

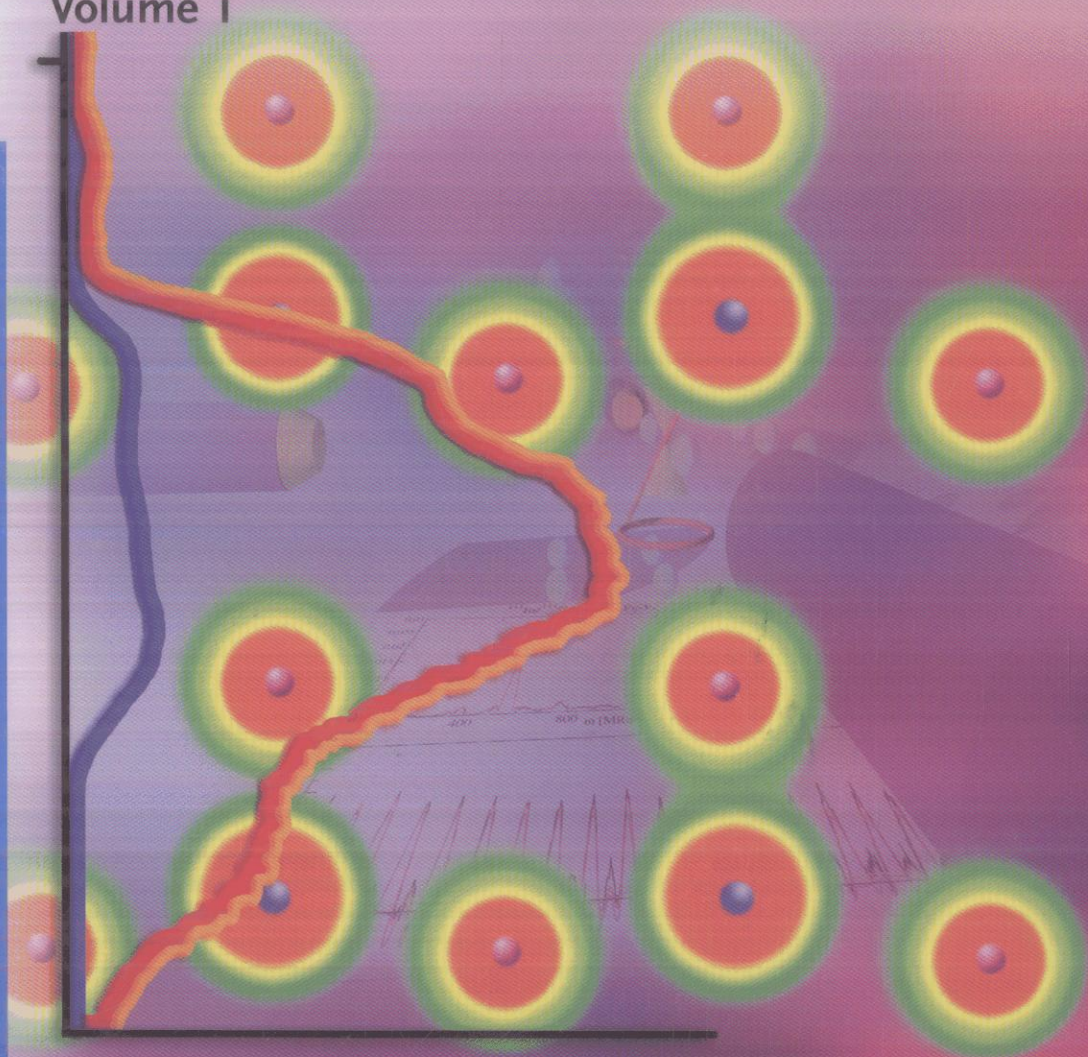
Edited by Rolf Schäfer, Peter C. Schmidt

 WILEY-VCH

Methods in Physical Chemistry

With a Foreword by Gerhard Ertl

Volume 1



Contents to Volume 1

List of Contributors XIX

Part I Gas Phase 1

1 Manipulating the Motion of Complex Molecules: Deflection, Focusing, and Deceleration of Molecular Beams for Quantum-State and Conformer Selection 3

