

Solid State Materials Chemistry

This book explores the fascinating world of functional materials from the perspective of those who are tasked with inventing them, solid state chemists. Written in a clear and accessible style, this book provides a modern-day treatment of solid state materials chemistry for graduate and advanced undergraduate level courses. With over 330 problems and 400 original figures, this essential reference covers a wide range of materials in a holistic manner, including inorganic and organic, crystalline and amorphous, bulk and nanocrystals.

The introductory chapters cover topics such as crystal structures, defects, diffusion in solids, chemical bonding, and electronic band structure. Later chapters focus on important classes of functional materials including pigments, phosphors, dielectric materials, magnets, metals, semiconductors, superconductors, nonlinear optical materials, battery materials, zeolites, metal–organic framework materials, and glasses. The technological applications and synthesis methods used to prepare the materials that drive modern society are highlighted throughout.

Patrick M. Woodward is a Professor in the Department of Chemistry and Biochemistry and holds a courtesy appointment in the Department of Physics at Ohio State University. He is best known for his studies of the structures and properties of perovskite-related materials. He has served as chair of the Solid State Chemistry Gordon Conference (2018), Associate Editor of the *Journal of Solid State Chemistry* (2006–2011), and Vice President of the Neutron Scattering Society of America (2014–2018). He is co-author of the widely used general chemistry textbook, *Chemistry: The Central Science* (Pearson Education Limited, 2018). Patrick is a recipient of an NSF Career Award (2001), a Sloan Research Fellowship (2004), a Leverhulme Visiting Professorship (2017), and is a Fellow of the American Chemical Society (2020).

Pavel Karen is a Professor in the Department of Chemistry at the University of Oslo. His interests include inorganic reaction chemistry, solid state synthesis methods, crystallography, phase relations and thermodynamics, and point-defect chemistry; all components of his teaching portfolio. He is interested in the relationship between structure and properties of less common inorganic solids, such as mixed-valence oxides. Crystal structures are studied by X-ray and neutron diffraction, local structures by Mössbauer spectroscopy, and valence-mixing by calorimetry. He is co-author of the chapter Phase Diagrams and Thermodynamic Properties in the *Handbook on the Physics and Chemistry of the Rare Earths, Volume 30, High-Temperature Superconductors* (Elsevier, 2000). Pavel is a member of the American Chemical Society, the American Crystallographic Association, and of the International

Union of Pure and Applied Chemistry's Division II and the Interdivisional Committee on Terminology, Nomenclature and Symbols.

John S. O. Evans is a Chemistry Professor at Durham University where he served as Head of Chemistry from 2009 to 2014. His research interests are in the synthesis and properties of (mainly) inorganic materials, their structural chemistry, and their real-world applications. In recent years he has worked, inter alia, on negative thermal expansion, symmetry properties of phase transitions, new oxide-chalcogenides and energy-related materials. He has a long-standing interest in developing powder diffraction methods and is co-author of *Rietveld Refinement: Practical Powder Diffraction Pattern Analysis using TOPAS* (De Gruyter, 2019). John was awarded the 1997 Meldola prize of the Royal Society of Chemistry, and was co-awarded the 2015 Royal Society of Chemistry Teamwork in Innovation Award for work with industry.

Thomas Vogt is the Educational Foundation Endowed Chair in the Department of Chemistry and Biochemistry, Director of the NanoCenter and adjunct Professor in the Department of Philosophy at the University of South Carolina. His work focuses on establishing structure–property relationships of solid state materials using X-ray and neutron scattering and electron microscopy. He is recognized as Fellow of the American Physical Society, the American Association for the Advancement of Science, the Institute of Advanced Study at Durham University, and the Neutron Scattering Society of America. Thomas received the Carolina Trustee Professorship of the Board of Trustees in 2018 as well as the University of South Carolina's Educational Foundation Award for Research in Science, Mathematics, and Engineering in 2019.

