

Contents

Foreword to Second Edition *xiii*
Foreword to First Edition *xv*
Preface to Third Edition *xix*
Preface to Second Edition *xx*
Preface to First Edition *xxi*
Acronyms *xxiii*

1	Crystallographic Considerations	1
1.1	Degrees of Crystallinity	1
1.1.1	Monocrystalline Solids	2
1.1.2	Quasicrystalline Solids	3
1.1.3	Polycrystalline Solids	4
1.1.4	Semicrystalline Solids	5
1.1.5	Amorphous Solids	8
1.2	Basic Crystallography	8
1.2.1	Crystal Geometry	8
1.2.1.1	Types of Crystallographic Symmetry	12
1.2.1.2	Space Group Symmetry	17
1.2.1.3	Lattice Planes and Directions	27
1.3	Single-Crystal Morphology and Its Relationship to Lattice Symmetry	32
1.4	Twinned Crystals, Grain Boundaries, and Bicrystallography	37
1.4.1	Twinned Crystals and Twinning	37
1.4.2	Crystallographic Orientation Relationships in Bicrystals	39
1.4.2.1	The Coincidence Site Lattice	39
1.4.2.2	Equivalent Axis–Angle Pairs	44
1.5	Amorphous Solids and Glasses	46
1.5.1	Oxide Glasses	49
1.5.2	Metallic Glasses and Metal–Organic Framework Glasses	51
1.5.3	Aerogels	53
	Practice Problems	53
	References	55
2	Microstructural Considerations	57
2.1	Materials Length Scales	57
2.1.1	Experimental Resolution of Material Features	61
2.2	Grain Boundaries in Polycrystalline Materials	63

2.2.1	Grain Boundary Orientations	63
2.2.2	Dislocation Model of Low Angle Grain Boundaries	65
2.2.3	Grain Boundary Energy	66
2.2.4	Special Types of “Low-Energy” Boundaries	68
2.2.5	Grain Boundary Dynamics	69
2.2.6	Representing Orientation Distributions in Polycrystalline Aggregates	70
2.3	Materials Processing and Microstructure	72
2.3.1	Conventional Solidification	72
2.3.1.1	Grain Homogeneity	74
2.3.1.2	Grain Morphology	76
2.3.1.3	Zone Melting Techniques	78
2.3.2	Deformation Processing	79
2.3.3	Consolidation Processing	79
2.3.4	Thin-Film Formation	80
2.3.4.1	Epitaxy	81
2.3.4.2	Polycrystalline PVD Thin Films	81
2.3.4.3	Polycrystalline CVD Thin Films	83
2.4	Microstructure and Materials Properties	83
2.4.1	Mechanical Properties	83
2.4.2	Transport Properties	86
2.4.3	Magnetic and Dielectric Properties	90
2.4.4	Chemical Properties	92
2.5	Microstructure Control and Design	93
	Practice Problems	96
	References	96
3	Crystal Structures and Binding Forces	99
3.1	Structure Description Methods	99
3.1.1	Close Packing	99
3.1.2	Polyhedra	103
3.1.3	The (Primitive) Unit Cell	103
3.1.4	Space Groups and Wyckoff Positions	104
3.1.5	Strukturbericht Symbols	104
3.1.6	Pearson Symbols	105
3.2	Cohesive Forces in Solids	106
3.2.1	Ionic Bonding	106
3.2.2	Covalent Bonding	108
3.2.3	Dative Bonds	110
3.2.4	Metallic Bonding	111
3.2.5	Atoms and Bonds as Electron Charge Density	112
3.3	Chemical Potential Energy	113
3.3.1	Lattice Energy for Ionic Crystals	114
3.3.2	The Born–Haber Cycle	119
3.3.3	Goldschmidt’s Rules and Pauling’s Rules	120
3.3.4	Total Energy	122
3.3.5	Electronic Origin of Coordination Polyhedra in Covalent Crystals	124
3.4	Common Structure Types	127

