

Contents

Preface XIII

Symbols and Abbreviations XV

1	Fundamentals of Magnetism	1
	<i>Jun Yamauchi</i>	
1.1	Magnetism of Materials	1
1.1.1	Historical Background	1
1.1.2	Magnetic Moment and its Energy in a Magnetic Field	3
1.1.3	Definitions of Magnetization and Magnetic Susceptibility	4
1.1.4	Diamagnetism and Paramagnetism	5
1.1.5	Classification of Magnetic Materials	6
1.1.6	Important Variables, Units, and Relations	7
1.2	Origins of Magnetism	8
1.2.1	Origins of Diamagnetism	8
1.2.2	Origins of Paramagnetism	10
1.2.3	Magnetic Moments	13
1.2.4	Specific Rules for Many Electrons	15
1.2.5	Magnetic Moments in General Cases	17
1.2.6	Zeeman Effect	18
1.2.7	Orbital Quenching	19
1.3	Temperature Dependence of Magnetic Susceptibility	21
1.3.1	The Langevin Function of Magnetization and the Curie Law	21
1.3.2	The Brillouin Function of Magnetization and the Curie Law	22
1.3.3	The Curie–Weiss Law	24
1.3.4	Magnetic Ordered State	26
1.3.5	Magnetic Interactions	30
1.3.5.1	Exchange Interaction	30
1.3.5.2	Dipolar Interaction	31
1.3.6	Spin Hamiltonian	34
1.3.7	Van Vleck Formula for Susceptibility	35
1.3.8	Some Examples of the van Vleck Formula	36
1.3.8.1	The Curie Law	36
1.3.8.2	Zero-Field Splitting Case	37

1.3.8.3	Spin Cluster Case—The Dimer Model	37
1.3.8.4	Multiple-spin Cluster Case—The Triangle or Others	39
1.3.8.5	Temperature-Independent Paramagnetism	39
1.3.9	Low-Dimensional Interaction Network	40
1.4	Experimental Magnetic Data Acquisition	43
1.4.1	Methods	43
1.4.2	Evaluations of Magnetic Susceptibility and Magnetic Moment	44
	References	45
2	Molecular Magnetism	47
	<i>Jun Yamauchi</i>	
2.1	Magnetic Origins from Atoms and Molecules	47
2.1.1	Historical Background	47
2.1.2	Spin States Derived from Chemical Bonds	48
2.1.3	Organic Free Radicals	50
2.1.4	Coordinate Compounds	50
2.2	Characteristics of Molecular Magnetism	51
2.2.1	Molecular Paramagnetism	51
2.2.2	Magnetic Properties of Organic Free Radicals	52
2.3	Nitroxide as a Building Block	53
2.3.1	Stability of the N–O Bond	53
2.3.2	Structural Resonance of the N–O Bond	54
2.3.3	Molecular and Magnetic Interactions between Nitroxides	55
2.3.4	Nitroxides as Building Block	56
2.4	Low-Dimensional Properties of Nitroxides	57
2.4.1	One-Dimensional Magnetism	57
2.4.1.1	TANOL (TEMPOL)	57
2.4.1.2	F ₃ PNN	59
2.4.2	Interchain Interaction and Spin Long-Range Ordering	60
2.4.3	Two-Dimensional Magnetism	63
2.4.3.1	DANO	63
2.4.3.2	p-NPNN	64
2.4.4	Coordination of Nitroxide with Metal Ions	65
2.4.4.1	Cu ²⁺ , Mn ²⁺ -TANOL (TEMPOL)	65
2.4.4.2	Mn ²⁺ -IPNN	66
	References	68
3	Fundamentals of Electron Spin Resonance (ESR)	71
	<i>Jun Yamauchi</i>	
3.1	Magnetic Resonance of Electron and Nuclear Spins	71
3.1.1	Historical Background	71
3.1.2	Classification of Magnetic Resonance	72
3.2	Principle of Electron Spin Resonance (ESR)	72
3.2.1	Principle of ESR from Spectroscopic Interpretation	72
3.2.2	Principle of ESR from Resonance Interpretation	74
3.2.3	Bloch Equation	77

