Method) 96
3.6 Temperature-Induced Phase Changes 98

4. Structure and Thermodynamics of Liquid Metals 102
4.1 Computer Simulations 103
4.2 Integral Equation Approach 104
4.3 Thermodynamic Perturbation Theories 107
4.3.1 Thermodynamic Variational Method for Liquids (Gibbs-Bogoljubov Method) 107
4.3.2 Repulsive Forces: Weeks-Chandler-Andersen Theory 110
4.3.3 Attractive Forces: Random Phase Approximation, Optimized Random Phase Approximation and Mean Spherical Approximation 113
4.4 Trends in Liquid Structures 121
4.5 Expanded Fluid Metals 125
4.6 Structure and Thermodynamics of Liquid Transition and Rare-Earth Metals 128
4.7 Atomic Motion in Liquid Metals 128

5. The pT Phase Diagram of Pure Metals 133
5.1 Solid-Liquid Trnasitions: The Total Energy Approach 133
5.2 Microscopic Theories of Melting and Freezing 137
5.3 The Liquid-Vapour Transition 142

6. Alloy Formation and Stability 145
6.1 Nearly-Free-Electron Approach to Alloy Formation 146
6.1.1 Criteria for Solubility in Homovalent Systems 146
6.1.2 Variations of the Atomic Volume in Heterovalent Alloy Systems 149
6.1.3 The Chemical Potential Model for the Heat of Formation 154
6.1.4 Band Picture for Simple-Metal Alloys 157
6.1.5 Real-Space Picture for Alloy Formation 159
6.1.6 A Brief Summary 162
6.2 Miedema's Semiempirical Theory of Alloy Formation 163
6.2.1 Microscopic Interpretation of Miedema's Alloying Rules: Simple Metals 164
6.2.2 Microscopic Interpretation of Miedema's Alloying Rules: Transition Metals 165

7. Solid Substitutional Alloys 169
7.1 Primary Solid Solutions 171
7.1.1 The Homovalent Case 171
7.1.2 The Heterovalent Case 177
7.2 Hume-Rothery Phases 180
7.3 Static Lattice Distortions 184
7.4 Ordering in Substitutional Alloys 188
7.4.1 Long-Range Order 190
7.4.2 Short-Range Order 195
7.4.3 Ordering in Substitutional Transition-Metal Alloys . 196
7.5 Thermodynamics of Alloys 197
7.5.1 Lattice Dynamics of Substitutional Alloys 197
7.5.2 Thermodynamic Perturbation Theory 202
7.5.3 Vibrational Dynamics and the Ordering Transition . 205

8. Intermetallic Compounds 207
8.1 Structure Maps 207
8.2 Empirical Pair-Potential Analysis of Intermetallic Phases .. 211
8.3 Classification of Intermetallic Phases According to Building Principles and Properties 214
8.4 Topologically Close-Packed Intermetallic Compounds (Frank-Kasper Phases) 215
8.4.1 Heat and Volume of Formation of Laves Phases 215
8.4.2 Structural Stability of Laves Phases 221
8.4.3 Other Topologically Close-Packed Compounds 227
8.4.4 Charge-Density Analysis of Bonding 230
8.4.5 Lattice Dynamics of Topologically Close-Packed Compounds 235

8.5 Intermetallic Phases with Large Band-Structure Stabilization 237
8.5.1 Charge-Density Analysis of Bonding in Zintl Phases 238
8.5.2 Lattice Dynamics of Zintl Phases 239

9. Liquid Alloys 241
9.1 Computer Simulations of Binary Liquid Alloys 243
9.2 Thermodynamic Variational Calculations 246
9.2.1 Systems with a Nearly Ideal Mixing Behaviour 247
9.2.2 Liquid Alloys with Strong Chemical Short-Range Order 254
9.2.3 Liquid Alloys with a Miscibility Gap 262
9.3 Thermodynamic Perturbation Theory 267
9.3.1 Repulsive Forces: Weeks-Chandler-Andersen Theory 267
9.3.2 Long-Range Forces: Optimized-Random-Phase Approximation 272
9.4 Structure and Thermodynamics of Liquid Transition-Metal Alloys 275
9.5 Collective Excitations in Liquid Alloys 278

10. Alloy Phase Diagrams 282
10.1 First Principles Calculations of Alloy Phase Diagrams 282
10.2 Chemical Short-Range Order and Alloy Phase Diagrams ... 285
10.2.1 Melting Extrema 286
10.2.2 Eutectic Diagrams 288
10.2.3 Compound Formation 288
10.2.4 Phase Separation in the Liquid State 289
10.3 Molecular Theory of the Freezing of Liquid Alloys 289

11. Beyond the Phase Diagram: The Formation and Properties of Metastable Phases 292
11.1 Amorphous Alloys – Metallic Glasses 292
11.1.1 Glass-Forming Ability 293
11.1.2 Atomic Structure of Metallic Glasses 298
11.1.3 Elementary Excitations in Metallic Glasses 307
11.2 Quasi-Crystals 309

12. Conclusions and Outlook 313

Appendices 315
A. Density-Functional Pseudopotentials 315
A.1 Optimized Pseudopotentials – the Operator Approach 319
A.2 Norm-Conserving Pseudopotentials – the Scattering Approach 323

B. Linear Response Theroy 325
C. Electrostatic Energies of Crystals and Liquids 331
C.1 The Madelung Constants of the Elemental Structures 331
C.2 The Madelung Constants of Binary Alloys and Intermetallic Compounds 335
C.3 Electrostatic Energies of Model Liquids and Liquid Mixtures 339
D. Liquid State Theory: Integral Equations, Variational Principles and Exactly Soluble Models 341
D.1 Correlation Functions and Equations of State 341
D.2 Integral Equations and Variational Principles for the Total and Direct Correlation Functions 343
D.3 Analytical Solutions for Model Liquids and Mixtures 350
D.3.1 Solution of the PY Equation for the Hard-Sphere Fluid 350
D.3.2 Solution of the PY Equation for Hard-Sphere Mixtures 352
D.3.3 The Solution of the MSA for Charged Hard Spheres with Yukawa Interactions 353
D.3.4 The Solution of the MSA for a Symmetric Mixture of Charged Hard Spheres with Yukawa Interactions 354

References 357

Subject Index 395