

Gerald F. Dionne

Magnetic Oxides

 Springer

Contents

1	Introductory Magnetism	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
2	Magnetic Ions in Oxides	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	σ and π 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
3	Magnetic Exchange in Oxides	107
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
4	Ferrimagnetism	151
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

- 5 Anisotropy and Magnetoelastic Properties 201**
 - 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
6	Electromagnetic Properties	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
7	Magneto-Optical Properties	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 $[\varepsilon]$ - $[\mu]$ 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
8	Spin Transport Properties	385
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
Index		461