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Handbook of Metal Physics

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Metallic Nanoparticles

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Metallic Nanoparticles

HANDBOOK OF METAL PHYSICS

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The Book Series 'Handbook of Metal Physics' is dedicated to my wife

Swayamprava

and to our children

Debasis, Mimi and Sandeep

Preface

Metal Physics is an interdisciplinary area covering Physics, Chemistry, Materials Science and Engineering. Due to the variety of exciting topics and the wide range of technological applications, this field is growing very rapidly. It encompasses a variety of fundamental properties of metals such as Electronic Structure, Magnetism, Superconductivity, as well as the properties of Semimetals, Defects and Alloys, and Surface Physics of Metals. Metal Physics also includes the properties of exotic materials such as High-Tc Superconductors, Heavy-Fermion Systems, Quasicrystals, Metallic Nanoparticles, Metallic Multilayers, Metallic Wires/Chains of Metals, Novel-Doped Semimetals, Photonic Crystals, Low-Dimensional Metals and Mesoscopic Systems. This is by no means an exhaustive list and more books in other areas will be published. I have taken a broader view and other topics, which are widely used to study the various properties of metals, will be included in the Book Series. During the past 25 years, there has been extensive theoretical and experimental research in each of the areas mentioned above. Each volume of this Book Series, which is self-contained and independent of the other volumes, is an attempt to highlight the significant work in that field. Therefore the order in which the different volumes will be published has no significance and depends only on the timeline in which the manuscripts are received.

The Book Series "Handbook of Metal Physics" is designed to facilitate the research of Ph.D. students, faculty and other researchers in a specific area in Metal Physics. The books will be published by Elsevier in hard cover copy. Each book will be written by either one or two authors who are experts and active researchers in that specific area covered by the book or multiple authors with a volume editor who will co-ordinate the progress of the book and edit it before submission for final editing. This choice has been made according to the complexity of the topic covered in a volume as well as the time that the experts in the respective fields were willing to commit. Each volume is essentially a summary as well as a critical review of the theoretical and experimental work in the topics covered by the book. There are extensive references after the end of each chapter to facilitate researchers in this rapidly growing interdisciplinary field. Since research in various sub-fields in Metal Physics is a rapidly growing area, it is planned that each book will be updated periodically to include the results of the latest research. Even though these books are primarily designed as reference books, some of these books can be used as advance graduate-level textbooks.

The outstanding features of this Book Series are the extensive research references at the end of each chapter, comprehensive review of the significant theoretical work, a summary of all important experiments, illustrations wherever necessary, and discussion of possible technological applications. This would spare the active researcher in a field to do extensive search of the literature before she or he would start planning to work on a new research topic or in writing a research paper on a piece of work already completed. The availability of the Book Series in hard copy would make this job much simpler.

Since each volume will have an introductory chapter written either by the author(s) or the volume editor, it is not my intention to write an introduction for each topic (except for the book being written by me). In fact, they are much better experts than me to write such introductory remarks.

Finally, I invite all students, faculty and other researchers, who would be reading the book(s) to communicate to me their comments. I would, particularly, welcome suggestions for improvement as well as any errors in references and printing.

Acknowledgements

I am grateful to all the eminent scientists who have agreed to contribute to the Book Series. All of them are active researchers and obviously extremely busy in teaching, supervising graduate students, publishing research papers, writing grant proposals and serving on committees. It is indeed gratifying that they have accepted my request to be either an author or volume editor of a book in the Series. The success of this Series lies in their hands and I am confident that each one of them will do a great job. In fact, I have been greatly impressed by the quality of the book "Metallic Nanoparticles" edited by Professor John Blackman of the University of Reading and the University of Leicester. He is one of the leading experts in the field of Theoretical Condensed Matter Physics and has made significant contributions to the research in the area of Metallic Nanoparticles. In addition to writing several chapters himself, he has assembled a team of experts from Oxford University, the University of Leicester, the University of Strathclyde in Glasgow and AstraZeneca International (all in the U.K.) to write the other chapters of the book.

