Frontiers of Science and Technology for the 21st Century
21世纪科技前沿丛书

Handbook of Advanced Magnetic Materials

Volume I Advanced Magnetic Materials: Nanostructural Effects

先进磁性材料手册

第1卷：先进磁性材料的纳米尺寸效应

Editors: David J. Sellmyer
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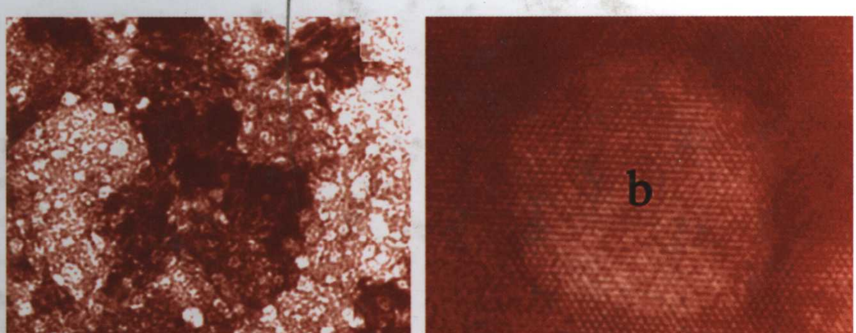

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内 容 简 介

本书的目的是对磁性材料研究的新近进展提供一种全面的理解。本书共分四卷，每一卷集中论述一个具体的研究领域。每一章首先对该章的基本概念和重要观念进行阐述，然后从实验和理论方面进行详细地说明，最后介绍该领域的发展前景以及新的思想。书中提供了详尽的参考文献，可供研究人员参考。

近年来纳米磁性材料的研究十分活跃，例如，颗粒体磁性材料的磁矫顽力随颗粒尺寸的减小而增大，到临界尺寸后又减小。为取得最佳磁耦和强磁体，其中的软磁相尺寸必须小于硬磁相磁筹界厚度的两倍。当颗粒尺寸减小到几个纳米时，就必需考虑量子效应。本卷重点阐述纳米尺寸效应对磁性材料的性能影响。

本书的读者对象为相关专业的研究生和研究人员。

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《Frontiers of Science and Technology for the 21st Century》

FOREWORD

Over the next several years, Tsinghua University Press will publish a series of books addressing progress in basic sciences and innovations in technology. We have made no attempt to pursue a comprehensive coverage of all disciplines of science and technology. Rather, topics for this series were selected with an emphasis on the currently active forefront of science and technology that will be contemporary in the next century. Most books in this series will deal with subjects of cross disciplines and newly emerging fields. Each book will be completed by individual authors or in a collaborative effort managed by an editor (s), and will be self-consistent, with contents systematically focused on review of the most recent advances and description of current progresses in the field. Sufficient introduction and references will be provided for readers with varying backgrounds. We have realize clearly the challenge of encompassing the diverse subjects of science and technology in one series. However, we hope that, through intensive collaboration between the authors and editors, high standards in editorial quality and scientific merit will be maintained for the entire series.

The international collaboration on this series has been coordinated by the Association of Chinese Scientists and Engineers-USA (ACSE). In the science community, authors voluntarily publish their results and discoveries in the full conviction that science should serve human society. The editors and authors of this series share this academic tradition, and many of them are fulfilling a spiritual commitment as well. For our editors and authors who were graduated from universities in China and further educated abroad in science and engineering, this is an opportunity to dedicate their work to the international education community and to commemorate the historical open-door movement that began in China two decades ago. When the human society enters the information age, there is no geographic boundary for science. The Editorial committee hopes that this series will promote further international collaboration in scientific research and education at the dawn of the new century.

The Editorial Committee
1999.6

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《21 世纪科技前沿》

丛 书 序 言

由清华大学出版社出版的这套丛书是基础科学和应用科学领域内的专门著作。除了可作为研究生教材外，也可作为科研和工程技术人员的参考书。在丛书的题材选择中，着重考虑目前比较活跃而且具有发展前景的新兴学科。因此，这套丛书大都涉及交叉和新兴学科的内容。编写的方式大多由主编策划并组织本学科有影响的专家共同执笔完成，从而使每一本书的系统性和各章节内容的连贯性得到了充分的兼顾。丛书涵盖学科的最新学术进展，兼顾到基本理论和新技术、新方法的介绍，并引入必要的导论和充分的参考文献以适应具有不同学术背景的读者。编撰一套容纳多学科的科技丛书是一项浩繁的工作，我们希望通过主编和作者的集体努力和精诚协作，使整套丛书的学术水准能够保持在较高的水平上。

