

Contents

1. Principles of Formation of the Atomic Structure of Crystals	1
1.1 The Structure of Atoms	1
1.1.1 A Crystal as an Assembly of Atoms	1
1.1.2 Electrons in an Atom	3
1.1.3 Multielectron Atoms and the Periodic System	7
1.2 Chemical Bonding Between Atoms	15
1.2.1 Types of Chemical Bonding	15
1.2.2 Ionic Bond	18
1.2.3 Covalent Bond. Valence-Bond Method	25
1.2.4 Hybridization. Conjugation	28
1.2.5 Molecular-Orbital (MO) Method	32
1.2.6 Covalent Bond in Crystals	37
1.2.7 Electron Density in a Covalent Bond	43
1.2.8 Metallic Bond	48
1.2.9 Weak (van der Waals) Bonds	51
1.2.10 Hydrogen Bonds	53
1.2.11 Magnetic Ordering	56
1.3 Energy of the Crystal Lattice	59
1.3.1 Experimental Determination of the Crystal Energy	59
1.3.2 Calculation of the Potential Energy	60
1.3.3 Organic Structures	65
1.4 Crystallochemical Radii Systems	67
1.4.1 Interatomic Distances	67
1.4.2 Atomic Radii	67
1.4.3 Ionic Radii	71
1.4.4 The System of Atomic-Ionic Radii of a Strong Bond	80
1.4.5 System of Intermolecular Radii	83
1.4.6 Weak- and Strong-Bond Radii	85
1.5 Geometric Regularities in the Atomic Structure of Crystals	87
1.5.1 The Physical and the Geometric Model of a Crystal	87
1.5.2 Structural Units of a Crystal	87
1.5.3 Maximum-Filling Principle	88
1.5.4 Relationship Between the Symmetry of Structural Units and Crystal Symmetry	90
1.5.5 Statistics of the Occurrence of Space Groups	94

1.5.6	Coordination	95
1.5.7	Classification of Structures According to the Dimensionality of Structural Groupings	96
1.5.8	Coordination Structures	98
1.5.9	Relationship Between Coordination and Atomic Sizes	98
1.5.10	Closest Packings	100
1.5.11	Structures of Compounds Based on Close Packing of Spheres	104
1.5.12	Insular, Chain and Layer Structures	106
1.6	Solid Solutions and Isomorphism	110
1.6.1	Isostructural Crystals	110
1.6.2	Isomorphism	111
1.6.3	Substitutional Solid Solutions	111
1.6.4	Interstitial Solid Solutions	116
1.6.5	Modulated and Incommensurate Structures	120
1.6.6	Composite Ultrastructures	122
2.	Principal Types of Crystal Structures	124
2.1	Crystal Structures of Elements	124
2.1.1	Principal Types of Structures of Elements	124
2.1.2	Cystallochemical Properties of Elements	132
2.2	Intermetallic Structures	134
2.2.1	Solid Solutions and Their Ordering	134
2.2.2	Electron Compounds	136
2.2.3	Intermetallic Compounds	138
2.3	Structures with Bonds of Ionic Nature	140
2.3.1	Structures of Halides, Oxides, and Salts	140
2.3.2	Silicates	144
2.3.3	Superionic Conductors	153
2.4	Covalent Structures	155
2.5	Structure of Complex and Related Compounds	161
2.5.1	Complex Compounds	161
2.5.2	Compounds with Metal Atom Clusters	165
2.5.3	Metal-Molecular Bonds (π Complexes of Transition Metals)	167
2.5.4	Compounds of Inert Elements.	168
2.6	Principles of Organic Crystal Chemistry	169
2.6.1	The Structure of Organic Molecules	169
2.6.2	Symmetry of Molecules	174
2.6.3	Packing of Molecules in a Crystal	176
2.6.4	Crystals with Hydrogen Bonds	182
2.6.5	Clathrate and Molecular Compounds	185
2.7	Structure of High-Polymer Substances	187
2.7.1	Noncrystallographic Ordering	187