Solid State Materials Chemistry

Patrick M. Woodward

Ohio State University

Pavel Karen

Universitetet i Oslo

John S. O. Evans

Durham University

Thomas Vogt

University of South Carolina



CAMBRIDGE
UNIVERSITY PRESS

Cambridge University Press
978-0-521-87325-3 — Solid State Materials Chemistry
Patrick M. Woodward, Pavel Karen, John S. O. Evans, Thomas Vogt
Frontmatter
[More Information](#)

CAMBRIDGE UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom
One Liberty Plaza, 20th Floor, New York, NY 10006, USA
477 Williamstown Road, Port Melbourne, VIC 3207, Australia
314-321, 3rd Floor, Plot 3, Splendor Forum, Jasola District Centre, New Delhi - 110025, India
103 Penang Road, #05-06/07, Visioncrest Commercial, Singapore 238467

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9780521873253

DOI: 10.1017/9781139025348

© Patrick M. Woodward, Pavel Karen, John S. O. Evans, and Thomas Vogt 2021

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2021

A catalogue record for this publication is available from the British Library

ISBN 978-0-521-87325-3 Hardback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party internet websites referred to in this publication, and does not guarantee that any content on such websites is, or will remain, accurate or appropriate.

Contents

Preface	<i>page</i> xvii
Acknowledgments	xix
1 Structures of Crystalline Materials	1
1.1 Symmetry	1
1.1.1 Translational Symmetry	2
1.1.2 Rotational Symmetry	3
1.1.3 Crystallographic Point Groups and Crystal Systems	5
1.1.4 Bravais Lattices	5
1.1.5 Introduction to Space Groups	8
1.1.6 Symmetry Elements That Combine Rotation and Translation	9
1.1.7 Space-Group Symbols	11
1.1.8 Description of a Crystal Structure	12
1.2 Databases	13
1.3 Composition	14
1.3.1 Coordination, Stoichiometry, and Connectivity	15
1.3.2 The Generalized 8–N Rule	17
1.4 Structural Principles	18
1.4.1 Packing of Spheres	19
1.4.2 Filling Holes	22
1.4.3 Network Structures	28
1.4.4 Polyhedral Structures	32
1.5 Structures of Selected Materials	38
1.5.1 The Spinel Structure	38
1.5.2 The Garnet Structure	39
1.5.3 Perovskite Structures	40
1.5.4 Silicates	44
1.5.5 Zeolites	46
1.5.6 Zintl Phases	47
1.6 Problems	48
1.7 Further Reading	51
1.8 References	51

vi Contents

2 Defects and More Complex Structures	54
2.1 Point Defects in Crystalline Elemental Solids	54
2.2 Intrinsic Point Defects in Compounds	55
2.3 Thermodynamics of Vacancy Formation	58
2.4 Extrinsic Defects	61
2.5 Solid Solutions and Vegard's Law	63
2.6 Kröger–Vink Notation	65
2.7 Line Defects in Metals	66
2.7.1 Edge Dislocations	66
2.7.2 Screw Dislocations	66
2.8 Planar Defects in Materials	67
2.8.1 Stacking Faults	67
2.8.2 Twinning	68
2.8.3 Antiphase Boundaries	72
2.8.4 Crystallographic Shear Structures	74
2.9 Gross Nonstoichiometry and Defect Ordering	75
2.10 Incommensurate Structures	78
2.11 Infinitely Adaptive Structures	80
2.12 Problems	81
2.13 Further Reading	85
2.14 References	85
3 Defect Chemistry and Nonstoichiometry	87
3.1 Narrow Nonstoichiometry in Oxides	87
3.1.1 Point Defects in a Pure Stoichiometric Oxide	87
3.1.2 Point Defects upon Oxidation/Reduction of the Stoichiometric Oxide	88
3.1.3 Equilibrium Equations for Oxidative and Reductive Nonstoichiometry	89
3.1.4 Defect Equilibria for Schottky-Type Redox Compensation	90
3.1.5 Acceptor-Doped Oxides	93
3.1.6 Donor-Doped Oxides	94
3.1.7 Solid Solubility of Dopants	94
3.1.8 Cautionary Note on Defect Models in Pure Oxides	96
3.2 Wide Nonstoichiometry in Oxides	98
3.3 Point Defects and Diffusion	99
3.3.1 Point-Defect Movements	101
3.3.2 Random Hopping	103
3.3.3 Hopping Under a Driving Force	104

