

## ELECTRONIC BASIS OF THE STRENGTH OF MATERIALS

This book is the first to relate the complete set of strength characteristics to the electronic structures of the constituent atoms. These relationships require knowledge of both the chemistry and physics of materials. Also, the book uses both classical and quantum mechanics since both are needed to describe the properties of atoms. The book begins with short reviews of the two mechanics. Following these reviews, the three major branches of the strength of materials are given their own sections. They are: the elastic stiffnesses; the plastic responses; and the nature of fracture.

Elastic deformation can be reduced to two pure types: volume changes, and shape changes (shears). The moduli (stiffnesses) associated with each of these can be quantitatively obtained by means of the Heisenberg Principle and the theory of polarizability. The analytic theories are simple enough to indicate the physical origins of these properties. The most important atomic properties are the valence electron densities, and the electronic polarizabilities. These lead to electron exchange forces, and photon exchange forces, respectively. Atomic, molecular, and plasmonic polarizabilities play important roles. The anomalously large shear stiffness of diamond is explained in terms of the distribution of electrons along the covalent bonds, resulting from electron correlation.

For plastic deformation, the critical role of dislocation mobility is discussed. In nearly perfect metal crystals (and ionic salts) there is no quasi-static resistance to dislocation motion (only electron and phonon viscosity). Resistance in imperfect crystals is caused by extrinsic factors. In nearly perfect covalent crystals (semiconductors), dislocation mobility is intrinsically limited by the localized chemical bonds. Using diamond as the prototype, a quantitative theory of intrinsic mobility is presented.

Fracture is discussed in terms of intrinsic surface energies and their effects on the fracture surface energies of real materials. Two simple approaches are discussed. One is based on the Heisenberg Principle, the other on the plasmon theory of Schmit and Lucas. The latter may be important for understanding ductility.

This book presents a comprehensive view of the relationships between the electronic structures of solids and the microscopic and macroscopic mechanical properties of solid materials. It will be of great value to academic and industrial research workers in the sciences of metallurgy, ceramics, micro-electronics, and polymers. It will serve well as a supplementary text for the teaching of solid mechanics.

# ELECTRONIC BASIS OF THE STRENGTH OF MATERIALS

JOHN J. GILMAN



Cambridge University Press  
 0521620058 - Electronic Basis of the Strength of Materials  
 John J. Gilman  
 Frontmatter  
[More information](#)

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE  
 The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS  
 The Edinburgh Building, Cambridge CB2 2RU, UK  
 40 West 20th Street, New York, NY 10011-4211, USA  
 477 Williamstown Road, Port Melbourne, VIC 3207, Australia  
 Ruiz de Alarcón 13, 28014 Madrid, Spain  
 Dock House, The Waterfront, Cape Town 8001, South Africa

<http://www.cambridge.org>

© John Gilman 2003

This book 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 2003

Printed in the United Kingdom at the University Press, Cambridge

*Typeface* Times 10/13 pt    *System* L<sup>A</sup>T<sub>E</sub>X 2<sub>ε</sub> [TB]

*A catalogue record for this book is available from the British Library*

*Library of Congress Cataloguing in Publication data*

Gilman, John J. (John Joseph)  
 Electronic basis of the strength of materials / John J. Gilman.  
 p.      cm.

Includes bibliographical references and index.