3.4.1	Iono-covalent Solids	128	2
3.4.1.1	AX Compounds	128	2.1
3.4.1.2	AX ₂ Compounds	130	2.2
3.4.1.3	AX ₆ Compounds	132	2.3
3.4.1.4	ABX ₂ Compounds	132	2.3.1
3.4.1.5	AB ₂ X ₄ Compounds (Spinel and Olivine Structures)	134	2.3.2
3.4.1.6	ABX ₃ Compounds (Perovskite and Related Phases)	135	2.4
3.4.1.7	A ₂ B ₂ O ₅ (ABO _{2.5}) Compounds (Oxygen-Deficient Perovskites)	137	2.5
3.4.1.8	A _x B _y O _z Compounds (Bronzes)	139	2.5.1
3.4.1.9	A ₂ B ₂ X ₇ Compounds (Pyrochlores)	139	2.5.2
3.4.1.10	Silicate Compounds	140	2.5.3
3.4.1.11	Porous Structures	141	2.5.4
3.4.2	Metal Carbides, Silicides, Borides, Hydrides, and Nitrides	144	2.6
3.4.3	Metallic Alloys and Intermetallic Compounds	144	
3.4.3.1	Zintl Phases	147	
3.4.3.2	Nonpolar Binary Intermetallic Phases	149	
3.4.3.3	Ternary Intermetallic Phases	151	
3.5	Structural Disturbances	153	6.1
3.5.1	Intrinsic Point Defects	154	6.2
3.5.2	Extrinsic Point Defects	155	6.2.1
3.5.3	Structural Distortions	156	6.2.2
3.5.4	Bond Valence Sum Calculations	158	6.2.3
3.6	Structure Control and Synthetic Strategies	162	6.2.4
	Practice Problems	165	6.3
	References	167	6.3.1
4	The Electronic Level I: An Overview of Band Theory	171	6.4
4.1	The Many-Body Schrödinger Equation and Hartree–Fock	171	6.4.1
4.2	Choice of Boundary Conditions: Born’s Conditions	177	6.4.1.1
4.3	Free-Electron Model for Metals: From Drude (Classical) to Sommerfeld (Fermi–Dirac)	179	6.4.1.2
4.4	Bloch’s Theorem, Bloch Waves, Energy Bands, and Fermi Energy	180	6.4.1.3
4.5	Reciprocal Space and Brillouin Zones	182	6.4.1.4
4.6	Choices of Basis Sets and Band Structure with Applicative Examples	188	6.4.2
4.6.1	From the Free-Electron Model to the Plane Wave Expansion	189	6.4.2.1
4.6.2	Fermi Surface, Brillouin Zone Boundaries, and Alkali Metals versus Copper	191	6.4.2.2
4.6.3	Understanding Metallic Phase Stability in Alloys	193	6.4.2.3
4.6.4	The Localized Orbital Basis Set Method	195	6.4.2.4
4.6.5	Understanding Band Structure Diagram with Rhenium Trioxide	196	6.4.2.5
4.6.6	Probing DOS Band Structure in Metallic Alloys	199	6.4.2.6
4.7	Breakdown of the Independent-Electron Approximation	200	6.4.3
4.8	Density Functional Theory: The Successor to the Hartree–Fock Approach in Materials Science	202	6.4.3.1
4.9	The Continuous Quest for Better DFT XC Functionals	205	6.4.3.2
4.10	Van der Waals Forces and DFT	208	6.4.3.3
	Practice Problems	210	7
	References	210	7.1

5	The Electronic Level II: The Tight-Binding Electronic Structure Approximation	213
5.1	The General LCAO Method	214
5.2	Extension of the LCAO Treatment to Crystalline Solids	219
5.3	Orbital Interactions in Monatomic Solids	221
5.3.1	σ -Bonding Interactions	221
5.3.2	π -Bonding Interactions	225
5.4	Tight-Binding Assumptions	229
5.5	Qualitative LCAO Band Structures	232
5.5.1	Illustration 1: Transition Metal Oxides with Vertex-Sharing Octahedra	236
5.5.2	Illustration 2: Reduced Dimensional Systems	238
5.5.3	Illustration 3: Transition Metal Monoxides with Edge-Sharing Octahedra	240
5.5.4	Corollary	243
5.6	Total Energy Tight-Binding Calculations	244
	Practice Problems	246
	References	246
6	Transport Properties	249
6.1	An Introduction to Tensors	249
6.2	Microscopic Theory of Electrical Transport in Ceramics: The Role of Point Defects	254
6.2.1	Oxygen-Deficient/Metal Excess and Metal-Deficient/Oxygen Excess Oxides	256
6.2.2	Substitutions by Aliovalent Cations with Valence Isoelectronicity	261
6.2.3	Substitutions by Isovalent Cations That Are Not Valence Isoelectronic	263
6.2.4	Nitrogen Vacancies in Nitrides	266
6.3	Thermal Conductivity	268
6.3.1	The Free Electron Contribution	269
6.3.2	The Phonon Contribution	271
6.4	Electrical Conductivity	274
6.4.1	Band Structure Considerations	278
6.4.1.1	Conductors	278
6.4.1.2	Insulators	279
6.4.1.3	Semiconductors	281
6.4.1.4	Semimetals	290
6.4.2	Thermoelectric, Photovoltaic, and Magnetotransport Properties	292
6.4.2.1	Thermoelectrics	292
6.4.2.2	Photovoltaics	298
6.4.2.3	Galvanomagnetic Effects and Magnetotransport Properties	301
6.4.3	Superconductors	303
6.4.4	Improving Bulk Electrical Conduction in Polycrystalline, Multiphasic, and Composite Materials	307
6.5	Mass Transport	308
6.5.1	Atomic Diffusion	309
6.5.2	Ionic Conduction	316
	Practice Problems	321
	References	322
7	Hopping Conduction and Metal–Insulator Transitions	325
7.1	Correlated Systems	327
7.1.1	The Mott–Hubbard Insulating State	329