	Contents	vii
3.3.4 Hopping Under a Concentration Gradient		105
3.3.5 Hopping Under an Electric Field		106
3.3.6 Relationship between Conductivity and Diffusivity		107
3.3.7 Ambipolar Diffusion		108
3.3.8 Temperature Dependence of Diffusivity		111
3.3.9 Diffusivity and Redox Defect Equilibria		111
3.3.10 Outline of Non-Steady-State Diffusion		112
3.3.11 Cautionary Note on Diffusion in Real Materials		114
3.4 Problems		115
3.5 Further Reading		118
3.6 References		118
4 Phase Diagrams and Phase Transitions		120
4.1 Phase Diagrams		120
4.2 Two-Component Phase Diagrams		123
4.2.1 Without Compound Formation		123
4.2.2 With Compound Formation		125
4.2.3 Solid-Solution Formation		128
4.3 Three-Component Phase Diagrams		131
4.4 Structural Phase Transitions		135
4.4.1 Classification of Phase Transitions		136
4.4.2 Symmetry and Order Parameters		137
4.4.3 Introduction to Landau Theory		140
4.4.4 Second-Order Transitions		141
4.4.5 First-Order and Tricritical Transitions		144
4.4.6 Phonons, Soft Modes, and Displacive Transitions		147
4.5 Problems		150
4.6 Further Reading		152
4.7 References		153
5 Chemical Bonding		154
5.1 Ionic Bonding		154
5.1.1 Coulombic Potential Energy		154
5.1.2 Lattice Energy and the Born–Mayer Equation		156
5.1.3 Experimental versus Calculated Lattice-Formation Energies		158
5.2 Atomic Orbitals		161
5.2.1 Energies of Atomic Orbitals		166
5.2.2 Sizes of Atomic Orbitals		168
5.3 Molecular-Orbital Theory		169
5.3.1 Homonuclear Diatomics: H_2^+ and H_2		169
5.3.2 The Heteronuclear Diatomic Case: HHe		173

viii Contents

5.3.3	Orbital Overlap and Symmetry	174
5.3.4	Combination of σ and π Bonding: O_2	175
5.3.5	Symmetry-Adapted Linear Combinations (SALCs)	177
5.3.6	Simple Polyatomic Molecules: BeH_2 and CH_4	179
5.3.7	Conjugated π Bonding: C_6H_6	181
5.3.8	Transition-Metal Complexes: $[CrCl_6]^{3-}$ and $[CoCl_4]^{2-}$	183
5.3.9	High- and Low-Spin Configurations	186
5.3.10	Jahn–Teller Distortions	188
5.4	Bond Valences	190
5.5	Problems	195
5.6	Further Reading	198
5.7	References	199
6	Electronic Band Structure	200
6.1	The Band Structure of a Hydrogen-Atom Chain	200
6.1.1	The Electronic Structures of Cyclic H_N Molecules	201
6.1.2	Translational Symmetry and the Bloch Function	202
6.1.3	The Quantum Number k	203
6.1.4	Visualizing Crystal Orbitals	204
6.1.5	Band-Structure Diagrams	207
6.1.6	Density-of-States (DOS) Plots	209
6.2	The Band Structure of a Chain of H_2 Molecules	210
6.3	Electrical and Optical Properties	213
6.3.1	Metals, Semiconductors, and Insulators	213
6.3.2	Direct- versus Indirect-Gap Semiconductors	214
6.4	Representing Band Structures in Higher Dimensions	215
6.4.1	Crystal Orbitals in Two Dimensions	215
6.4.2	Crystal Orbitals in Three Dimensions	219
6.5	Band Structures of Two-Dimensional Materials	220
6.5.1	Graphene	221
6.5.2	CuO_2^{2-} Square Lattice	223
6.6	Band Structures of Three-Dimensional Materials	227
6.6.1	α -Polonium	227
6.6.2	Diamond	228
6.6.3	Elemental Semiconductors	230
6.6.4	Rhenium Trioxide	231
6.6.5	Perovskites	233
6.7	Problems	237
6.8	Further Reading	241
6.9	References	242