3.2.3.1	Solutions of the Bloch Equation	77
3.2.3.2	Absorption Line Shape	78
3.2.3.3	Relaxation Times	81
3.2.4	Modified Bloch Equation	82
3.2.5	Hyperfine Interaction	84
3.2.5.1	Interaction of the Electron Spin with Nuclear Spins	84
3.2.5.2	Hyperfine Splitting	85
3.2.5.3	Hydrogen Atom ($S = 1/2$ and $I = 1/2$)	87
3.2.5.4	Spin Polarization Mechanism	88
3.2.6	Fine Structure	90
3.2.7	Dynamical Phenomena	91
3.2.7.1	Correlation Time	91
3.2.7.2	Rotational Correlation Time	92
3.2.7.3	Chemical Exchange	94
3.3	Anisotropic Parameters in Crystal	94
3.3.1	g-Anisotropy	94
3.3.2	A-Anisotropy	96
3.3.3	D-Anisotropy	99
3.3.4	Anisotropic Parameters from ESR Powder Pattern	99
3.4	Pulsed ESR	102
3.4.1	Fundamental Concept of FT-ESR	102
3.4.2	Electron Spin Echo (ESE)	104
3.4.2.1	Two-Pulse Method	104
3.4.2.2	Three-Pulse Method	105
3.4.2.3	Inversion Recovery Method	106
3.4.2.4	Echo-Detected ESR (ED-ESR)	106
3.4.2.5	Nutation Spectroscopy	107
3.4.3	ESEEM	108
3.5	Double Resonance	108
3.5.1	ENDOR	108
3.5.2	TRIPLE	110
3.5.3	ELDOR	111
3.5.4	Pulsed Methods for Double Resonance	113
3.6	ESR of Magnetic Materials	114
3.6.1	Low-Dimensional Magnetic Materials	114
3.6.2	Ferromagnetic Resonance (FMR)	115
3.6.3	Antiferromagnetic Resonance (AFMR)	116
3.6.4	Ferrimagnetic Resonance	118
	References	118
4	Recent Advantages in ESR Techniques Used in Nitroxide Applications	121
	<i>Alex I. Smirnov</i>	
4.1	Introduction	121
4.2	Macromolecular Distance Constraints from Spin-Labeling Magnetic Resonance Experiments	122
4.2.1	Continuous Wave ESR of Nitroxide-Nitroxide Pairs	123

- 4.2.2 Continuous Wave ESR of Nitroxide-Metal Ion Pairs 125
- 4.2.3 Time Domain Magnetic Resonance of Spin Pairs 128
- 4.2.3.1 Nitroxide Spin Labels in Protein Structure Determination by NMR 128
- 4.2.3.2 Electronic Relaxation Enhancement in Spin Pairs 130
- 4.2.3.3 Pulsed Double Electron-Electron Resonance 131
- 4.2.3.4 ESR Double Quantum Coherence Experiments 133
- 4.2.4 Distance and Angular Constraints by ESR of Spin Pairs at High Magnetic Fields 134
- 4.3 Multiquantum ESR 135
- 4.4 Spin-Labeling ESR of Macroscopically Aligned Lipid Bilayers and Membrane Proteins 136
- 4.4.1 Mechanical Alignment of Lipid Bilayers on Planar Surfaces 136
- 4.4.2 Alignment of Discoidal Bilayered Micelles by Magnetic Forces 138
- 4.4.3 Nanopore-Confined Cylindrical Bilayers 139
- 4.5 Spin-labeling ESR at High Magnetic Fields 141
- 4.5.1 Spin-Labeling HF and Multifrequency ESR in Studying Molecular Dynamics 142
- 4.5.1.1 Stochastic Liouville Theory of Slow Motion ESR Spectra Simulations 143
- 4.5.1.2 Molecular Dynamics Simulation Methods 145
- 4.5.2 High Field ESR in Studying Nitroxide Microenvironment 146
- 4.5.2.1 Probing Local Polarity and Proticity of Membrane and Proteins 146
- 4.5.2.2 Site-Directed pH-Sensitive Spin-labeling: Differentiating Local pK and Polarity Effects by High-Field ESR 150
- 4.6 Perspectives 152
- Acknowledgements 154
- References 154

5 Preparations, Reactions, and Properties of Functional Nitroxide Radicals 161

Shin'ichi Nakatsuji

- 5.1 Short Historical Survey and General Preparative Methods of NRs 161
- 5.2 Early Progress toward FNRs for Organic Magnetic Materials 164
- 5.3 Organic Ferromagnets Based on NRs 165
- 5.4 Charge-Transfer Complexes/Radical Ion Salts Based on NR 168
- 5.5 Donors and Acceptors Carrying NRs and the Derived CT Complexes/Radical Salts 172
- 5.6 Supramolecular Spin Systems Carrying NRs 175
- 5.7 Photochromic Spin Systems Carrying NRs 184
- 5.8 FNRs for Biomedical Applications 191
- 5.9 Functional Nitrones 196
- 5.10 Conclusion 197
- References 198

