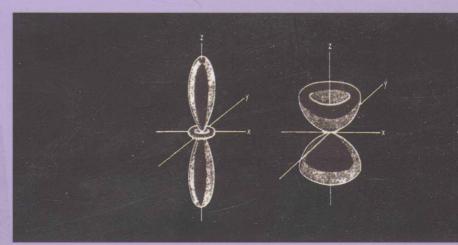
K. H. J. Buschow, F. R. De Boer

Physics of Magnetism and Magnetic Materials

磁性物理学和磁性材料



Physics of Magnetism and Magnetic Materials

K. H. J. Buschow

Van der Waals-Zeeman Instituut Universiteit van Amsterdam Amsterdam, The Netherlands

and

F. R. de Boer

Van der Waals-Zeeman Instituut Universiteit van Amsterdam Amsterdam, The Netherlands



Kluwer Academic/Plenum Publishers New York, Boston, Dordrecht, London, Moscow

Library of Congress Cataloging-in-Publication Data

Buschow, K.H. J.

Physics of magnetism and magnetic materials/K.H.J. Buschow & F.R. de Boer.

p. cm.

Includes bibliographical references and index.

ISBN 0-306-47421-2

1. Magnetism. 2. Magnetic materials. I. Boer, F. R. de (Frank R.) II. Title.

QC753.2 .B88 2003 538—dc21

2002034118

Reprint from English language edition:

Physics of Magnetism and Magnetic Materials
by K. H. J. Buschow. E. R. De Boer
Copyright © 2003, Springer US
Springer US is a part of Springer Science+Business Media
All Rights Reserved

This reprint has been authorized by Springer Science & Business Media for distribution in China Mainland only and not for export therefrom.

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher, with the exception of any material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work.

图书在版编目 (CIP) 数据

磁性物理学和磁性材料 = Physics of Magnetism and Magnetic Materials: 英文/(荷)布朔 (Buschow, K. H. J.)著.—影印本.—北京:世界图书出版公司北京公司, 2012.8

ISBN 978 -7 -5100 -5045 -9

I. ①磁··· II. ①布··· III. ①磁学—英文②磁性材料—英文 IV. ①0441. 2 ②TM27

中国版本图书馆 CIP 数据核字 (2012) 第 186174 号

书 名: Physics of Magnetism and Magnetic Materials

作 者: K. H. J. Buschow, F. R. De Boer

中 译 名: 磁性物理学和磁性材料

责任编辑: 高蓉 刘慧

出版者: 世界图书出版公司北京公司

印刷者: 三河市国英印务有限公司

发 行: 世界图书出版公司北京公司(北京朝内大街 137 号 100010)

联系电话: 010-64021602, 010-64015659

电子信箱: kjb@ wpcbj. com. en

开 本: 24 开

印 张: 8

版 次: 2013年1月

版权登记: 图字: 01 - 2012 - 5876

书 号: 978-7-5100-5045-9 定 价: 35.00元

Physics of Magnet and Magnetic Mate

Contents

Chapter 1. Introduction	1
Chapter 2. The Origin of Atomic Moments	3
2.1. Spin and Orbital States of Electrons	3
2.2. The Vector Model of Atoms	5
Chapter 3. Paramagnetism of Free Ions	11
3.1. The Brillouin Function	11
3.2. The Curie Law	13
References	17
Chapter 4. The Magnetically Ordered State	19
4.1. The Heisenberg Exchange Interaction and the Weiss Field	19
4.2. Ferromagnetism	22
4.3. Antiferromagnetism	26
4.4. Ferrimagnetism	34
References	41
Chapter 5. Crystal Fields	43
5.1. Introduction	43
5.2. Quantum-Mechanical Treatment	44
5.3. Experimental Determination of Crystal-Field Parameters	50
5.4. The Point-Charge Approximation and Its Limitations	52
5.5. Crystal-Field-Induced Anisotropy	54
5.6. A Simplified View of 4f-Electron Anisotropy	56
References	57
Chapter 6. Diamagnetism	59
Reference	61

