

CONTENTS

Preface..... v

Contributors..... xvii

1. Nuclear Magnetic Resonance Spectroscopy..... 1

Eduardo Ribeiro deAzevedo and Tito José Bonagamba

1.1 Introduction	1
1.2 Properties of Nuclear Spins	1
1.3 Nuclear Spin Interactions in Solids	2
1.3.1 General Structure of the Internal Hamiltonians	5
1.3.2 Behavior of Internal Hamiltonians under Rotations.....	6
1.4 Quantum Mechanical Calculations.....	8
1.4.1 Quantum Mechanical Description of NMR	9
1.4.2 The NMR Signal—Zeeman Interaction	13
1.5 High Resolution Solid State NMR Methods	13
1.5.1 Dipolar Decoupling	14
1.5.2 Magic-Angle Spinning (MAS).....	14
1.5.3 Cross-Polarization (CP).....	19
1.5.4 The CP-MAS Experiment	19
1.5.5 NMR Spectra.....	20
1.6 Principles of Two-Dimensional Spectroscopy	22
1.7 Molecular Dynamics and Local Molecular Conformation in Solid Materials	23
1.7.1 Lineshape Analysis	23
1.7.2 Two-Dimensional Exchange NMR Experiments.....	32
1.7.3 One-Dimensional Exchange NMR Experiments	45
1.7.4 Conformation-NMR	53
References	59

2. Nuclear Quadrupole Resonance Spectroscopy..... 65

Bryan H. Suits

2.1 Introduction	65
2.2 Basic Theory.....	66
2.2.1 The Nuclear Electric Quadrupole Interaction	66
2.2.2 Energy Levels and Transition Frequencies	70
2.2.3 Excitation and Detection	72
2.2.4 The Effect of a Small Static Magnetic Field	77
2.2.5 Linewidths and Relaxation Times.....	79
2.3 Instrumentation.....	82
2.3.1 CW Spectrometers.....	83
2.3.2 Pulsed Spectrometers	84

2.3.3 Field Cycling NQR Spectrometers.....	87
2.3.4 Some Less Common NQR Detection Schemes	88
2.4 Interpretation of Coupling Constants	89
2.4.1 Molecular Crystals and Covalently Bonded Groups.....	90
2.4.2 Ionic Crystals.....	91
2.4.3 Metals.....	92
2.4.4 Sternheimer Shielding/Antishielding	92
2.5 Summary	93
References	94
Bibliography.....	96

3. Electron Paramagnetic Resonance Spectroscopy 97

Sergei A. Dikanov and Antony R. Crofts

3.1 Introduction	97
3.2 Theoretical Background	98
3.2.1 EPR Condition	98
3.2.2 Continuous Wave-EPR	99
3.2.3 EPR Lineshape: Relaxation Times.....	99
3.2.4 EPR Spin-Hamiltonian	102
3.2.5 Electron-Nuclear Interactions: Hyperfine Structure.....	106
3.2.6 Homogeneous and Inhomogeneous Line Broadening.....	111
3.2.7 Pulsed-EPR	111
3.3 Experimental	119
3.3.1 Design of CW-EPR Spectrometer.....	119
3.3.2 Design of Pulsed-EPR Spectrometer.....	121
3.3.3 Resonators	121
3.3.4 EPR Bands, Multifrequency Experiments.....	122
3.4 Applications of EPR Spectroscopy.....	123
3.4.1 CW-EPR and Pulsed-EPR in Single Crystals	123
3.4.2 Orientation-Disordered Samples	127
3.4.3 Two-Dimensional ESEEM.....	140
3.4.4 Measurement of Relaxation Times in CW- and Pulsed-EPR	143
3.4.5 Interaction Between Electron Spins	145
References	146

4. ENDOR Spectroscopy 151

Lowell D. Kispert and Lidia Piekara-Sady

4.1 Introduction	151
4.2 Experimental Conditions for ENDOR.....	156
4.2.1 Sensitivity, Magnetic Field Homogeneity, and Stability.....	157
4.2.2 Sample Size.....	158
4.2.3 Introduction of RF Power into Cavity	158