Jochen Küpper, Frank Filsinger, Gerard Meijer, and Henrik Stapelfeldt

- 1.1 Introduction: Controlled Molecules 4
- 1.2 Experimental Methods 4
 - 1.2.1 Large Neutral Molecules in the Gas Phase 6
 - 1.2.2 Manipulation of Molecular Beams with Electric and Magnetic Fields 8
 - 1.2.3 Alignment and Orientation of Molecular Ensembles 13
- 1.3 Experimental Details 15
 - 1.3.1 Deflection 15
 - 1.3.2 Alternating-Gradient Focusing 17
 - 1.3.3 Alternating-Gradient Deceleration 18
- 1.4 Selected Applications 18
 - 1.4.1 Cluster and Biomolecules Deflection 18
 - 1.4.2 Conformer Selection 19
 - 1.4.3 Three-Dimensional Orientation 20
 - 1.4.4 Molecular-Frame Photoelectron Angular Distributions 22
- 1.5 Conclusions and Perspectives 23
- References 24

2 Laser Ionization Spectroscopy 29

Hans Georg Breunig and Karl-Michael Weitzel

- 2.1 Introduction 29
- 2.2 Basic Principles 30
- 2.3 Experimental Methods 31
 - 2.3.1 Single-Photon Ionization 31
 - 2.3.2 Resonance Enhanced Multiphoton Ionization 32

2.3.3	Ion-Dip Spectroscopy	38
2.3.4	Pulsed-Field Ionization	39
2.3.5	Strong-Field Ionization	41
2.3.6	Time-of-Flight Mass Spectrometer	45
2.4	Case Studies	45
2.4.1	Identification of Substances and Structural Isomers	45
2.4.2	Trace Analysis of Molecules	50
2.4.3	Laser Ionization as a Source of State-Selected Ions	51
2.5	Conclusions and Perspectives	55
2.6	Supplementary Material	55
	References	60
3	Mass Spectrometry for Ion Chemistry and Links from the Gas Phase to “Real” Processes	63
	<i>Detlef Schröder</i>	
3.1	Introduction	63
3.2	Key Experimental Methods	66
3.3	Ion Structures	69
3.3.1	Differentiation of $C_7H_7^+$ Isomers	69
3.3.2	Generation, Characterization, and Spectroscopy of $[FeCH_4O]^+$ Ions	71
3.4	Ion Energetics	72
3.4.1	Threshold Ionization and “Titration” of Reaction Barriers	73
3.4.2	Thermochemistry of $FeO_mH_n^{-/0/+ /2+}$ Ions (“Gaseous Rust”)	76
3.5	Reactions of Neutral Molecules Studied by Mass Spectrometry	77
3.5.1	Electron-Transfer Mass Spectrometry	77
3.5.2	Charge-Tagging Methods	78
3.6	Ion Catalysis	79
3.7	Summary and Perspectives	80
	References	82
	Part II Condensed-Phase	85
4	Solid State NMR: a Versatile Tool in Solid State Chemistry and Materials Science	87
	<i>Gunther Brunklaus, Hans-Wolfgang Spiess, and Hellmut Eckert</i>	
4.1	Introduction	87
4.2	Basic Principles	89
4.2.1	Nuclear Magnetism and Precession	89
4.2.2	Signal Excitation and Detection	90
4.2.3	Relaxation Phenomena	92
4.2.4	Internal Interactions	94
4.3	Experimental Techniques	99
4.3.1	Sample Spinning Techniques	100
4.3.2	Spin Echo Decay Methods	103

4.3.3	Hetero- and Homonuclear Decoupling	104
4.3.4	Multi-Dimensional NMR	105
4.3.5	Coherence Transfer Techniques	109
4.3.6	Recoupling of Homonuclear Magnetic Dipole–Dipole Interactions	110
4.3.7	Recoupling of Heteronuclear Magnetic Dipole–Dipole Interactions	116
4.4	Selected Applications	120
4.4.1	Glasses	120
4.4.2	Supramolecular Systems	131
4.5	Conclusion	144
4.6	Supplementary Material	145
	References	152
5	EPR–ESR–EMR, an Ongoing Success Story	159
	<i>Klaus-Peter Dinse and Gunnar Jeschke</i>	
5.1	Introduction	160
5.2	Basic Principles	160
5.3	Experimental Methods	164
5.3.1	Continuous Wave EMR at High Fields and Frequencies	164
5.3.2	Pulsed EMR	168
5.3.3	Merging EPR and NMR: Pulsed ENDOR	172
5.4	Case Studies	173
5.4.1	Physics	173
5.4.2	Chemistry	177
5.4.3	Biology	179
5.5	Conclusions and Perspectives	182
5.6	Supplementary Material	182
	References	188
6	Broadband Conductivity Spectroscopy for Studying the Dynamics of Mobile Ions in Materials with Disordered Structures	191
	<i>Klaus Funke</i>	
6.1	Introduction: “Microscopy in Time” in Disordered Ionic Materials	192
6.2	Experimental Techniques: Spanning More Than 17 Decades in Frequency	197
6.2.1	General	197
6.2.2	Complex Conductivities from Waveguide Spectroscopy	199
6.2.3	Complex Conductivities from Fourier Transform Infrared Spectroscopy	202
6.3	Linear Response Theory: Current Density and Conductivity	204
6.4	Conductivity Spectra: Universal Properties Detected	207
6.4.1	Time–Temperature Superposition	207
6.4.2	“First” Universality	209