vi CONTENTS

Chapter 7. Itinerant-Electron Magnetism	63
7.1. Introduction	63
7.2. Susceptibility Enhancement	65
7.3. Strong and Weak Ferromagnetism	66
7.4. Intersublattice Coupling in Alloys of Rare Earths and 3d Metals	70
References	73
Chapter 8. Some Basic Concepts and Units	75
References	83
References	63
Classes O. Management Trabairment	85
Chapter 9. Measurement Techniques	
9.1. The Susceptibility Balance	85
9.2. The Faraday Method	86
9.3. The Vibrating-Sample Magnetometer	87
9.4. The SQUID Magnetometer	89
References	89
Chapter 10. Caloric Effects in Magnetic Materials	91
10.1. The Specific-Heat Anomaly	91
10.2. The Magnetocaloric Effect	93
References	95
Chapter 11. Magnetic Anisotropy	97
References	
TOTOLOGO	102
Chapter 12. Permanent Magnets	105
•	105
	105
12.3. Domains and Domain Walls	
A THE ACT OF THE PROPERTY OF T	112
12.5. Magnetic Anisotropy and Exchange Coupling in Permanent-Magnet	115
Materials Based on Rare-Earth Compounds	
12.6. Manufacturing Technologies of Rare-Earth-Based Magnets	
12.7. Hard Ferrites	
12.8. Alnico Magnets	
References	128
Chapter 13. High-Density Recording Materials	131
13.1. Introduction	131
13.2. Magneto-Optical Recording Materials	
13.3. Materials for High-Density Magnetic Recording	139
References	145

CONTENTS vii

Chapter 14. Soft-Magnetic Materials	147							
14.1. Introduction	147							
14.2. Survey of Materials	148							
14.3. The Random-Anisotropy Model								
14.4. Dependence of Soft-Magnetic Properties on Grain Size	158							
14.5. Head Materials and Their Applications	159							
14.5.1 High-Density Magnetic-Induction Heads	159							
14.5.2 Magnetoresistive Heads								
References	163							
Chapter 15. Invar Alloys	165							
References								
Chapter 16. Magnetostrictive Materials	171							
References	175							
Reterences	1,5							
Author Index	177							
Author index	1//							
Subject Index	179							

Introduction

The first accounts of magnetism date back to the ancient Greeks who also gave magnetism its name. It derives from Magnesia, a Greek town and province in Asia Minor, the etymological origin of the word "magnet" meaning "the stone from Magnesia." This stone consisted of magnetite (Fe₃O₄) and it was known that a piece of iron would become magnetized when rubbed with it.

More serious efforts to use the power hidden in magnetic materials were made only much later. For instance, in the 18th century smaller pieces of magnetic materials were combined into a larger magnet body that was found to have quite a substantial lifting power. Progress in magnetism was made after Oersted discovered in 1820 that a magnetic field could be generated with an electric current. Sturgeon successfully used this knowledge to produce the first electromagnet in 1825. Although many famous scientists tackled the phenomenon of magnetism from the theoretical side (Gauss, Maxwell, and Faraday) it is mainly 20th century physicists who must take the credit for giving a proper description of magnetic materials and for laying the foundations of modern technology. Curie and Weiss succeeded in clarifying the phenomenon of spontaneous magnetization and its temperature dependence. The existence of magnetic domains was postulated by Weiss to explain how a material could be magnetized and nevertheless have a net magnetization of zero. The properties of the walls of such magnetic domains were studied in detail by Bloch, Landau, and Néel.

Magnetic materials can be regarded now as being indispensable in modern technology. They are components of many electromechanical and electronic devices. For instance, an average home contains more than fifty of such devices of which ten are in a standard family car. Magnetic materials are also used as components in a wide range of industrial and medical equipment. Permanent magnet materials are essential in devices for storing energy in a static magnetic field. Major applications involve the conversion of mechanical to electrical energy and vice versa, or the exertion of a force on soft ferromagnetic objects. The applications of magnetic materials in information technology are continuously growing.

In this treatment, a survey will be given of the most common modern magnetic materials and their applications. The latter comprise not only permanent magnets and invar alloys but also include vertical and longitudinal magnetic recording media, magneto-optical recording media, and head materials. Many of the potential readers of this treatise may have developed considerable skill in handling the often-complex equipment of modern

information technology without having any knowledge of the materials used for data storage in these systems and the physical principles behind the writing and the reading of the data. Special attention is therefore devoted to these subjects.

