Imperfections in Crystalline Solids

This textbook provides students with a complete working knowledge of the properties of imperfections in crystalline solids. Readers will learn how to apply the fundamental principles of mechanics and thermodynamics to defect properties in materials science, gaining all the knowledge and tools needed to put this into practice in their own research.

Beginning with an introduction to defects and a brief review of basic elasticity theory and statistical thermodynamics, the authors go on to guide the reader in a step-by-step way through point, line, and planar defects, with an emphasis on their structural, thermodynamic, and kinetic properties.

Numerous end-of-chapter exercises enable students to put their knowledge into practice, and with solutions for instructors and MATLAB programs available online, this is an essential text for advanced undergraduate and introductory graduate courses in crystal defects, as well as being ideal for self-study.

Wei Cai is an Associate Professor in the Department of Mechanical Engineering at Stanford University. He received the Presidential Early Career Award for Scientists and Engineers in 2004, the American Society of Engineering Education Beer and Johnston New Mechanics Educator Award in 2009, and the American Society of Mechanical Engineers Hughes Young Investigator Award in 2013.

William D. Nix has been teaching courses on imperfections in crystalline solids at Stanford for more than 50 years. His teaching awards include the Bradley Stoughton Award for Young Teachers of Metallurgy, the Albert Easton White Distinguished Teacher Award, and The Educator Award from The Metallurgical Society. He has also received many awards for his research and is a Fellow of the American Academy of Arts and Sciences and a member of both the National Academy of Engineering and the National Academy of Sciences.

"This book captures the spirit of the legendary Stanford lecture course on the subject. It combines scientific authority with linguistic elegance and is suitable for students and specialists alike – a joy to read."

Eduard Arzt, Saarland University

"This authoritative book provides a thorough and quantitative description of imperfections in crystalline materials with clear text and illustrations. Students and practitioners of materials science and engineering and other related fields will benefit immensely by applying the fundamental concepts presented in the book to scientific research problems and engineering practice."

Subra Suresh, Carnegie Mellon University

"This invaluable textbook introduces knowledge of the complicated imperfections in crystalline solids and their properties unambiguously and completely, which is extremely useful for students and professionals in the field of materials science and engineering."

**K. Lu, Shenyang National Laboratory for Materials Science,
Chinese Academy of Science**

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To my parents, for their encouragement and support.
Wei Cai

To my family, for their patience with my obsessions.
William D. Nix

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Preface

This book is mainly written for senior undergraduate and junior graduate students wanting to gain an understanding of the behavior of defects in crystalline materials using the fundamental principles of mechanics and thermodynamics. We choose the word *imperfections* to emphasize that the crystalline materials in which these defects are found are nearly perfect. In other words, the densities of these defects are usually very low. Yet, they can greatly alter and even control the properties of the host crystal. It can be said that the main purpose of the entire field of materials science is to modify the properties of materials through the control of their defects.

The book is written based on a set of lecture notes of a course (MSE206 Imperfections in Crystalline Solids) that one of us (WDN) taught in the Materials Science and Engineering Department of Stanford University for more than 50 years. This course is now taught in the Mechanical Engineering Department (as ME209 by WC). We wanted to turn these lecture notes into a textbook so that it can be used by students and instructors in other universities who are interested in learning/teaching this subject.

The scope of this book has significant overlap with two important books in this area: *Introduction to Dislocations* by Hull and Bacon, and *Theory of Dislocations* by Hirth and Lothe. The book by Hull and Bacon provides a clear introduction for junior undergraduate students to the field of defects in crystals, while the book by Hirth and Lothe is a monograph and a valuable reference to experienced researchers in this field. It has long been recognized by the community that what we lack is a textbook that bridges the gap between these two books, a textbook that can be used in the teaching of core senior undergraduate/junior graduate courses on defects in crystals.

To this end, we can share the personal experience of one of us (WC) while he was a graduate student himself (at MIT). Realizing that his PhD thesis research would deal with the modeling of crystalline defects, he first read through *Introduction to Dislocations* by Hull and Bacon. The book provided a very useful introduction, but after reading it, he still did not feel quite "ready" for his research tasks. So he realized it was necessary to delve into *Theory of Dislocations* by Hirth and Lothe. But that proved to be a significant challenge, especially for a junior graduate student. Looking back, it appears that a significant part of his needs as a starting graduate student could have been met if he had had the opportunity to take the MSE206 course, being offered at the other end of the continent. The possibility of helping those students in a similar situation provided a strong personal motivation for him to help turn the lecture notes of MSE206 into this book.