编辑《21 世纪科技前沿》丛书是由"旅美中国科学家工程师协会"发起的一项国际科技界的合作。传递信息，加强交流，促进新世纪的科技繁荣是编著者们参与此项工作的共同信念。此外，这套丛书还具有特别的纪念意义。20 年前，历史的进程使成千上万的中国学生、学者有机会走出国门，到世界各地学习和从事科学研究。今天，活跃在世界科技前沿领域的中华学子们没有忘记振兴祖国科技教育事业的责任和推动国际学术交流与合作的义务。正是基于这一共同的心愿，大家积极参与这套系列丛书的撰写、组稿和编辑工作。为此，我们愿以这套丛书来纪念中国改革开放 20 周年。

编 委 会
1999. 6

Preface

In December 2002, the world's first commercial magnetic levitation supertrain went into operation in Shanghai. The train is held just above the rails by magnetic levitation (maglev) and can travel at a speed of 400 km/hr completing the 30km journey from the city to the airport in minutes. Now consumers are enjoying 50 GB hard drives compared to 0.5 GB hard drives ten years ago. Achievements in magnetic materials research have made dreams of a few decades ago reality. The objective of this book is to provide a comprehensive review of recent progress in magnetic materials research. The whole book consists of four volumes, each volume focusing on a specific field. Graduate students and professional researchers are targeted as the readers. Each chapter will have an introduction to give a clear definition of basic and important concepts of the topic. The details of the topic are then elucidated theoretically and experimentally. New ideas for further advancement are then discussed. Sufficient references are also included for those who wish to read the original work. Many of the authors are well known senior scientists. We have also chosen some accomplished young scientists to provide reviews on new and active topics.

In the last decade, one of the most significant thrust areas of materials research has been nanostructured magnetic materials. There are several critical sizes that control the behavior of a magnetic material. For example, the coercivity of a magnetic material made of particles increases with decreasing particle size, reaching a maximum where coherent rotation of a single-domain particle is realized, and then decreases with further decrease of the particle size. For a composite made of a magnetically hard phase and soft phase, when the grain size of the soft phase is sufficiently large, the soft and hard phases reverse independently. However, when the grain size of the soft phase is reduced to a size of about twice the domain wall thickness of the hard phase, the soft and hard phases will be exchange-coupled and behave as if a single magnetic phase is present. Such behavior can be used to increase the energy product of high-performance permanent magnets. Size effects become critical when dimensions approach a few nanometers, where quantum phenomena appear. The first volume of the book has therefore been devoted to the recent development of nanostructured magnetic materials, emphasizing size effects.

Our understanding of magnetism has advanced with the establishment of the theory of atomic magnetic moments and itinerant magnetism. In general, the magnetism of a bulk material can be considered as the superposition of atomic magnetic moments plus itinerant magnetism due to conduction electrons. In practical applications the situation becomes much more complicated. The boundary conditions have to be taken into account. This includes the size of the crystals, second-phase effects and intrinsic properties of each phase. The effects of magnetic relaxation over long periods of time can be critical to understanding. Simulation is a powerful tool for exploration and explanation of properties of various magnetic materials. Simulation also provides insight for further development of new materials. Naturally, before any simulation can be started, a model must be constructed. This requires that the material be well characterized. Therefore the second volume of the book provides a comprehensive review of both experimental methods and simulation techniques for the characterization of magnetic materials. After an introduction, each section gives a detailed description of the method and the following sections provide examples and results of the method. Finally further development of the method will be discussed.

The success of each type of magnetic material depends on its properties and cost which are directly related to its fabrication process. Processing of a material can be critical for development of artificial materials such as multilayer films, clusters, etc. Moreover, cost-effective processing usually determines whether a material can be commercialized. In recent years processing of materials has continuously evolved from improvement of traditional methods to more sophisticated and novel methods. The objective of the third volume of the book is to provide a comprehensive review of recent developments in processing of advanced magnetic materials. Each chapter will have an introduction and a section to provide a detailed description of the processing method. The following sections give detailed descriptions of the processing, properties and applications of the relevant materials. Finally the potential and limitation of the processing method will be discussed.