Although the topic Magnetic Materials is of a highly interdisciplinary nature and combines features of crystal chemistry, metallurgy, and solid state physics, the main emphasis will be placed here on those fundamental aspects of magnetism of the solid state that form the basis for the various applications mentioned and from which the most salient of their properties can be understood.

It will be clear that all these matters cannot be properly treated without a discussion of some basic features of magnetism. In the first part a brief survey will therefore be given of the origin of magnetic moments, the most common types of magnetic ordering, and molecular field theory. Attention will also be paid to crystal field theory since it is a prerequisite for a good understanding of the origin of magnetocrystalline anisotropy in modern permanent magnet materials. The various magnetic materials, their special properties, and the concomitant applications will then be treated in the second part.

The Origin of Atomic Moments

2.1. SPIN AND ORBITAL STATES OF ELECTRONS

In the following, it is assumed that the reader has some elementary knowledge of quantum mechanics. In this section, the vector model of magnetic atoms will be briefly reviewed which may serve as reference for the more detailed description of the magnetic behavior of localized moment systems described further on. Our main interest in the vector model of magnetic atoms entails the spin states and orbital states of free atoms, their coupling, and the ultimate total moment of the atoms.

The elementary quantum-mechanical treatment of atoms by means of the Schrödinger equation has led to information on the energy levels that can be occupied by the electrons. The states are characterized by four quantum numbers:

- 1. The total or principal quantum number n with values $1, 2, 3, \ldots$ determines the size of the orbit and defines its energy. This latter energy pertains to one electron traveling about the nucleus as in a hydrogen atom. In case more than one electron is present, the energy of the orbit becomes slightly modified through interactions with other electrons, as will be discussed later. Electrons in orbits with $n = 1, 2, 3, \ldots$ are referred to as occupying K, L, M, \ldots shells, respectively.
- 2. The orbital angular momentum quantum number l describes the angular momentum of the orbital motion. For a given value of l, the angular momentum of an electron due to its orbital motion equals $\hbar\sqrt{l(l+1)}$. The number l can take one of the integral values $0, 1, 2, 3, \ldots, n-1$ depending on the shape of the orbit. The electrons with $l=0,1,2,3,4,\ldots$ are referred to as s, p, d, f, g,...electrons, respectively. For example, the M shell (n=3) can accommodate s, p, and d electrons.
- 3. The magnetic quantum number m_l describes the component of the orbital angular momentum l along a particular direction. In most cases, this so-called quantization direction is chosen along that of an applied field. Also, the quantum numbers m_l can take exclusively integral values. For a given value of l, one has the following possibilities: $m_l = l, l 1, \ldots, 0, \ldots, -l + 1, -l$. For instance, for a d electron the permissible values of the angular momentum along a field direction are $2\hbar$, \hbar , $0, -\hbar$, and $-2\hbar$. Therefore, on the basis of the vector model of the atom, the plane of the electronic orbit can adopt only certain possible orientations. In other words, the atom is spatially quantized. This is illustrated by means of Fig. 2.1.1.

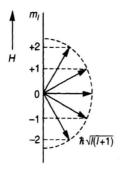


Figure 2.1.1. Vector model of the atom applied to the situation l=2 and nonzero external field.

4. The spin quantum number m_s describes the component of the electron spin s along a particular direction, usually the direction of the applied field. The electron spin s is the intrinsic angular momentum corresponding with the rotation (or spinning) of each electron about an internal axis. The allowed values of m_s are $\pm 1/2$, and the corresponding components of the spin angular momentum are $\pm \hbar/2$.

