Materials Engineering

Bonding, Structure, and Structure–Property Relationships

Designed for both one- and two-semester courses, this textbook provides a succinct and easy-to-read introduction to crystal structures and structure-property relations. By linking together the fundamentals of bond strength and the arrangement of atoms in space with the mechanical, optical, magnetic, and electrical properties that they control, students will gain an intuitive understanding of how different materials are suited to particular applications. The systematics of crystal structures are described for both organic and inorganic materials, with coverage including small molecular crystals, polymers, metals, ceramics, and semiconductors. Hundreds of figures and practice problems help students gain an advanced, 3D understanding of how structure governs behavior, and a wealth of examples throughout show how the underlying theory is translated into practical devices. With solutions, video lectures, and PowerPoints available online for instructors, this is an excellent resource for graduates and senior undergraduates studying materials science and engineering.

Susan Trolier-Mckinstry is the Steward S. Flaschen Professor of Ceramic Science and Engineering, Professor of Electrical Engineering, and Director of the Nanofabrication Facility at Pennsylvania State University. She was also the 2017 President of the Materials Research Society (MRS), and is a fellow of the IEEE, MRS, and the American Ceramic Society.

The late **Robert E. Newnham** was a professor in the Department of Materials Science and Engineering at Pennsylvania State University and a member of the National Academy of Engineering. He was the recipient of numerous awards, including the John Jeppson Medal from the American Ceramic Society and the Turnbull Lecturer Award from the Materials Research Society.

Materials Engineering

Bonding, Structure, and Structure–Property Relationships

SUSAN TROLIER-McKINSTRY
Pennsylvania State University

ROBERT E. NEWNHAM
Pennsylvania State University

CAMBRIDGE
UNIVERSITY PRESS

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

79 Anson Road, #06–04/06, Singapore 079906

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/9781107103788
DOI: 10.1017/9781316217818

First published 2018

Printed in the United States of America by Sheridan Books, Inc., 2017

A catalog record for this publication is available from the British Library.

Library of Congress Cataloging-in-Publication Data
Names: Trolier-McKinstry, Susan, 1965– author. | Newnham, Robert E. (Robert Everest), 1929–2009 author.
Title: Materials engineering : bonding, structure, and structure–property relationships / Susan Trolier-McKinstry, Pennsylvania State University, Robert Newnham, Pennsylvania State University.
Description: Cambridge, United Kingdom ; New York, NY, USA : Cambridge University Press, [2017] | Includes bibliographical references and index.
Identifiers: LCCN 2017024291 | ISBN 9781107103788 (hardback : alk. paper)
Subjects: LCSH: Materials.
Classification: LCC TA403 .T746 2017 | DDC 620.1/1–dc23 LC record available at https://lccn.loc.gov/2017024291

ISBN 978-1-107-10378-8 Hardback

Additional resources available at www.cambridge.org/trolier-mckinstry

This book is dedicated to the memory of Professor Robert E. Newnham, an extraordinary scientist, engineer, and educator.

For my family. Thank you for your patience and your love.

Susan Trolier-McKinstry

Cambridge University Press
978-1-107-10378-8 — Materials Engineering
Susan Trolier-McKinstry , Robert E. Newnham
Frontmatter
More Information

Contents

Foreword

Use of this Book for Different Classes

The intended audience is primarily undergraduate or beginning graduate students in materials science and engineering. That said, the book is written in such a way that it could be used as a text for a single class in materials to be taught to engineering students in other disciplines (civil, electrical, and mechanical, in particular).

Professor Newnham was a great believer in looking at structure models of crystals, dreaming he was an ångström (Å) high – walking around inside the crystals, hopping across grain boundaries and domain walls, pushing on the atomic bonds. Both he and I have thought about crystals, ceramics, metals, semiconductors, polymers, and their properties for many years. The ability to visualize crystal structures and the connectivity of strong and weak bonds in materials provides tremendous insight. Hence, this text is liberally illustrated with figures of crystal structures, all of which were drawn using CrystalMaker™. Numerous good drawing programs exist; students are strongly urged to explore both three dimensional hand models as well as computer packages so that they can develop an intuitive understanding of symmetry.

The modus operandi of materials research and development programs is to seek fundamental understanding while working toward an engineering goal and remaining alert for new applications. One of the best ways of introducing this line of thinking is to develop an understanding of the structure–property relationships.

I use this book to teach both undergraduate and graduate classes in Crystal Chemistry at Penn State.

The undergraduate course is a junior level class, intended to provide many of the underpinnings of the field to the student. The perspective begins from the structure and bonding of the solid, and uses this to provide students with an intuitive understanding of how materials are designed or chosen for particular applications.

Prerequisite knowledge includes:

- some chemistry (typically two semesters of College Chemistry)
- vector math
- some physics (particularly a class in waves, so that the ideas of phonons and photons are not new).

Course Objectives

(a) To identify important raw materials and minerals as well as their names and chemical formulas.

(b) To describe the crystal structure of important materials and to be able to build their atomic models.

