

# Magnetic Oxides

Gerald F. Dionne

# Magnetic Oxides

 Springer

Gerald F. Dionne  
Massachusetts Institute of Technology  
244 Wood Street  
Lexington, MA 02420  
dionne@ll.mit.edu

ISBN 978-1-4419-0053-1            e-ISBN 978-1-4419-0054-8  
DOI 10.1007/978-1-4419-0054-8  
Springer New York Dordrecht Heidelberg London

Library of Congress Control Number: 2009935694

© Springer Science+Business Media, LLC 2009

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, LLC, 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks, and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed on acid-free paper

Springer is part of Springer Science+Business Media ([www.springer.com](http://www.springer.com))

*The author dedicates this book to*

*Rev. Hugh McPhee, S.J.,  
former Dean of Science at Loyola College  
in Montreal,*

*who once advised a liberal arts student  
that science could offer a clearer window  
on the world.*

# Preface

The inspirations for this book probably began in 1961 when I left a promising career as a semiconductor device engineer in the Rte 128 cauldron of the Boston area to pursue a new challenge at the McGill University Eaton Electronics Research Laboratory. Three years later I wrote a Ph.D. thesis on paramagnetic resonance and 3 years after I was adding to that experience as a Staff Member with MIT Lincoln Laboratory, where the scope of my obligations gradually broadened from microwave magnetic resonance to the physics and chemistry of ferrites and related magnetic oxide systems. At the time of this writing, I continue there as a resident consultant and also as a research affiliate with the MIT Department of Materials Science and Engineering.

Magnetic resonance has played a vital role in the study of magnetism in oxides and other insulating compounds that began during World War II and flourished globally for a quarter century. During this halcyon period, texts on magnetism became abundant as many of the pioneers took pen in hand to leave a treasure of elegantly presented reference literature as the 1960s drew to a close. By the mid-1970s, the once-fledgling field of semiconductor electronics that I had abandoned was overwhelming almost all competing technologies, including those with a magnetic component. For the better part of the two decades between the end of the Vietnam war and the discoveries of high-temperature superconductivity and giant magnetoresistance in transition-metal oxides in the early 1990s, fundamental investigations of magnetic compounds were nearly dormant.

The content and organization of this volume are intended to serve two purposes: (1) bridging of the intellectual gap left by the 20 years of reduced inquiry into magnetic phenomena, and (2) restoration of the molecular approach to the study of magnetic insulators that function more by local rather than the collective electron interactions that are more characteristic of metals and semiconductors.

The level of discussion presumes the reader to have some familiarity with atomic physics and basic quantum mechanics. Chapter 1 is an abbreviated introduction to magnetism. The discussion begins with a reminder of some fundamental definitions and selected subjects that can be found in most standard textbooks. However, two topics are treated in greater depth. A generic description of the quantum origins of magnetic exchange introduces the antisymmetry requirements of the hybrid eigenstates that determine the stabilization of parallel (metal) or antiparallel (insulator)

spin alignment. This general theory is intended to support the later discussion of superexchange that is approached with a model that is more specific to magnetic oxides. An introduction to magnetic resonance and relaxation derived from classical Larmor precession serves a similar purpose for the examination of the broad subject of electromagnetism in ferrites. The physics and chemistry of magnetism in oxide compounds is covered in Chaps. 2, 3, and 4 in terms of localized ion and molecular-orbital models of molecular bonding. Chapter 5 addresses the secondary magnetic phenomena of anisotropy and magnetostriction from the standpoint of local orbital interactions with crystal fields and spin-orbit coupling that produces self-induced magnetoelastic effects. Traditional phenomenological theories are then reviewed in preparation for the examination of electromagnetic properties in Chap. 6. In Chaps. 7 and 8, magneto-optics and polarized spin transport that will be of increasing importance in the age of molecular-scale structures are described in the conceptual context of the earlier chapters.