6.4.3	“Second” Universality	210
6.5	“First” Universality: Spectra and Modeling	212
6.5.1	Different Approaches	212
6.5.2	The MIGRATION Concept	213
6.5.3	Permittivity and Localized Mean Square Displacement	216
6.5.4	Non-Arrhenius DC Conductivities	218
6.6	“Second” Universality: Spectra and Modeling	220
6.6.1	Approaches for Modeling	220
6.6.2	Time-Dependent Double-Well Potentials	221
6.6.3	NCL-Type Effects Detected at High Frequencies	223
6.6.4	A New Picture Emerges for the Low-Temperature NCL Effect	224
	References	228
7	X-Ray Absorption Spectroscopy – the Method and Its Applications	231
	<i>Matthias Bauer and Helmut Bertagnolli</i>	
7.1	Introduction	232
7.2	Basic Principles – the EXAFS Equation	232
7.3	Experimental Methods	236
7.3.1	Experimental Design	236
7.3.2	Data Reduction and Evaluation	237
7.3.3	Data Analysis and Interpretation	241
7.4	Case Studies	246
7.4.1	Material Science	246
7.4.2	Nanoparticles and Heterogeneous Catalysis	250
7.4.3	Homogeneous Catalysis	258
7.4.4	Biochemistry	262
7.5	Conclusion	267
	References	267
8	Diffraction Methods: Structure Determination and Phase Analysis of Solids	271
	<i>Barbara Albert</i>	
8.1	Introduction: Diffraction – What for?	271
8.2	Basic Principles of the Elastic Interaction of Radiation and Periodic Arrays of Atoms	273
8.2.1	Scattering – Diffraction	273
8.2.2	Crystalline Solids and Symmetry	275
8.3	Methods and Their Applications	277
8.3.1	Generation and Detection of X-Rays and Neutrons	277
8.3.2	Single Crystal Analysis – Structure Determination and Refinement	278
8.3.3	Powder Diffractometry – Finger Print, Phase Analysis, or Structure Determination	283

8.4	Summary: Diffractometry-Where To?	293
	References	293
9	Small-Angle X-Ray and Neutron Scattering – Two Complementary Methods to Study Soft Matter Structure	297
	<i>Martin Engel, Tinka Spehr, and Bernd Stühn</i>	
9.1	Introduction	298
9.2	Basic Theory of Small-Angle Scattering	300
9.2.1	Calculation of the Interference Pattern	301
9.3	X-Rays and Neutrons	306
9.3.1	X-Rays	306
9.3.2	Neutrons	309
9.4	Selected Applications	314
9.4.1	Ion-Track Etched Polycarbonate Nanopores	314
9.4.2	Water-in-Oil Droplet Microemulsions	317
9.5	Conclusions	322
	References	324
10	Perturbed γ–γ Angular Correlation	325
	<i>Jens Röder and Klaus-Dieter Becker</i>	
10.1	Introduction	325
10.2	Basic Principles	326
10.2.1	PAC Basics	326
10.2.2	Angular Correlation in the Emission of γ -Rays	327
10.2.3	Nuclear Interactions	332
10.2.4	The PAC Experiment	335
10.3	Case Studies	337
10.3.1	Local Magnetic Fields in Iron	337
10.3.2	Spin Transitions in LaCoO_3	338
10.3.3	Structural Refinements of Sesquioxides, M_2O_3	340
10.3.4	Surface Studies	341
10.3.5	Reactivity of Thin Films	343
10.3.6	Strained Silicon	344
10.3.7	Diffusion	345
10.4	Conclusions and Perspectives	347
	References	348
11	Mössbauer Spectroscopy	351
	<i>Philipp Gütlich and Christian Schröder</i>	
11.1	Introduction	352
11.2	Basic Principles	353
11.2.1	Mössbauer Isotopes	353
11.2.2	The Mössbauer Effect	354
11.3	Experimental Methods	355
11.3.1	Mössbauer Spectrometer	355