The properties of a magnetic material can be characterized by intrinsic properties such as anisotropy, saturation magnetization and extrinsic properties such as coercivity. The properties of a magnetic material can be affected by its chemical composition and processing route. With the continuous search for new materials and invention of new processing routes, magnetic properties of materials cover a wide spectrum of soft magnetic materials, hard magnetic materials, recording materials, sensor materials and others. The objective of the fourth volume of this book is to provide a comprehensive review of recent development of various magnetic materials and their applications. Each chapter will have an introduction of the materials and the principals of their applications. The following sections give a detailed description of the processing, properties and applications. Finally the potential and limitation of the materials will be discussed.

NASA is considering the launching of spacecraft by maglev. The first stage rocket, which accounts for two-thirds of the cost and is lost every launch, would be replaced by a maglev track. Using a 50 ft track NASA scientists have accelerated a model spacecraft to 96kph in less than half a second. In the last few decades the knowledge of mankind has been expanding rapidly into deep space measured by light years and the nano world where building blocks of atoms are being engineered. Magnetism and magnetic materials are among the most intriguing and fascinating science and engineering fields. Undoubtedly advances in magnetic materials research will continue to fuel our understanding of the universe in the new century. We hope this book will provide a useful reference for researchers working at the frontier of magnetic materials research.

We would like to express our sincere thanks to all our devoted authors, technical editors, and publishers for making this book possible.

The editors

Contents

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1 Intrinsic and Extrinsic Properties of Advanced Magnetic Materials

R. Skomski and D. J. Sellmyer

1.1 Introduction

Magnetic materials have inspired human imagination for millennia, and for many centuries they have stimulated progress in science and technology. For a long time, focus has been on naturally occurring magnetic materials, such as iron and magnetite (see Fig. 1.1). In the last few decades, there has been a revolution in the development of magnetic materials. On one hand, atomic-scale quantum-mechanical and relativistic effects have been exploited to create high-performance magnetic materials, such as the alloys $SmCo_5$ and $Nd_2Fe_{14}B$, which are used to produce permanent magnets. On the other hand, geometrically well-defined nanostructures such as multilayers, particle arrays and bulk composites, are now actively explored and used to fabricate magnetic materials for a wide range of applications (Coehoorn et al., 1988; Baibich et al., 1988; Skomski and Coey, 1993; McCurrie, 1994; Himpsel et al., 1998; Comstock, 1999; Wood, 2000; Weller et al., 2000; Ziese and Thornton, 2001; Sellmyer et al., 2002).

In magnetism, there is a fundamental distinction between intrinsic and extrinsic properties. Intrinsic properties, such as the spontaneous magnetization M_s, the Curie temperature T_C, and magnetocrystalline anisotropy, are realized on atomic length and time scales but describe infinite crystals. They can, in general, be considered as equilibrium properties. For example, the magnetization of α-Fe single crystals, $\mu_0 M_s = 2.15$ T, is associated with the body-centered cubic structure of elemental iron. (For magnetic units, see Appendix 1.1.) By contrast, extrinsic magnetic properties, such as the coercivity H_c and the remanence M_r, reflect the magnet's real-structure (morphology) (Bloch, 1932; Landau and Lifshitz, 1935; Kersten, 1943; Skomski and Coey, 1999). The strong real-structure dependence of extrinsic properties is seen, for example, from the fact that the coercivity of technical iron doubles by adding 0.01 wt.% nitrogen (Kersten, 1943). By comparison, intrinsic properties are not affected by small concentrations of defects. Extrinsic phenomena are, in general, nonequilibrium phenomena, closely related to magnetic hysteresis.

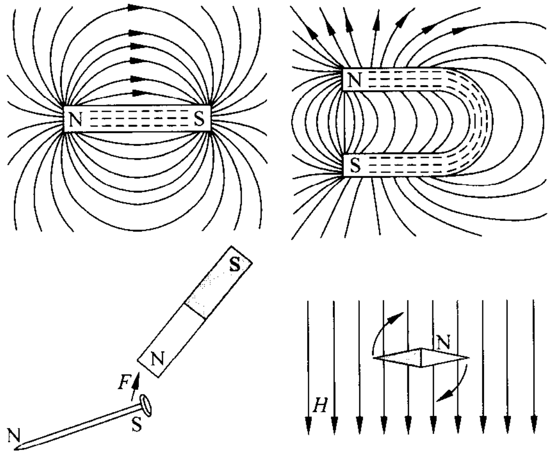

Figure 1. 1 Popular magnetism. Compiled from 20th-century middle-school textbooks, this figure correctly illustrates some phenomenological aspects of magnetism (magnetic field, Zeeman interaction, flux closure, difference between hard and soft magnets) but ignores the atomic origin of intrinsic magnetism (magnetic moment, magnetocrystalline anisotropy) and the nanoscale origin of hysteresis (granular anisotropy fluctuations, grain boundaries).