As the preparation of this monograph draws to a close, I reflect on the journey that brought me to this point. From the frequency of their citations, the reader is certain to recognize the reliance on the seminal works of John Van Vleck, Maurice Pryce, John Goodenough, and Ernst Schlœmann, as well as the classic textbooks of Alan Morrish, Sōshin Chikazumi, Carl Ballhausen, Benjamin Lax and Kenneth Button, and many others. There were also collaborations with academia, industry, and government that are too numerous to list in any detail. However, I cannot pass up this opportunity to acknowledge the guidance of my doctoral thesis advisor Garnet Woonton and his colleague Maurice Pryce who was a most encouraging external examiner. Lincoln Laboratory's radar leaders John Allen, Carl Blake, Donald Temme, and Roger Sudbury who supported me and my vigorous colleagues Jerald Weiss, James Fitzgerald, Daniel Oates, and Russell West (of Trans-Tech, Inc.). Then there was the mentorship of John Goodenough and Benjamin Lax and the MIT campus affiliations with Mildred and Gene Dresselhaus, and Caroline Ross. Finally, I must mention the associations with Kristl Hathaway, Gary Prinz, and Stuart Wolf of the US Departments of the Navy and DARPA, and the assistance of Elaine Tham and Lauren Danahy of Springer US.

Lexington  
MA

*Gerald F. Dionne*

# Contents

<b>1</b>	<b>Introductory Magnetism</b> .....	1
1.1	Fundamental Concepts and Definitions .....	1
1.1.1	Basic Electrostatics.....	2
1.1.2	Basic Magnetostatics .....	3
1.1.3	Demagnetization in Uniformly Magnetized Bodies .....	4
1.1.4	Domains in Partially Magnetized Bodies .....	6
1.2	Induced Magnetism.....	8
1.2.1	Diamagnetism and Paramagnetism .....	8
1.2.2	Temperature Dependence of Susceptibility .....	11
1.3	Spontaneous Magnetism .....	15
1.3.1	Classical Ferromagnetism and Antiferromagnetism.....	15
1.3.2	Solutions of the Brillouin–Weiss Equation .....	16
1.3.3	Quantum Origins of the Molecular Field .....	19
1.3.4	The Ising Approximation .....	24
1.4	Gyromagnetism.....	25
1.4.1	Larmor Precession and Resonance .....	26
1.4.2	Phenomenological Relaxation Theory .....	27
1.4.3	Complex Susceptibility Theory.....	29
1.4.4	Resonance Line Shapes .....	33
	Appendix 1A Spin–Lattice Contribution to Linewidth .....	34
	References.....	35
<b>2</b>	<b>Magnetic Ions in Oxides</b> .....	37
2.1	The Transition Metals .....	37
2.1.1	The Periodic Table .....	38
2.1.2	Iron Group $3d^n$ Ions .....	40
2.1.3	Rare Earth $4f^n$ Ions.....	42
2.1.4	$4d^n$ and $5d^n$ Ions .....	42
2.2	Oxygen Coordinations .....	43
2.2.1	Crystal Systems and Point Groups .....	44
2.2.2	Cubic Symmetry .....	45
2.2.3	Lower Symmetries .....	47
2.3	Crystal Electric Fields .....	48
2.3.1	Angular Momentum States .....	49

2.3.2	Crystal Field Hamiltonian .....	50
2.3.3	Hierarchy of Perturbations .....	54
2.3.4	Weak-Field Solutions .....	55
2.3.5	Group Theory and Lower Symmetry .....	64
2.3.6	Strong Field Solutions and Term Diagrams .....	68
2.3.7	Rare-Earth Ion Solutions .....	71
2.4	Orbital Energy Stabilization .....	73
2.4.1	One-Electron Model .....	73
2.4.2	High- and Low-Spin States .....	75
2.4.3	Orbit–Lattice Stabilization (Jahn–Teller Effects) .....	79
2.4.4	Spin–Orbit–Lattice Stabilization .....	82
2.5	Covalent Stabilization .....	88
2.5.1	Molecular-Orbital Theory .....	89
2.5.2	Determinant Method .....	91
2.5.3	$\sigma$ and $\pi$ Bonds and the Molecular Orbital Diagram .....	95
2.5.4	Valence Bond Method .....	99
Appendix 2A	Homonuclear Molecule Ion .....	102
Appendix 2B	Valence-Bond Diatomic Molecule .....	103
References	.....	105
<b>3</b>	<b>Magnetic Exchange in Oxides</b> .....	<b>107</b>
3.1	Interionic Magnetic Exchange .....	108
3.1.1	Molecular-Orbital Exchange Approximation .....	109
3.1.2	Valence-Bond Solutions .....	113
3.1.3	Spin Alignment in Oxides .....	119
3.1.4	Ferromagnetism by Spin Transfer .....	121
3.1.5	Goodenough–Kanamori Rules .....	125
3.2	Antiferromagnetism .....	129
3.2.1	Superexchange and Molecular Fields .....	129
3.2.2	Molecular Field Theory of Antiferromagnetism .....	131
3.2.3	Antiferromagnetic Spin Configurations .....	135
3.3	Antiferromagnetic Oxides .....	139
3.3.1	One-Metal Oxides .....	139
3.3.2	$ABO_3$ and $A_2BO_4$ Perovskites .....	140
3.3.3	The Mixed-Valence Manganite Anomaly .....	143
Appendix 3A	Analysis of $M^{2+}O^{2-}$ Exchange Interactions .....	146
Appendix 3B	Curie Temperature Model for (La,Ca) $MnO_3$ .....	147
References	.....	149
<b>4</b>	<b>Ferrimagnetism</b> .....	<b>151</b>
4.1	Ferrimagnetic Order .....	151
4.1.1	Generic Ferrimagnetic Systems .....	152
4.1.2	Molecular Field Theory of Ferrimagnetism .....	153
4.1.3	Magnetic Frustration and Spin Canting .....	157



