

Contents

Preface	V
List of Contributors	XV
1 Bimetallic Magnets: Present and Perspectives	1
1.1 Introduction	1
1.2 Bimetallic Magnetic Materials Derived from Oxamato-based Complexes	2
1.2.1 Dimensionality and Magnetic Properties	2
1.2.2 Modulation of the Magnetic Properties	17
1.2.3 Dimensionality Modulation by a Dehydration-Polymerization Process	20
1.2.4 Alternative Techniques for the Studies of Exchange-coupled Systems	26
1.3 Bimetallic Magnets Based on Second- and Third-row Transition Metal Ions	28
1.3.1 Examples of Ru(III)-based Compounds	28
1.3.2 Mo, Nb, and W-cyanometalate-based Magnets	31
1.3.3 Light-induced Magnetism	36
1.4 Concluding Remarks	37
References	38
2 Copper(II) Nitroxide Molecular Spin-transition Complexes	41
2.1 Introduction	41
2.2 Nitroxide Free Radicals as Building Blocks for Metal-containing Magnetic Species	42
2.2.1 Electronic Structure	43
2.2.2 Coordination Properties	43
2.3 Molecular Spin Transition Species	46
2.3.1 Discrete Species	46
2.3.2 One-dimensional Species	50
2.4 Conclusion	61
References	62
3 Theoretical Study of the Electronic Structure of and Magnetic Interactions in Purely Organic Nitronyl Nitroxide Crystals	65
3.1 Introduction	65
3.2 Electronic Structure of Nitronyl Nitroxide Radicals	68

3.2.1	Fundamentals	68
3.2.2	<i>Ab-initio</i> Computation of the Electronic Structure of Nitronyl Nitroxide Radicals	73
3.2.3	Spin Distribution in Nitronyl Nitroxide Radicals	78
3.3	Magnetic Interactions in Purely Organic Molecular Crystals	88
3.3.1	Basics of the Magnetism in Purely Organic Molecular Crystals	88
3.3.2	The McConnell-I Mechanism: A Rigorous Theoretical Analysis	90
3.3.3	Theoretical Analysis of Through-space Intermolecular Interactions	94
3.3.4	Experimental Magneto-structural Correlations	102
3.3.5	Theoretical Magneto-structural Correlations	105
	References	113
4	Exact and Approximate Theoretical Techniques for Quantum Magnetism in Low Dimensions	119
4.1	Introduction	119
4.2	Exact Calculations	121
4.3	Applications to Spin Clusters	125
4.4	Field Theoretic Studies of Spin Chains	129
4.4.1	Nonlinear σ -model	130
4.4.2	Bosonization	133
4.5	Density Matrix Renormalization Group Method	137
4.5.1	Implementation of the DMRG Method	139
4.5.2	Finite Size DMRG Algorithm	140
4.5.3	Calculation of Properties in the DMRG Basis	142
4.5.4	Remarks on the Applications of DMRG	142
4.6	Frustrated and Dimerized Spin Chains	144
4.7	Alternating (S_1, S_2) Ferrimagnetic Spin Chains	148
4.7.1	Ground State and Excitation Spectrum	149
4.7.2	Low-temperature Thermodynamic Properties	155
4.8	Magnetization Properties of a Spin Ladder	160
	References	168
5	Magnetic Properties of Self-assembled $[2 \times 2]$ and $[3 \times 3]$ Grids	173
5.1	Introduction	173
5.2	Polytopic Ligands and Grid Complexes	174
5.2.1	$[2 \times 2]$ Ligands	175
5.2.2	Representative $[2 \times 2]$ Complexes	176
5.2.3	$[3 \times 3]$ Ligands and their Complexes	187
5.3	Magnetic Properties of Grid Complexes	189
5.3.1	$[2 \times 2]$ Complexes	189
5.3.2	$[3 \times 3]$ Complexes	191
5.3.3	Magnetic Properties of $[2 \times 2]$ and $[3 \times 3]$ Grids	192

5.3.4	Potential Applications of Magnetic Grids to Nanoscale Technology	201
	References	202
6	Biogenic Magnets	205
6.1	Introduction	205
6.1.1	Magnetotactic Bacteria	205
6.1.2	Magnetosomes	206
6.1.3	Magnetite Magnetosomes	207
6.1.4	Greigite Magnetosomes	208
6.2	Magnetic Properties of Magnetosomes	209
6.2.1	Magnetic Microstates and Crystal Size	209
6.2.2	Single-domain (SD) and Multi-domain (MD) States	211
6.2.3	Superparamagnetic (SPM) State	211
6.2.4	Theoretical Domain Calculations: Butler–Banerjee Model	213
6.2.5	Local Energy Minima and Metastable SD States: Micromagnetic Models	214
6.2.6	Magnetic Anisotropy of Magnetosomes	215
6.2.7	Magnetosome Chains	217
6.2.8	Magnetic Properties of Magnetosomes at Ambient Temperatures	217
6.2.9	Low-temperature (<300 K) Magnetic Properties	218
6.2.10	Magnetosomes and Micromagnetism	220
6.2.11	Magnetosome Magnetization from Electron Holography	220
6.3	Mechanism of Bacterial Magnetotaxis	223
6.3.1	Passive Orientation by the Geomagnetic Field	223
6.3.2	Magneto-aerotaxis	225
6.4	Conclusion	227
	References	228
7	Magnetic Ordering due to Dipolar Interaction in Low Dimensional Materials	233
7.1	Introduction	233
7.2	Magnetic Ordering in Pure Dipole Systems	234
7.2.1	The Dipole–Dipole Interaction – A Well Known Hamiltonian?	234
7.2.2	Ordering Temperature – The Mean-field Approach	235
7.2.3	Dipolar Ordering in 3D Systems	238
7.2.4	Dipolar Ordering in 2D Systems	243
7.3	Strongly Correlated Extended Objects	246
7.3.1	Stacking of Magnetic Planes	246
7.3.2	3D of 1D – Bunching of Wires or Chains	248
7.3.3	2D of 1D – Planar Arrays of Magnetic Wires	250
7.3.4	2D of 0D – Planar Arrays of Magnetic Dots	252
7.3.5	1D of 0D – Lines of Magnetic Dots	254
7.4	Weakly Correlated Extended Systems	255