4.2.4 RF Power Level: CW versus Pulsed Schemes	159
4.2.5 Mode of Detection and Modulation Scheme.....	159
4.2.6 ENDOR Mechanism	159
4.2.7 Extension of ENDOR: TRIPLE Resonance.....	162
4.3 ENDOR in the Solid State	163
4.3.1 Single Crystals.....	164
4.3.2 Organic Free Radicals	167
4.3.3 Transition Metal Ions	169
4.3.4 Disordered Solids	173
4.4 Pulsed ENDOR.....	177
4.5 Applications.....	180
4.5.1 Organic Radicals in Organic Host Crystals.....	181
4.5.2 Radicals Trapped in Matrices.....	186
4.5.3 Triplet-State Radicals in Crystals, Polycrystalline Samples	186
4.5.4 Free Radicals in Biological Systems	187
4.5.5 Polymeric Systems	188
4.5.6 Inorganic Radicals in Irradiated Inorganic Single Crystals.....	189
4.5.7 Inorganic Paramagnetic Complexes in Organic Single Crystals....	189
4.5.8 F and H Centers in Inorganic Host Crystals	189
4.5.9 Paramagnetic Inorganic Ions in Organic Host Crystals.....	190
4.5.10 Transition Metal Ion Complexes in Frozen Solutions and Powders	190
4.5.11 Defects and Complexes on Surfaces	190
4.5.12 Impurity Centers in Semiconductor Host Crystals.....	191
4.5.13 Spin Centers in Silicon and Borate Systems	192
4.5.14 Paramagnetic Centers in Cubic Host Crystals.....	192
4.5.15 Perovskite-Type Materials	192
References	193

5. Mössbauer Spectroscopy..... 201

J.M. Cadogan and D.H. Ryan

5.1 Introduction	201
5.1.1 Recoilless Processes	201
5.1.2 Doppler Velocity	203
5.1.3 Lineshape	203
5.1.4 Hyperfine Interactions	203
5.2 Methodology	212
5.2.1 Drives	214
5.2.2 Detectors	215
5.2.3 Data Collection.....	218
5.2.4 Calibration.....	220
5.2.5 Sources	222
5.2.6 Cryostats.....	225
5.2.7 Emission-Based Techniques	229

5.3 Applications.....	234
5.3.1 Magnetism.....	234
5.3.2 Magnetic Reorientations	237
5.3.3 Crystal Fields.....	239
5.3.4 Phase Analysis.....	239
5.3.5 Amorphous Materials.....	241
5.3.6 Electronic Relaxation	245
5.3.7 Electronic Valence	245
5.3.8 Industrial Applications	248
5.4 Concluding Remarks	254
References	254
6. Crystal Field Spectroscopy	257
<i>Albert Furrer and Andrew Podlesnyak</i>	
6.1 Introduction	257
6.2 The Crystal Field Interaction.....	259
6.2.1 Basic Formalism.....	259
6.2.2 Model Calculations of the Crystal Field Interaction	263
6.2.3 Parametrization of the Crystal Field Interaction	266
6.2.4 Extrapolation Schemes	267
6.2.5 Calculation of Thermodynamic Magnetic Properties.....	268
6.3 Experimental Techniques	268
6.3.1 Introductory Remarks.....	268
6.3.2 Neutron Spectroscopy	269
6.3.3 Raman Spectroscopy	276
6.3.4 Point-Contact Spectroscopy	278
6.4 Determination of Crystal Field Parameters from Experimental Data	280
6.4.1 A Simple Two-Parameter Crystal Field Problem.....	280
6.4.2 A Complicated Many-Parameter Crystal Field Problem.....	283
6.5 Interactions of Crystal Field Split Ions.....	287
6.5.1 Introductory Remarks.....	287
6.5.2 Interaction with Phonons.....	287
6.5.3 Interaction with Conduction Electrons.....	288
6.5.4 Magnetic Exchange Interaction.....	290
6.6 Crystal Field Effects Related to High-Temperature Superconductivity.....	291
6.6.1 Introductory Remarks.....	291
6.6.2 The Crystal Field as a Local Probe: Evidence for Materials Inhomogeneities.....	292
6.6.3 Relaxation Phenomena to Probe the Pseudogap	297
6.7 Concluding Remarks	300
References	301

