Handbook of Magnetic Materials

Edited by

K.H.J. Buschow

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Volume 23

Editor

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Preface

The *Handbook of Magnetic Materials* series is a continuation of the *Handbook of Ferromagnetic Materials*. When Peter Wohlfarth started the latter series, his original aim was to combine new developments in magnetism with the achievements of earlier compilations, producing a worthy successor to Bozorth's classical and monumental book *Ferromagnetism*. This is the main reason that Ferromagnetic Materials was initially chosen as title for the handbook series although the latter aimed at giving a more complete cross-section of magnetism than Bozorth's book. In the last few decades, magnetism has seen an enormous expansion into a variety of different areas of research, comprising the magnetism of several classes of novel materials that share with truly ferromagnetic materials only the presence of magnetic moments. For this reason, the editor and the publisher carefully reconsidered the title of the series and changed it to the Handbook of Magnetic Materials. It is with much pleasure that I now introduce Volume 23.

Chapter 1 of this volume deals with supermagnetism. The advent of nanoscale materials has led to important improvements in materials properties and to new aspects in the understanding of matter in various fields of physics, chemistry and material science. Of particular interest are the achievements reached with magnetic nanoscale materials. Here it should be mentioned that the synthesis of magnetic nanomaterials has been a challenge in its own right, where many advances have been reached in the last two decades. Hand in hand with these advances in synthesis methods, a much better understanding of the electrical, magnetic, optical, and mechanical properties was reached that in turn made it possible that novel experimental techniques have been developed, leading to a much better characterization of nanoscale materials. It appeared that finite size effects, surface effects, and interparticle interactions are the main issues that dominate the magnetic properties of magnetic nanoparticles. The much reduced particle size is responsible for the so-called quantum confinement to able to control the nanoscale properties to a large extent. By contrast, surface effects result in symmetry breaking of the crystal structure at the nanoparticles' boundaries. Numerous review articles have been published in the past few decades dealing with the synthesis, properties, and applications of magnetic nanoparticles. Here the magnetic properties of nanoparticle assemblies of variant concentrations are reviewed. There is a discussion on how interparticle interactions of different strengths give rise to a variety of magnetic states such as superparamagnetism, superspin glass behavior, and superferromagnetism, which together form the field of supermagnetism. The review highlights the most important developments in the field. After introducing the basic magnetic properties of single domain nanoparticles, their mutual interactions and specific characterization methods are outlined. The types of different supermagnetic states mentioned are discussed with much attention being paid to the behavior of discontinuous metal-insulator multilayers as being universally representative. Superspin glass systems show all of the characteristic glassy properties including frustration, non-ergodicity and aging. Superferromagnetic domains in a non-percolated nanoparticle assembly are comparable to conventional ones in a continuous ferromagnetic film with the decisive difference that the atomic spins are replaced by the superspins of the single-domain nanoparticles. Correlated granular ferromagnets and self-assembled magnetic supracrystals also show various supermagnetic states depending on their superstructure and composition and may offer a wide application potential as multifunctional nanoparticle materials. At the end of this Chapter the current state of understanding is highlighted and some challenges in this field are mentioned that need to be addressed in the future.

In Chapter 2 a comprehensive review is given of non-Fermi liquid behavior in heavy fermion systems. Over many decades the Landau Fermi liquid theory has successfully been employed in explaining the low-energy behavior of most common metallic systems. At low temperatures this Fermi liquid behavior can be characterized by a linear temperature dependence of the specific heat with a renormalized specific-heat coefficient, by a generally weakly temperature-dependent but enhanced magnetic susceptibility and by an electrical resistivity consisting of a constant term and a term that increases quadratically in T. In the last few decades numerous U, Ce and Yb based heavy fermion systems have been reported to show deviations from Fermi liquid behavior. These deviations have been indicated as non-Fermi liquid behavior and often display a log(T)-dependence in the specific heat when plotted over T, a singular behavior of the magnetic susceptibility, and a resistivity showing a power-law dependence in T. In numerous investigations the breakdown of the Fermi liquid behavior was studied in systems where it was reached by varying the chemical pressure in alloys via element substitution or by changing the hydrostatic pressure or the magnetic field. These systems are often close to the onset of antiferromagnetism and the non-Fermi liquid behavior is considered to be due to the presence of a quantum critical point, although the latter point itself is experimentally elusive because it occurs at $T = 0$. A review of the experimental and theoretical studies dealing with this interesting class of materials is presented here. First fundamental aspects of Landau's phenomenological theory are briefly reviewed, followed by a presentation of the microscopic origin of heavy electrons through the Kondo and Anderson lattices. It is discussed how in terms of Doniach's picture the competition of the Kondo effect with the Ruderman–Kittel–Kasuya–Yosida interaction leads to a magnetically ordered phase and a Fermi liquid phase separated by a quantum critical point, the instability of the Fermi liquid being the origin of the non-Fermi liquid behavior. It is stressed that quantum critical points and non-Fermi liquid behavior can be viewed as a natural occurrence in low-dimensional critical phenomena. The discussion includes several examples such as the multichannel Kondo model, Luttinger liquids, the anisotropic Heisenberg chain, and long-range order in two dimensions. Also disorder driven quantum criticality is briefly addressed and the results are analyzed for a microscopic model for quantum criticality due to nested Fermi surfaces.