2.7.2	Structure of Chain Molecules of High Polymers	187
2.7.3	Structure of a Polymer Substance	192
2.7.4	Polymer Crystals	193
2.7.5	Disordering in Polymer Structures	196
2.8	Structure of Liquid Crystals	200
2.8.1	Molecule Packing in Liquid Crystals	200
2.8.2	Types of Liquid-Crystal Ordering	201
2.9	Structures of Substances of Biological Origin	210
2.9.1	Types of Biological Molecules	210
2.9.2	Principles of Protein Structure	212
2.9.3	Fibrous Proteins	220
2.9.4	Globular Proteins	222
2.9.5	Structure of Nucleic Acids	250
2.9.6	Structure of Viruses	258
3.	Band Energy Structure of Crystals	271
3.1	Electron Motion in the Ideal Crystal	271
3.1.1	Schrödinger Equation and Born-Karman Boundary Conditions	271
3.1.2	Energy Spectrum of an Electron	276
3.2	Brillouin Zones	278
3.2.1	Energy Spectrum of an Electron in the Weak-Bond Approximation	278
3.2.2	Faces of Brillouin Zones and the Laue Condition	281
3.2.3	Band Boundaries and the Structure Factor	283
3.3	Isoenergetic Surfaces. Fermi Surface and Band Structure	284
3.3.1	Energy Spectrum of an Electron in the Strong-Bond Approximation	284
3.3.2	Fermi Surfaces	286
4.	Lattice Dynamics and Phase Transitions	289
4.1	Atomic Vibrations in a Crystal	289
4.1.1	Vibrations of a Linear Atomic Chain	289
4.1.2	Vibration Branches	290
4.1.3	Phonons	292
4.2	Heat Capacity, Thermal Expansion, and Thermal Conductivity of Crystals	293
4.2.1	Heat Capacity	293
4.2.2	Linear Thermal Expansion	294
4.2.3	Thermal Conductivity	295
4.3	Polymorphism. Phase Transitions	296
4.3.1	Phase Transitions of the First and Second Order	298
4.3.2	Phase Transitions and the Structure	299

4.4	Atomic Vibrations and Polymorphous Transitions	302
4.5	Ordering-Type Phase Transitions	306
4.6	Phase Transitions and Electron–Phonon Interaction	309
4.6.1	Contribution of Electrons to the Free Energy of the Crystal	309
4.6.2	Interband Electron–Phonon Interaction	310
4.6.3	Photostimulated Phase Transitions	314
4.6.4	Curie Temperature and the Energy Gap Width	315
4.7	Debye’s Equation of State and Grüneisen’s Formula	316
4.8	Phase Transitions and Crystal Symmetry	318
4.8.1	Second-Order Phase Transitions	318
4.8.2	Description of Second-Order Transitions with an Allowance for the Symmetry	321
4.8.3	Phase Transitions Without Changing the Number of Atoms in the Unit Cell of a Crystal	323
4.8.4	Changes in Crystal Properties on Phase Transitions	326
4.8.5	Properties of Twins (Domains) Forming on Phase Transformations	327
4.8.6	Stability of the Homogeneous State of the Low-Symmetry Phase	328
5.	The Structure of Real Crystals	330
5.1	Classification of Crystal Lattice Defects	330
5.2	Point Defects of the Crystal Lattice	331
5.2.1	Vacancies and Interstitial Atoms	331
5.2.2	Role of Impurities, Electrons, and Holes	337
5.2.3	Effect of External Influences	339
5.3	Dislocations	341
5.3.1	Burgers Circuit and Vector	341
5.3.2	Elastic Field of Straight Dislocation	344
5.3.3	Dislocation Reactions	349
5.3.4	Polygonal Dislocations	350
5.3.5	Curved Dislocations.	355
5.4	Stacking Faults and Partial Dislocations	357
5.5	Continuum Description of Dislocations	364
5.5.1	Dislocation-Density Tensor	364
5.5.2	Example: A Dislocation Row	366
5.5.3	Scalar Dislocation Density	367
5.6	Subgrain Boundaries (Mosaic Structures) in Crystals	367
5.6.1	Examples of Subgrain Boundaries: A Tilt Boundary and a Twist Boundary	367
5.6.2	The Dislocation Structure of the Subgrain Boundary in General	369
5.6.3	Subgrain Boundary Energy	372
5.6.4	Incoherent Boundaries	373