ISBN 0 521 62005 8

1. Strength of materials.    2. Electronic structure.    I. Title.

TA405 .G54    2003

620.1'12 – dc21    2002073591

ISBN 0 521 62005 8 hardback

## Contents

	<i>Preface</i>	<i>page ix</i>
<b>Section I</b>	<b>Introduction</b>	1
<b>Section II</b>	<b>Elements of solid mechanics</b>	5
	1 Nature of elastic stiffness	5
	2 Generalized stress	9
	2.1 Specification of a plane	10
	2.2 Resolution of an area element	11
	2.3 Resolution of a force element	12
	2.4 Definition of the local state of stress	12
	2.5 Principal stresses	14
	3 Generalized strain	16
	4 Elastic coefficients	20
	4.1 Cubic crystals	23
	4.2 Strain energy	24
	4.3 Contracted notation	24
	4.4 Young's modulus	25
	4.5 Cauchy's relations	27
<b>Section III</b>	<b>Elements of electron mechanics</b>	31
	5 Properties of electrons	31
	6 Quantum states	37
	6.1 Wave-like fields	38
	6.2 Particle on a ring	40
	6.3 Particle on a sphere	42
	6.4 The most simple atom (hydrogen)	45
	6.5 Electron spin	49
	6.6 The Pauli Principle	50
	6.7 Summing up	51
	7 Periodic patterns of electrons	52
	8 Heisenberg's Principle	56
	8.1 Heisenberg hydrogen atom	60

<b>Section IV</b>	<b>Elastic stiffness</b>	63
	9 Cohesion of atoms	63
	9.1 Limiting bond types	66
	9.2 Covalent bonds	67
	9.3 The importance of symmetry factors	69
	9.4 Ionic bonding	73
	9.5 Metallic bonding	73
	9.6 London forces	74
	9.7 Hydrogen bonding	75
	9.8 Magnetic contributions to cohesion	75
	10 Intramolecular cohesion	77
	10.1 Covalent diatomic molecules (time independent)	77
	10.2 Time dependent theory (resonance)	80
	10.3 Polyatomic molecules	87
	11 Intermolecular cohesion	97
	11.1 London forces	97
	11.2 Polarizability	100
	11.3 Casimir forces	103
	11.4 Derjaguin forces	103
	11.5 Dipole–dipole crystals	103
	11.6 Hydrogen bonds	106
	12 Bulk modulus	110
	12.1 Bulk stiffnesses of the elements (chemical factors)	111
	12.2 Metals	113
	12.3 Simple metals	113
	12.4 Alkali metals	115
	12.5 Transition metals	117
	12.6 Theory of the bulk modulus (simple metals)	121
	12.7 The lanthanides	128
	12.8 Hard metals (metalloid–metal interstitial compounds)	128
	12.9 Intermetallic compounds	129
	12.10 Covalent crystals	129
	12.11 Ionic crystals	133
	12.12 Fluorites	137
	12.13 Chalcogenides (oxygen column of the Periodic Table)	137
	12.14 Silicates	138
	12.15 Molecular crystals	139
	13 Shear modulus	142
	13.1 General comments	142
	13.2 Shear stiffnesses	143
	13.3 The Cauchy relations	146

*Contents*

vii

13.4	Simple metals	147
13.5	Failure of radial potentials	150
13.6	Alkali metals	153
13.7	Compounds	155
13.8	Ionic crystals	159
13.9	Covalent crystals	162
13.10	Isotope effect	169
13.11	Quasicrystals	169
13.12	Polymers	170
13.13	Atomic vibrations	171
14	Entropic elasticity (polymers)	174
14.1	Introduction	174
14.2	Enthalpic stiffness	175
14.3	Entropic stiffness	175
14.4	Rubbery elasticity	176
15	Universality and unification	179
15.1	Bulk modulus	180
15.2	Shear stiffness	181
15.3	Plastic resistance (physical hardness)	181
15.4	Shear-induced phase transitions	182
15.5	Shear-induced chemical reactions	182
<b>Section V</b>	<b>Plastic strength</b>	185
16	Macroscopic plastic deformation	185
16.1	Distinction between elastic and plastic deformations	187
16.2	Plastic equation of state	188
16.3	Modes of plastic deformation	189
17	Microscopic plastic deformation	193
17.1	Plasticity as linear transport	193
17.2	Multiplication of dislocations	195
17.3	Some kinematics	198
17.4	Importance of dislocation mobility	199
18	Dislocation mobility	201
18.1	Introduction	201
18.2	Mobilities, general	201
18.3	Dislocations with low mobilities	204
18.4	Steadiness of motion	205
18.5	Resistance to individual dislocation motion	206
18.6	Chemical theory of dislocation mobility	224
18.7	Molecular solids	234
18.8	Alloys and intermetallic compounds	236
18.9	Oxide crystals (including silicates)	238