11.3.2	Recording Mössbauer Spectra	357
11.3.3	Hyperfine Interactions and Mössbauer Parameters	359
11.4	Case Studies and Selected Applications	365
11.4.1	Basic Information on Structure and Bonding	365
11.4.2	Switchable Molecules: Spin Crossover	370
11.4.3	Mössbauer Emission Spectroscopy – After-Effects of Nuclear Decay	377
11.4.4	Industrial Applications	380
11.4.5	Miniaturized Portable Mössbauer Spectroscopy	381
11.5	Outlook	387
	References	387
12	Electron Energy Loss Spectroscopy as an Experimental Probe for the Crystal Structure and Electronic Situation of Solids	391
	<i>Kathrin Hofmann</i>	
12.1	Introduction	391
12.2	Basics of EELS	394
12.2.1	Theoretical Background	394
12.2.2	The Energy-Loss Spectrum	397
12.2.3	The Use of Core-Loss Edges	400
12.2.4	Fine Structure of Core-Loss Edges	402
12.3	Selected Applications of EELS	409
12.3.1	General Remarks	409
12.3.2	Determination of the Composition	409
12.3.3	Determination of the Valence State	410
12.3.4	Structural Investigations	410
12.4	Outlook	414
	References	415

Contents to Volume 2

List of Contributors XIX

Part III Interfaces 419

13	Raman Spectroscopy: Principles, Benefits, and Applications	421
	<i>Melissa M. Mariani and Volker Deckert</i>	
13.1	Introduction	422
13.2	Basic Principles: Raman Scattering	422
13.3	Experimental Methods	426
13.3.1	General Aspects	426
13.3.2	Raman Instrumentation	428
13.3.3	Coupling Raman with Microscopy	434
13.3.4	Benefits of Raman Spectroscopy	435

13.4	Applications of Raman Spectroscopy	436
13.4.1	Chemical Applications	436
13.4.2	Biological Applications	437
13.4.3	Variations of Raman Spectroscopy	438
13.4.4	Data Analysis	440
13.5	Conclusion	441
	References	442
14	Diffuse Reflectance Infrared Fourier Transform Spectroscopy: an <i>In situ</i> Method for the Study of the Nature and Dynamics of Surface Intermediates	445
	<i>Alfons Drochner and G. Herbert Vogel</i>	
14.1	Introduction	446
14.1.1	IR Spectroscopy of Solids	446
14.2	Basic Principles	448
14.3	Experimental Set-Up	454
14.3.1	DRIFTS Accessories	460
14.3.2	DRIFTS Reactor Cells for Heterogeneous Catalysis	461
14.4	Application Examples	463
14.4.1	NO _x Reduction	463
14.4.2	Quantification of Oxygen Surface Groups	470
14.5	Summary	473
	References	474
15	Photoelectron Spectroscopy in Materials Science and Physical Chemistry: Analysis of Composition, Chemical Bonding, and Electronic Structure of Surfaces and Interfaces	477
	<i>Andreas Klein, Thomas Mayer, Andreas Thissen, and Wolfram Jaegermann</i>	
15.1	Introduction	478
15.2	Experimental Procedure	479
15.2.1	Basic Set-Up and Operation Principle	479
15.2.2	Sample Preparation	483
15.3	Case Studies: XPS	488
15.3.1	Analysis of Peak Intensities	488
15.3.2	Analysis of Energy Shifts	492
15.3.3	Interface Analysis	501
15.4	Case Studies: UPS	503
15.5	Conclusions and Perspectives	505
15.6	Supplementary Material	506
	References	509