7.1.2	Charge-Transfer Insulators	334	
7.1.3	Marginal Metals	334	
7.2	Anderson Localization	336	
7.3	Experimentally Distinguishing Disorder from Electron Correlation	340	
7.4	Tuning the M–I Transition	343	
7.5	Other Types of Electronic Transitions	345	
	Practice Problems	347	
	References	347	
8	Magnetic and Dielectric Properties	349	
8.1	Phenomenological Description of Magnetic Behavior	351	
8.1.1	Magnetization Curves	354	
8.1.2	Susceptibility Curves	355	
8.2	Atomic States and Term Symbols of Free Ions	359	
8.3	Atomic Origin of Paramagnetism	365	
8.3.1	Orbital Angular Momentum Contribution: The Free Ion Case	366	
8.3.2	Spin Angular Momentum Contribution: The Free Ion Case	367	
8.3.3	Total Magnetic Moment: The Free Ion Case	368	
8.3.4	Spin–Orbit Coupling: The Free Ion Case	368	
8.3.5	Single Ions in Crystals	371	
8.3.5.1	Orbital Momentum Quenching	371	
8.3.5.2	Spin Momentum Quenching	373	
8.3.5.3	The Effect of JT Distortions	373	
8.3.6	Solids	374	
8.4	Diamagnetism	376	
8.5	Spontaneous Magnetic Ordering	377	
8.5.1	Exchange Interactions	379	
8.5.1.1	Direct Exchange and Superexchange Interactions in Magnetic Insulators	382	
8.5.1.2	Indirect Exchange Interactions	387	
8.5.2	Itinerant Ferromagnetism	390	
8.5.3	Noncollinear Spin Configurations and Magnetocrystalline Anisotropy	394	
8.5.3.1	Geometric Frustration	394	
8.5.3.2	Magnetic Anisotropy	397	
8.5.3.3	Magnetic Domains	398	
8.5.4	Ferromagnetic Properties of Amorphous Metals	401	
8.6	Magnetotransport Properties	401	
8.6.1	The Double Exchange Mechanism	402	
8.6.2	The Half-Metallic Ferromagnet Model	403	
8.7	Magnetostriction	404	
8.8	Dielectric Properties	405	
8.8.1	The Microscopic Equations	407	
8.8.2	Piezoelectricity	408	
8.8.3	Pyroelectricity	414	
8.8.4	Ferroelectricity	416	
	Practice Problems	421	
	References	422	

9	Optical Properties of Materials	425
9.1	Maxwell's Equations	425
9.2	Refractive Index	428
9.3	Absorption	436
9.4	Nonlinear Effects	441
9.5	Summary	446
	Practice Problems	446
	References	447
10	Mechanical Properties	449
10.1	Stress and Strain	449
10.2	Elasticity	452
10.2.1	The Elasticity Tensors	455
10.2.2	Elastically Isotropic and Anisotropic Solids	459
10.2.3	The Relation Between Elasticity and the Cohesive Forces in a Solid	465
10.2.3.1	Bulk Modulus	466
10.2.3.2	Rigidity (Shear) Modulus	467
10.2.3.3	Young's Modulus	470
10.2.4	Superelasticity, Pseudoelasticity, and the Shape Memory Effect	473
10.3	Plasticity	475
10.3.1	The Dislocation-Based Mechanism to Plastic Deformation	481
10.3.2	Polycrystalline Metals	487
10.3.3	Brittle and Semi-brittle Solids	489
10.3.4	The Correlation Between the Electronic Structure and the Plasticity of Materials	490
10.4	Fracture	491
	Practice Problems	494
	References	495
11	Phase Equilibria, Phase Diagrams, and Phase Modeling	499
11.1	Thermodynamic Systems and Equilibrium	500
11.1.1	Equilibrium Thermodynamics	504
11.2	Thermodynamic Potentials and the Laws	507
11.3	Understanding Phase Diagrams	510
11.3.1	Unary Systems	510
11.3.2	Binary Systems	511
11.3.3	Ternary Systems	518
11.3.4	Metastable Equilibria	522
11.4	Experimental Phase Diagram Determinations	522
11.5	Phase Diagram Modeling	523
11.5.1	Gibbs Energy Expressions for Mixtures and Solid Solutions	524
11.5.2	Gibbs Energy Expressions for Phases with Long-Range Order	527
11.5.3	Other Contributions to the Gibbs Energy	530
11.5.4	Phase Diagram Extrapolations: The CALPHAD Method	531
	Practice Problems	534
	References	535
12	Synthetic Strategies	537
12.1	Synthetic Strategies	538
12.1.1	Direct Combination	538

