

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 Transitions: 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 Theory.....	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