The idea of editing a Book Series on Metal Physics was conceived during a meeting with Dr. Charon Duermeijer, publisher of Elsevier (she was Physics Editor at that time). After several rounds of discussions (via e-mail), the Book Series took shape in another meeting where she met some of the prospective authors/volume editors. She has been a constant source of encouragement, inspiration and great support while I was identifying and contacting various experts in the different areas covered by this extensive field of Metal Physics. It is indeed not easy to persuade active researchers (scattered around the globe) to write or even edit an advance research-level book. She had enough patience to wait for me to finalize a list of authors and volume editors. I am indeed grateful to her for her confidence in me.

I am also grateful to Dr. Anita Koch, Manager, Editorial Services, Books of Elsevier, who has helped me whenever I have requested her, i.e. in arranging to write new contracts, postponing submission deadlines, as well as making many helpful suggestions.

She has been very gracious and prompt in her replies to my numerous questions. I have profited from conversations with my friends who have helped me in identifying potential authors as well as suitable topics in my endeavor to edit such an ambitious Book Series. I am particularly grateful to Professor Larry Pinsky (Chair) and Professor Gemunu Gunaratne (Associate Chair) of the Department of Physics of University of Houston for their hospitality, encouragement and continuing help.

Finally, I express my gratitude to my wife and children who have loved me all these years even though I have spent most of my time in the physics department(s) learning physics, doing research, supervising graduate students, publishing research papers and writing grant proposals. There is no way I can compensate for the lost time except to dedicate this Book Series to them. I am thankful to my daughter-in-law Roopa who has tried her best to make me computer literate and in the process has helped me a lot in my present endeavor. My fondest dream is that when my grandchildren Annika and Millan attend college in 2021 and Kishen and Nirvaan in 2024, this Book Series would have grown both in quantity and quality (obviously with a new Series Editor in place) and at least one of them would be attracted to study the subject after reading a few of these books.

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Volume Preface

Nanoscience is generally defined as the study of phenomena on the scale 1–100 nm. Metallic nanoparticles in that size range are clusters containing a few to about 10^7 atoms. Metallic nanoparticles display fascinating properties that are quite different from those of individual atoms or bulk materials. At the lower end of the size range (say <100 atoms), their properties are affected by the discreteness of their electronic energy levels, which contrasts with the continuum of energy states found in bulk materials. The existence of a surface has a major influence. Atoms at the surface are in a different environment from those in bulk and this will modify the overall electronic, chemical and magnetic properties of the cluster (even for clusters of 2000 atoms, about 20% of the atoms lie on the surface). Throughout the size range, the surface is defining an entity that is smaller than the wavelength of light, and this results in optical properties that are different from those of the bulk material.

Understanding the novel behaviour of these systems provides a challenge to the experimental and theoretical techniques of fundamental science, but coupled with this is their huge potential in nanotechnology. Applications, or potential applications, are diverse. They include, for example, catalysis, chemical and biological sensors, systems for nanoelectronics and nanostructured magnetism (e.g. data storage devices) and, in medicine, there is interest in their potential as agents for drug delivery.

This book describes the production and detection of metallic nanoparticles, their optical, chemical and magnetic properties, theoretical models for describing their structure and properties, and a number of their important applications. A vital first step in understanding the properties of nanoparticles is to study their behaviour as free particles, but in most situations they are deposited on a substrate or embedded in a matrix of another material and it is necessary to study the influence of the environment. In many applications, the attachment of chemical or biological molecules to the nanoparticles is of major interest. These various aspects are discussed.

The book will provide a reference work for researchers who are active in the field, but it is also aimed at newcomers such as research students entering a Ph.D. programme in nanoscience or workers in fields other than physics or chemistry who are users of nanoparticles and wish to gain a deeper understanding of the fundamental science. With the newcomer in mind, we have included an overview of the background to a number of the topics so that these topics should be accessible without the need to consult a more basic text. We have also provided references to books and review articles that may be useful to those readers who wish to pursue particular aspects in more detail.

Nanoscience and nanotechnology are inherently multidisciplinary. The fundamental understanding about the nature of metallic nanoparticles has largely come from the physics and chemistry communities, although interest in nanoparticles and their exploitation spreads across many branches of science. The authors of this volume are physicists and chemists, both experimentalists and theorists. Paul Mulheran and John Blackman are both theoretical/computational physicists, although Mulheran is now based in a Department of Chemical and Process Engineering. Chris Binns and Edman Tsang are both experimentalists, Binns in physics and Tsang in chemistry. Two of Tsang's co-authors (Oduro and Yu) are members of his group and his other co-author (Tam) is based at AstraZeneca, an international pharmaceutical company.