4.2	Theory of Superexchange Dilution .....	161
4.2.1	Superexchange Energy Stabilization .....	161
4.2.2	Molecular Field Coefficients.....	164
4.2.3	Solution for Yttrium Iron Garnet .....	165
4.3	Ferrimagnetic Oxides.....	168
4.3.1	Spinel Ferrites $A [B_2] O_4$ .....	169
4.3.2	Garnet Ferrites $\{c_3\} [a_2] (d_3) O_{12}$ .....	175
4.3.3	Rare-Earth Garnet Ferrites .....	180
4.3.4	Rare-Earth Canting Effect .....	184
4.3.5	Hexagonal Ferrites .....	190
4.3.6	Orthoferrites .....	193
Appendix 4A	Molecular Field Analysis of LiZnTi Ferrite .....	193
Appendix 4B	High-Magnetization Limits .....	195
Appendix 4C	Brillouin Functions in Exchange Energy Format .....	196
References	.....	197
<b>5</b>	<b>Anisotropy and Magnetoelastic Properties</b> .....	<b>201</b>
5.1	Quantum Paramagnetism of Single Ions .....	202
5.1.1	Theory of Anisotropic g Factors.....	202
5.1.2	Conventional Perturbation Solutions .....	205
5.1.3	The Spin Hamiltonian for $3d^n$ Ions .....	209
5.1.4	The Crystal-Field Hamiltonian for $4f^n$ Ions.....	210
5.2	Anisotropy of Single Ions .....	212
5.2.1	$3d^1$ and $3d^6$ D-State Triplet .....	213
5.2.2	$3d^4$ and $3d^9$ D-State Doublet (J–T Effect) .....	217
5.2.3	$3d^2$ and $3d^7$ F-State Triplet .....	219
5.2.4	$3d^3$ and $3d^8$ F-State Singlet.....	220
5.2.5	$3d^5$ S-State Singlet .....	222
5.2.6	$4f^n$ Ion Anisotropy .....	226
5.3	Magnetocrystalline Anisotropy and Magnetostriction .....	228
5.3.1	Phenomenological Anisotropy Theory .....	229
5.3.2	Phenomenological Magnetostriction Theory .....	231
5.3.3	Dipolar Pair Model of Magnetic Anisotropy.....	234
5.3.4	Single-Ion Model of Ferrimagnetic Anisotropy .....	236
5.3.5	Cooperative Single-Ion Effects: Anisotropy .....	241
5.3.6	Cooperative Single-Ion Effects: Magnetostriction.....	246
5.4	Magnetization Process and Hysteresis.....	250
5.4.1	Initial Permeability and Coercivity .....	251
5.4.2	Anisotropy Field and Remanence Ratio.....	254
5.4.3	Approach to Saturation .....	256
5.4.4	Demagnetization and Permanent Magnets .....	258
Appendix 5A	Four-Level Degenerate Perturbation Solution for $d^1$ .....	261

