

---

# Contents

Preface.....	xi
Author .....	xv
<b>Chapter 1</b> General Principles of Pulsed NMR and NMR Techniques .....	1
1.1 Early History of NMR in the Solid State .....	2
1.2 Nuclei in the External Magnetic Field.....	3
1.3 Effects of Radio Frequency Pulses.....	9
1.4 From Macroscopic Magnetization to Nuclear Relaxation and Shapes of NMR Signals.....	12
1.4.1 Common Representations of Molecular Motions and Their Influence on NMR .....	14
1.4.2 Contribution of Molecular Mobility to Spin–Spin and Spin–Lattice Nuclear Relaxation.....	17
1.5 Parameters Characterizing Nuclei in the External Magnetic Field .....	20
1.5.1 Chemical Shift.....	20
1.5.2 Spin–Spin Coupling .....	22
1.5.3 Quadrupolar Coupling .....	24
1.6 Introducing NMR Equipment and NMR Experiments .....	26
1.6.1 Magnets and NMR Probes .....	28
1.6.2 Homogeneity of the External Magnetic Field and Digital Resolution in NMR Spectra .....	30
1.6.3 Dead Time of NMR Spectrometers: Intensity of Signals and Distortion of Baselines in NMR Spectra .....	30
1.7 Main Principles of Two-Dimensional NMR .....	32
1.8 Enhancement of Sensitivity in NMR.....	34
References .....	35
<b>Chapter 2</b> On Amorphous Materials as Potential Objects in Solid-State NMR Studies: Common and Key Problems .....	37
2.1 Hybrid Materials.....	38
2.2 Polymer Solids.....	40
2.3 Systems Based on Nanostructures.....	41
2.4 Wood and Wood Components .....	42
2.5 Glasses .....	44
2.6 Zeolites .....	45

2.7	Design of Porous and Layered Molecular Systems .....	47
2.7.1	General Problems in Structural Characterizations of Amorphous Porous Materials .....	48
2.7.2	Some Key Structural Issues in Characterizations of Amorphous Materials Modified by Metal Ions and Methods for Structure Solution .....	50
	References .....	54
<b>Chapter 3</b>	<b>Features of Solid-State NMR: Diamagnetic Materials .....</b>	<b>57</b>
3.1	From Isotropic Chemical Shifts to Magnetic Shielding Tensors .....	57
3.1.1	Visualization of Chemical Shift Tensors and Determination of Their Orientations.....	62
3.2	Nuclei with a Spin of 1/2 .....	66
3.3	Quadrupolar Nuclei in Solids .....	70
3.3.1	Two Categories of Quadrupolar Nuclei.....	72
3.4	Detection of NMR Signals in Solids: Common Aspects .....	73
3.4.1	Wide-Line NMR .....	73
3.4.2	Direct Excitation .....	74
3.4.3	Cross-Polarization .....	76
3.4.4	Cross-Polarization with Quadrupolar Nuclei .....	79
3.5	High-Power Decoupling .....	81
3.6	Multi-Quantum NMR Experiments .....	83
3.7	Dipolar Recoupling NMR Techniques .....	85
3.8	Sideband Manipulations .....	90
3.9	Zero-Field Solid-State NMR Experiments.....	92
3.10	Solid-State NMR Imaging.....	94
	References .....	96
<b>Chapter 4</b>	<b>Practice of Multinuclear NMR in Diamagnetic Solids: General Information and Examples of Applications .....</b>	<b>99</b>
4.1	Structural Information by Increasing the Spectral Resolution in Multinuclear Solid-State NMR .....	99
4.1.1	Spectral Resolution for Nonquadrupolar Nuclei .....	100
4.1.2	Signal Assignments .....	102
4.1.3	Resolving Quadrupolar Nuclei.....	104
4.2	Probing Proximities of Nuclei and Measurements of Internuclear Distances in Diamagnetic Solids .....	106
4.3	<sup>31</sup> P Solid-State NMR .....	111
4.4	Solid-State NMR of Halogen Nuclei and Oxygen.....	116
4.5	Solid-State NMR of Oxide Materials: Nuclei <sup>51</sup> V, <sup>93</sup> Nb, and <sup>181</sup> Ta.....	123
4.6	Solid-State <sup>13</sup> C NMR: Wood and Wood Products.....	127
4.7	<sup>2</sup> H NMR in Solids at Deuterium Natural Abundance .....	129