(c) To learn the systematics of crystal and glass chemistry.
(d) To understand how physical and chemical properties are related to crystal structure and microstructure.
(e) To appreciate the engineering significance of these ideas and how they relate to industrial products: past, present, and future.

Course Outcomes

(a) Students should be able to write and balance chemical formulae for commercially important raw and engineered materials.
(b) Students should be able to build important crystal structures and understand the impact of bond length, coordination, and symmetry on the resultant physical properties.
(c) Given an initial chemistry, students should be able to apply Pauling's rules to determine anion and cation coordinations, and should be able to make intelligent suppositions about the resulting crystal structure. Similarly, on the basis of Zachariasen's rules, students should be able to assess the likelihood of easy glass formation in a particular materials system.
(d) Students should understand the rules governing the stability of crystal structures as a function of temperature, pressure, and composition changes.
(e) Students should understand the basic mechanisms controlling a wide variety of physical properties, and should be able to correlate this information with crystal structures to predict materials properties.
(f) Students should begin to understand how materials are chosen and designed for particular engineering applications.

The best way of visualizing the atomic structures of materials is to build models. It is easy to see why graphite is a good lubricant, how slip occurs in metals, and why barium titanate develops a spontaneous polarization. Table F.1 lists the models built in the introductory course. Thirty hours of model building are accompanied by information discussing atomic coordination, chemical bonding, crystallographic symmetry, and structure–property relations. Raw material specimens and commercial products are circulated amongst the students to emphasize the usefulness of the materials being modeled. Of course, the structures selected can be modified to best suit particular disciplines: in classes taught to civil engineers, it is recommended that the cement structures alite, belite, and tobermorite be substituted for the last lab listed.

The first four laboratory sessions are devoted to basic structures illustrating the five principal types of chemical bonding. After that point, more sophisticated model building is pursued. It is important to move beyond the elementary crystal structures of rocksalt, diamond, and the metal structures. In building the models, we use the Orbit and Minit Molecular Building Systems™ utilizing flexible plastic straws and connectors, available from Cochranes of Oxford, Ltd. It is critical to utilize a building system that allows coordinations from 1 to 12.

Discussions of anisotropy develop naturally from crystal models. A simple example comes from the structures of graphite and boron nitride. Thermal conductivity coefficients are much higher parallel to the layers than in the perpendicular direction.

Table F.1 Crystal structures assembled in introductory crystal chemistry

Ionic solids	Halite and fluorite
Covalent crystals	Diamond, zincblende, and wurtzite
Metals	Copper (FCC), iron (BCC), and magnesium (HCP)
Molecular solids	Ice, pentacene, and coupling agents
Polymers	Polyethylene, polypropylene, polystyrene, and silicones
Structures with anisotropy	Rutile, graphite, and hexagonal BN
Octahedral coordinations	Brucite, gibbsite, and corundum
Classification of silicate structures	Isolated silicates, ring structures, single and double chains, zeolites
Layer silicates	Kaolinite, serpentine, talc, micas
Silica phases and stuffed derivatives	Cristobalite, tridymite, and their stuffed derivatives
Raw materials	Feldspars, beryl, and cordierite
Optical and electronic ceramics	Calcite and perovskite
Magnetic structures and defects	Spinels, β-alumina, edge and screw dislocations
Pb^{2+} and B^{3+} coordinations, and non-oxide ceramics	PbO, borax, and silicon nitride

Table F.2 Selected empirical rules of thumb of importance in materials science and engineering

- Goldschmidt's rules for atomic coordination changes at high temperature and pressure.
- Hume-Rothery and Brewer predictions for metallic structures and solid solutions.
- Line and Matthiessen rules for electrical conductivity of alloys.
- Mooser–Pearson rules for semiconductors.
- Pauling's rules for ionic coordination and crystal structures.
- Shewmon and Tamman rules for diffusion coefficients and annealing temperatures.
- Trouton formula for latent heat of evaporation and boiling point.
- Weidenmann–Franz law relating thermal and electrical conductivity of metals.
- Zachariasen's rules for oxide glass formation and structure.

This structure–property relationship can be further amplified with discussions of the correlations between thermal conductivity and chemical bonding, and with bond length.

"Rules of thumb" help put students in touch with reality, since most involve properties of practical importance. They provide the physical and chemical intuition required for back of the envelope calculations, and for rapid recall at technical meetings. Table F.2 lists several of these rules. Common sense ideas like these also facilitate discussion of more theoretical concepts, and provide a link to the advances in materials modeling.

For the graduate course, the outline is as follows.

