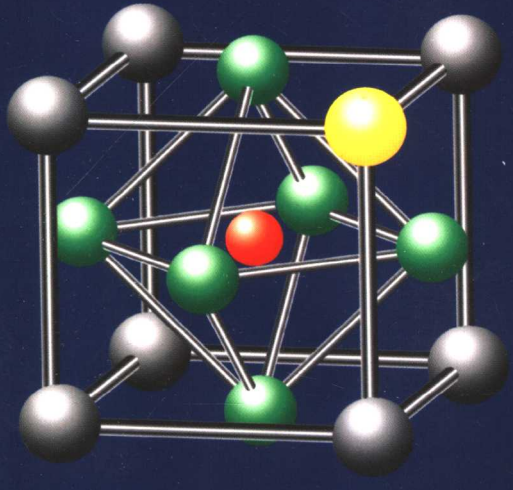
经典电介质科学丛书
Classic Dielectric Science Book Series
丛书主编 姚熹 (Yao Xi, Series Editor)

金属氧化物中的缺陷化学

The Defect Chemistry of Metal Oxides

（影印版）

〔美〕D. M. Smyth 著



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D. M. Smyth
Lehigh University

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内容提要

本书是由国际知名学者、美国里海大学保罗·B·莱因霍尔德材料科学与工程和化学荣誉退休教授 D. M. Smyth 所著的唯一一本介绍固体无机化合物尤其是金属氧化物化学平衡的著作。对没有多少缺陷化学背景的学生而言，本书解释了如何应用基本原理以及如何解释材料的相关行为。本书讨论的主题包括晶格和电子缺陷、掺杂效应、非化学计量性以及质量与电荷的输运，并特别强调了成分元素的一般化学性能与它们的化合物的缺陷化学和输运性能之间的关系。本书覆盖了缺陷形成种类、掺杂效应、化学计量的偏离程度和方向、受主和施主浓度以及其他主题。最后一章对二氧化钛、氧化钴和氧化镍以及钛酸钡这三个体系做了最新的介绍和详细的分析。

本书是同类出版物中唯一一本为学生设计了习题的教材。它可满足材料科学与工程、化学和地球化学等学科中不同课程的需要，同时也可以作为研究人员和教师的有益的参考书。

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作者简介
ABOUT THE AUTHOR

D. M. 史密斯，生于1930年，现为美国里海大学保罗·B·莱因霍尔德材料科学与工程和化学荣誉退休教授。研究方向为电子陶瓷中的固态化学和缺陷化学。1990年当选美国陶瓷学会会士。1996年因其在电子陶瓷元件中的固态化学方面所做出的杰出贡献当选美国国家工程院院士。

D. M. Smyth was born in 1930. He is Paul B. Reinhold Professor Emeritus of materials science and engineering and of chemistry, Lehigh University, USA. His research interests are focused on the solid state chemistry and defect chemistry of electronic ceramics. He was elected as a **Fellow** of the American Ceramic Society in 1990. In recognition of his excellent contribution to the solid state chemistry of electronic components based on ceramic materials, he was elected as a **Member** of the National Academy of Engineering (USA) in 1996.

丛书主编简介
ABOUT THE SERIES EDITOR

姚熹，1935年生于中国江苏苏州。1957年毕业于交通大学电机系，1982年获美国宾夕法尼亚州立大学固态科学博士学位。1957年至今在西安交通大学任教，现任西安交通大学教授。1989年当选国际陶瓷科学院首批院士。1991年当选中国科学院院士。2002年当选美国陶瓷学会会士。

Yao Xi was born in 1935 in Suzhou, Jiangsu, China. He graduated from the department of electrical engineering, Jiaotong University in 1957, and received his Ph. D. of solid state science from the Pennsylvania State University in 1982. He has been a professor of Xi'an Jiaotong University since 1984. Dr. Yao was elected as an **Academician** in the first election of the World Academy of Ceramics in 1989. He also was elected as a **Member** of the Chinese Academy of Sciences in 1991 and a **Fellow** of the American Ceramic Society in 2002.