According to Pauli's principle (used on p. 10) it is not possible for two electrons to occupy the same state, that is, the states of two electrons are characterized by different sets of the quantum numbers n, l, m_l , and m_s . The maximum number of electrons occupying a given shell is therefore

$$2\sum_{l=0}^{n-1} (2l+1) = 2n^2. (2.1.1)$$

The moving electron can basically be considered as a current flowing in a wire that coincides with the electron orbit. The corresponding magnetic effects can then be derived by considering the equivalent magnetic shell. An electron with an orbital angular momentum $\hbar l$ has an associated magnetic moment

$$\vec{\mu}_l = -\frac{|e|}{2m}\hbar \vec{l} = -\mu_B \vec{l},$$
 (2.1.2)

where μ_{B} is called the Bohr magneton. The absolute value of the magnetic moment is given by

$$|\vec{\mu}_l| = \mu_B \sqrt{l(l+1)}$$
 (2.1.3)

and its projection along the direction of the applied field is

$$\mu_{lz} = -m_l \mu_B. \tag{2.1.4}$$

The situation is different for the spin angular momentum. In this case, the associated magnetic moment is

$$\vec{\mu}_s = -g_e \frac{|e|}{2m} \hbar \vec{s} = -g_e \mu_B \vec{s}, \qquad (2.1.5)$$



Figure 2.1.2. Effect of a magnetic field on the energy levels of the two electron states with $m_s = +1/2$ and $m_s = -1/2$.

where g_e (=2.002290716 (10)) is the spectroscopic splitting factor (or the *g*-factor for the free electron). The component in the field direction is

$$\mu_{sz} = -g_e m_s \mu_B. \tag{2.1.6}$$

The energy of a magnetic moment $\vec{\mu}$ in a magnetic field \vec{H} is given by the Hamiltonian

$$H = -\mu_0 \vec{\mu} \cdot \vec{H} = -\vec{\mu} \cdot \vec{B}, \qquad (2.1.7)$$

where \vec{B} is the flux density or the magnetic induction and $\mu_0 = 4\pi \times 10^{-7} \,\mathrm{T}\,\mathrm{m}\,\mathrm{A}^{-1}$ is the vacuum permeability. The lowest energy E_0 , the ground-state energy, is reached for $\vec{\mu}$ and \vec{H} parallel. Using Eq. (2.1.6) and $m_s = -1/2$, one finds for one single electron

$$E_0 = -\mu_0 \mu_{sz} H = +g_e m_s \mu_0 \mu_B H = -\frac{1}{2} g_e \mu_0 \mu_B H. \tag{2.1.8}$$

For an electron with spin quantum number $m_s = +1/2$, the energy equals $+\frac{1}{2}g_e\mu_0\mu_B H$. This corresponds to an antiparallel alignment of the magnetic spin moment with respect to the field.

In the absence of a magnetic field, the two states characterized by $m_s = \pm 1/2$ are degenerate, that is, they have the same energy. Application of a magnetic field lifts this degeneracy, as illustrated in Fig. 2.1.2. It is good to realize that the magnetic field need not necessarily be an external field. It can also be a field produced by the orbital motion of the electron (Ampère's law, see also the beginning of Chapter 8). The field is then proportional to the orbital angular momentum l and, using Eqs. (2.1.5) and (2.1.7), the energies are proportional to $\vec{s} \cdot \vec{l}$. In this case, the degeneracy is said to be lifted by the spin-orbit interaction.

2.2. THE VECTOR MODEL OF ATOMS

When describing the atomic origin of magnetism, one has to consider orbital and spin motions of the electrons and the interaction between them. The total orbital angular momentum of a given atom is defined as

$$\vec{L} = \sum_{i} \vec{l}_i, \tag{2.2.1}$$

where the summation extends over all electrons. Here, one has to bear in mind that the summation over a complete shell is zero, the only contributions coming from incomplete

shells. The same arguments apply to the total spin angular momentum, defined as

$$\vec{S} = \sum_{i} \vec{s}_i. \tag{2.2.2}$$

The resultants \vec{S} and \vec{L} thus formed are rather loosely coupled through the spin-orbit interaction to form the resultant total angular momentum \vec{J} :

