Contents

List of Contributors *xi*

Preface *xiii*

Contents of Volume I *xvii*

14 The Bond-Valence Method: An Empirical Approach to Chemical Structure and Bonding

I. D. BROWN

I. Summary 1
II. Introduction 2
III. Basic Concepts of the Bond-Valence Theory 2
IV. Correlations with Experiment 3
V. Distortion Theorem 6
VI. The Valence-Matching Principle 7
VII. The Chemistry of Solids with Water 11
VIII. Prediction of Structure 15
IX. Acid–Acid Bonds and Lone Pairs 16

X. Conclusions 17
Appendix: Parameters for Calculating Bond Valences 18
References 29

15 Interatomic Distance Predictions for Computer Simulation of Crystal Structures

WERNER H. BAUR

I. Computer Simulation 31
II. Predictions of Interatomic Distances 35
III. Conclusion 49
References 50

16 Bond Distances in Sulfides and a Preliminary Table of Sulfide Crystal Radii

R. D. SHANNON

I. Introduction 53
II. Procedure 54
III. Results and Discussion 60
References 69

17 Energetics of Phase Transitions in AX, ABO_3, and AB_2O_4 Compounds

ALEXANDRA NAVROTSKY

I. Introduction 71
II. AX Structures 72
III. ABO_3 Structures 79
IV. AB_2O_4 Structures: Olivine (α), Spinel (γ), and Modified Spinel (β) 85
V. Entropies of High-Pressure Phase Transitions: Some Crystal Chemical Considerations 88

VI. Conclusions 91
References 92

18 Crystal Chemical Effects on Geophysical Equilibria

JOHN C. JAMIESON, MURLI H. MANGHNANI, AND L. C. MING

I. Introduction 95
II. Polymorphism in the Compounds of the Model Equilibria 99
III. Geophysical Consequences of Polymorphism in the Model Reactions 105
IV. Crystal Chemical Conclusions 106
References 106

19 Module Structure Variation with Temperature, Pressure, and Composition: A Key to the Stability of Modular Structures

R. M. HAZEN AND L. W. FINGER

I. Introduction 109
II. Variations of Crystal Structure 110
III. Stability of Modular Arrangements 113
IV. Conclusions 115
References 116

20 Theoretical Prediction of Ordered Superstructures in Metallic Alloys

J. M. SANCHEZ AND D. DE FONTAINE

I. Introduction 117
II. The State of Order 119
III. Examples and Applications of the Theory 125
IV. Conclusion 131
References 131

21 Graph Theoretic Enumeration of Structure Types: A Review

T. J. McLARNAN AND P. B. MOORE

I. Introduction 133
II. Mathematical Methods 135
III. Crystallographic Applications 143
IV. Unsolved Problems 160
References 164

22 Polytypism in Complex Crystals: Contrasts between Mica and Classical Polytypes

JAMES B. THOMPSON, JR.

I. Introduction 168
II. Idealized Mica Polytypes 169
III. The Mica Space Groups 175
IV. Less Idealized Micas 182
V. The Classical Polytypes 187
VI. Imperfect Polytypes 190
References 195

23 The Influence of Cation Properties on the Conformation of Silicate and Phosphate Anions

FRIEDRICH LIEBAU

I. Introduction and Methods 197
II. Computational Results of the Regression Analysis of Single-Chain Silicates and Phosphates 205
III. Interpretation of the Results of the Regression Analysis 211
IV. Consequences and Predictions Based on the Results of the Regression Analyses 217
V. Summary 231
References 232

24 The Description of Complex Alloy Structures

STEN ANDERSSON

I. Introduction 233
II. The Geometry in One, Two, and Three Dimensions 235
III. The Tetrahedrally Close-Packed Alloy Structures 235
IV. Intergrowth and Some Cubic Structures 244
V. Conclusions 256
References 257

25 Structural Features of Rare-Earth-Rich–Transition-Metal Alloys

E. PARTHÉ

I. Introduction 259
II. Formation of Rare-Earth–Transition-Metal Compounds 260
III. Rare-Earth Alloy Structures Characterized by Centered Trigonal Rare-Earth Prisms 263
IV. Structures Built Up with Trigonal Prisms R_6T and Cubes R_8R 289
V. Structures without Trigonal Prisms 290
VI. Concluding Remarks 294
References 295

26 On Polycompounds: Polycationic and Polyanionic Tetrelides, Pnictides, and Chalcogenides

F. HULLIGER

I. Introduction 297
II. The Mooser–Pearson Rule 298
III. The Occurrence of M–M and X–X Bonds in Relation to the Periodic Table 301

IV. Derivation of Polyanionic Coordinations and Structures 340
V. Semiconductor → Metal Transitions 345
References 348

Index 353