内容简介
BRIEF INTRODUCTION

本书是唯一一本介绍固体无机化合物尤其是金属氧化物化学平衡的著作。对没有多少缺陷化学背景的学生而言，本书解释了如何应用基本原理以及如何解释材料的相关行为。本书讨论的主题包括晶格和电子缺陷、掺杂效应、非化学计量性以及质量与电荷的输运，并特别强调了成分元素的一般化学性能与它们的化合物的缺陷化学和输运性能之间的关系。本书覆盖了缺陷形成种类、掺杂效应、化学计量的偏离程度和方向、受主和施主浓度以及其他主题。最后一章对二氧化钛、氧化钴和氧化镍以及钛酸钡这三个体系做了最新的介绍和详细的分析。本书是同类出版物中唯一一本为学生设计了习题的教材。它可满足材料科学与工程、化学和地球化学等学科中不同课程的需要，同时也可作为研究人员和教师的有益的参考书。

This book is a unique introduction to the equilibrium chemistry of solid inorganic compounds with a focus on metal oxides. Accessible to students with little or no background in defect chemistry, it explains how to apply basic principles and interpret the related behavior of materials. Topics discussed include lattice and electronic defects, doping effects, nonstoichiometry, and mass and charge transport. The text distinctly emphasizes the correlation between the general chemical properties of the constituent elements and the defect chemistry and transport properties of their compounds. It covers the types of defects formed, the effects of dopants, the amount and direction of nonstoichiometry, the depths of acceptor and donor levels, and more. Concluding chapters present up-to-date and detailed analyses of three systems: titanium dioxide, cobalt oxide and nickel oxide, and barium titanate. This book is the only book of its kind that incorporates sample problems for students to solve. Suitable for a variety of courses in materials science and engineering, chemistry, and geochemistry, it also serves as a valuable reference for researchers and instructors.

Preface to the Classic Dielectric Science Book Series

Fifty years ago, I was sitting in a class at Jiaotong University in Shanghai, China taking a course called "DIELECTRIC PHYSICS" lectured by the late Professor Chen Jidan. I was one of the thirty students sitting in his class taking the course. This was the first time DIELECTRIC study was introduced to Chinese Universities. Since then, dielectric study became one of the major concerns of the science and technology community of China in developing its electrical and electronic engineering. Fifty years past, thousands of students, graduate students, professors, scientists and engineers have been engaged in the studies and applications of dielectrics in this country. In the past fifty years, the Xi'an Jiaotong University, Shanghai Jiaotong University, Electronic Science and Technological University, Shandong University, Zhongshan University, Sichuan University, Nanjing University, Tongji University and the Shanghai Institute of Ceramics, the Beijing Institute of Physics of the Chinese Academy of Sciences were heavily involved in dielectric studies and gave their various contributions to the development of dielectric study in China. Now, China is probably one of the most important countries in dielectric studies among the list of the ex Soviet Union and the United Kingdom. Late Professor Chen was the pioneer and founder of DIELECTRIC studies in China. The staidness, sureness and solemnness of his academic attitude are the invaluable treasure of the Chinese dielectric community. I would like to take the chance of writing this preface to pay my sincere respect to the late Professor Chen.

However, as a branch of solid state science, the advancement of dielectric science is not well satisfied as widely expected. Our basic understanding on the electro-physical process within real dielectrics

beyond the classical electro-magnetic theory is still rather poor. For example, the way how the charge assemblies respond to the external stimuli of electric field and the way of the communication and interaction among charge assemblies in real dielectrics are yet to be explored. Our understanding on local field, defects, inhomogeneous, space charges in real dielectric materials is to be profounded. As to the structure-property relationship of dielectric materials is still rather superficial. We are still struggling on how to calculate the dielectric constants of alkali-halogen crystals, water and other high dielectric constant materials. In contrast with other fields of solid state science such as metal, semiconductor and magnetics, dielectrics are probably the worst understood arena of solid state materials. The current status of dielectric science is not satisfied at all. Big efforts should be taken to catch up with the development of modern science and technology in this 21st century.