6	Nitroxide Spin Probes for Studies of Molecular Dynamics and Microstructure	205
	<i>Gertz I. Likhtenshtein</i>	
6.1	Nitroxide Molecular Dynamics	205
6.1.1	Introduction	205
6.1.2	Molecular Dynamics of Surrounding Molecules	206
6.1.2.1	Microviscosity and Fluidity	206
6.1.2.2	Motion of Macromoles as a Whole and Segmental Dynamics	207
6.1.2.3	Low-Amplitude High-Frequency Motion and Phonon Dynamics	208
6.2	The Spin Label-Spin Probe Methods	212
6.3	Spin Oximetry	215
6.4	Determination of the Immersion Depth of Radical and Fluorescent Centers	217
6.4.1	Analysis of Power Saturation Curves in Solids by CW ESR	217
6.4.2	Determination of Depth of Immersion of a Luminescent Chromophore and a Radical Using Dynamic Exchange Interactions	218
6.5	Nitroxide as Polarity Probes	220
6.6	Electrostatic Effects in Molecules in Solutions	221
6.6.1	Effect of Charge on Dipolar Interactions Between Protons and a Paramagnetic Species	221
6.6.2	Impact of Charge on Spin Exchange Interactions Between Radicals and Paramagnetic Complexes	223
6.7	Spin-Triplet-Fluorescence-Photochrome Method	224
6.8	Dual Fluorophore-Nitroxide as Molecular Dynamics Probes	227
6.9	Nitroxide Spin pH Probes	230
6.10	Nitroxides as Spin Probes for SH Groups	231
	References	232
7	Nitroxide Redox Probes and Traps, Nitron Spin Traps	239
	<i>Gertz I. Likhtenshtein</i>	
7.1	Nitroxide Redox Probes	239
7.1.1	Introduction	239
7.1.2	Quantitative Characterization of Antioxidant Status	240
7.1.3	Antioxidant Activity	242
7.1.3.1	SOD Mimetic Activity	242
7.1.3.2	Spin Trapping by Nitroxides	244
7.2	Nitron Spin Trapping	247
7.2.1	Introduction	247
7.2.2	Chemical Structure and Reactions of Nitrones with Radicals	248
7.2.3	Non-Radical Reactions of Nitrones	253
7.2.4	Nitric Oxide Trapping	254
7.2.5	Thermodynamics and Kinetics of Nitron Reactions	254
7.3	Dual Fluorophore-Nitroxides (FNRO·) as Redox Sensors and Spin Traps	256

7.3.1	Introduction	256
7.3.2	Analysis of Antioxidant Status	257
7.3.3	Analysis of Superoxide and Nitric Oxide by Pyren-Nitronyl	261
7.3.3.1	Superoxide Analysis	261
7.3.3.2	Nitric Oxide Analysis	262
7.3.4	Dual Molecules as Spin Traps	263
	References	264

8 Nitroxides in Physicochemistry 269

Gertz I. Likhtenshtein

8.1	Polymers	269
8.1.1	Introduction	269
8.1.2	Polymerization: Nitroxides Mediated Living Polymerization (NMLP)	269
8.1.2.1	Phenomenon of and Chemistry of Nitroxide Mediated Living Polymerization	270
8.1.2.2	Thermodynamic and Kinetics	272
8.1.3	Molecular Dynamics and Microstructure of Polymers	274
8.1.3.1	Introduction	274
8.1.3.2	Polymers Segmental Dynamics	276
8.1.3.3	Spatial and Orientational Distribution of Nitroxides	279
8.2	Nitroxides in Photochemistry and Photophysics	279
8.2.1	Fluorescence Quenching, Photoelectron Transfer and Photoreduction	279
8.2.1.1	Dual Fluorophore-Nitroxide Compounds	279
8.2.1.2	Nitroxides in Multispin Systems	284
8.2.1.3	Spin Trapping in Photochemical Reactions	285
8.3	Complexes Transition Metals with Nitroxide Ligands	287
8.4	Nitroxides in Inorganic Chemistry	292
8.4.1	Langmuir-Blodgett (LB) Films on Inorganic Substrates	293
8.4.2	Surface Microstructure and Dynamics	294
8.4.3	Nanoparticles	295
8.4.4	Local Acidity	296
	References	297

