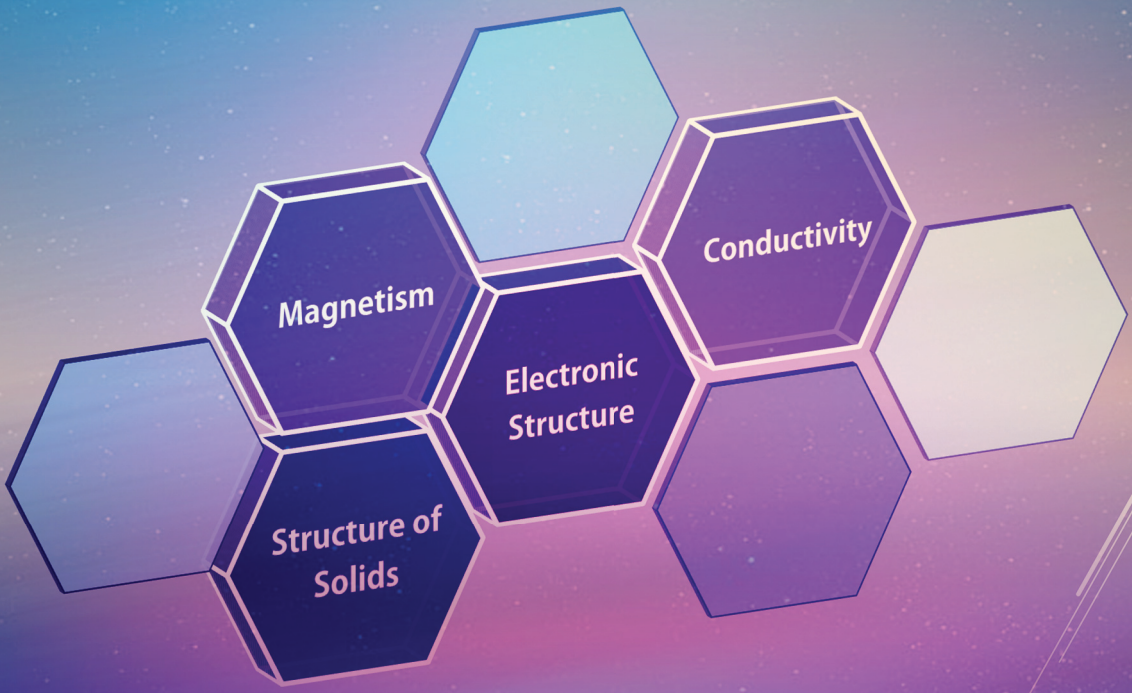
Electronic Structure of Materials

Challenges and Developments

edited by

Natalia Chezhina | Dmitry Korolev



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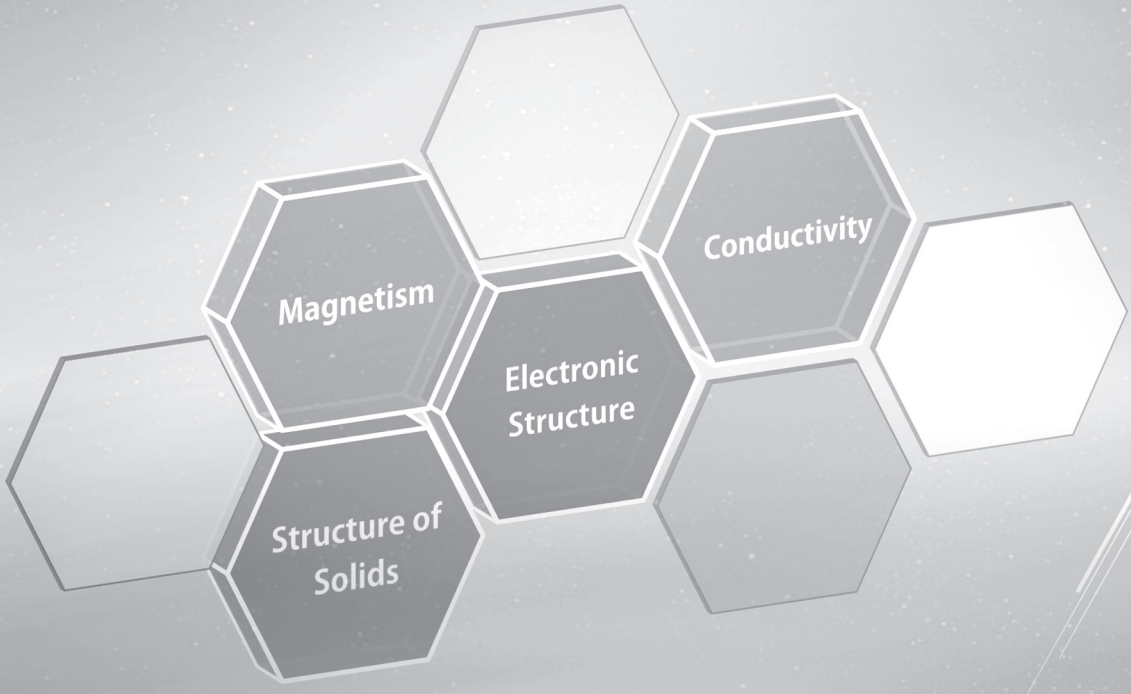