Definition of Crystal Chemistry
Elements of Crystallography
  Symmetry
  Space Groups and Point Groups
  Coordination

- Bonding
  - Covalent Bonding
  - Ionic Bonding
  - Metallic Bonding
  - Hydrogen Bonding
  - Van der Waals Bonding
  - Ionic and Atomic Radii
  - Crystal Field Theory
  - Molecular Orbital Theory
  - Band Theory
- Defects
- Structure Prediction
  - Pauling's Rules
  - Bond Valence Sums
  - 8 – *N* Rule
  - Metal Structure Prediction
  - Structure Field Maps
  - Pressure–Temperature Variations
- Important Structure Types
  - Ionically Bonded Materials
  - Metallically Bonded Materials
  - Covalently Bonded Materials
  - Small Molecule Crystals
  - Polymers
  - Glasses
- Structure–Property Relations
  - Neumann's Law
  - Thermal Properties
  - Electrical Conductivity
  - Dielectric Properties
  - Optical Properties
  - Magnetism
  - Mechanical Properties

This book will not describe two of the other pillars of materials science and engineering: processing and its link to microstructure, and materials characterization.

Acknowledgements

Portions of this book were adapted from previous works by Professor Robert E. Newnham. We gratefully acknowledge Elsevier for permission to adapt material from R. E. Newnham, "Phase diagrams and crystal chemistry," in *Phase Diagrams: Materials Science and Technology, Volume V*, Academic Press, NewYork (1978). We are similarly grateful to Springer-Verlag for permission to reuse and adapt material from R. E. Newnham, *Structure–Property Relations*, Springer-Verlag (1975).

Professor Newnham knew the name and chemical formula of all the minerals, and usually knew the crystal structure. He combined this knowledge with a breadth of understanding of the fundamental mechanisms responsible for various properties. As a result, he was often able to predict the likely material response from the chemical formula, and use this to solve engineering problems.

Bob received numerous prizes and honors over the course of his career, including the Franklin Medal for Electrical Engineering for development of the composite transducers now ubiquitous in medical ultrasound. One of the stories that he told over the years about the genesis of the idea was that he recognized that SbSI, a one-dimensional ferroelectric, had some of the key properties: strong bonding along the axis of the SbSI chains that produced a strong piezoelectric response in that direction; weak bonding between the chains that degraded the coupling to motion perpendicular to the chains. Then, it was simply a matter of artificially creating the desired connectivity in a material that is less electrically leaky. At this point, there are thousands to millions of people whose lives have been saved by this inspired application of structure–property relations.

It was Bob's hope as well as mine, that this book would inspire more generations of scientists to learn about structures and structure–property relations.

There are a great many people to thank for helping make this book a reality.

A small army of proofreaders has helped improve the text over the years – from students in MATSE 400 or MATSE 512 at Penn State, to Igor Levin, Cihangir Duran, Barry Scheetz, Della Roy, Paolo Colombo, Allison Beese, Michael Hickner, Robert Hickey, Wanlin Zhu, Thomas N. Jackson, Jon-Paul Maria, Jon Ihlfeld, Kim Trolier, and Michael Trolier. Thank you, thank you, thank you! Remaining errors are my responsibility.

This manuscript is strongly dependent on figures. The crystal structures were rendered in Crystal Maker™. Several people helped with figures along the way, including Ryan Haislmaier, Aileen McKinstry, Nathan McKinstry, and Herb McKinstry.

Finally, my family has been both enormously patient and supportive of the time it has taken to finish this. You all are my heroes.

Acknowledgements from the Family of Professor Robert Newnham

On behalf of Professor Robert Newnham's family, we would like to thank his friend and valued colleague, Professor Susan Trolier-McKinstry, for her work in carrying on our father's legacy. At the time of his death in 2009, Dad and Susan had written only about a quarter of this book, so it is very generous of her to share full co-author credit with my father on this final version, which is largely her work.

Susan's dedication does an excellent job in describing our father's scientific legacy. But there was much more to him than his work. First, he was a very kind and devoted family man, and is warmly remembered by his children, Randall and Rosemary, their spouses, Janet and Patrick, his grandchildren, Johnathan Robert, Henry Everest, and Eleanor Patricia, and a large extended family. He and our mother Patricia treated Dad's colleagues as family, too, including them in hikes, picnics, and family holiday celebrations. They enjoyed visiting his academic "children" and "grandchildren" all over the world. Second, he always approached his work – and his life – with a sense of imagination and fun, which we hope readers of this book will be able to share. For example, he opened the Preface of his first book with these words, to explain how he developed his love of structures as a child:

> As a boy I loved to build model airplanes, not the snap-together plastic models of today, but the old-fashioned Spads and Sopwith Camels made of balsa wood and tissue paper. I dreamed of Eddie Rickenbacker and dogfights with the Red Baron as I sat there sniffing airplane glue. Mother thought I would never grow up to make an honest living, and mothers are never wrong. Thirty years later I sit in a research laboratory surrounded by crystal models and dream of what it would be like to be one Angstrom tall, to rearrange atoms with pick and shovel, and make funny things happen inside.[1]

Reading these words again, we can picture our father laughing as he wrote them, before turning to work on another of the carefully constructed crystal models which littered his office. We hope this book will inspire you to cultivate some of the same joy and wonder in the natural world that our father felt since he was a little boy.

Randall and Rosemary Newnham, July 2016

[1] Robert E. Newnham, *Structure–Property Relations*. Berlin: Springer-Verlag (1975).