

**TREATISE ON
SOLID STATE CHEMISTRY**

**Volume 3
Crystalline and
Noncrystalline Solids**

TREATISE ON SOLID STATE CHEMISTRY

Volume 3 Crystalline and Noncrystalline Solids

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**TREATISE ON
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Volume 3
Crystalline and
Noncrystalline Solids

TREATISE ON SOLID STATE CHEMISTRY

- Volume 1 • The Chemical Structure of Solids
- Volume 2 • Defects in Solids
- Volume 3 • Crystalline and Noncrystalline Solids
- Volume 4 • Reactivity of Solids
- Volume 5 • Changes of State
- Volume 6A • Surfaces I
- Volume 6B • Surfaces II

Foreword

The last quarter-century has been marked by the extremely rapid growth of the solid-state sciences. They include what is now the largest subfield of physics, and the materials engineering sciences have likewise flourished. And, playing an active role throughout this vast area of science and engineering have been very large numbers of chemists. Yet, even though the role of chemistry in the solid-state sciences has been a vital one and the solid-state sciences have, in turn, made enormous contributions to chemical thought, solid-state chemistry has not been recognized by the general body of chemists as a major subfield of chemistry. Solid-state chemistry is not even well defined as to content. Some, for example, would have it include only the quantum chemistry of solids and would reject thermodynamics and phase equilibria; this is nonsense. Solid-state chemistry has many facets, and one of the purposes of this *Treatise* is to help define the field.

Perhaps the most general characteristic of solid-state chemistry, and one which helps differentiate it from solid-state physics, is its focus on the chemical composition and atomic configuration of real solids and on the relationship of composition and structure to the chemical and physical properties of the solid. Real solids are usually extremely complex and exhibit almost infinite variety in their compositional and structural features.

Chemistry has never hesitated about the role of applied science, and solid-state chemistry is no exception. Hence, we have chosen to include in the field not only basic science but also the more fundamental aspects of the materials engineering sciences.

The central theme of the *Treatise* is the exposition of unifying principles in the chemistry, physical chemistry, and chemical physics of solids. Examples are provided only to illustrate these principles. It has, throughout, a chemical viewpoint; there is, perforce, substantial overlap with some areas of solid-

Foreword

state physics and metallurgy but a uniquely chemical perspective underlies the whole. Each chapter seeks to be as definitive as possible in its particular segment of the field.

The *Treatise* is intended for advanced workers in the field. The scope of the work is such that all solid-state chemists, as well as solid-state scientists and engineers in allied disciplines, should find in it much that is new to them in areas outside their own specializations; they should also find that the treatment of their own particular areas of interest offers enlightening perspectives.

Certain standard subjects, such as crystal structures, have been omitted because they are so well covered in many readily available standard references and are a part of the background of all solid-state scientists. Certain limited redundancies are intended, partly because they occur in different volumes of the series, but mainly because some subjects need to be examined from different viewpoints and in different contexts. The first three volumes deal with the structure of solids and its relation to properties. Volumes 4 and 5 cover broad areas of chemical dynamics in bulk solids. Volume 6 treats both structure and chemical dynamics of surfaces.

N.B.H.

Preface to Volume 3

Volumes 1 and 2 of this Treatise were concerned with both perfect and imperfect crystalline solids, all exhibiting simple crystal lattices and with the imperfect solid taken to mean a solid with a modest concentration of simple defects, i.e., point defects or dislocations. Certain classes of solids, including major classes of practical materials, fall outside the range covered by this structural description. The reason for this varies widely; thus, periodic structural features can be used to distinguish unusual classes of crystalline solids, the solid can be built up from molecular units, the defects can be extended in nature, or the solid may exhibit a semicrystalline or a completely amorphous structure. In this volume, several classes of solids of this type are examined.