9 Organic Functional Materials Containing Chiral Nitroxide Radical Units 303

Rui Tamura

9.1	Introduction	303
9.2	Synthesis and Structure of Chiral NRs	304
9.2.1	Chiral Five-Membered Cyclic NRs	304
9.2.1.1	Chiral α -NNs	304
9.2.1.2	Chiral PROXYLs	305
9.2.1.3	Chiral DOXYLs	313
9.2.2	Chiral Six-Membered Cyclic NRs	314

9.2.3	Miscellaneous Examples	314
9.3	Magnetic Properties of Chiral NRs in the Solid State	315
9.3.1	Chiral Nitoxide-Mn ²⁺ Complex Magnets	315
9.3.2	Chiral Multispin System	316
9.4	Properties of Chiral NRs in the Liquid Crystalline State	318
9.4.1	DOXYL and TEMPO Liquid Crystals	318
9.4.2	PROXYL Liquid Crystals	320
9.4.2.1	Phase-Transition Behavior	320
9.4.2.2	Ferroelectric Properties	322
9.4.2.3	Nonlinear Mesoscopic-Ferromagnetic Interactions	323
9.5	Application of Redox Properties of NRs	323
9.5.1	Oxidation Catalyst	323
9.5.1.1	Achiral Catalyst	323
9.5.1.2	Chiral Catalyst	325
9.5.2	Radical Battery	325
9.6	Conclusion	326
	References	327
10	Spin Labeling in Biochemistry and Biophysics	331
	<i>Gertz I. Likhtenshtein</i>	
10.1	Proteins and Enzymes	331
10.1.1	Intramolecular Dynamics and Conformational Transition in Enzymes	332
10.1.1.1	Introduction	332
10.1.1.2	Low-Temperature Molecular Dynamics	332
10.1.1.3	Protein Dynamics at Ambient Temperature	334
10.1.2	Conformational Changes in Proteins and Enzymes, and Mechanism of Intramolecular Dynamics	336
10.1.3	Structure of the Enzymes' Active Centers	338
10.1.4	Site-Directed Spin-Labeling (SDSL)	340
10.1.4.1	Introduction	340
10.1.4.2	Soluble Proteins	341
10.1.4.3	Rhodopsin and Bacteriorhodopsin	344
10.1.4.4	Muscle Proteins	344
10.1.4.5	Membrane Proteins	345
10.2	Biomembranes	346
10.2.1	Structure and Dynamics	347
10.2.1.1	Location of Labels, Water, and Oxygen in Membranes	347
10.2.1.2	Membrane Microstructure	348
10.2.2	Membrane Dynamics	349
10.2.3	Proteins and Peptides in Membranes	350
10.3	Nucleic Acids	354
10.3.1	Introduction	354
10.3.2	DNA	355

10.3.3	RNA	358
10.4	Polysacchrides and Dextrins	360
10.4.1	Cotton and Cellulose	360
10.4.2	Cyclodextrins	362
	References	363
11	Biomedical and Medical Applications of Nitroxides	371
	<i>Gertz I. Likhtenshtein</i>	
11.1	Cells and Tissues. Biomedical Aspects	371
11.1.1	Cell Membrane Fluidity	371
11.1.2	Cells Redox Status	372
11.1.3	Nitroxides as Cell Protectors	373
11.2	Nitroxides <i>In Vivo</i>	374
11.2.1	Introduction	374
11.2.2	Nitroxide <i>In Vivo</i> Biochemistry. Biomedical Aspects	375
11.2.2.1	Antioxidant Activity of Nitroxides	375
11.2.2.2	Detection of Reactive Radicals: Spin-Trapping	376
11.2.2.3	Spin Farmokinetics <i>In Vivo</i>	378
11.2.2.4	Spin pH Probing	380
11.2.2.5	Spin Imaging	381
11.2.2.6	Nitroxide Spin Probe Oximetry	383
11.3	Medical Application of Nitroxides	385
11.3.1	Nitroxides and Nitrons as Drugs	385
11.3.2	Protection in Animal Model Diseases	386
11.3.3	Human Diseases. Therapeutic Aspects	388
11.3.4	Nitroxides in Clinics	389
11.4	Areas Related to Future Development of Nitroxide Applications in Biomedicine	391
	References	393
12	Conclusion	401
	Index	405