Appendix 5B	$T_{2g}$ Solution for $d^1$ in an Exchange Field	263
Appendix 5C	Orbital States of $d^5$ in a Cubic Field	265
Appendix 5D	Angular Dependence of Cubic Anisotropy Fields	267
References		269
<b>6</b>	<b>Electromagnetic Properties</b>	273
6.1	Magnetic Relaxation	274
6.1.1	Nonresonant Longitudinal Relaxation	274
6.1.2	Quantum Mechanisms of Spin–Lattice Relaxation	278
6.1.3	Perturbation Theories of Spin–Phonon Interaction	286
6.2	Gyromagnetic Resonance and Relaxation	287
6.2.1	Paramagnetic Resonance	288
6.2.2	Ferromagnetic Resonance	292
6.2.3	Uniform Precession Damping	295
6.2.4	Inhomogeneous Resonance Line Broadening	297
6.2.5	Fast-Relaxing Ion Effects	300
6.2.6	The Exchange Isolation Effect	306
6.3	Exchange-Coupled Modes (Spin Waves)	307
6.3.1	Uniform Precession Decoherence (Degenerate Spin Waves)	307
6.3.2	Instability Threshold (Classical Approximation)	311
6.3.3	Instability Threshold (Nonlinear Spin Waves)	315
6.3.4	Magnetostatic Modes	317
6.4	Permeability and Propagation	318
6.4.1	Low-Frequency Longitudinal Permeability	318
6.4.2	High-Frequency Transverse Limits	322
6.4.3	Snoek’s Law Considerations	324
6.4.4	Circular Polarization and Nonreciprocal Properties	327
6.4.5	Linear Polarization and Faraday Rotation	332
Appendix 6A	Transverse Permeability Tensor	333
Appendix 6B	Classical Instability Threshold	336
Appendix 6C	Domain Wall Susceptibility Equation	338
References		340
<b>7</b>	<b>Magneto-Optical Properties</b>	343
7.1	Infrared Exchange Resonance	344
7.1.1	Classical Precession Model	344
7.1.2	Quantum Spin Transition Model	346
7.1.3	Experimental Exchange Spectra	351
7.2	Combined Permeability and Permittivity	352
7.2.1	The $[\varepsilon] \cdot [\mu]$ Tensor Solutions	352
7.2.2	Propagation Parameters and Faraday Rotation	353
7.3	Magneto-Optical Spectra	355
7.3.1	Electric-Dipole Transitions	355
7.3.2	Yttrium Iron Garnet Spectra (Paramagnetic)	360

7.3.3	Iron Garnets with Bismuth Ions (Diamagnetic).....	366
7.3.4	$Fe^{3+}$ - $Bi^{3+}$ Hybrid Excited States .....	371
7.3.5	Intersublattice Transitions and the $\Delta S = 0$ Rule.....	376
Appendix 7A Magnetic Circular Birefringence and Dichroism .....		381
References.....		382
<b>8</b>	<b>Spin Transport Properties .....</b>	<b>385</b>
8.1	Polarons and Charge Transfer.....	386
8.1.1	Transfer Among Equivalent Energy Sites (Small Polarons) .....	388
8.1.2	Transfer to Higher Energy Sites (Large Polarons) .....	389
8.1.3	Transfer by Covalent Tunneling .....	392
8.1.4	The Holstein Polaron Theory .....	394
8.2	Metallic Oxides with Polarized Spins .....	396
8.2.1	Simple Oxides .....	397
8.2.2	Complex Oxides .....	397
8.2.3	Classical Resistivity-Temperature Model.....	400
8.3	Magnetoresistance in Oxides (CMR).....	401
8.3.1	Manganese-Ion Exchange Interactions .....	402
8.3.2	Magnetoresistivity-Temperature Model .....	405
8.3.3	Dilute Magnetic Oxides .....	410
8.4	Superconductivity in Oxides .....	413
8.4.1	Classical Foundations .....	413
8.4.2	Zero-Spin Polarons and Magnetic Frustration .....	419
8.4.3	Large-Polaron Superconductivity .....	423
8.4.4	Normal Resistivity and Critical Temperature .....	426
8.4.5	Layered Cuprate Superconductors .....	430
8.5	Supercurrents and Magnetic Fields .....	439
8.5.1	Supercurrent Formation .....	439
8.5.2	Condensation Energy .....	442
8.5.3	London Penetration Depth .....	443
8.5.4	Critical Magnetic Field .....	445
8.5.5	Critical Current Density.....	447
8.5.6	Coherence Length .....	450
8.5.7	Type-II Superconductors .....	452
Appendix 8A Magnetic Levitation .....		455
References.....		456
<b>Index .....</b>		<b>461</b>