We have attempted to give the book coherence so that it does not read as independent and disconnected chapters. If we have succeeded in this objective, it has been facilitated largely because of existing research collaborations between the contributors.

The authors would like to thank their families for their support and patience while this book was being assembled. Inevitably time spent in writing is time sacrificed elsewhere.

Finally, as editor of this volume, I would like to acknowledge the support of Prasanta Misra (the series editor of the *Handbook of Metal Physics*) and Anita Koch (of *Elsevier*) for their encouragement in bringing this book to fruition.

John A. Blackman
Volume Editor

Contents

As defined above, nanoscience is nothing new. Faraday [2] studied colloidal gold particles and lectured on his investigations in 1857. The motivation for his study was the red colour of the gold particles, a striking contrast to the familiar yellow appearance of gold in its bulk form. By a similar argument, the use of small metal particles (smaller than 100 nm) to produce decorative effects in stained glass for church windows or in pottery glazes would date nanotechnology back to mediaeval times or even earlier [3,4].

However, it is the recent invention of a variety of tools for studying systems at the atomic level, coupled with the development of techniques for producing nanoparticles, that has led to the emergence of nanoscience as a new field of study. Of primary importance are the scanning probe microscopes, that make it possible not just to "see" individual atoms and molecules on the surfaces of materials but to move them on the nanoscale as well. The scanning tunnelling microscope (STM), the first scanning probe microscope, appeared in 1982 [5,6] and, in 1986, Gerd Binnig and Heinrich Rohrer were awarded the Nobel Prize in physics for its design. Important also is the ability to study the properties of isolated nanoclusters. Even if the technological interest is in clusters on a surface or embedded in a material, an investigation in their isolated state unencumbered by the background material is an essential first step for understanding their properties. New sources to produce clusters in the gas phase were developed during the 1960s and 1970s [7], but it was in the 1980s that Knight's group [8] first produced clusters of alkali metals with up to about 100 atoms and systematically studied their properties.

Nano-objects have a size that is intermediate between atoms (or molecules) and bulk matter. Even for clusters of 1000 atoms, more than one-quarter of the atoms lie on the surface, resulting in properties that are very different from those of atoms or bulk. The properties vary strongly with the size, shape and composition of the nanoparticle. This has been exploited, certainly since the 1960s, in heterogeneous catalysis [9]. Catalysts comprise metallic nanoparticles dispersed on a porous material, with optimisation for the best reaction rate and selectivity largely by trial and error. However, the catalysts can now be fully characterised using the available nanoscience techniques.

More recently, there have been developments towards biological and medical uses of nanoparticles. The entrapment of anticancer drugs in nanoparticles, and the decoration of the particles with molecular ligands for the targeting of cancerous cells, offers the prospect of more effective cancer therapy with reduced side-effects [10]. An alternative strategy for the use of nanoparticles in cancer treatment is photothermal tumour ablation [11]. Nanoparticles absorb laser light at a characteristic frequency and the associated heating can be used to destroy solid tumours. The aim would be to tune the particle to a frequency for which the absorption by tissue is low.

The binding of biological molecules (DNA) to metallic nanoparticles provides the basis for a number of possible applications. DNA is highly programmable and this characteristic can, in principle, be exploited to self-assemble functionalised nanoparticles into structures with more complex architecture [12]. One possible use is as sensors of biological or chemical molecules.

There is considerable potential for exploiting the magnetic properties of nanoscale structures in spintronics (also known as magnetoelectronics) [13].

High-density data storage is one of the goals, and possible systems for quantum information devices [14] are being explored that are based on the quantum tunnelling of the magnetisation of a cluster through a magnetic anisotropy barrier. The most successful spintronics device to date is the spin valve. This is based on two magnetic layers, one hard and one soft magnetically. An external magnetic field can switch the direction of the magnetisation of the soft layer while leaving that of the other layer unchanged. The switch is accompanied by a sharp increase in the electrical resistance due to spin-dependent scattering of the electrons.

1.2. A note on etymology, neologisms and terminology

The prefix nano- is variously said to derive from the Greek word νάνος or the Latin word nannus, both meaning dwarf. It was adopted as an official SI prefix, meaning 10^{-9} of an SI base unit, at the 11th Conférence Générale des Poids et Mesures (CGPM) in 1960 (Comptes Rendus de la CGPM, 87, Rés. 12) [15,16], although it had informal status before that.