5.7	Twins	375
5.7.1	Twinning Operations	376
5.7.2	Twinning with a Change in Crystal Shape	378
5.7.3	Twinning Without a Change in Shape	382
5.8	Direct Observation of Lattice Defects	384
5.8.1	Ionic Microscopy	385
5.8.2	Electron Microscopy	385
5.8.3	X-Ray Topography	340
5.8.4	Photoelasticity Method	396
5.8.5	Selective Etching Method	347
5.8.6	Investigation of the Crystal Surface	398
6.	Advances in Structural Crystallography	400
6.1	Development of Structure Analysis. Data Banks	400
6.2	Fullerenes and Fullerides	402
6.2.1	Fullerenes	402
6.2.2	C ₆₀ Crystals	405
6.3	Crystal Chemistry of Silicates and Related Compounds	404
6.3.1	Main Features of the Silicate Structures	404
6.3.2	Insular Anionic Tetrahedron Complexes in Silicates	410
6.3.3	Anionic Tetrahedron Complexes in the Form of Rings and Chains	411
6.3.4	Framework Silicates	413
6.3.5	Theoretical Methods for the Calculation of Silicate Structures	414
6.4	Structure of Superconductors	416
6.4.1	Superconductivity	416
6.4.2	High-Temperature Superconductors (HTSCs)	419
6.4.3	Structure of MeCuO ₄ High-T _c Superconductors	421
6.4.4	Atomic Structure of Y–Ba–Cu Phases	422
6.4.5	Atomic Structure of Tl-Phases of High-T _c Superconductors	423
6.4.6	Specific Features of the Structure of HTSCs	428
6.5	Modular Structures, Blocks, and Fragments	429
6.5.1	The Notion of Modular Structures (MS)	429
6.5.2	Relationship Between Different Types of Modular Structures	431
6.5.3	Symbolic Notations of MS	434
6.5.4	Structure-Property Relations for MS	435
6.6	X-Ray Analysis for Studying Chemical Bonding	435
6.7	Organic Crystal Chemistry	442
6.7.1	Organic Structures	442
6.7.2	Large Organic Molecules	442
6.7.3	Secondary Bonds	445

6.8	Structure Investigation of Biomolecular Crystals	447
6.8.1	Progress in the Methods of X-Ray Macromolecular Crystallography	447
6.8.2	Investigation of Protein Structure by the Nuclear Magnetic Resonance (NMR) Method	451
6.8.3	Dynamics of Protein Molecules	453
6.8.4	Data on the Structure of Large Proteins	457
6.8.5	X-Ray Investigation of Ribosomes	462
6.8.6	Virus Structures	462
6.9	Ordering in Liquid Crystals	467
6.9.1	Smectic A Polymorphism in Liquid Crystals (LC) Containing Polar Molecules	468
6.9.2	Smectic Lamellar Crystalline Phases and Hexatics	470
6.9.3	Freely Suspended Smectic Films	472
6.9.4	Cholesteric Blue Phases	472
6.9.5	Other Liquid Crystalline Phases	473
6.10	Langmuir-Blodgett Films	475
6.10.1	Principles of Formation	475
6.10.2	Chemical Composition, Properties and Applications of LB Films	475
6.10.3	Structure of LB Films	477
6.10.4	Multicomponent Langmuir-Blodgett Films. Superlattices	482
6.11	Photo- and Thermostimulated Phase Transitions in Ferroelectrics	485
6.11.1	Photostimulated Phase Transitions in Ferroelectrics	485
6.11.2	Thermostimulated Phase Transitions in Ferroelectrics . . .	490
	References	493
	Bibliography	509
	Subject Index	515

Modern Crystallography 2

Structure of Crystals

Vainshtein, B.K.; Fridkin, V.M.; Indenbom, V.L.

2000, XX, 521 p., Hardcover

ISBN: 978-3-540-67474-0