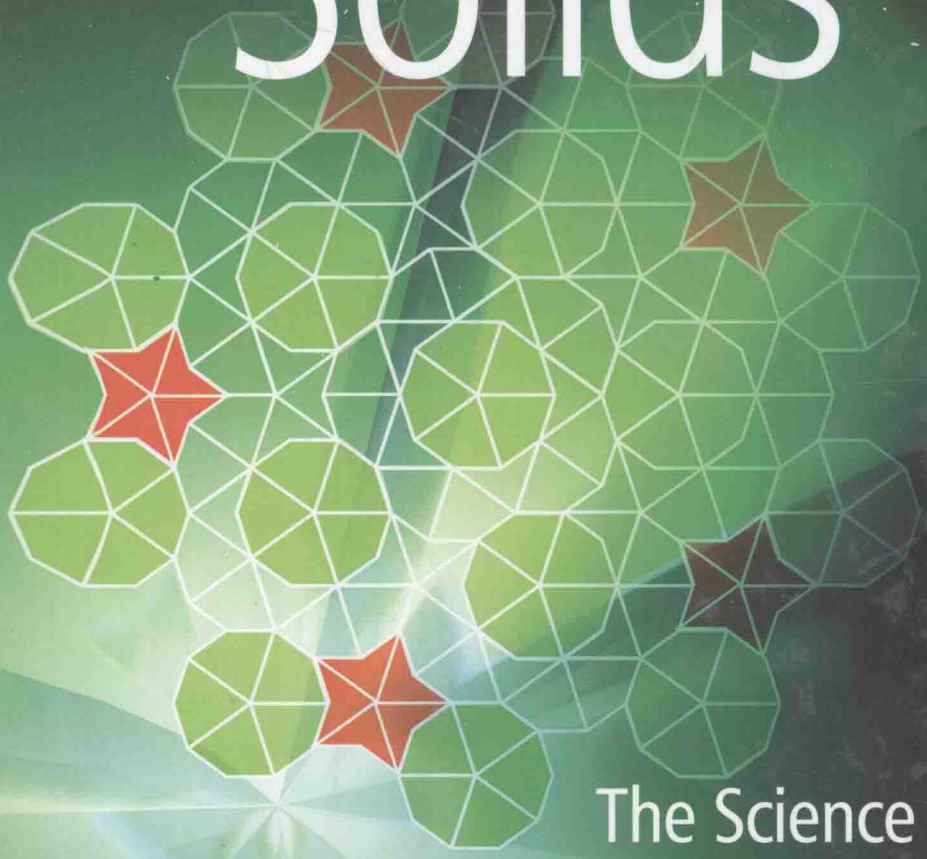
Richard J. D. Tilley

Second Edition

Understanding Solids



The Science of Materials

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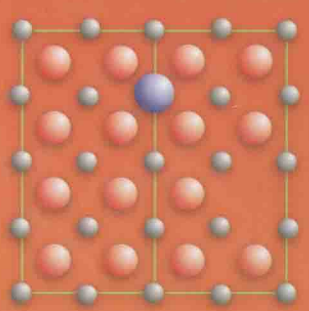

Understanding Solids

The Science of Materials

2nd edition

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Understanding Solids

For Anne

Preface to the Second Edition

In this edition the structure of the First Edition has been retained. However, in the intervening years an enormous number of new experimental and theoretical studies have appeared in the literature, and although this is an introductory text, many of these new studies merit reporting. The additions are spread throughout the text, but can be roughly divided into four groups. The first area is computational science and engineering. Computer simulations of the behaviour of solids, from the engineering of large-scale structures using finite element analysis, via atomistic simulation and molecular dynamics, used to study features such as elastic behaviour and dislocation movement, through to the calculation of the electronic properties of solids via density functional theory, are used routinely in almost all disciplines that are related to the subject matter of this book. The computer calculation of phase diagrams (CALPHAD) also comes into this category. An indication of the principles underlying these programmes of work is given to underpin the computational "black boxes" available (Chapters 1, 2, 4 and 10).

Another area of change is that concerned with nanoscale properties. Here, not only is the primary literature growing rapidly but there are a rapidly increasing number of specialised books that deal with the subject. Some of the properties that are affected by small scales are described, including the magnetic and ferroelectric properties of thin films and superlattices (Chapters 11 and 12) and nanoparticle colours (Chapter 14).

Point defects are key components for the manipulation of the physical properties of solids, and this area has been supplemented. The universally used Kroger-Vink notation for point defects has been defined (Chapter 3). The interplay between defect populations and ionic conductivity (Chapter 7), relaxor ferroelectrics (Chapter 11), the electronic and magnetic properties of cobaltites and manganites, including colossal magnetoresistance (Chapter 12, 13), cuprate superconductors (Chapter 13) and thermoelectric properties (Chapter 15) are described.

New text has also been added to cover a number of important crystallographically related topics. These include quasicrystals (Chapter 3), phase transformations including first- and second-order transitions, displacive versus reconstructive transitions and order–disorder transitions, and martensitic transitions (Chapter 9), and coverage of crystal symmetry with respect to piezoelectricity (Chapter 11).