18.10	Glasses	239
18.11	Self-interactions (strain hardening)	240
18.12	Activation of motion	241
<b>Section VI</b>	<b>Fracture resistance</b>	247
19	Mechanics of cracks	247
19.1	Elements of cracking	247
19.2	Fracture surface energies	249
19.3	Inelastic effects	251
19.4	Environmental factors	252
20	Surface and interfacial energies	254
20.1	Introduction	254
20.2	Surface states	255
20.3	Surface energies	257
20.4	Surface energy from the Heisenberg Principle	258
20.5	Surface energy from elastic stiffness	260
20.6	Surface energy from plasmon theory	261
20.7	Interfacial energies from plasmon theory	262
20.8	Long-range attraction of cleavage faces	262
20.9	Importance of polarizability	265
21	Fracturing rates	267
21.1	Introduction	267
21.2	Thermal activation	267
21.3	Fracture via tunneling	269
21.4	Zener tunneling	271
21.5	Conformance of experimental data with the tunneling equation	272
	<i>Index</i>	277

## Preface

In the middle of the twentieth century it was recognized that the theory of the mechanics of continua (particularly solid mechanics) is not adequate to account for the strength properties of materials. It was clear that structural considerations at the microscopic and nanoscopic levels of aggregation are not only important but are essential to an understanding of the strengths of materials. It also came to be realized, as a result of the fact that plastic shear deformation is usually heterogeneous, that a space can be continuous but not simply connected, that is, dislocated. Also, in crystals, such dislocations are quantized, having constant displacements equal to the magnitudes of translation vectors of the crystal structure.

Although structural geometry plays an essential role in determining mechanical behavior, it leaves a number of questions unanswered. The answers to these questions can only be found by considering the electronic structure that underlies the geometric factors. Since the behavior of electrons is not described by classical mechanics, this necessitates the use of quantum mechanics to obtain answers to the various unanswered questions. For example, why is the shear stiffness of diamond greater than its volumetric stiffness? Why do the most simple metals, the alkalis, have body-centered cubic crystal structures which are not atomically close packed? Why is pure silicon brittle, while pure nickel is quite ductile? They both have the same crystal structure, so why is pure TiC hard, while pure NaCl is soft? Why do intermetallic compounds often change their color when they are plastically deformed? What determines the temperature dependences of yield stresses? Why are grain boundaries weak? What activates plastic flow and crack growth at low temperatures where there are no thermal fluctuations? Only the subatomic behavior of electrons can account for these phenomena. This is the theme of this book.

I recall seeing a review of a book (*Electronic Structure and the Properties of Solids*) by Walter Harrison that called it “idiosyncratic”. It is that, but it is also comprehensive and instructive as only a lifetime of scholarship could make it. This book is also idiosyncratic. That is, it is one person’s view of a vast and complex subject. Whether it is instructive is a verdict to be brought by readers.

This book differs from most books dealing with electronic structure which introduce the formalities of quantum mechanics, and then circumvent them with approximations and numerical computations. Here, it is assumed that solids are so complex that it is better to make the approximations first, and then try to show that they are consistent with the basic



rules of quantum mechanics, and that they yield properties consistent with the measured values. In this regard much use is made of Heisenberg's Theorem in its exact form, so there is nothing uncertain about it. It is an approximate solution of Schrödinger's equation.

Perhaps the most controversial topic in the book is that of dislocation mobility. Together with W.G. Johnston, the author made the first direct measurements of dislocation mobility, and therefore has some knowledge of its intricacies. The latter have not been described consistently in much of the extant literature. A purpose of this book is to correct this.

Sometimes explicitly, and often implicitly, the electronic properties on which the strength properties depend are the valence charge density, and the electronic polarizability. The reader should have a better appreciation of this after reading this book. Since these are also the electronic properties that primarily determine the optical and the chemical properties, this demonstrates the unity that exists among the various properties.