China is probably the country having the largest community of dielectric study in the world. Many of the old generation have devoted their career life focused on dielectrics in the past several decades. Next generation of dielectric study is now getting more mature and stronger. They have got better training and better working condition than their old generation. The Chinese dielectric community should be able to render more contribution to the advancement of dielectric science. However, dielectric science is now not yet in the main stream of solid state science. Many of the important publications were published twenty to sixty years ago in English. The first published book by P. Debye, Polar Molecules, was published in 1928. These important classics are not easily available to young scholars nowadays. To promote the dielectric studies in China, Electronic Materials Research Laboratory at Xi'an Jiaotong University proposed a publication project to introduce the most important classical publications on dielectrics from abroad and publish them in China, subjected to the consent of their original publishers. I am very pleased that the Xi'an Jiaotong University Press (XJTU Press) kindly agrees to support the publication project of Classical Dielectric Science Book Series (CDSBS). We will carefully select the subjects and topics based on our

best knowledge and judgment to keep the CDSBS including all the important and useful publications, while still keeping it concise. Needless to say, due to the restriction of our knowledge and information, there might be pretermissions in searching and collection. Any suggestion and recommendation from the reader of the series would be highly appreciated.

I would like to take the chance to thank the Chinese publisher, the Xi'an Jiaotong University Press, for their kind support of the project and their far sighted vision in promoting academic excellence, as well as the original publishers, such as the Oxford University Press and etc. for their generous consideration to permit the publication of their books in China. Highest esteem will be dedicated to the authors of the books. We may not be able to give our thanks to them individually. We gratitude them and hope them happy and healthy. I would also acknowledge Dr. Wei Xiaoyong and Dr. Xu Zhuo as well as the editors of the book series Ms Zhao Liping and Mr. He Fengtao for their enthusiastic and hard works to promote the CDSBS project being realized.

Yao Xi

Electronic Materials Research Laboratory,
Xi'an Jiaotong University
April 20, 2006

Preface to the Chinese Printing

I am delighted that my book on defect chemistry is being reprinted in China and will now be more accessible to students and scientists there. I have a missionary's enthusiasm for spreading the truth about this important, but often neglected subject. Improving the book's availability in China is especially gratifying to me because of the many excellent students, postdoctoral associates, and scientists from China with whom I have collaborated over the years. I understand that my book will be one of several in the field of dielectrics to be reprinted in China, and I congratulate Professor Yao Xi and his colleagues for initiating this important program.

It has always been a mystery to me why defect chemistry is so often abused in the literature. I review manuscripts for several scientific journals and it is seldom that I find the subject properly applied by those who have not devoted themselves to a thorough study of the field. Part of the problem may be that the concepts seem deceptively simple. Students in my classes have generally found that each progressive step is quite simple and logical, but then have trouble fitting these together into a coherent package. At almost all universities, the teaching of defect chemistry is limited to a few lectures in courses on diffusion, electrical properties, or more general physical properties. That is not adequate, and gives a false sense of understanding of the subject. This book is an attempt to develop the subject in more progressive detail, starting with very simple and obvious rules and concepts and building to ever more complex treatment. The material is not difficult but contains a lot of detail. Behind it all are a few simple rules: the conservation of mass, charge, and crystal structure.

My visits to China and interactions with its students and scientists have had a strong influence on my career, and on my world-view. I have been impressed with how the application of strong intellect and very hard

work have led to the growth of both the confidence and the contributions of Chinese science. I hope that my book can make some small contribution to further advances.

D. M. Smyth

Bethlehem, Pennsylvania, USA
May 26, 2006.