Other new topics include lithium-air batteries (Chapter 8), increased discussion of elastic moduli and their measurement using ultrasonic waves (Chapter 10), the newly appreciated physical property of flexoelectricity (Chapter 11), crystal field effects, the magnetic properties of garnets and photoinduced magnetism (Chapter 12), dye-sensitized solar cells (Chapter 14), zero thermal expanding solids (Chapter 15), increased discussion of nuclear stability and radioisotope dating (Chapter 16).

The text on all these topics is necessarily compact, but can be supplemented by reference to extensive additional sources listed in the Further Reading sections.

Because of this expansion of material, of necessity some sections of the original have had to be excised. For the same reason, much of the supplementary information in the first edition has been

removed or incorporated into the relevant chapters. In making these changes, all the material has been rewritten and rearranged to the extent that no single page of this edition is identical to any in the first edition. In addition, all figures have been redrawn in colour. These, together with the solutions to the Introductory Questions and Problems and Exercises, are to be found on a companion web site (http://www.wiley.com/go/tilleysolids2e).

It is a pleasure to acknowledge the help from the staff at John Wiley, including Rebecca Stubbs, Emma Strickland and Sarah Tilley, all of whom were enthusiastic about this project and fielded my many queries efficiently. The staff of the Trevithick library in Cardiff University provided, as always, help in tracking down obscure references. Professor F.S. Stone and Dr D.F. Klemperer were generous in their encouragement. Finally I must acknowledge my wife Anne, who has continually supported and helped in more ways that it is possible to record.

R.J.D. Tilley
August 2012

Preface to the First Edition

This book originated in lectures to undergraduate students in materials science, which were later extended to geology, physics and engineering students. The subject matter is concerned with the structures and properties of solids. The material is presented with a science bias, and is aimed not only at students taking traditional materials science and engineering courses, but also courses in the rapidly expanding fields of materials chemistry and physics. The coverage aims to be complementary to established books in materials science and engineering. The level is designed to be introductory in nature, and as far as is practical, the book is self-contained. The chapters are provided with questions designed to reinforce the concepts presented. These are in two parts. A multiple choice 'Quick Quiz' is designed to be tackled rapidly, and aims to uncover weaknesses in a student's grasp of the fundamental concepts described. The 'Calculations and Questions' are more traditional, containing numerical examples to test the understanding of formulae, and derivations that are not carried out in the main body of the text. Many chapters contain one or more appendices that bear directly upon the material, but which would disrupt the flow of the subject matter if included within the chapter itself. These are meant to provide more depth than is possible otherwise. Further Reading allows students to take matters a little further. With only one exception, the references are to printed information. In general, it would be expected that a student would initially turn to the Internet for information. Sources here are rapidly located and this avenue of exploration has been left to the student.

The subject matter is divided into five sections. Part 1 covers the building blocks of solids. Here the topics centre upon atoms and bonding, and the patterns of structure that result. In this section, the important concepts of microstructure and macrostructure are developed, leading naturally to an understanding of why nanostructures possess unique properties. Defects that are of importance are also described here. Part 2 is concerned with the traditional triumvirate of metals, ceramics and polymers, together with a brief introduction to composite materials. The subject is condensed into a single chapter. It provides an overview of a comparative nature, focused upon giving a broad appreciation of why the fundamental groups of materials appear to differ so much, and laying the foundations for why some, such as ceramic superconductors, seem to behave so differently from their congeners. Part 3 has a more chemical bias, and describes reactions and transformations. The principles of diffusion are outlined in Chapter 7; electrochemical ideas, which lead naturally to batteries, corrosion and electroplating, are described in Chapter 8. Solid-state transformations, which impinge upon areas as diverse as shape memory alloys, semiconductor doping and sintering, are introduced in Chapter 9. Part 4 is a description of the physical properties of solids, and complements the chemical aspects detailed in Part 3. The topics covered are those of importance to both science and technology, mechanical, Chapter 10, insulators, Chapter 11, magnetic, Chapter 12, electronic, Chapter 13, optical, Chapter 14, and thermal, Chapter 15. Part 5 is concerned with radioactivity. This topic is of enormous importance, and

in particular the disposal of nuclear waste in solid form is of pressing concern.

The material in all of the later sections is founded upon the concepts presented in Part 1, that is, properties are explained as arising naturally from the atomic constituents, the chemical bonding, the microstructures and defects present in the solid. This leads naturally to an understanding of why nanostructures have seemingly different properties from bulk solids. Because of this, nanostructures are not gathered together in one section, but considered throughout the book, in the context of the better-known macroscopic properties of the material.

It is a pleasure to acknowledge the help of Dr A. Slade and Mrs Celia Carden of John Wiley, who have given continual encouragement and assistance to this venture. Ms Rachael Catt read the complete manuscript with meticulous care, exposed ambiguities and inconsistencies in both text and figures, and added materially to the final version. Mr Allan Coughlin read large parts of earlier drafts, clarified many obscurities and suggested many improvements. Mr Rolfe Jones has provided information and micrographs of solids whenever called upon. As always, my family has been ever-supportive during the writing of this book, and my wife Anne has endured the hours of being a computer widow without complaint. To all of these, my heartfelt thanks.

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