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Preface

This book shows the specialists in the field of materials chemistry the importance and necessity of studying the electron structure of solid oxide systems, promising from the point of view of application in various fields. The everlasting problem of selecting the qualitative and quantitative composition of materials may be solved only on the basis of the exhaustive knowledge of their crystal and electron structure and of the model simulation of the influence of various elements on the target properties of oxide ceramics. A great diversity of crystal structures and physical and chemical properties of oxide systems used as materials nowadays made the authors to concentrate on a certain number of systems that are the most popular in modern material technologies. All the parts of the book are associated with the method of magnetic dilution as the most universal method for studying the electron structure of solids. The method was advanced as early as in 1960, in particular, by Professor S. M. Ariya and is still being developed in Saint Petersburg state University by the group of magnetochemistry of solids. In these years, the mathematical and physical apparatus of the magnetic dilution method has been developed together with the development of the theory of magnetochemistry. The book shows the expediency of using various physical methods with the aim of revealing the chemical structure of particular solid oxide systems depending on their chemical composition and crystal structure and provides a clue for selecting optimal compositions for obtaining special properties of target materials.

The authors express their profound gratitude to Evgenii Shchipunov, whose highest skills were provided for all the experiments, especially the operation of magnetic devices. We are grateful to Professors V. N. Pak, R. S. Bubnova, S. K. Filatov, and S. I Andronenko, Associate Professors M. G. Krzhizhanovskaya, N. V. Platonova, and I. A. Kasatkin, Dr. S. V. Nekipelov (Syktyvkar State University), and scientific coworker D. A. Spiridonova for scientific cooperation at various stages of studies. Special thanks

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Natalia Chezhina
Dmitry Korolev

Introduction

Nowadays oxide materials have acquired great interest among researchers and in the industry. Gone are the times when ceramics were associated with building materials, utensils, and other even less prestigious applications. Now complex oxides are widely used as materials for oxygen sensors and oxygen-conducting membranes of catalytic reactors, and photocatalyzers in the UV and visual regions of the spectrum. Recent discoveries of high-temperature superconductivity in oxide systems of colossal magneto resistance in lanthanum manganites gave a great impetus to the search of new compounds demonstrating unusual and promising physicochemical properties. The challenges in the field of energy sources started a completely new and wide problem of development in the compositions for the technologies of solid oxide fuel cells (SOFC).