4.8	Between Solution- and Solid-State NMR: Nanoparticles and Suspensions.....	131
	References .....	137
<b>Chapter 5</b>	<b>Dynamics in Diamagnetic Materials from Solid-State NMR: Methods, Measurements, and Analysis.....</b>	<b>139</b>
5.1	Variable-Temperature Solid-State NMR Experiments and a Line-Shape Analysis.....	141
5.1.1	Dynamics in Polymeric Materials from a Line-Shape Analysis.....	143
5.2	Molecular Mobility from the Solid-State NMR Relaxation ....	145
5.2.1	Measurements of Relaxation Times and Errors of the Measurements .....	145
5.2.2	How Molecular Motions Affect Nuclear Relaxation ....	149
5.2.2.1	Correlation Time Distribution versus Single Correlation Time .....	151
5.2.3	Relaxation Approaches: Methodology and Examples .....	153
5.3	One- and Two-Dimensional Exchange Solid-State NMR Spectroscopy .....	156
5.4	Molecular Mobility from the Cross-Polarization NMR Experiments .....	158
5.5	Molecular Mobility from Magnetic Relaxation Dispersion Experiments .....	160
	References .....	163
<b>Chapter 6</b>	<b>Strategies in Solid-State Multinuclear NMR: Studies of Diamagnetic Porous Materials.....</b>	<b>165</b>
6.1	Porosity of Materials from NMR .....	165
6.1.1	NMR Cryoporometry.....	168
6.1.2	NMR Relaxometry.....	171
6.1.3	NMR Behavior of Gases in Pore Spaces.....	173
6.2	Structural Features of Silica Lattice and Surface by Solid-State $^1\text{H}$ $^{29}\text{Si}$ , $^{27}\text{Al}$ , and $^{17}\text{O}$ NMR Spectra.....	176
6.2.1	Distribution of Diamagnetic Metal Ions from Solid-State NMR.....	181
6.3	Molecular Mobility in Diamagnetic Porous Materials.....	186
	References .....	189
<b>Chapter 7</b>	<b>Paramagnetic Effects in Solid-State NMR .....</b>	<b>191</b>
7.1	Theoretical Aspects.....	193
7.1.1	Chemical Shifts and Magnetic Shielding Tensors in the Presence of Unpaired Electrons.....	193

7.2	Nuclear Relaxation in the Presence of Unpaired Electrons....	197
7.2.1	Spin Diffusion .....	198
7.2.2	Nuclear Relaxation via Nucleus–Electron Dipolar and Contact Interactions .....	199
7.3	Practical Consequences from the Theory of Paramagnetic Effects .....	200
7.4	$^1\text{H}$ , $^{31}\text{P}$ , $^{13}\text{C}$ , $^2\text{H}$ , $^{29}\text{Si}$ , $^7\text{Li}$ , and $^6\text{Li}$ NMR Spectra of Paramagnetic Solids .....	205
7.5	$^{51}\text{V}$ and $^{55}\text{Mn}$ NMR Spectra of Paramagnetic Solids .....	210
7.5.1	Analyzing the Nature of Metal Ions by Their Direct Observation in Solid-State NMR Spectra.....	212
7.6	Special NMR Techniques for Observations of “Invisible” Target Nuclei.....	215
7.7	Relaxation Measurements and Relaxation Times in Paramagnetic Solids .....	217
7.7.1	Solid-State $T_1$ Measurements .....	224
7.7.2	Spin–Spin Relaxation Times and Anomalies in Solid-State $T_2$ Measurements.....	225
	References .....	228

<b>Chapter 8</b>	Strategy in NMR Studies of Amorphous Porous Paramagnetic Materials.....	231
8.1	Intense Sideband Patterns in MAS NMR Spectra of Paramagnetic Amorphous Materials and Their Analysis .....	231
8.2	Direct Detection of the Nuclei Closest to Paramagnetic Ions in Porous Materials by the Hahn-Echo Mapping NMR Experiments .....	236
8.3	NMR Relaxation Approaches to Structure of Porous Amorphous Paramagnetic Silica-Based Materials: From Experiments to Models and Interpretations.....	240
8.3.1	Factors Affecting Relaxation Times in Porous Solids ...	241
8.3.2	Spin–Lattice Relaxation Times in Porous Silica-Based Materials and Concentrations of Paramagnetic Ions.....	242
8.3.3	$^{29}\text{Si}$ Spin–Lattice and Spin–Spin Relaxation in Static and Spinning Porous Amorphous Paramagnetic Silica-Based Materials .....	243
8.3.4	$T_1$ Criteria for Locations of Paramagnetic Ions: Relaxation of Isotropic Resonances .....	247
8.3.5	$T_1$ Criteria Based on Relaxation of Sideband Patterns in MAS Spectra of Porous Paramagnetic Materials.....	251
8.3.6	BMS Effects and NMR Relaxation of Sideband Patterns in MAS Spectra of Porous Paramagnetic Materials.....	254

8.4	Protocol for Quantification of “Invisible Nuclei” in MAS NMR.....	255
8.5	Concluding Remarks .....	256
	References .....	257
<b>Index</b> .....		<b>259</b>