7. Scanning Tunneling Spectroscopy (STS)	305
<i>K.W. Hips</i>	
7.1 Introduction	305
7.2 The Scanning Tunneling Microscope (STM).....	307
7.2.1 Commercial Instruments	312
7.2.2 Tips.....	313
7.3 Scanning Tunneling Spectroscopy (STS) of Semiconductors and Metals	315
7.4 Electron Tunneling Spectroscopy of Adsorbed Molecules	319
7.5 Practical Considerations Relating to STM-IETS and STM-OMTS	326
7.5.1 STM-Based Orbital-Mediated Tunneling Spectra and Electrochemistry	328
7.5.2 STM-Based OMTS and Ultraviolet Photoemission Spectroscopy	332
7.5.3 OMTS as a Chemical Analysis Tool: Direct Spectral Characterization	337
7.5.4 OMTS as a Chemical Analysis Tool: Bias-Dependent Imaging.....	342
7.5.5 OMTS as a Submolecular Electron Transport Mapping Tool.....	343
7.6 Some Concluding Points	345
References	346
8. Resonance Acoustic Spectroscopy.....	351
<i>Farhang Honarvar and Esmaeil Enjilela</i>	
8.1 Introduction	351
8.2 Scattering of Waves.....	352
8.2.1 Physics of Acoustic Resonance Scattering.....	352
8.2.2 Acoustic Wave Scattering from Elastic Targets.....	354
8.3 Mathematical Models	356
8.3.1 Resonance Scattering Theory (RST).....	368
8.4 Method of Isolation and Identification of Resonances (MIIR).....	371
8.4.1 Introduction	371
8.4.2 Quasi-Harmonic MIIR	371
8.4.3 Short-Pulse MIIR	375
8.5 Experimental and Numerical Results	377
8.5.1 Introduction	377
8.5.2 Characterization of Target Shape by RAS	377
8.5.3 Material Characterization by Resonance Acoustic Spectroscopy (MCRAS).....	381
8.5.4 Nondestructive Evaluation (NDE) of Clad Rods by RAS.....	385
8.5.5 Nondestructive Evaluation of Epon-815 Clad Steel Rod by RAS	386
8.5.6 Characterization of Cladding Delamination	388

8.5.7 Nondestructive Evaluation (NDE) of Explosively Welded Clad Rods by RAS	390
8.5.8 Nondestructive Evaluation of Fiber-Reinforced Composite Rods	395
8.5.9 Nondestructive Evaluation of Continuously Cast Rods by RAS ...	399
References.....	407
9. Fourier Transform Infrared Spectroscopy	411
<i>Neena Jaggi and D.R. Vij</i>	
9.1 Introduction	411
9.2 Historical Background.....	413
9.3 FT-IR Spectroscopy.....	416
9.3.1 Basic Integral Equation	417
9.3.2 Experimental Setup	419
9.3.3 Advantages.....	421
9.3.4 Other Aspects	427
9.4 Applications.....	436
9.4.1 Atmospheric Pollution.....	438
9.4.2 Study of Planetary Atmosphere.....	440
9.4.3 Surface Studies.....	443
9.4.4 Characterization of Optical Fibers	444
9.4.5 Vibrational Analysis of Molecules.....	444
9.4.6 Study of Biological Molecules	445
9.4.7 Study of Polymers	446
References	447
10. Auger Electron Spectroscopy	451
<i>Richard P. Gunawardane and Christopher R. Arumainayagam</i>	
10.1 Introduction	451
10.2 Historical Perspective.....	454
10.3 Basic Principles of AES	454
10.3.1 X-Ray Notation	454
10.3.2 Auger Transitions.....	455
10.3.3 Kinetic Energies of Auger Electrons.....	457
10.4 Instrumentation.....	459
10.4.1 Electron Optical Column.....	459
10.4.2 Ion Optical Column.....	461
10.4.3 Electron Energy Analyzers.....	462
10.4.4 Electron Detector.....	464
10.4.5 Computer Control and Data Display Systems.....	464
10.5 Experimental Procedures Including Sample Preparation	465
10.5.1 Sample.....	465
10.5.2 Beam Effects and Surface Damage	465

