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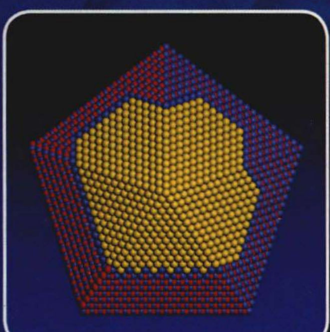
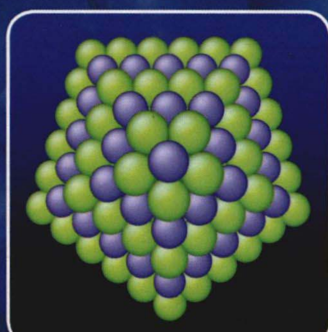
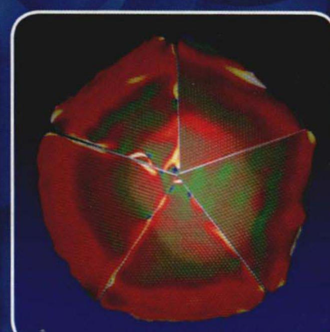
Nanoalloys

From Fundamentals to Emergent Applications

Edited by Florent Calvo

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Nanoalloys

Foreword

Matter at the nanoscale exhibits some remarkable and unexpected properties that differ sharply from the behavior of bulk materials. For example, science students have been taught for centuries that gold is a "noble metal," that is, that it is very unreactive. However, nanoparticles of gold turn out to be extremely effective catalysts, for reasons that are only now beginning to be understood. Another remarkable example is the melting behavior of clusters of about 100 atoms of gallium or of tin. Since the mid-nineteenth century, we have understood that small particles melt at lower temperatures than their bulk counterparts, but these specific nanoparticles totally violate that dogma, and melt at temperatures higher than the corresponding bulk melting points. In short, even homogeneous metal nanoparticles are a fascinating and challenging form of matter that we are only in first stage of understanding.

Metal alloys at the nanoscale are an even more dramatic challenge. The variability of their composition and structure, the dependence of their behavior on those characteristics and the size of the nanoparticle, present us with a complexity, and, at the same time, a capacity to control properties, that we perhaps have never seen in any other form of matter. Most biomolecules are very complex, but making small changes in their composition or structure typically prevents them from functioning. Metal alloy nanoparticles can be changed a little in composition or structure and may well have only slightly altered properties—or may undergo very significant changes in behavior. We are just beginning to understand the nature of bonding in these systems, and of their kinetic behavior. As we learn more, and learn to control their composition, size and structure, we will develop the capability to make nanoscale devices with capabilities that are still unforeseen. This book describes how this field, potentially both deep in fundamentals and broad in applicability, is opening.

This book addresses the full range of the subject of nanoalloys. The first two chapters deal with their controlled synthesis, a major challenge. The next two address the theoretical and experimental approaches to understanding the electronic and geometric structures of nanoalloys. Then a series of chapters examine their properties—thermodynamic, kinetic, optical and magnetic, and then their behavior as catalysts. The penultimate chapter examines nanoalloys' roles in living organisms, and the final chapter discusses their use as building blocks in composite systems.

R. Stephen Berry

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Introduction

The last decade has seen a booming development of nanosciences, which now stand as their own field across physics, material sciences, chemistry and medicine. Nanoscale objects include organic particles such as fullerenes, carbon nanotubes or even graphene, semiconducting devices such as quantum dots for electronic or photonic applications, and even hydrogen-bonded compounds like water droplets for their relevance as nucleation seeds in atmospheric processes. The interplay between atomic and electronic structures makes metal nanoparticles highly versatile, already with many uses as catalysts, magnetic devices or optical probes. Although dating back to the mid nineteenth century and their discovery by Faraday, nanoparticles have become a major scientific topic when researchers gained the ability to synthesize them and, more importantly, to observe and understand their fascinating properties.

The most distinctive feature of nanoscale materials is the size dependence often displayed by these properties. Size dependence is usually quantitative: the optical response, the catalytic reactivity, or the magnetic moment exhibit variations that vary with the nanoparticle size, smoothly at first in the so-called scalable regime, then nonmonotonically when the particle becomes small enough. Under some circumstances, the dependence is more qualitative and can arise from some changes in chemical bonding. Besides its size, the shape of a nanoparticle can also affect its property, opening interesting avenues of research, e.g. in the design of photoelectronic devices such as nanoantennas.

Mixing several metals together provides another opportunity for tuning a physical or chemical property at the nanoscale. This ambition is rooted in the achievements of early metallurgists from the Bronze age who found several millennia ago that the strength and durability of their materials could be enhanced by mixing different metals. Metal alloys at the nanoscale are a prime example of nanoalloys in which the relative composition is a new variable to be varied, expectantly having a profound influence on the desired property along with size itself. However, it should be made clear here that nanoalloys do not only refer to mixed, nanoscale alloys. For sake of a general definition (and perhaps by lack of a more rigorous term), nanoalloys are currently understood as multimetallic nanoparticles, with no assumption about the chemical order within them. Fully phase-separated particles, such as core/shell compounds, represent an important class of nanoalloys, among other possible arrangements.

Adding the dimension of composition to the existing roles of size and structure entails a significant complexity, which could only be addressed after research on pure metal nanoparticles had reached some level of maturity. Tackling this complexity by experimental or theoretical means requires dedicated tools that build upon methods available for monometallic systems, as well as methods more specific to the presence of several metals. One first objective of the present book is to provide a broad introduction to such methods, either for synthesis purposes or for fundamental investigations. Beyond fundamentals, and although a relatively young discipline, nanoalloys have also started to receive a considerable attention for their potential interest in several applied fields, for energy production, magnetic storage, or biomedicine. These topics are closely related to specific chemical or physical issues but deserved dissertations of their own.

This book was designed with the aim to present and discuss the major topics of relevance for nanoalloys, at a time where literature on the subject remains scarce. A particular attention was paid to both experimental and theoretical aspects, under the form of broad reviews that cover the most recent advances. The book is organized into 11 chapters covering the most fundamental aspects of nanoalloys related to their synthesis (Chapters 1 and 2) and characterization (Chapter 4), as well as their theoretical study (Chapter 3). Aspects related to their thermodynamics (Chapter 5) and kinetics (Chapter 6) are covered as well. The gear then moves to more specific topics, including optics (Chapter 7), magnetism (Chapter 8), and catalysis (Chapter 9), and finally to biomedical applications (Chapter 10) and the technologically relevant issue of self-assembly (Chapter 11).

The contributors of the book are all world experts in their respective fields, and it is a pleasure to thank them for their fine work. Prof. R. Stephen Berry, who has pioneered the study of the physics and chemistry of atomic clusters, is also gratefully acknowledged for his foreword.

August 30, 2012.

Florent Calvo

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