Chapter 3 reviews the magnetic and physical properties of cobalt perovskites. The cobalt oxides with the perovskite structure form a large group of exciting materials. They have been the subject of many studies because this group harbors a plethora of complex compositional, structural, magnetic, and electrical-transport properties. To date there are still many ongoing studies, many of which deal with controversial aspects. It interesting to note that apart from the cobalt perovskites there exist an equally interesting group of structurally related materials formed by the manganite perovskites, materials for which the physics is notably different. The properties of these manganite perovskites have been reviewed in Volume 22 of this handbook. The extraordinary rich physics of cobalt perovskites is strongly related to their specific crystal chemistry which in turn originates from the electronic properties of cobalt. This transition metal component can be present in different oxidation states such as Co^{2+}, Co^{3+}, Co^{4+}. This opens the possibility of the formation of a large variety of different coordinations, including those of tetrahedral, octahedral, square pyramidal, trigonal bipyramidal symmetry. The upshot is that mixed-valency perovskites can be formed in which oxygen deficiency plays an important role. This oxygen deficiency, in turn, can give rise to the interesting phenomenon of ordering–disordering of oxygen vacancies in non-stoichiometric compounds. All these features can occur to different degrees in the various cobalt perovskites, depending strongly on the nature of the third component (such as for instance rare earths or alkaline earths) in these mixed oxide materials. An additional feature arises from the crystal field splitting of the 3D orbitals of the Co atoms. This leads to triply degenerate t_{2g} levels and doubly degenerate e_g levels. Depending on the oxidation state of the Co atoms, these states are increasingly occupied with electrons when moving in the sequence Co^{4+}, Co^{3+}, Co^{2+}. As a consequence, various spin states may develop, including high spin ($S = 3/2$), intermediate spin ($S = 1$), and low spin ($S = 1/2$). Which of these spin states is reached depends on how the degree of occupation of the t_{2g} levels and e_g levels is realized, which can be influenced by various external circumstances. This opens the possibility of spin state transitions brought about for instance by varying the temperature, the pressure or the magnetic field. Needless to say, this can have serious consequences for the magnetic and transport properties. As follows from the above, there is an enormous wealth of physical phenomena observed experimentally in the various types of perovskites as reviewed here. In this chapter the authors have concentrated on the stoichiometric perovskites of the types $LnCoO_3$ and $Ln_{1-x}A_xCoO_3$, where cobalt is only in octahedral coordination, and on the oxygen deficient perovskites of the types $Sr_{1-x}Ln_xCoO_{3-\delta}$ and $LnBaCo_2O_{5+\delta}$, where cobalt exhibits at least two sorts of coordination with possible order–disorder oxygen vacancies phenomena. All reviewed experimental accomplishments are discussed in the framework of the current physical understanding.

Chapter 4 deals with ferrites. These materials are of long standing interest in the field of magnetism, as witnessed, for instance, by several reviews on ferrite properties and their application presented already in Volumes 2 and 3 of this Handbook. The advent of nanotechnology revealed that substantial improvements in magnetic and high-frequency properties can be reached, which, in turn, have led to novel types of application of many ferrites. This has necessitated a reconsideration of the ferrite reviews presented in earlier chapters of the Handbook. An updated review on high-frequency ferrites was published recently in Volume 20. Generally, it can be said that the past decade has seen the development of novel types of magnetic materials. Especially nanosized ferrites have attracted much interest as strategic materials that can be applied in a large variety of different fields. In the last chapter of this volume, the authors briefly discuss the importance and need of bulk and nanoferrites and their use in various fields such as communication, microwaves, electromagnetic shielding, memory devices, multiferroics, spintronics devices, humidity/gas sensing, drug delivery, hyperthermia, and biosensors. For some selected fields the authors present a more detailed discussion of fabrication techniques and the resulting specific magnetic and electrical properties along with the application of ferrite nanostructures or nanomaterials. The chapter is interspersed with fundamental aspects and typical experimental approaches of a few well-established techniques of nanoparticle syntheses particularly used for ferrites.

Volume 23 of the Handbook on the Properties of Magnetic Materials, like the preceding volumes, has a dual purpose. As a textbook, it is intended to be of assistance to those who wish to be introduced to a given topic in the field of magnetism without the need to read the vast amount of literature published. As a reference work, it is intended for scientists active in magnetism research. To this dual purpose, Volume 23 of the Handbook comprises topical review articles written by leading authorities. In each of these articles, an extensive description is given in graphical as well as in tabular form, much emphasis being placed on the discussion of the experimental material in the framework of physics, chemistry, and material science. The task to provide the readership with novel trends and achievements in magnetism would have been extremely difficult without the professionalism of the North Holland Physics Division of Elsevier B.V.

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