Contents of Volume 3

Chapter 1

Metastable Phases Produced by Rapid Quenching from the Vapor and the Liquid 1

A. K. Sinha, B. C. Giessen, and D. E. Polk

1. Introduction	1
1.1. Definition	1
1.2. Kinetic Considerations	2
1.3. Free Energy and Phase Diagram Considerations	3
1.4. Energetic Considerations	8
1.5. Structural Considerations	9
1.6. Classification of Metastable Phases and Outline of Chapter	10
2. Experimental Techniques	11
2.1. Evaporation	11
2.2. Sputtering	13
2.3. Electrodeposition	16
2.4. Rapid Liquid Quenching	17
3. Amorphous Phases	19
3.1. Elemental Amorphous Phases	20
3.2. Alloy Amorphous Phases	24
3.3. Structural Analysis	26
3.4. Electrical Properties	30
3.5. Magnetic Properties	32
3.6. Transformation Kinetics	35

Contents of Volume 3

4.	Metastable Elemental and Near-Elemental Crystalline Phases . .	36
4.1.	Topologically Close-Packed Structures.	36
4.2.	Spherically Close-Packed Structures.	44
5.	Metastable Crystalline Intermediate Alloy Phases	48
5.1.	Occurrence and Study of Intermediate Alloy Phases	48
5.2.	Structures and Crystal Chemistry of Metastable Intermediate Phases.	51
5.3.	Further Structural Relationships.	57
6.	Supersaturated Terminal or Intermediate Solid Solutions	61
6.1.	Occurrence and Study of Extended Solid Solutions	61
6.2.	Crystal Chemistry and Properties of Metastable Solid Solutions.	64
7.	Concluding Remarks.	75
7.1.	Significance of Research on Metastable Phases.	75
7.2.	Review of Metastable Phase Formation.	76
7.3.	Alternate Methods and Products of Metastable Phase Preparation.	77
7.4.	Present and Suggested Applications of Metastable Phases	78
7.5.	Areas for Further Research	79
	Acknowledgment	80
	References.	81

Chapter 2

Inclusion Compounds **89**

F. R. Gamble and T. H. Geballe

1.	Introduction	89
2.	Metallic Clathrates.	90
2.1.	Electrical Properties.	94
2.2.	Low-Temperature Heat Capacity	94
3.	Boron Compounds.	95
3.1.	Icosahedral Grouping	95
3.2.	Octahedral Grouping	96
4.	Graphite Intercalation Compounds.	106
4.1.	Introduction	106
4.2.	Compounds with Electron Donors	107
4.3.	Compounds with Electron Acceptors	111
4.4.	Order–Disorder Transitions.	111
4.5.	Reaction Mechanisms.	112
4.6.	Fermi Surface and Transport Measurements.	115
4.7.	Superconductivity	120
4.8.	Spin Resonance	120
4.9.	Magnetic Properties.	121

5. Chalcogenide Intercalation Compounds.....	124
5.1. The Layered Chalcogenides.....	124
5.2. The Intercalation Compounds of Layered Dichalcogenides and Elemental Metals.....	127
5.3. Molecular Intercalates.....	134
6. Layered Halide and Similar Intercalation Compounds.....	144
7. Tungsten Bronzes and Similar Compounds.....	148
Epilogue.....	155
References.....	155

Chapter 3

**The Structural Chemistry of Some Complex Oxides: Ordered and
Disordered Extended Defects** **167**

LeRoy Eyring and Leung-Tak Tai

1. Introduction.....	167
1.1. Types of Defects in Crystals.....	167
1.2. Methods of Observing Extended Defects.....	170
2. Complex Structures Based on Crystallographic Shear.....	173
2.1. Introduction.....	173
2.2. Compounds Containing One-Dimensional Crystallogra- phic Shear.....	183
2.3. Compounds Containing Two-Dimensional Crystallogra- phic Shear.....	201
2.4. Disorder in Block Structures.....	210
2.5. Disorder in Systems Related to the Tetragonal Tungsten Bronze.....	216
3. The Fluorite-Related Structures.....	223
3.1. Introduction.....	223
3.2. The Relationship between the Fluorite and Other Structures.....	227
3.3. Fluorite-Related Phases with Excess Oxygen.....	229
3.4. The Fluorite-Related Homologous Series.....	231
4. Extended Defects in the NaCl Structure Type.....	238
4.1. Nonstoichiometry and Defect Structure of Titanium and Vanadium Monoxides.....	238
4.2. The Defect Structure of Fe_{1-x}O	240
5. Stoichiometry and Structure of Highly Conducting Solid Electro- lytes.....	242
5.1. The Structure of Calcia-Stabilized Zirconia.....	242
5.2. The Structure of Some Beta-Aluminas.....	244
5.3. The Structure of Halide and Chalcogenide Solid Electro- lytes.....	246
Acknowledgment.....	248
References.....	249