16	Photoelectron Microscopy: Imaging Tools for the Study of Surface Reactions with Temporal and Spatial Resolution	513
	<i>Eva Mutoro, Bjoern Luerßen, Sebastian Günther, and Jürgen Janek</i>	
16.1	Introduction	515
16.2	Basic Principles: Photoelectron-Based Analytical Techniques	515
16.3	Experimental Methods	518
16.3.1	Ultraviolet Photoelectron Spectroscopy and X-Ray Photoelectron Spectroscopy	518
16.3.2	Scanning Photoelectron Microscopy	522
16.3.3	Photoelectron Emission Microscopy	523
16.4	Case Studies (Selected Applications)	526
16.4.1	Chemical Waves in the $\text{NO} + \text{H}_2$ Reaction on Rh(110)	526
16.4.2	Electrode Reactions: Photoelectron Microscopy and Electrochemistry	533
16.4.3	Recent Developments in Instrumentation and Application	537
16.5	Conclusions and Perspectives	539
16.6	Supplementary Material	540
	References	544
17	Secondary Ion Mass Spectrometry – a Powerful Tool for Studying Elemental Distributions over Various Length Scales	547
	<i>Roger A. De Souza and Manfred Martin</i>	
17.1	Introduction	548
17.2	Basic Principles	548
17.2.1	The General Principle of Analysis	548
17.2.2	The SIMS Phenomenon	549
17.3	Experimental Methods	554
17.3.1	SIMS Machines and Modes of Operation	554
17.4	Case Studies	556
17.4.1	Oxygen Tracer Diffusion in LiNbO_3 : Depth Profiling	556
17.4.2	Oxygen Diffusion in Fe-Doped SrTiO_3	559
17.4.3	Cation Diffusion in LSGM: 3D Analysis – Depth Profiling with Image Analysis	562
17.4.4	Nitrogen in YSZ: Depth Profiles and Quantification	566
17.4.5	Elemental Distribution in Plants: Imaging Analysis	568
17.5	Conclusions and Perspectives	569
17.6	Supplementary Material	569
	References	573
18	Application of the Quartz Microbalance in Electrochemistry	575
	<i>Karl Doblhofer and Konrad G. Weil</i>	
18.1	Introduction	575
18.2	Basic Principles	576
18.2.1	Piezoelectricity of Quartz in Static Electric Fields	576
18.2.2	Piezoelectricity of Quartz in Oscillating Electric Fields	577

18.2.3	The Mass Load Dependence of the Resonance Frequency	578
18.2.4	Measurements of the Resonance Frequency	579
18.2.5	Quartz Oscillators in Viscous Media	581
18.3	Experimental Methods	582
18.3.1	Metalization of the Quartz Surfaces	582
18.3.2	The Electrochemical Cell	583
18.3.3	Calibration of the Microbalance	584
18.4	Case Studies	585
18.4.1	The Effect of Surface Roughness	585
18.4.2	Corrosion Studies	586
18.4.3	Metal Deposition	589
18.4.4	Oscillating Electrochemical Reactions	592
18.4.5	Self-Assembled Monolayers	593
18.5	Conclusions and Perspectives	595
18.6	Supplementary Material	595
	References	600
19	The Scanning Tunneling Microscope in Electrochemistry: an Atomistic View of Electrochemistry	603
	<i>Dieter M. Kolb and Marie Anne Schneeweiss</i>	
19.1	Introduction	603
19.2	Basic Principles	604
19.2.1	The Scanning Tunneling Microscope	604
19.2.2	Some Basics of Electrochemistry	607
19.3	Experimental Methods	609
19.4	Case Studies	610
19.4.1	The Reconstruction of Gold Surfaces	611
19.4.2	Ordered Adlayers of Ions and Organic Molecules	613
19.4.3	Metal Deposition	614
19.4.4	Nanostructuring of Surfaces with an STM	617
19.5	Conclusion and Perspectives	620
19.6	Supplementary Material	621
	References	623
20	Low-Energy Electron Diffraction: Crystallography of Surfaces and Interfaces	625
	<i>Georg Held</i>	
20.1	Introduction	625
20.2	Basic Principles	627
20.2.1	Surface Periodicity and Reciprocal Lattice	627
20.2.2	Superstructures	630
20.2.3	Spot Intensity versus Energy	630
20.2.4	Spot Profiles	631
20.3	Experiment	632
20.4	Applications	633

20.4.1	Leed Pattern: CO on Ni{111}	634
20.4.2	Spot Profiles	636
20.4.3	LEED-IV Structure Determination	637
20.4.4	LEED-IV on Disordered Layers	639
20.5	Conclusions and Perspectives	640
	References	641