The Oxford English Dictionary (OED) [17] credits Taniguchi [18] with the first use of the word "nanotechnology" in 1974, followed sometime after by Drexler [19] in a book entitled *Engines of Creation*. Interestingly, the OED does not see fit to include "nanoscience" in its compilation of nano- words, although the term was certainly in use by the early 1990s [20,21].

Taniguchi, a precision engineer, had in mind technologies operating to tolerances of less than 100 nm, whereas Drexler's idea of nanotechnology concerned the manipulation and assembly of structures at the molecular scale, a concept already discussed in 1959 by Feynman in a lecture entitled *There's Plenty of Room at the Bottom* [22]. One of the legacies of Drexler's imaginative work is the term "grey goo", which describes a nightmare scenario where nanorobots run out of control and destroy everything while replicating themselves. Unfortunately the term can be (and has been) used to spice up articles about nanoscience in the sensational press and give it a negative slant, inhibiting sensible discussion.

Although nanoscience and nanotechnology are generally the preferred words used to describe national research programmes [23], the terms are so broad that the umbrella covers many topics that have little in common. As a consequence, the prefix is increasingly appearing in front of traditional disciplines as in nanophysics, nanomaterials or nanomedicine. Doubtless the use of the word nano in product names [24], such as the iPod and the car from Tata Motors, provides further confusion for those who are not part of the scientific community.

We shall be concerned in this book with metallic nanoparticles. The scope of material covered is summarised in the rest of this chapter. A brief note on terminology concludes this section. Two main approaches are used in creating nanostructures: "bottom-up" and "top-down". The top-down method involves starting with a larger piece of material and forming a nanostructure from it by removing material through etching or machining. The various lithography techniques (e.g. electron beam and focused ion beam (FIB) lithography) use etching, and are examples of top-down techniques. In the bottom-up approach, molecules or nanoparticles are produced by chemical synthesis or other means, followed by self-assembly into ordered structures by physical or chemical interactions between the units. Feynman was anticipating the bottom-up approach.

1.3. Metallic nanoparticles

Nanoscale particles or clusters (we use the terms interchangeably) can be formed from most elements of the periodic table, and they can be classified as metallic, semiconductor, ionic, rare gas or molecular according to their constituents. Carbon nanoclusters form a special class that includes the famous buckyball (C_{60}), related fullerenes and the carbon nanotubes. Clusters are characterised as homogeneous if they contain a single type of atom, or heterogeneous if they comprise more than one constituent. They may be neutral or charged (anions or cations).

1.3.1. Size and surface/volume ratio

This book is concerned specifically with metallic nanoparticles, their properties, means of production, experimental techniques for studying them, models for describing them and some of their applications. It is instructive first to give a rough estimate of the size of these objects. The simplest description is the liquid drop model (LDM). In the LDM, we ignore the internal structure of the cluster and simply represent it as a sphere of radius R, the size of which is related to the number of atoms N. The relation can be written in terms of the Wigner–Seitz radius r_s. The Wigner–Seitz radius comes from solid state physics [25] and is defined as the radius of a sphere whose volume, v, is equal to the volume occupied by one atom in the bulk material. Strictly, it is the volume per valence electron, but the distinction is immaterial for monovalent metals. Then, setting the volume of the cluster equal to Nv, it immediately follows that

$$R = N^{1/3} r_s. \tag{1.1}$$

Wigner–Seitz radii are usually expressed in atomic units (au). The au of length is the Bohr radius: 1 au = 0.05292 nm. The diameters ($2R$) of Cu and Au clusters as a function of the number of atoms are shown in Table 1.1. We have included $N = 10$ in the table, but it should be noted that there are large departures from the simple picture at small sizes. This is particularly true for Au, which tends to form a planar cluster even at $N = 10$.

The surface of a cluster is the most obvious feature that distinguishes it from bulk material. The fraction of atoms that are on the surface is a measure of how much the cluster differs from the bulk. To get an estimate of this, we can cut out a regularly shaped object from a face-centred cubic (fcc) lattice and count the number of surface atoms for different size clusters. Atom-centred clusters thus formed have six square and eight triangular faces and look like the illustration in Figure 1.1.