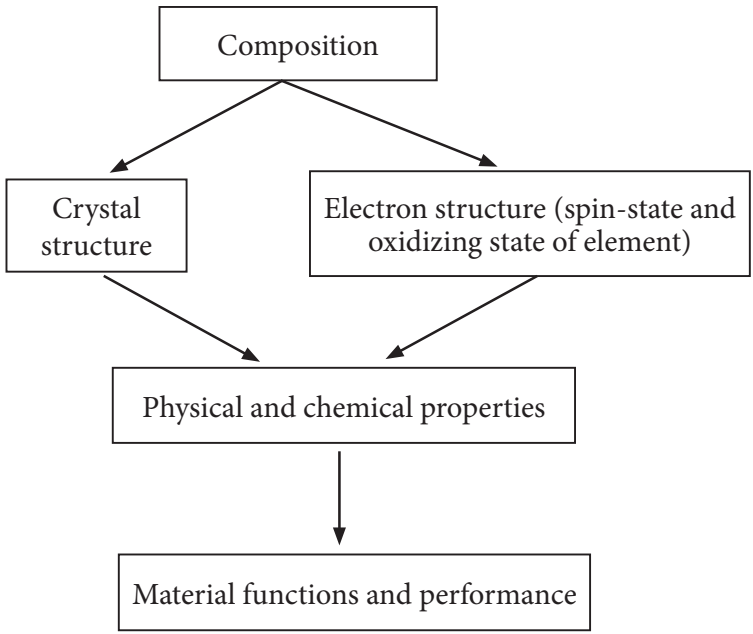
All the above-mentioned oxide systems have various structures, and their applications are different. Moreover, almost all the systems are multicomponent, which means that they are solid solutions including transition and rare earth elements somehow distributed over various sublattices in the complex oxides. A large series of structures, especially perovskite like, are tolerant to substitution varying both by the nature of the substituent and by their concentration. Up to now the search for optimal compositions has been carried out purely experimentally, which resulted in a wide series of published works recommending better compositions for a particular property, e.g. electron-ionic conductivity, ionic conductivity, magneto resistivity, and so on. Taking into account the fact that in the Periodic Table of elements the number of possible dopants in the metal sublattice amounts to about a hundred, and sometimes several elements are introduced simultaneously, the more so, the ratio between several dopants may vary in wide regions, the number of possible compositions tends to infinity.

Therefore, the problem of selecting the compositions of oxide ceramics requires attaining theoretical grounds. A large number of questions must be answered in doing this. In the systems

containing *d*- or *f*-elements, these questions may be summed up as following if not exclusively.

1. What are the oxidation and spin states of paramagnetic elements, and how does the crystal structure of the oxide system influence them and how does the electron structure of paramagnetic elements influence the crystal structure of oxide materials?
2. What are the interatomic interactions between paramagnetic atoms, and what effect do they have on the physical and chemical properties of oxide systems?
3. How do diamagnetic elements of the oxide system influence both above-mentioned characteristics?
4. How do all these factors affect the performance (magnetic, electric, catalytic, and so on) of the target materials?

In other words, with the aim of laying the pathway to selecting the composition of ceramics with predetermined physical and chemical characteristics, we must solve the problems thoroughly connected with each other in various ways:



The interrelation between the composition (both qualitative and quantitative) and the crystal structure is successfully studied by the X-ray method exquisitely developed nowadays and allowing the structure refinement to be made for powder samples. The problem of electron structure and its interrelation with crystal structure and physicochemical properties is more complicated and can be solved by a number of physical methods sensitive to the state of paramagnetic atoms and interatomic interactions. All of them have special features when applied to solid state and various limits of their application.

For example, such an extremely sensitive physical method as electron spin resonance (ESR) could be used for solving the above-mentioned problems, but not all the paramagnetic centers give signals in ESR. Ni^{2+} is active in ESR, but not always, mostly when the atom is in a regular octahedral surrounding, Ni^{3+} low spin give a good signal, but Ni^{3+} high spin does not. Mn^{2+} and Mn^{4+} are active in ESR even at room temperature, but Mn^{3+} may be seen only at very low temperatures, close to liquid helium. This means that we can use this method only if we have a signal in ESR, but if we have no signal we cannot conclude sometimes that there is no paramagnetic atom in the particular oxidation or spin state. Nuclear magnetic resonance has even narrower application, since only a limited number of atoms have nonzero nuclear spin and the presence of paramagnetic atoms in the system extremely complicates the resolution of the spectra and their interpretation. Mossbauer spectra can be successfully applied to iron-containing systems, no other paramagnetic elements can be detected. However, even with iron the method has some limitations associated with other diamagnetic elements, such as lead and strontium, which damp down the signal of iron.

In other words, all these physical methods, sensitive to the electron structure in themselves, may be used only as auxiliary methods for studying particular oxide systems, the more so that there always must be some regularities in electron structures and properties as function of the origin of paramagnetic element e.g. of its position in the Periodic table. The same can be applied to optic spectra in the IR or visual region widely used for the interpretation of the chemical structure of complex compounds, since in the solids owing to exchange line breadth the interpretation of the results may be dubious.

The method of static magnetic susceptibility may be reckoned as a universal method for studying the electron structure of inorganic compounds for the following reasons. Magnetic susceptibility is the value showing the difference between the magnetic fields in vacuum and in a substance. Since this value cannot be equal to zero, the problem consists of adequate analysis of the observed effect and of creating quantum-mechanical models for its interpretation. Let us make a short insight into the fundamentals of magneto chemistry and consider its application in the solid state in more details.