7 Optical Materials	243
7.1 Light, Color, and Electronic Excitations	243
7.2 Pigments, Dyes, and Gemstones	245
7.3 Transitions between <i>d</i> Orbitals (<i>d</i> -to- <i>d</i> Excitations)	246
7.3.1 Ligand- and Crystal-Field Theory	246
7.3.2 Absorption Spectra and Spectroscopic Terms	248
7.3.3 Correlation Diagrams	252
7.3.4 Selection Rules and Absorption Intensity	255
7.4 Charge-Transfer Excitations	258
7.4.1 Ligand-to-Metal Charge Transfer	259
7.4.2 Metal-to-Metal Charge Transfer	260
7.5 Compound Semiconductors	261
7.5.1 Optical Absorbance, Band Gap, and Color	262
7.5.2 Electronegativity, Orbital Overlap, and Band Gap	263
7.6 Conjugated Organic Molecules	265
7.7 Luminescence	267
7.8 Photoluminescence	268
7.8.1 Components of a Phosphor	268
7.8.2 Radiative Return to the Ground State	270
7.8.3 Thermal Quenching	272
7.8.4 Lanthanoid Activators	274
7.8.5 Non-Lanthanoid Activators	279
7.8.6 Energy Transfer	281
7.8.7 Sensitizers	283
7.8.8 Concentration Quenching and Cross Relaxation	284
7.8.9 Up-Conversion Photoluminescence	285
7.9 Electroluminescence	287
7.9.1 Inorganic Light-Emitting Diodes (LEDs)	287
7.9.2 Organic Light-Emitting Diodes (OLEDs)	289
7.10 Materials for Lighting	291
7.10.1 Fluorescent Lamp Phosphors	292
7.10.2 Phosphor-Converted LEDs for White Light	293
7.11 Problems	294
7.12 Further Reading	298
7.13 References	299
8 Dielectrics and Nonlinear Optical Materials	301
8.1 Dielectric Properties	301
8.1.1 Dielectric Permittivity and Susceptibility	302

x Contents

8.1.2	Polarization and the Clausius–Mossotti Equation	303
8.1.3	Microscopic Mechanisms of Polarizability	305
8.1.4	Frequency Dependence of the Dielectric Response	306
8.1.5	Dielectric Loss	308
8.2	Dielectric Polarizabilities and the Additivity Rule	309
8.3	Crystallographic Symmetry and Dielectric Properties	313
8.4	Pyroelectricity and Ferroelectricity	314
8.4.1	Ferroelectricity in BaTiO ₃	314
8.4.2	Antiferroelectricity	319
8.5	Piezoelectricity	321
8.6	Local Bonding Considerations in Non-Centrosymmetric Materials	324
8.6.1	Second-Order Jahn–Teller Distortions with d^0 Cations	325
8.6.2	Second-Order Jahn–Teller Distortions with s^2p^0 Cations	327
8.7	Nonlinear Optical Materials	330
8.8	Nonlinear Susceptibility and Phase Matching	331
8.9	Important SHG Materials	334
8.9.1	KH ₂ PO ₄	336
8.9.2	KTiOPO ₄	336
8.9.3	Niobates and Tantalates	338
8.9.4	Organic and Polymer NLO Materials	339
8.9.5	Borates	340
8.10	Problems	343
8.11	Further Reading	346
8.12	References	346
9	Magnetic Materials	349
9.1	Magnetic Materials and Their Applications	349
9.2	Physics of Magnetism	349
9.2.1	Bar Magnets and Atomic Magnets	349
9.2.2	Magnetic Intensity, Induction, Energy, Susceptibility, and Permeability	352
9.2.3	Unit Systems in Magnetism	355
9.3	Types of Magnetic Materials	356
9.4	Atomic Origins of Magnetism	357
9.4.1	Electron Movements Contributing to Magnetism and Their Quantization	357
9.4.2	Atomic Magnetic Moments	359
9.4.3	Magnetic Moments for $3d$ Ions in Compounds	363
9.4.4	Magnetic Moments for $4f$ Ions in Compounds	366
9.4.5	Note on Magnetic Moments of $4d$ and $5d$ Metals in Compounds	366