The involvement of nanoscale phenomena leads to the question: How many atoms are necessary to form a magnetic body, which can be considered as quasi-infinite? The answer depends on the considered magnetic property. Intrinsic properties tend to approach their bulk values on fairly small length scales. For example, "long-range" thermodynamic fluctuations, as involved in the realization of the Curie temperature, and deviations from the Bloch character of metallic wave functions yield only small corrections when the size of the magnetic particle exceeds about 1 nm. In the case of extrinsic properties, nanostructural effects are important on much larger length scales, typically at least several nm. One example is the enhancement of permanent magnet energy-product in exchange-coupled hard-soft nanocomposites (Skomski and Coey, 1993), for example in Fe-Pt composite films (Liu et al., 1998). This effect, where adding a soft phase improves the permanent-magnet performance of a hard phase, is realized on length scales of the order of 10 nm.

The scope of this chapter is to provide an introduction into the wide range of physical properties, nanogeometries, chemical compositions, and applications of magnetic materials of current interest in science and technology. Emphasis is on the physical nature of the phenomena. Numerical calculations and computer experiments (Daalderop et al., 1990; Coehoorn, 1989; Bland and Heinrich, 1994; Schrefl et al., 1994; Steinbeck et al., 1996; Sabiryanov and Jaswal, 1998a, 1998b; Sandratskii, 1998; Schrefl and Fidler, 1998; Lyberatos, 2000; Hertel, 2001) are of great importance in advanced magnetism, but the discussion of numerical details goes beyond the scope of this chapter. Section 1.2 deals with the atomic aspects of magnetism; Section 1.3 is devoted to the phenomenon of hysteresis; Section 1.4 briefly discusses the main classes of magnetic materials; and Section 1.5 is devoted to nanomagnetic effects.

1.2 Intrinsic Properties

Intrinsic properties refer to the atomic origin of magnetism and involve quantum phenomena such as exchange, crystal-field interaction, interatomic hopping and spin-orbit coupling (Ising, 1925; Heisenberg, 1928; Bloch, 1929; Brooks, 1940; Slater, 1953). The understanding of some problems of intrinsic magnetism, such as exchange (Heisenberg, 1928), dates back to the very early days of quantum mechanics, whereas the understanding and exploitation of the large magnetic anisotropy of advanced magnetic materials is a comparatively recent event. Intrinsic properties themselves are interesting figures of merit, but they also affect the hysteresis loop by entering the micromagnetic equations as parameters. In this section, we focus on the magnetic dipole moment per atom, the spontaneous magnetization, the magnetocrystalline anisotropy and the exchange stiffness.

1.2.1 Magnetic Moment

The moment of magnetic solids nearly exclusively originates from the partly filled inner electron shells of transition-metal atoms. Of particular importance are the iron-series transition-metal elements (3d elements) Fe, Co and Ni, and the rare-earth or 4f elements, such as Nd, Sm, Gd and Dy. On the other hand, palladium-series (4d), platinum-series (5d), and actinide (5f) elements, have a magnetic moment in suitable crystalline environments. The inner-shell electrons give rise to a magnetic moment m, which is often measured in Bohr magnetons per formula unit ($\mu_B = 9.2740 \times 10^{-24}\ \mathrm{Am}^2$). An alternative way of characterizing a material's net moment is to consider the spontaneous magnetization $M_s = m/V$, measured in A/m, or its flux-density equivalent $\mu_0 M_s$, measured in T. Here V is a small volume element containing at least one unit cell.

There are two sources of the atomic magnetic moment m: currents associated with the orbital motion of the electrons (orbital moment l) and the electron spin (spin moment s). The magnetism of free atoms or ions is governed by Hund's rules, which predict the spin and orbital moment as a function of the number inner-shell electrons (Kittel, 1986). Hund's rules are

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