$$\vec{J} = \vec{L} + \vec{S}. \tag{2.2.3}$$

This type of coupling is referred to as Russell-Saunders coupling and it has been proved to be applicable to most magnetic atoms. J can assume values ranging from J=(L-S), (L-S+1), to (L+S-1), (L+S). Such a group of levels is called a multiplet. The level lowest in energy is called the ground-state multiplet level. The splitting into the different kinds of multiplet levels occurs because the angular momenta \vec{L} and \vec{S} interact with each other via the spin-orbit interaction with interaction energy $\lambda \vec{L} \cdot \vec{S}$ (λ is the spin-orbit coupling constant). Owing to this interaction, the vectors \vec{L} and \vec{S} exert a torque on each other which causes them to precess around the constant vector \vec{J} . This leads to a situation as shown in Fig. 2.2.1, where the dipole moments $\vec{\mu}_L = -\mu_B \vec{L}$ and $\vec{\mu}_S = -g_e \mu_B \vec{S}$, corresponding to the orbital and spin momentum, also precess around \vec{J} . It is important to realize that the total momentum $\vec{\mu}_{tot} = \vec{\mu}_L + \vec{\mu}_S$ is not collinear with \vec{J} but is tilted toward the spin owing to its larger gyromagnetic ratio. It may be seen in Fig. 2.2.1 that the vector $\vec{\mu}_{tot}$ makes an angle θ with \vec{J} and also precesses around \vec{J} . The precession frequency is usually quite high so that only the component of $\vec{\mu}_{tot}$ along \vec{J} is observed, while the other component averages out to zero. The magnetic properties are therefore determined by the quantity

$$\vec{\mu} = \vec{\mu}_{tot} \cos \theta = -g_J \mu_B J. \tag{2.2.4}$$

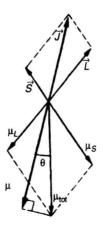


Figure 2.2.1. Spin-orbit interaction between the angular momenta \vec{S} and \vec{L} .

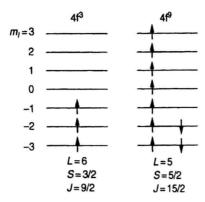


Figure 2.2.2. Application of Hund's rules to find the ground-state multiplet for an atom with three 4f electrons $(4f^3)$ and nine 4f electrons $(4f^9)$.

It can be shown that

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. (2.2.5)$$

This factor is called the Landé spectroscopic g-factor.

For a given atom, one usually knows the number of electrons residing in an incomplete electron shell, the latter being specified by its quantum numbers. We then may use Hund's rules to predict the values of L, S, and J for the free atom in its ground state. Hund's rules are:

- (1) The value of S takes its maximum as far as allowed by the exclusion principle.
- (2) The value of L also takes its maximum as far as allowed by rule (1).
- (3) If the shell is less than half full, the ground-state multiplet level has J = L S, but if the shell is more than half full the ground-state multiplet level has J = L + S.

The most convenient way to apply Hund's rules is as follows. First, one constructs the level scheme associated with the quantum number l. This leads to 2l+1 levels, as shown for f electrons (l=3) in Fig. 2.2.2. Next, these levels are filled with the electrons, keeping the spins of the electrons parallel as far as possible (rule 1) and then filling the consecutive lowest levels first (rule 2). If one considers an atom having more than 2l+1 electrons in shell l, the application of rule 1 implies that first all 2l+1 levels are filled with electrons with parallel spins before the remainder of electrons with opposite spins are accommodated in the lowest, already partly occupied, levels. Two examples of 4f-electron systems are shown in Fig. 2.2.2. The value of L is obtained from inspection of the m_l values of the occupied levels whereas S is equal to $\frac{1}{2} \times$ (net number of spin-up electrons). The J values are then obtained from rule 3.

Most of the lanthanide elements have an incompletely filled 4f shell. It can be easily verified that the application of Hund's rules leads to the ground states as listed in Table 2.2.1. The variation of L and S across the lanthanide series is illustrated also in Fig. 2.2.3.

The same method can be used to find the ground-state multiplet level of the 3d ions in the iron-group salts. In this case, it is the incomplete 3d shell, which is gradually filled up.