	Contents	xi
9.5 Diamagnetism		367
9.6 Paramagnetism		367
9.6.1 Curie and Curie–Weiss Paramagnetism		368
9.6.2 Pauli Paramagnetism		371
9.7 Antiferromagnetism		372
9.8 Superexchange Interactions		374
9.9 Ferromagnetism		377
9.9.1 Ferromagnetic Insulators and Half-Metals		381
9.9.2 Ferromagnetic Metals		382
9.9.3 Superferromagnets		384
9.10 Ferrimagnetism		385
9.11 Frustrated Systems and Spin Glasses		387
9.12 Magnetoelectric Multiferroics		388
9.13 Molecular and Organic Magnets		389
9.14 Problems		391
9.15 Further Reading		394
9.16 References		394
10 Conducting Materials		396
10.1 Conducting Materials		396
10.2 Metals		398
10.2.1 Drude Model		398
10.2.2 Free-Electron Model		402
10.2.3 Fermi–Dirac Distribution		403
10.2.4 Carrier Concentration		405
10.2.5 Carrier Mobility and Effective Mass		406
10.2.6 Fermi Velocity		407
10.2.7 Scattering Mechanisms		409
10.2.8 Band Structure and Conductivity of Aluminum		411
10.2.9 Band Structures and Conductivity of Transition Metals		412
10.3 Semiconductors		414
10.3.1 Carrier Concentrations in Intrinsic Semiconductors		414
10.3.2 Doping		416
10.3.3 Carrier Concentrations and Fermi Energies in Doped Semiconductors		419
10.3.4 Conductivity		421
10.3.5 p–n Junctions		422
10.3.6 Light-Emitting Diodes and Photovoltaic Cells		425
10.3.7 Transistors		426

xii Contents

10.4	Transition-Metal Compounds	428
10.4.1	Electron Repulsion: The Hubbard Model	428
10.4.2	Transition-Metal Compounds with the NaCl-Type Structure	431
10.4.3	Transition-Metal Compounds with the Perovskite Structure	434
10.5	Organic Conductors	437
10.5.1	Conducting Polymers	438
10.5.2	Polycyclic Aromatic Hydrocarbons	441
10.5.3	Charge-Transfer Salts	443
10.6	Carbon	445
10.6.1	Graphene	445
10.6.2	Carbon Nanotubes	447
10.7	Problems	451
10.8	Further Reading	454
10.9	References	455
11	Magnetotransport Materials	457
11.1	Magnetotransport and Its Applications	457
11.2	Charge, Orbital, and Spin Ordering in Iron Oxides	458
11.2.1	The Verwey Transition in Magnetite, Fe_3O_4	458
11.2.2	Double-Cell Perovskite, YBaFe_2O_5	460
11.2.3	CaFeO_3 and SrFeO_3	462
11.3	Charge and Orbital Ordering in Perovskite-Type Manganites	465
11.3.1	Spin and Orbital Ordering in CaMnO_3 and LaMnO_3	465
11.3.2	The $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ Phase Diagram	468
11.3.3	Tuning the Colossal Magnetoresistance	470
11.4	Half-Metals and Spin-Polarized Transport	472
11.4.1	Magnetoresistant Properties of Half-Metals	472
11.4.2	CrO_2	476
11.4.3	Heusler Alloys	477
11.4.4	Half-Metals with Valence-Mixing Itinerant Electrons	480
11.5	Problems	481
11.6	Further Reading	483
11.7	References	483
12	Superconductivity	486
12.1	Overview of Superconductivity	486
12.2	Properties of Superconductors	488
12.3	Origins of Superconductivity and BCS Theory	492
12.4	C_{60} -Derived Superconductors	500
12.5	Molecular Superconductors	505

