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978-0-521-47214-2 - Physics and Chemistry at Oxide Surfaces
Claudine Noguera
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This book summarizes the present state of knowledge on the microscopic behaviour of oxide surfaces.

The first chapter of the book summarizes classical approaches, introduces the concept of ionicity, and describes the mixed iono–covalent character of the oxygen cation bond in bulk materials. The next three chapters focus on the characteristics of the atomic structure (relaxation, rumpling and reconstruction effects), the electronic structure (band width, gap width, etc.) and the excitations of clean surfaces. Metal–oxide interfaces are considered in the fifth chapter with special emphasis on the microscopic interfacial interactions responsible for adhesion. The last chapter develops the concepts underlying acid–base reactions on oxide surfaces, which are used in catalysis, in adhesion science, and in colloid physics, and discusses their applicability to the adsorption of hydroxyl groups. A comprehensive list of references is included.

This book will be of interest to graduate students or researchers, to experimentalists and theorists in solid state physics, chemistry and physical chemistry.

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PHYSICS AND CHEMISTRY AT OXIDE SURFACES

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Nuestras horas son minutos
Cuando esperamos saber,
Y siglos cuando sabemos
Lo que se puede apprender.

Antonio Machado
Proverbios y Cantares
(Campos de Castilla)

Hours are minutes
When we hope to know,
And centuries when we know
What can be learned.

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Preface

Although oxides have been the subject of active research for many years, they have attracted an increasing interest in the last decade. One reason for this interest is the discovery of superconductivity in copper oxide based materials, in 1986, with critical temperatures higher than the temperature of liquid nitrogen. Simple oxides have also been more thoroughly studied and a detailed analysis of their surface properties has been undertaken, thanks to several technological advances made during this period. The success in compensating charging effects, for example, has allowed spectroscopic measurements to be performed. Photoemission, x-ray absorption, Auger spectroscopy and low-energy electron diffraction now yield quantitative information, as they do for semi-conductors and metals. Topographic images of insulating surfaces can be recorded with an atomic force microscope. On the theoretical side, advanced numerical codes have been developed, which solve the electronic structure, optimize the geometry, and start accounting for dynamical effects in an *ab initio* way. The results presently available allow a first synthesis of the field.

The interest and the richness of the field of oxide surfaces lies in its inter-disciplinary nature and in the diversity of questions it raises, both on a fundamental and on an applied level. For example, geophysicists and geologists consider in detail the surface properties and porosity of the rocks of our earth, made of complex oxides whose properties are, to a large extent, controlled by the grain boundaries and internal surfaces. The mineral reactivity also interests the toxicologists, who try to understand the interactions between small particles and the biological medium. Small oxide particles may be found in colloidal suspensions, and the surface reactions, which take place at the interface with the solution, determine in a large part the nature and strength of the particle–particle interactions and thus the stability of the suspension. Oxides are also good catalysts, which are largely used, for example, in petrochemistry. Specific experimental

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techniques have been developed to quantify the acidity or basicity of their surface sites and to establish a correlation between their catalytic activity and their surface geometry. In the multi-layered materials produced in modern industry, oxides are often used as supports for thin metallic films or grafted polymeric layers, as intercalation layers in electronic devices, etc. They are often present, although in an uncontrolled way, whenever a material is in contact with the ambiant atmosphere. They play a fundamental role in corrosion processes and the surface properties of real materials, such as the friction coefficient, etc., are *in fine* determined by them. Finally, they offer a large field of investigations to surface physicists, who have developed concepts and obtained many results on metals and semi-conductor surfaces, but who are still trying to answer elementary questions on oxide surface characteristics – e.g. density of states, gap width, stoichiometry of the outer layers, reconstructions, defects.

In this vast context, the present book is restricted to well-defined themes, which have been the subject of recent developments and for which a microscopic understanding is emerging. The oxides which will be discussed are 'simple' insulating oxides, with cations from the four first columns of the periodic table or from one of the transition series, provided that they are in a closed-shell configuration – such as TiO_2. Those oxides whose insulating character results from strong electron correlations will be discarded. Their *bulk* electronic structure remains a challenge for the theoreticians and little information on their surfaces is known. For a long time, all 'simple' insulating oxides were believed to be highly ionic, and were described by classical electrostatic models. More recently, electronic structure calculations have proved that most oxides are only partially ionic, but the relative weight of covalent and electrostatic interactions in these materials remains a subject of controversy. The first chapter of this book summarizes the classical approaches, makes a presentation of the concept of ionicity and proposes a quantum model, which accounts for the mixed iono–covalent character of the oxygen–cation bonds in the bulk. The three following chapters focus on the atomic structure – relaxation, rumpling and reconstruction effects; the electronic structure – band width, gap width, etc.; and the excitations of clean surfaces. Interfaces between a metal and an oxide are considered in the fifth chapter, with a special stress put on the microscopic interfacial interactions responsible for adhesion. Although the relevance of some parameters to wetting and growth processes is indicated, all the kinetic aspects – growth of a metallic deposit on an oxide or superficial oxidation of a metal – are excluded. The last chapter develops the concepts underlying acid–base reactions, which are used in catalysis, in adhesion science and in colloid physics. It points out their relevance to chemisorption processes, and more specifically to the adsorption of hydroxyl groups on oxide surfaces.

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The aim of this book is to draw a panorama of the field, to ask questions, to indicate tracks for future research, rather than to present a final picture, which has still to be built up. Due to the connections with many disciplinary fields, it has not been possible to make an exhaustive bibliography. Many review papers or books are quoted, in which the reader will be able to trace the original papers. For the sake of synthesis and pedagogy, systematic features are stressed, relevant parameters are derived and a comparison is made between the concepts used in 'this' or 'that' research area. Theoretical models are proposed to synthesize the experimental or numerical results obtained on given systems and to obtain a consistent picture. Although they can only account for the gross features and the trends, they do represent an advance on the long way of the conceptualization of knowledge. The analytical support is highly inhomogeneous: some questions are developed at length; others are sketched only quickly and will leave the reader unsatisfied. It is the sign that much work remains to be done.

The French version of this book was written after a series of lectures given in 1992–3, in Orsay, to undergraduate students in solid state physics. The audience contained students preparing their theses, as well as researchers: solid state physicists, geophysicists, electrochemists and chemists, experimentalists or theoreticians. A special effort was thus made to settle the background necessary to a complete understanding, without assuming any advanced knowledge. I am deeply indebted to all the participants who encouraged me with their attendance and helped me with their questions. Many thanks are also due to my own PhD students who have shared my queries during the last years.

The final version of this book benefited greatly from discussions, comments and encouragements from some of my colleagues. Among them, I am especially grateful to J. Friedel, J. Jupille, S. and A. Chopin, P. Dubost, E. Ilisca, J. P. Pouget, J. P. Roux, A. Auroux and J. Schultz, who read part or the whole of the French draft, D. W. Jepsen who kindly read and corrected the English version, and C. Godrèche and P. Manneville whose help was invaluable in disentangling the subtleties of TEX formatting.

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