7.4.1	Low Dimensional Molecular-based Magnets	255
7.4.2	3D Ordering Due to Dipolar Interaction – A Model	261
7.5	Conclusion	265
	References	266
8	Spin Transition Phenomena	271
8.1	Introduction	271
8.2	Physical Characterization	272
8.2.1	Occurrence of Thermal Spin Transition	272
8.2.2	Magnetic Susceptibility Measurements	274
8.2.3	Optical Spectroscopy	275
8.2.4	Vibrational Spectroscopy	276
8.2.5	⁵⁷ Fe Mössbauer Spectroscopy	277
8.2.6	Calorimetry	279
8.2.7	Diffraction Methods	280
8.2.8	X-ray Absorption Spectroscopy	281
8.2.9	Positron-annihilation Spectroscopy	282
8.2.10	Nuclear Resonant Scattering of Synchrotron Radiation	283
8.2.11	Magnetic Resonance Studies (NMR, EPR)	284
8.3	Highlights of Past Research	285
8.3.1	Chemical Influence on Spin-crossover Behavior	285
8.3.2	Structural Insights	289
8.3.3	Influence of Crystal Quality	291
8.3.4	Theoretical Approaches to Spin Transition Phenomena	292
8.3.5	Influence of a Magnetic Field	299
8.3.6	Two-step Spin Transition	299
8.3.7	LIESST Experiments	306
8.3.8	Formation of Correlations During HS → LS relaxation	309
8.3.9	Nuclear Decay-induced Spin Crossover	313
8.4	New Trends in Spin Crossover Research	320
8.4.1	New Types of Spin Crossover Material	320
8.4.2	New Effects and Phenomena	326
	References	334
9	Interpretation and Calculation of Spin-Hamiltonian Parameters in Transition Metal Complexes	345
9.1	Introduction	345
9.2	The Spin-Hamiltonian	347
9.2.1	The SH	347
9.2.2	Eigenstates of the SH	348
9.2.3	Matrix Elements of the SH	349
9.2.4	Comments	352
9.3	The Physical Origin of Spin-Hamiltonian Parameters	352
9.3.1	Many-electron Wavefunctions and the Zeroth-order Hamiltonian	352
9.3.2	Perturbing Operators for Magnetic Interactions	355
9.3.3	Theory of Effective Hamiltonians	361

9.3.4	Equations for Spin-Hamiltonian Parameters	363
9.3.5	Formulation in Terms of Molecular Orbitals	371
9.4	Ligand Field and Covalency Effects on SH Parameters	380
9.4.1	Molecular Orbitals for Inorganic Complexes	380
9.4.2	Ligand Field Energies	381
9.4.3	Matrix Elements over Molecular Orbitals	385
9.4.4	“Central Field” versus “Symmetry Restricted” Covalency .	392
9.4.5	Ligand-field Theory of Zero-field Splittings	395
9.4.6	Ligand-field Theory of the g-Tensor	396
9.4.7	Ligand-field Theory of Hyperfine Couplings	397
9.4.8	Table of Hyperfine Parameters	399
9.4.9	Examples of Ligand-field Expressions for Spin Hamiltonian Parameters	401
9.5	Case Studies of SH Parameters	414
9.5.1	CuCl_4^{2-} and the Blue Active Site: g and A^M Values	415
9.5.2	FeCl_4^- and the $\text{Fe}(\text{SR})_4^-$ Active Site: Zero-field Splitting (ZFS)	420
9.6	Computational Approaches to SH Parameters	423
9.6.1	Hartree–Fock Theory	424
9.6.2	Configuration Interaction	426
9.6.3	Density Functional Theory	427
9.6.4	Coupled-perturbed SCF Theory	428
9.6.5	Relativistic Methods	432
9.6.6	Calculation of Zero-field Splittings	433
9.6.7	Calculation of g-Values	435
9.6.8	Calculation of Hyperfine Couplings	444
9.7	Concluding Remarks	455
9.8	Appendix: Calculation of Spin–Orbit Coupling Matrix Elements . .	456
	References	458
10	Chemical Reactions in Applied Magnetic Fields	467
10.1	Introduction	467
10.2	Gas-phase Reactions	467
10.2.1	Gaseous Combustion	467
10.2.2	Carbon Nanotube and Fullerene Synthesis	468
10.2.3	Liquid-phase Reactions	470
10.2.4	Asymmetric Synthesis	470
10.2.5	Electrodeposition	471
10.3	Solid-phase Reactions	472
10.3.1	Self-propagating High-temperature Synthesis (SHS)	472
10.3.2	SHS Reactions in High Fields (1 to 20 T)	475
10.3.3	Time-resolved X-ray Diffraction Studies	476
10.3.4	Possible Field-dependent Reaction Mechanisms	479
10.4	Conclusions	479
	References	480
	Index	483