

Contents

1 Atom	1
1.1 Ionization Potentials and Electron Affinities	1
1.1.1 Ionization Potentials of Atoms	1
1.1.2 Electron Affinity	7
1.1.3 Effective Nuclear Charge	12
1.2 Absolute Dimensions of Atoms	15
1.3 Radii of Atoms in Molecules and Crystals	19
1.3.1 Historical Outline	19
1.3.2 Metallic Radii	21
1.3.3 Covalent Radii	24
1.4 Radii of Ions in Molecules and Crystals	26
1.4.1 Methods of Estimating Ionic Radii	26
1.4.2 Experimental (bonded) Ionic Radii	31
1.4.3 Energy-Derived Ionic Radii	32
1.4.4 Ultimate Ionic Radii	34
1.4.5 Concluding Remarks	34
Appendix	35
References	43
2 Chemical Bond	51
2.1 Historical Development of the Concept	51
2.2 Types of Bonds: Covalent, Ionic, Polar, Metallic	53
2.2.1 Ionic Bond	54
2.2.2 Covalent Bond	56
2.2.3 Polar Bond, Effective Charges of Atoms	60
2.2.4 Metallic Bond	68
2.2.5 Effective Valences of Atoms	71
2.3 Energies of the Chemical Interaction of Atoms	73
2.3.1 Bond Energies in Molecules and Radicals	73
2.3.2 Bond Energies in Crystals	85
2.3.3 Crystal Lattice Energies	87

2.3.4	Band Gaps in Solids	91
2.4	Concept of Electronegativity	96
2.4.1	Discussion About Electronegativity	96
2.4.2	Thermochemical Electronegativities	97
2.4.3	Ionization Electronegativities	101
2.4.4	Geometrical Electronegativities	106
2.4.5	Recommended System of Electronegativities of Atoms and Radicals	111
2.4.6	Equalization of Electronegativities and Atomic Charges	111
2.5	Effective Charges of Atoms and Chemical Behavior	117
2.6	Change of Chemical Bond Character under Pressure	119
2.7	Conclusions	122
	Appendix	122
	References	138
3	“Small” Molecule	159
3.1	Introduction	159
3.2	Inorganic Molecules and Radicals	161
3.2.1	Bond Distances	161
3.2.2	Bond Angles. VSEPR Concept	168
3.2.3	Non-Stoichiometric and Unusual Molecules	171
3.3	Organic Molecules	172
3.4	Organometallic Compounds	177
3.5	Clusters	186
3.5.1	Boron Clusters	186
3.5.2	Transition Metal Clusters	188
3.5.3	Clusters of Main Group Elements	193
3.5.4	Fullerenes	194
3.6	Coordination Compounds	197
	Appendix	200
	References	213
4	Intermolecular Forces	227
4.1	Van der Waals Interaction	227
4.2	Interdependence of the Lengths of Covalent and van der Waals Bonds	234
4.3	Van der Waals Radii	236
4.3.1	Introduction	236
4.3.2	Crystallographic van der Waals Radii	237
4.3.3	Equilibrium Radii of Atoms	242
4.3.4	Anisotropic van der Waals Radii	243
4.3.5	Concluding Remarks	246
4.4	Donor–Acceptor Interactions	247
4.5	Hydrogen Bond	249
	Appendix	253
	References	268

5	Crystal Structure – Idealised	275
5.1	Structures of Elements	275
5.1.1	Structures of Metals	276
5.1.2	Structures of Non-Metals	282
5.2	Binary Inorganic Crystalline Compounds	289
5.2.1	Crystal Structures of Halides, Oxides, Chalcogenides, Pnictides	289
5.2.2	Structures of Compounds with Diverse Bonds	301
5.3	Interconversions of Crystal Structures	302
5.4	Effective Coordination Number	303
5.5	Bond Valence (Bond Strength, Bond Order)	306
5.6	Ternary Compounds	309
5.7	Structural Features of Silicates	310
	Appendix	311
	References	318
6	Crystal Structure: Real	331
6.1	Thermal Motion	331
6.2	Lindemann's Hypothesis	334
6.3	Defects in Crystals	341
6.3.1	Classification of Defects	341
6.3.2	Defects Induced by Shock Waves	343
6.3.3	Real Structure and Melting of Solids	345
6.4	Isomorphism and Solid Solutions	347
	Appendix	351
	References	354
7	Amorphous State	359
7.1	Dispersing Powders	359
7.2	Amorphous Solids, Glasses	362
7.3	Structure of Melts	364
7.4	Structure of Aqueous Solutions	368
	Appendix	372
	References	375
8	Between Molecule and Solid	381
8.1	Energetic Properties of Clusters and Nanoparticles	381
8.1.1	Melting Temperatures and Heats Under Transition from Bulk to Nanophases	382
8.1.2	Energy Variation Under Transition from Bulk to Clusters	383
8.2	Changes of the Atomic Structure on Transition from Bulk Solids to Nanophases	385
8.3	Size Effect in the Dielectric Permittivity of Crystals	385
8.3.1	Effect of the Energy Factor	386
8.3.2	Effect of the Phase Composition on ϵ of Barium Titanate	387

8.3.3 Dielectric Behavior of Ceramic Materials	388
8.3.4 Dielectric Properties of Multi-Phase Systems	390
8.4 Conclusions	392
References	392
9 Phase Transition	397
9.1 Polymorphism	397
9.1.1 Polyamorphism	400
9.2 Energies of Phase Transitions	402
9.2.1 Melting Heats of Compounds	402
9.2.2 Sublimation Heats of Elements and Compounds	404
9.2.3 Evaporation Heats of Compounds	406
9.2.4 Enthalpies of Phase Transformations	409
References	410
10 Extreme Conditions	415
10.1 Polymorphic Transformations Under High Static Pressures	416
10.2 Pressure-induced Amorphization and Polyamorphism	424
10.3 Effect of the Crystal Size on the Pressure of Phase Transition	425
10.4 Solid Phase Transformations Under High Dynamic Pressures	428
10.5 Detonation Transformation and Synthesis of Diamond and <i>c</i> -BN ...	439
10.6 Equations of State of Solids	441
Appendix	446
References	460
11 Structure and Optical Properties	475
11.1 Refractive Index	476
11.1.1 Definitions, Anisotropy, Theory	476
11.1.2 Influence of Composition, Structures and Thermodynamic Conditions on Refractive Indices	480
11.2 Polarization and Dipole Moments	482
11.3 Molecular Refraction: Experiment and Calculation	489
11.3.1 Formulae of Refraction	489
11.3.2 Dependence of Refractions on the Structure and Thermodynamic Parameters	490
11.3.3 Atomic and Covalent Refractions	492
11.3.4 Ionic Refractions	495
11.3.5 Bond Refractions	499
11.4 Structural Application of Refractometry	501
11.5 Structural Applications of Spectroscopy	504
11.6 Optical Electronegativities	511
Appendix	514
References	527
Index	539

Introduction to Structural Chemistry

Batsanov, S.S.; Batsanov, A.S.

2012, X, 542 p., Hardcover

ISBN: 978-94-007-4770-8