Part IV Biomolecules and Materials 643

21	Femtosecond Vibrational Spectroscopies and Applications to Hydrogen-Bond Dynamics in Condensed Phases	645
	<i>Jörg Lindner and Peter Vöhringer</i>	
21.1	Introduction	646
21.2	Vibrational Pump–Probe Spectroscopy	647
21.2.1	Infrared Pump–Probe Spectroscopy	648
21.2.2	Coherent Anti-Stokes Raman Scattering	653
21.2.3	Raman-Induced Optical Kerr Effect and Impulsive Stimulated Raman Scattering	657
21.3	Applications	663
21.3.1	Hydrogen Bonding	663
21.3.2	Optical Kerr Effect of Water	667
21.3.3	Vibrational Relaxation in Water	669
21.3.4	Vibrational Relaxation in Ammonia	674
21.3.5	Vibrational Dynamics of H-Bond Wires	678
21.4	Summary	682
	References	683
22	THz Technology and THz Spectroscopy: Modeling and Experiments to Study Solvation Dynamics of Biomolecules	687
	<i>David M. Leitner, Martin Gruebele, and Martina Havenith-Newen</i>	
22.1	THz Technology	687
22.2	THz Spectroscopy	693
22.3	THz Spectroscopy of Solvated Probes	695
22.4	Biomolecule Solvation and Terahertz Dynamics: Important Concepts	699
22.5	Precise Measurements of the THz Absorption Coefficient	702
22.6	THz Spectroscopy of Solvated Proteins	705
22.7	KITA: Kinetic THz Absorption Spectroscopy	706
22.8	Further Application of THz Absorption Spectroscopy	708
	References	709
23	Single-Molecule Fluorescence Spectroscopy: The Ultimate Limit of Analytical Chemistry in the Condensed Phase	711
	<i>Dirk-Peter Herten, Arina Rybina, Jessica Balbo, and Gregor Jung</i>	
23.1	Introduction	712

23.2	Basic Principles	712
23.2.1	History Survey	712
23.2.2	The Fluorophor and Photophysical Processes	713
23.2.3	Background and Noise	715
23.3	Methods	716
23.4	Single Quantum Systems: Anti-Bunching, Blinking, Anisotropy	721
23.4.1	Novel Phenomena: Non-Classical Light	723
23.5	Conclusions and Perspectives	725
23.6	Related Fields of Research	725
23.6.1	Probes, Switches, and Conductors – Photophysics	725
23.6.2	Single-Molecule Tracking	729
	References	732
24	Scanning Probe Methods: From Microscopy to Sensing	737
	<i>Rüdiger Berger, Jochen Gutmann, and Rolf Schäfer</i>	
24.1	Introduction	738
24.2	Basic Principles and Experimental Techniques	739
24.2.1	Working Principle of Scanning Probe Microscopy	739
24.2.2	Scanning Probe Microscopy	740
24.2.3	Force Spectroscopy	741
24.2.4	Mass Sensing	743
24.2.5	Surface Stress	743
24.2.6	Calorimetry	744
24.3	Applications	745
24.3.1	Imaging in Solution	745
24.3.2	Binding Forces and Off-Rates	746
24.3.3	Gravimetry	750
24.3.4	Biosensors (Nose)	752
24.3.5	Thermochemistry	754
24.4	Summary and Conclusion	756
	References	758
25	Superconducting Quantum Interference Device Magnetometry	763
	<i>Heiko Lueken</i>	
25.1	Introduction	763
25.2	Basic Principles	764
25.2.1	Magnetic Quantities and Units [5, 6]	764
25.2.2	Classification of Magnetic Materials	768
25.3	Experimental Magnetometrical Methods	777
25.3.1	Direct Current Method	777
25.3.2	Alternating Current Method	778
25.3.3	Magnetometry at High Fields	780
25.4	Selected Applications	781
25.4.1	Diamagnetic Materials	781
25.4.2	Metamagnetic $\text{Sc}_2\text{MnRh}_5\text{B}_2$	781

25.4.3	Superparamagnets	783
25.4.4	Spin Glasses	785
25.4.5	Single-Molecule Magnets	787
25.4.6	Magnetometry at High Fields	790
25.5	Supplementary Material	791
	References	792

26	Transmission Electron Microscopy	797
	<i>Hans-Joachim Kleebe, Stefan Lauterbach, and Mathis M. Müller</i>	
26.1	Introduction	797
26.1.1	Why Electrons?	798
26.2	Components of a TEM Instrument	799
26.2.1	Lens Aberrations	802
26.3	Specimen Preparation	803
26.4	Electron Diffraction	806
26.5	Image Contrast	813
26.6	High Resolution Imaging	816
26.7	Summary	820
	References	820

Appendix	823
-----------------	------------

Index	829
--------------	------------