12.1.2	Low Temperature	540
12.1.2.1	Sol–Gel	540
12.1.2.2	Solvothermal	543
12.1.2.3	Intercalation	544
12.1.3	Defects	546
12.1.4	Combinatorial Synthesis	548
12.1.5	Spinodal Decomposition	548
12.1.6	Thin Films	550
12.1.7	Photonic Materials	552
12.1.8	Nanosynthesis	553
12.1.8.1	Liquid Phase Techniques	554
12.1.8.2	Vapor/Aerosol Methods	556
12.1.8.3	Combined Strategies	556
12.2	Summary	558
	Practice Problems	559
	References	559
13	An Introduction to Nanomaterials	563
13.1	History of Nanotechnology	564
13.2	Nanomaterials Properties	565
13.2.1	Electrical Properties	566
13.2.2	Magnetic Properties	567
13.2.3	Optical Properties	567
13.2.4	Thermal Properties	568
13.2.5	Mechanical Properties	569
13.2.6	Chemical Reactivity	570
13.3	More on Nanomaterials Preparative Techniques	572
13.3.1	Top-Down Methods for the Fabrication of Nanocrystalline Materials	572
13.3.1.1	Nanostructured Thin Films	572
13.3.1.2	Nanocrystalline Bulk Phases	573
13.3.2	Bottom-Up Methods for the Synthesis of Nanostructured Solids	574
13.3.2.1	Precipitation	575
13.3.2.2	Hydrothermal Techniques	576
13.3.2.3	Micelle-Assisted Routes	577
13.3.2.4	Thermolysis, Photolysis, and Sonolysis	580
13.3.2.5	Sol–Gel Methods	581
13.3.2.6	Polyol Method	582
13.3.2.7	High-Temperature Organic Polyol Reactions (IBM Nanoparticle Synthesis)	584
13.3.2.8	Additive Manufacturing (3D Printing)	584
	References	586
14	Introduction to Computational Materials Science	589
14.1	A Short History of Computational Materials Science	590
14.1.1	1945–1965: The Dawn of Computational Materials Science	591
14.1.2	1965–2000: Steady Progress Through Continued Advances in Hardware and Software	595
14.1.3	2000–Present: High-Performance and Cloud Computing	598
14.2	Spatial and Temporal Scales, Computational Expense, and Reliability of Solid-State Calculations	600

14.3	Illustrative Examples	604
14.3.1	Exploration of the Local Atomic Structure in Multi-principal Element Alloys by Quantum Molecular Dynamics	604
14.3.2	Magnetic Properties of a Series of Double Perovskite Oxides A_2BCO_6 ($A = \text{Sr, Ca}$; $B = \text{Cr}$; $C = \text{Mo, Re, W}$) by Monte Carlo Simulations in the Framework of the Ising Model	606
14.3.3	Crystal Plasticity Finite Element Method (CPFEM) Analysis for Modeling Plasticity in Polycrystalline Alloys	613
	References	617
15	Case Study I: TiO_2	619
15.1	Crystallography	619
15.2	Microstructure	623
15.3	Bonding	626
15.4	Electronic Structure	627
15.5	Transport	628
15.6	Metal–Insulator Transitions	632
15.7	Magnetic and Dielectric Properties	632
15.8	Optical Properties	634
15.9	Mechanical Properties	635
15.10	Phase Equilibria	636
15.11	Synthesis	638
15.12	Nanomaterial	639
	Practice Questions	639
	References	640
16	Case Study II: GaN	643
16.1	Crystallography	643
16.2	Microstructure	646
16.3	Bonding	647
16.4	Electronic Structure	647
16.5	Transport	648
16.6	Metal–Insulator Transitions	650
16.7	Magnetic and Dielectric Properties	652
16.8	Optical Properties	652
16.9	Mechanical Properties	653
16.10	Phase Equilibria	654
16.11	Synthesis	654
16.12	Nanomaterial	656
	Practice Questions	657
	References	658
	Appendix A: List of the 230 Space Groups	659
	Appendix B: The 32 Crystal Systems and the 47 Possible Forms	665
	Appendix C: Principles of Tensors	667
	Appendix D: Solutions to Practice Problems	679
	Index	683