12.6	BaBiO ₃ Perovskite Superconductors	509
12.7	Cuprate Superconductors	511
12.7.1	La ₂ CuO ₄ “214” Materials	512
12.7.2	YBa ₂ Cu ₃ O _{7-δ} “YBCO” or “123” Materials	513
12.7.3	Other Cuprates	516
12.7.4	Electronic Properties of Cuprates	517
12.8	Iron Pnictides and Related Superconductors	521
12.9	Problems	523
12.10	Further Reading	526
12.11	References	526
13	Energy Materials: Ionic Conductors, Mixed Conductors, and Intercalation Chemistry	529
13.1	Electrochemical Cells and Batteries	529
13.2	Fuel Cells	532
13.3	Conductivity in Ionic Compounds	533
13.4	Superionic Conductors	536
13.4.1	AgI: A Cation Superionic Conductor	536
13.4.2	PbF ₂ : An Anionic Superionic Conductor	539
13.5	Cation Conductors	540
13.5.1	Sodium β-alumina	540
13.5.2	Other Ceramic Cation Conductors	542
13.5.3	Polymeric Cation Conductors	543
13.6	Proton Conductors	545
13.6.1	Water-Containing Proton Conductors	546
13.6.2	Acid Salts	547
13.6.3	Perovskite Proton Conductors	548
13.7	Oxide-Ion Conductors	549
13.7.1	Fluorite-Type Oxide-Ion Conductors	552
13.7.2	Perovskite, Aurivillius, Brownmillerite, and Other Oxide Conductors	553
13.7.3	SOFC Electrode Materials and Mixed Conductors	555
13.8	Intercalation Chemistry and Its Applications	555
13.8.1	Graphite Intercalation Chemistry	556
13.8.2	Lithium Intercalation Chemistry and Battery Electrodes	559
13.8.3	Lithium-Ion Batteries with Oxide Cathodes	561
13.8.4	Electrochemical Characteristics of Lithium Batteries	568
13.8.5	Other Lithium Battery Electrode Materials	569
13.9	Problems	573
13.10	Further Reading	576
13.11	References	576

xiv Contents

14 Zeolites and Other Porous Materials	579
14.1 Zeolites	579
14.1.1 Representative Structures of Zeolites	581
14.1.2 Roles of Template Molecules in Zeolite Synthesis	586
14.1.3 Zeolites in Catalysis	588
14.1.4 Ion-Exchange Properties	593
14.1.5 Drying Agents, Molecular Sieving, and Sorption	595
14.1.6 AlPOs and Related Materials	596
14.2 Mesoporous Aluminosilicates	597
14.3 Other Porous Oxide Materials	600
14.4 Metal–Organic Frameworks (MOFs)	605
14.4.1 MOF Structures	605
14.4.2 Some Applications of MOFs	608
14.5 Problems	612
14.6 Further Reading	615
14.7 References	616
15 Amorphous and Disordered Materials	619
15.1 The Atomic Structure of Glasses	620
15.2 Topology and the Structure of Glasses	622
15.3 Oxide Glasses	625
15.4 Optical Properties and Refractive Index	625
15.5 Optical Fibers	631
15.6 Nucleation and Growth	633
15.7 The Glass Transition	634
15.8 Strong and Fragile Behavior of Liquids and Melts	639
15.9 Low-Temperature Dynamics of Amorphous Materials	642
15.10 Electronic Properties: Anderson Localization	644
15.11 Metallic Glasses	647
15.12 Problems	651
15.13 Further Reading	652
15.14 References	652
Appendix A: Crystallographic Point Groups in Schönflies Symbolism	655
Appendix B: International Tables for Crystallography	656
Appendix C: Nomenclature of Silicates	661
Appendix D: Bond-Valence Parameters in Solids	662
Appendix E: The Effect of a Magnetic Field on a Moving Charge	663
Appendix F: Coupling j – j	664

Appendix G: The Langevin Function	665
Appendix H: The Brillouin Function	666
Appendix I: Measuring and Analyzing Magnetic Properties	670
Appendix J: Fundamental Constants of Exact Value	672
References for Appendices	673
Index	674