			(0)	-, -	(- , -/,				
Ion	4f ⁿ	Ground term	L	S	J	8	$g\sqrt{J(J+1)}$	gJ	G*
La ³⁺	0	¹ S ₀	0	0	_	0	0	0	0
Ce ³⁺	1	$^{2}F_{5/2}$	1/2	3	5/2	6/7	2.54	2.14	0.011
Pr^{3+}	2	³ H ₄	1	5	4	4/5	3.58	3.20	0.051
Nd^{3+}	3	4l _{9/2}	3/2	6	9/2	8/11	3.62	3.28	0.116
Pm^{3+}	4	³ I ₄	2	6	4	3/5	2.68	2.40	0.217
Sm^{3+}	5	6H5/2	5/2	5	5/2	2/7	0.84	0.72	0.283
Eu ³⁺	6	'Fo	3	3	0	0	0	0	0
Gd^{3+}	7	8S7/2	7/2	0	7/2	2	7.94	7	1
Tb^{3+}	8	'F ₆	3	3	6	3/2	9.72	9	0.667
Dy^{3+}	9	$^{6}H_{15/2}$	5/2	5	15/2	4/3	10.63	10	0.450
Ho ³⁺	10	$^{5}I_{8}$	2	6	8	5/4	10.60	10	0.286
Er^{3+}	11	4I _{15/2}	3/2	6	15/2	6/5	9.59	9	0.162
Tm^{3+}	12	³ H ₆	1	5	6	7/6	7.57	7	0.074
Yb^{3+}	13	$^{2}F_{7/2}$	1/2	3	7/2	8/7	4.54	4	0.020
Lu ³⁺	14	$^{1}S_{0}$	0	0	0	_	0	0	0

Table 2.2.1. Selected ionic properties of the rare-earth elements. The quantity G^* represents the De Gennes factor $G = (g_I - 1)^2 J(J + 1)$, normalized to the value for Gd^{3+}

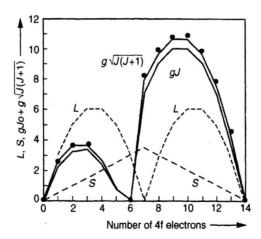


Figure 2.2.3. Variation of L, S, gJ, and $g\sqrt{J(J+1)}$ across the lanthanide series. The latter values are compared with experimental results obtained from χ^{-1} versus T plots (see Section 3.1) of various rare-earth tri-aluminides, represented as filled circles.

As seen in Tables 2.2.1 and 2.2.2, the maximum S value is reached in each case when the shells are half filled (five 3d electrons or seven 4f electrons).

In most cases, the energy separation between the ground-state multiplet level and the other levels of the same multiplet are large compared to kT. For describing the magnetic properties of the ions at 0 K, it is therefore sufficient to consider only the ground

Z	Ion	Ground term	L	S	J	M _{eff,exp}	$g\sqrt{J(J+1)}$ $g\sqrt{L(L+1)}$		$\frac{2\sqrt{S(S+1)}}{4S(S+1)}$
18	K^+, V^{5+}	$^{1}S_{0}$	0	0	0	diam.	0	0	0
19	Sc^{2+} , Ti^{3+} , V^{4+}	$^{2}D_{3/2}$	2	1/2	3/2	1.73	1.55	3.01	1.78
20	Ti^{2+}, V^{3+}	$^{3}F_{2}$	3	1	2	2.83	1.63	4.49	2.83
21	V^{2+} , Cr^{3+} , Mn^{4+}	$^{4}F_{3/2}$	3	3/2	3/2	3.82	0.70	5.21	3.87
22	Cr^{2+} , Mn^{3+}	$^{5}D_{0}$	2	2	0	4.81	0	5.50	4.91
23	Mn^{2+} , Fe^{3+}	$^{6}S_{5/2}$	0	5/2	5/2	5.85	5.92	5.92	5.92
24	Fe ²⁺	5D_4	2	2	4	5.52 - 5.22	6.71	5.50	4.91
25	Co ²⁺	$^{4}F_{9/2}$	3	3/2	9/2	5.20 - 4.43	6.63	5.21	3.87
26	Ni ²⁺	$^{3}F_{4}$	3	1	4	3.23	5.59	4.49	2.83
27	Cu ²⁺	$^{2}D_{5/2}$	2	1/2	5/2	2.02 - 1.81	3.55	3.01	1.73

Table 2.2.2. Selected ionic properties of iron-group elements containing Z electrons

level characterized by the angular momentum quantum number J listed in Tables 2.2.1 and 2.2.2.

For completeness it is mentioned here that the components of the total angular momentum \vec{J} along a particular direction are described by the magnetic quantum number m_J . In most cases, the quantization direction is chosen along the direction of the field. For practical reason, we will drop the subscript J and write simply m to indicate the magnetic quantum number associated with the total angular momentum \vec{J} .