10.5.3 AES Modifications and Combinations with Other Techniques	466
10.6 Auger Spectra: Direct and Derivative Forms	466
10.7 Applications.....	468
10.7.1 Qualitative Analysis	468
10.7.2 Quantitative Analysis	468
10.7.3 Chemical Information	472
10.7.4 Auger Depth Profiling	473
10.7.5 Auger Images and Linescans.....	476
10.7.6 Research and Industry	477
10.8 Recent Advances	479
10.8.1 Positron-Annihilation-Induced AES	480
10.8.2 Auger Photoelectron Coincidence Spectroscopy	480
10.9 Conclusions	481
References	481
11. X-Ray Photoelectron Spectroscopy.....	485
<i>Hsiao-Lu Lee and Nolan T. Flynn</i>	
11.1 Introduction and Basic Theory	485
11.2 Historical Perspective.....	486
11.3 Instrumentation.....	486
11.3.1 Vacuum System.....	487
11.3.2 X-Ray Source	489
11.3.3 Electron Energy Analyzer	492
11.4 Sample Selection and Preparation.....	492
11.4.1 Sample Charging	493
11.4.2 X-Ray Beam Effects.....	495
11.5 Spectral Analysis	496
11.5.1 Core Level Splitting	498
11.5.2 Linewidths.....	500
11.5.3 Elemental Analysis: Qualitative and Quantitative	500
11.5.4 Secondary Structure	501
11.6 XPS Imaging	502
11.7 Angle-Resolved XPS.....	504
11.8 Recent Advances and Applications	504
11.9 Conclusions	506
References	506
12. Luminescence Spectroscopy	509
<i>Baldassare Di Bartolo and John Collins</i>	
12.1 Introduction	509
12.1.1 Basic Concepts	509
12.1.2 History	510

12.2 Spontaneous Emission, Absorption, and Induced Emission	511
12.2.1 Classical Bound, Radiating Electron.....	511
12.2.2 Quantum Mechanical Radiative Decay.....	513
12.2.3 Absorption and Emission	516
12.2.4 Absorption Coefficient and Absorption Cross-Section.....	518
12.3 Measurements and Techniques.....	519
12.3.1 Absorption Spectra.....	519
12.3.2 Luminescence Spectra.....	521
12.3.3 Excitation Spectra	522
12.3.4 Responses to Pulsed Excitation.....	522
12.4 Localized Systems.....	523
12.4.1 Introduction	523
12.4.2 The Hamiltonian of an Ion in a Solid.....	524
12.4.3 Rare Earth Ions in Solids.....	524
12.4.4 Transition Metal Ions in Solids	528
12.4.5 Color Centers in Solids	535
12.5 Processes in Localized System Service	539
12.5.1 Introduction	539
12.5.2 Radiative Decay	540
12.5.3 Multiphonon Decay	542
12.5.4 Vibronic Transitions.....	545
12.5.5 Energy Transfer.....	547
12.5.6 Upconversion	548
12.5.7 Line Broadening and Shifting with Temperature.....	549
12.6 Delocalized Systems.....	551
12.6.1 Density of One-Electron States and Fermi Probability Distribution	551
12.6.2 Classification of Crystalline Solids	552
12.6.3 Intrinsic Semiconductors.....	554
12.6.4 Doped Semiconductors	556
12.6.5 Model for a Doped Semiconductor	557
12.7 Processes in Delocalized Systems	560
12.7.1 Direct Gap and Indirect Gap Semiconductors.....	560
12.7.2 Excitation in Insulators and Large Band Gap Semiconductors....	561
12.7.3 Radiative Transitions in Pure Semiconductors	562
12.7.4 Doped Semiconductors	564
12.7.5 Radiative Transitions Across the Band Gap.....	565
12.7.6 Non-Radiative Processes	566
12.7.7 p-n Junctions	567
12.8 Direction of Future Efforts	571
12.8.1 Why Luminescence?	571
12.8.2 Challenges and Future Work.....	571
References	574
Bibliography	575