Contents of Volume 3

Chapter 4

Interstitial Phases

253

A. L. Bowman and N. H. Krikorian

1. Introduction	253
2. Crystallography of Interstitial Phases	255
2.1. Geometrical Basis of Close Packing	256
2.2. The Radius Ratio	258
2.3. Crystal Structures of Interstitial Phases	259
2.4. Polymorphism in Interstitial Compounds	266
2.5. Ternary Interstitial Phases	267
3. Properties of Interstitial Phases	268
3.1. Phase Diagrams	268
3.2. Melting Points	272
3.3. Thermodynamic Properties	273
3.4. Hardness	276
3.5. Thermal Expansion	279
3.6. Electrical Resistivity	280
3.7. Superconductivity	281
3.8. Diffusion	283
3.9. Bonding	283
4. Summary	284
References	285

Chapter 5

Inorganic Amorphous Solids and Glass-Ceramic Materials

293

D. R. Uhlmann

1. Introduction	293
2. Atomic Structure of Glasses	295
2.1. Models of Glass Structure	296
2.2. Structure of Oxide Glasses	298
2.3. Structure of Nonoxide Glasses	303
2.4. Effects of Pressure, Thermal History, and Irradiation	305
3. Submicrostructure of Glasses	306
3.1. Introduction	306
3.2. Spinodal Decomposition vs. Nucleation Growth Coalescence	311
4. Electronic Structure of Glasses	316
4.1. Introduction	316
4.2. Density of States	316
5. Glass Formation	318
6. Macrostructure of Glasses	322

7. Glass-Ceramic Materials	325
7.1. Commercial Glass-Ceramic Systems	326
7.2. Microstructural Features and Properties	328
8. Concluding Discussion	329
References	330

Chapter 6

The Morphology of Crystalline Synthetic Polymers 335

F. Khoury and E. Passaglia

1. Introduction	335
1.1. General and Historical	335
1.2. Scope of the Chapter	337
2. Crystallinity in Polymers	338
2.1. Requisites for Crystallization	338
2.2. Polymer Crystal Structures	347
2.3. Degree of Crystallinity	355
3. The Morphology of Polymers Crystallized from Solution	357
3.1. Preliminary Remarks	357
3.2. Crystallization Procedures, with Comments on Polydispersity in the Molecular Weight of Polymers and the Incidence of Fractionation during Crystallization	358
3.3. Optical and Electron Microscopy, with Comments on the Susceptibility of Polymers to Electron Irradiation	359
3.4. Polymer Crystals	362
4. The Morphology of Polymers Crystallized from the Melt	441
4.1. Preliminary Remarks	441
4.2. General Comments on Spherulites and Their Structures	442
4.3. The Fine Structure of Polymer Spherulites	445
4.4. Crystallization under Pressure	476
5. Concluding Remarks	480
Acknowledgments	481
References	481

Chapter 7

The Rate of Crystallization of Linear Polymers with Chain Folding 497

John D. Hoffman, G. Thomas Davis, and John I. Lauritzen, Jr.

1. Introduction	497
1.1. Aims and Objectives	497
1.2. Nature of Crystallizable Linear Macromolecules	500
1.3. Chain-Folded Crystals from Bulk and Dilute Solutions	503

Contents of Volume 3

2.	Thermodynamic Preliminaries and Work of Chain Folding	528
2.1.	Fold Surface Free Energies from Melting Point and Crystal Thickness Data.	528
2.2.	Melting Behavior	531
2.3.	Interpretation of σ_e in Terms of Fold Structure	537
2.4.	The Driving Force for Crystallization in Strongly Sub-cooled Systems.	540
3.	Theory of Growth and Lamellar Thickness.	541
3.1.	Approach and Model	541
3.2.	Calculation of the Total Flux.	545
3.3.	Initial Lamellar Thickness	548
3.4.	Growth Rate.	553
3.5.	Interpretation of ψ	561
3.6.	Effect of Chain Ends.	564
4.	Comparison of Theory and Experiment	565
4.1.	Objectives	565
4.2.	Growth Rate versus Crystallization Temperature Curves	566
4.3.	Polymers Where Data Allow Test of Expressions for Both Growth Rate and Lamellar Thickness	574
4.4.	The Fold Period as a Function of the Undercooling in Dilute Solutions: Verification of $l_g^* = (C_1/\Delta T) + C_2$	584
4.5.	Generalized Treatment to Obtain Work of Chain Folding from K_g	587
5.	Theories with Fluctuations of Fold Period.	592
6.	Homogeneous Nucleation in Polymers.	597
	Acknowledgments	604
	Note Added in Proof.	605
	References.	605