This book is dedicated to my wife,
Elisabeth Luce Smyth,
my partner in life.

Preface

This book is designed to help those with little or no background in the field of defect chemistry to apply its principles and to interpret the related behavior of materials. It is the product of a course for advanced undergraduates and graduate students that was taught by the author at Lehigh University for over twenty years. The course is highly interdisciplinary and has been attended by students from the departments of chemical engineering, chemistry, electrical engineering and computer science, geology, materials science and engineering, and physics. The only prerequisite is introductory chemistry, although some very basic thermodynamics will be helpful. The book is intended for use either as a text for a similar course or as a reference work that covers the major principles of defect chemistry. While it starts from a very basic level, it proceeds to fairly advanced interpretations and should also be of use to those with some acquaintance with the field. Unfortunately, only rarely is an entire course devoted to defect chemistry, a field commonly covered in two to four weeks in courses on diffusion, electrical properties, or more general physical properties. That brief exposure almost always proves to be inadequate for any useful application of the material. It is to be hoped that the availability of a book designed to be an introductory text will encourage more thorough coverage.

The subject is developed in a very systematic and sequential way, and an attempt has been made to define terms and symbols clearly and consistently. Hopefully this will help to bring some order to a somewhat chaotic state of terminology and notation. The defect notation used throughout is that proposed forty years ago by Kröger and Vink. It is clear and self-consistent, and, in the opinion of the author, no deviation from it should be tolerated in any publication.

For those who have some background in defect chemistry, it will not be necessary to plow dutifully through the book from beginning to end, or even through complete chapters, since many sections have been designed to be reasonably complete by themselves. A few problems have been included. It is the experience of the author that while readers may feel that they understand the material, there may still be a problem in applying it to real or hypothetical cases. Attempts to do the problems often lead to a much better understanding.

Much of the treatment of defect chemistry can be shortened by recognizing that once an adequate number of simultaneous equations have been established, they can be fed into a computer that will tabulate or plot out the results. However, this does not lead to an understanding of the chemical interactions of the system. For that reason, this book takes the more laborious and traditional approach of breaking

the system down into its component parts so that the chemistry is fully exposed to view.

Special acknowledgment must be given to two books that have proved to be particularly helpful in the development of both the course and this book. *Introduction to Solid State Physics*, by Charles Kittel (3rd edition, John Wiley & Sons, New York, 1966) has an unusually lucid treatment of the electronic properties of semiconducting solids, and chapters by A. D. Franklin, R. G. Fuller, and A. S. Nowick in *Point Defects in Solids*, Volume 1, *General and Ionic Crystals* (edited by J. H. Crawford Jr. and L. M. Slifkin, Plenum Press, New York, 1972) have been particularly useful as sources of experimental data and illustrative examples.

The book has benefited greatly from the patience of the students who have been subjected to the evolution of understanding and presentation that inevitably grows out of the teaching interaction. It has also been a special privilege to share the learning process with so many dedicated graduate students and postdoctoral associates who have worked in the author's laboratory at Lehigh. Also most helpful have been discussions and friendly arguments with many colleagues, including Harlan Anderson, Nick Eror, George Shirn, and Terry Tripp at the now defunct Research and Development Laboratories of the Sprague Electric Company, and later, at Lehigh University, especially Sid Butler, Helen Chan, Martin Harmer, and the late Frank Feigl. In addition, a substantial portion of this book was written while the author was on leave at the Sandia National Laboratories in Albuquerque, New Mexico, and the opportunity to collaborate with the research activities there, especially with Duane Dimos, Bill Hammetter, Bruce Tuttle, and Bill Warren, is deeply appreciated. I am also grateful to Ms. Sharon Balogh for the beautiful line drawings. Finally, and most importantly, none of this could have been accomplished without the support and patience of my wife, Betty, who has suffered through years of trying to communicate while my brain was wandering through some crystalline lattice looking for vacancies, interstitials, and stray electrons.

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