13. Laser-Induced Fluorescence Spectroscopy	577
<i>G. Geipel</i>	
13.1 Introduction	577
13.2 Experimental Setup	578
13.3 Fluorescence Spectroscopy of Minerals	579
13.4 Fluorescence Spectroscopy of Surface Species and in Solid Phases....	584
13.5 Fluorescence Spectroscopy of Frozen Samples.....	586
13.6 Fluorescence Spectroscopy of Non-Actinide Solid Matrices	589
13.7 Outlook	591
References	591
14. Soft X-Ray Emission and Resonant Inelastic Scattering Spectroscopy	595
<i>E.J. Nordgren, S.M. Butorin, L.C. Duda, and J.-H. Guo</i>	
14.1 Introduction	595
14.2 Properties of X-Ray Spectra	597
14.3 Resonant Inelastic X-Ray Scattering	602
14.4 Experimental Techniques	605
14.4.1 Grating Spectrometers for Soft X-Ray Emission	605
14.4.2 Samples at Ambient Conditions	608
14.5 Applications.....	609
14.5.1 Surfaces, Interfaces, and Thin Films	609
14.5.2 Nano Structures	615
14.5.3 Transition Metal Systems	619
14.6 Summary	654
References	654
15. Laser Raman Spectroscopy	661
<i>Alfons Schulte and Yu Guo</i>	
15.1 Introduction	661
15.2 Spontaneous Raman Scattering	663
15.3 Experimental Approaches	666
15.4 Applications.....	670
15.4.1 Glasses for Raman Gain	671
15.4.2 Chalcogenide Glasses.....	673
15.4.3 Chalcogenide Thin Films—Waveguide Raman	675
15.4.3 High-Pressure Raman Spectroscopy of Proteins	677
15.4.4 Micro-Raman Spectroscopy	680
15.5 Conclusions and Outlook	685
References	685

16. Polarization Spectroscopy of Ordered Samples	689
<i>Peter W. Thulstrup and Erik W. Thulstrup</i>	
16.1 Introduction	689
16.1.1 Linearly Polarized Light.....	689
16.1.2 Transition Moment Directions	690
16.1.3 Spectroscopy with Linearly Polarized Light	694
16.2 Occurrence, Production, and Optical Properties of Aligned Solid Samples.....	696
16.2.1 Perfectly and Partially Aligned Samples.....	696
16.2.2 Solutes in Partially Aligning Solvents.....	697
16.3 One-Photon Spectroscopy: Linear Dichroism.....	699
16.3.1 Optical Spectroscopy with Linearly Polarized Light: Experimental Needs	699
16.3.2 Mathematical Descriptions of Aligned, Uniaxial Samples	700
16.3.3 LD Spectra of Aligned, Uniaxial Samples	702
16.3.4 Transition Moment Directions and Reduced Spectra: Symmetrical Molecules	704
16.3.5 Transition Moment Directions: Molecules of Lower Symmetry	715
16.3.6 Non-Uniaxial Samples	720
16.4 Two-Photon Spectroscopy.....	721
16.5 Conclusions	726
References	726