Preface

Functional materials are an integral part of daily life. As an example, consider the materials that underpin smartphone technology. The integrated circuitry is made from complex patterns of semiconductors, metallic conductors, and insulators. Organic light-emitting diodes convert electrical signals from the processor into a vibrant high-resolution color display. The display is protected by a screen made from tough but lightweight Gorilla[®] glass, which is coated with a transparent conducting oxide to make the screen responsive to the touch of a finger. Magnetic materials are used in the speakers, a lithium-ion battery powers the device, specific dielectric materials are used to receive and isolate a call once the signal reaches a base station, and the list goes on.

This book explores the fascinating world of functional materials from the perspective of those who are tasked with inventing them, solid state chemists. We therefore adopt the chemist's definition of a material as a substance whose structure and properties are controlled at the atomic level to produce a specific function. Returning to our example, a modern smartphone contains over half of the non-radioactive elements on the periodic table. A few are used in their elemental form, but in most cases the desired function can only be achieved by combining elements to form compounds. With the periodic table as a palette, how does the chemist design and synthesize the mind-boggling variety of functional materials that future technologies depend upon? That question is the topic this book explores.

The book is written specifically with teaching in mind and is intended primarily for use in upper-level undergraduate or graduate level courses. While our perspective is that of a chemist, the book is accessible to physicists and engineers as well. Mathematical details are given where they add deeper understanding, but the focus is always on relating the properties of a material to the characteristics of the atoms and molecules from which it is built.

The first six chapters cover the fundamentals of extended solids: crystal structures, defects, reactivity, phase diagrams, phase transitions, chemical bonding, and band structure. The remaining chapters, each of which is organized around a specific property or class of materials, show how the properties of modern functional materials can be understood from these fundamental concepts. Recognizing that the field of solid state chemistry is much more expansive than can be covered in a single course, the later chapters are designed to be largely independent of each other. This organization provides the instructor freedom to tailor a course to cover those materials that are most relevant for their students.

Coverage of inorganic and organic materials is interwoven throughout the book to place the emphasis on properties. To keep the scope at a manageable level, neither synthesis nor

xviii Preface

characterization are covered in detail. Instead, boxes on synthetic methods and characterization methods are placed throughout the book to highlight specific examples. In a similar vein, boxes are used to describe how the properties of nanoscale solids differ from bulk materials (Nanoscale Concepts), and to highlight important technological applications of materials (Materials Spotlight). Students learn by practice, and, in this spirit, we have included dozens of problems at the end of each chapter to allow students to test their understanding of the concepts covered in the chapter. Instructors can obtain a full set of worked solutions on request.

We hope that this book will be a valuable source of learning for the next generations of solid state scientists and engineers and a resource for those who already work in this fascinating field.

**Patrick Woodward
Pavel Karen
John Evans
Thomas Vogt**

Acknowledgments

We are indebted to several organizations and countless people for their support and encouragement. PMW would like to acknowledge the Leverhulme Foundation for supporting his stay at Durham University as a Visiting Professor during the 2017–2018 academic year. TV spent the beginning of 2018 as a Fellow at Durham University’s Institute of Advanced Study. He is grateful to Linda Crowe and the rest of the team at the institute, as well as David Wilkinson, Principal at St. John’s College, for their warm hospitality and for providing an environment so conducive to scholarly work. These overlapping stays in Durham were instrumental in making the final push to finish this book. PMW is grateful for many years of support from the Solid State Materials Chemistry program of the National Science Foundation. PMW and JSOE thank Arthur Sleight for inspiration and early career mentoring. In these data-dominated times, PK is grateful to the now Professor Jiří Hanika for teaching Fortran programming in the 1970/1 course Computational Technology at the VŠCHT in Prague, and to the now Ing. František Hovorka, CSc, for the idea of taking an external typing course during the sophomore year 1967/8 at the SPŠCH Praha. We all would like to thank both colleagues and students who provided key feedback on early versions of the chapters. Finally, we thank our families for their patience and support over this long journey.