The ultimate goal of this book is to develop confidence in students, so that they not only *know* how defects behave in crystalline materials, but also can *apply* a set of fundamental principles to explain these behaviors, to make some (albeit approximate) predictions, and to analyze similar situations they may encounter in the future. In other words, we hope that students will develop sufficient confidence to do something with the material they have learned. To achieve this goal, most of the analyses in this book are described at a slow pace, in a step-by-step fashion, with the intention that the student can follow the steps by him/herself and will be able to apply the same approach to similar situations. The exercise problems at the end of each chapter then provide the practice necessary for mastery. The mathematics used in the analysis is kept at a level accessible to a senior undergraduate student in science or engineering.

An obvious challenge faced by this approach is that, if we describe each topic in such great detail, we cannot possibly cover many topics in a reasonably sized book. Consequently, we chose to focus on a smaller set of topics than what might appear in a broad book on defects in crystals. The motto we adopted for this book project was: we want to be *tutorial rather than encyclopedic*. When deciding on which topics to include, preference was placed on the ones that could be analyzed using the fundamental principles introduced in previous chapters.

Much emphasis in this book is placed on developing intuition. We believe it to be an important skill, which also brings a great deal of satisfaction, to be able to develop approximate, but simple, estimates of various quantities of interest, such as the fraction of vacancies in a crystal near its melting temperature. Intuition is developed (and confidence strengthened) when we have a habit of making these rough estimates and comparing them with experimental data. It is also a great way to integrate the various subjects discussed in this book and see how they fit together.

Among the existing books on this topic, this book is somewhat special in terms of the number of illustrations (300+) and number of exercise problems (300+). The more than 50 years of teaching MSE206 have resulted in the wealth of materials available for this book. We believe illustrations and diagrams are very important in conveying the essence of the subject. Therefore, we have made all the figures in this book freely available as PDF files on the book website (http://ics-book.stanford.edu), so that the reader can view them on a computer screen at arbitrary magnification.

The book consists of 14 chapters, which are grouped into four parts. Part I introduces the fundamental mechanics and statistical-thermodynamic principles that will be used in the subsequent parts of the book. In the teaching of a course, these subjects are usually covered by previous courses in the curriculum. They are included in this book to serve as a review and a quick reference for the readers. Parts II, III, and IV of the book then apply these fundamental principles to point, line, and planar defects, respectively, in crystalline materials. A summary is included at the end of each chapter. The reader can use the summary to check whether he/she has received the main messages we wish to deliver in each chapter. We emphasize that working on the exercise problems at the end of each chapter is essential for a full mastery of the subject.

While the content of this book is based on a one quarter, first year graduate level course that has been given at Stanford for many years, not all of the topics found in the book were ever presented in a given quarter. Two or more quarters would be needed to cover everything. But we anticipate that not everyone will be equally interested in all aspects of defects. Teachers will naturally want to spend more time on some topics and less, or none at all, on others. In that case, parts of the book can serve as the text for the course, with the unused parts of the books serving as a reference for the book owners if they subsequently wish to delve into different areas of crystal defects. Also, teachers might even wish to cover only elementary fundamentals in some areas, usually at the beginning of the chapters, while going to the advanced fundamentals near the ends of the chapters on topics of greater interest.

We want to thank the thousands of students who have either taken MSE206 at Stanford University or used the course notes over the past 50+ years, and have helped to shape the lecture materials that ultimately led to this book. We also thank a group of dedicated former and current students, Wendelin Wright (Bucknell University), Gang Feng (Villanova University), Seok-Woo Lee (University of Connecticut), Ill Ryu (Brown University), William Kuykendall, Ryan Sills, and Yanming Wang, who devoted their time to read the nearly final version of this book and provided valuable suggestions. WC wishes to thank Sidney Yip of MIT and Vasily V. Bulatov of LLNL for introducing him to this field, and for instilling in him a writing style of plain English and clarity. WDN wishes to thank Robert A. Huggins of Stanford for introducing him to materials science more than 55 years ago and for encouraging him in this field, and Oleg D. Sherby of Stanford for introducing the field of dislocations to him and giving him the chance to learn to teach this exciting subject.

Finally, we wish to thank the following individuals for granting us permission to use various images for the illustrations on the cover of the book: Yayu Wang of Tsinghua University for the image of point defects in $Ca_2CuO_2Cl_2$; Sang Chul Lee of Stanford University for the TEM image of a dislocation at the interface of a film of Sm doped Ceria on a Yttrium Stabilized Zirconia substrate; Wayne King of the Lawrence Livermore National Laboratory for the image of a $\Sigma 11$ grain boundary in aluminum; and James LeBeau of North Carolina State University for the image of twin boundaries in NiFeCrCo.