Chapter 8

Organic Molecular Crystals: Anthracene **615**

R. G. Kepler

1.	Introduction	615
2.	The Molecule	618
3.	The Crystal	620
4.	Optical Absorption	623
4.1.	Singlet Excitons	624
4.2.	Triplet Excitons	627
5.	Fluorescence.	629
6.	Energy Transport.	631
6.1.	Singlet Excitons	632
6.2.	Triplet Excitons	638

7.	Electrons and Holes	645
7.1.	Electron and Hole Transport	645
7.2.	Electron and Hole Generation	651
8.	Theory	661
8.1.	Excitons	661
8.2.	Electrons and Holes	665
	References	667

Chapter 9

Organic Molecular Crystals: Charge-Transfer Complexes **679**
 Zoltán G. Soos and Douglas J. Klein

1.	Introduction	679
1.1.	Contrast of Solution and Solid-State Complexes	679
1.2.	Molecular-Exciton Approach	681
1.3.	π -Molecular Ion-Radical Solids	683
1.4.	Hubbard Models and CT Crystals	685
1.5.	Relation to Other Work: Scope of the Review	687
2.	Development of Phenomenological Theory	690
2.1.	The Ion-Radical Dimer	690
2.2.	Intermolecular Forces	693
2.3.	Orthonormal Basis for Dimers	696
2.4.	Site Representation for Molecular Crystals	697
2.5.	Minimum Basis for CT Crystals	699
2.6.	Fermion Representation of \mathcal{H}	702
2.7.	Matrix Elements	703
2.8.	Charge-Transfer Hamiltonian	707
3.	Classification of π -Molecular CT Crystals	708
3.1.	Structural Variations of Molecular Stacks	708
3.2.	Collective Physical Properties	711
3.3.	Mixed, Simple Stacks: Neutral or Ionic	713
3.4.	Crystals of Dimers and Complex CT Crystals	717
3.5.	FR Crystals with Simple, Regular Stacks	720
3.6.	Segregated Simple Alternating Stacks	723
3.7.	Complex, Regular FR Stacks: Fractional Charges	725
3.8.	Complex, Segregated, Alternating FR Stacks	727
4.	Electronic Properties of Ion-Radical Crystals	729
4.1.	Excitations of the CT Hamiltonian	729
4.2.	Optical Properties: CT Bands	732
4.3.	Electric Conduction	734
4.4.	Magnetic Properties: Antiferromagnetic Exchange	736
4.5.	One-Dimensionality and Spin Dynamics	740

Contents of Volume 3

5. Quantum Computations	743
5.1. Approximate Molecular Computations	743
5.2. Crystal-Perturbed States	745
5.3. Improved Matrix Elements	749
5.4. Hubbard and Heisenberg Models	753
5.5. Hubbard Model Computations	755
6. Conclusions	757
Acknowledgments	758
References	759
Index	769

Metastable Phases Produced by Rapid Quenching from the Vapor and the Liquid

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1. Introduction

1.1. Definition

Though some metastable phases are obtained readily, e.g., common inorganic oxide glasses or some phases present in many varieties of steels, the phases of interest here are those which can be obtained only through the use of high effective quenching rates from the vapor or liquid phase. This includes many thin-film phases obtained by evaporation or sputtering and not-so-thin film phases obtained by rapid cooling from the melt and by electrodeposition from a liquid electrolyte. In the case of evaporation or sputtering of a metal, the substrate is exposed to a gaseous ambient containing metal as well as nonmetal atoms, whereas in the case of rapid quenching from the melt and electrodeposition, the ambient of the substrate is made up of a crystallographically uncorrelated assembly of atoms in the liquid phase or in solution.

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