Nuclear Magnetic Resonance in Solids

Edited by

Lieven Van Gerven

Laboratorium voor Vaste Stof-Fysika en Magnetisme Katholieke Universiteit Leuven Leuven, Belgium

> Bibliothek FB7 Physikal. Chemie / Chem. Technologie

> Technische Hochschule Darmstadt

Van 3

Inventar Nr. 10522/PC

PLENUM PRESS • NEW YORK AND LONDON Published in cooperation with NATO Scientific Affairs Division

Contents

1

DEDICATION

Chapter I: PRINCIPLES: TEMPERATURES, STRUCTURES, MOTIONS

GENERAL ASPECTS OF NUCLEAR MAGNETIC RESONANCE IN SOLIDS	
C.P. Slichter	3
Introduction	3
The contrast with high resolution NMR	3
The flavor of the problems studied	4
The special solid state aspects of the coupling of a nucleus to its surroundings - Line position and shape	5
INTRODUCTION TO SPIN TEMPERATURES AND THEIR RELATION TO THE BLOCH EQUATIONS	
C.P. Slichter	17
A prediction from the Bloch equations	17
The concept of spin temperature in the laboratory frame in the absence of alternating magnetic fields	19
Adiabatic and sudden changes	21
Magnetic resonance and saturation	25
Redfield theory neglecting lattice coupling	28
The approach to equilibrium for weak H ₁	32
1	34
Conditions for validity of the Redfield hypothesis	
Spin-lattice effects	34
Spin-locking, T ₁₀ , and slow motion	37

ix

SINGLE CRYSTALS, POWDERS, AND ANISOTROPY EFFECTS C.P. Slichter	4 1
A single crystal example	41
The spectra of powder samples	49
NMR PARAMETERS FOR STUDYING STRUCTURE AND MOTION W. Müller-Warmuth	55
Introduction	55
Dipolar interactions	57
Quadrupole effects	64
Anisotropic chemical shift effects	68
THE EFFECT OF MOLECULAR MOTION ON LINE WIDTHS AND RELAXATION TIMES	
S. Clough	71
Summary	71
Introduction	71
The example	73
Internuclear interactions	74
Motionally adapted dipolar Hamiltonian	75
A second type of motion	77
Collective interaction constants	78
Effect of motion on spin diffusion	80
A COMPARISON BETWEEN CLASSICAL THEORY OF MOTIONAL NARROWING AND NARROWING DUE TO QUANTUM MECHANICAL TUNNELLING MOTION	
S. Clough	83
Summary	83
Introduction	83
The relationship between classical and quantum motion	84
Motional narrowing	86
Classical model	86
Tunnelling model	87

х

÷

ì

Ś

Ĭ

1

3

Practical examples of tunnelling motions in molecular solids	89
Spin species and the role of the exclusion principle	92
Measurement of tunnelling frequency by NMR	92
Appendix A	93
Appendix B	94
Appendix C	95

Chapter II: SYSTEMS: PHONONS, NON-METALS, METALS

MAGNETIC RESONANCE AND RELAXATION: A PROBE OF THE	
PHONON SPECTRUM R. Orbach	99
MAGNETIC RESONANCE AND STRUCTURAL PHASE TRANSITIONS R. Blinc	113
	, i i j
Introduction	113
Order parameter determination by magnetic resonance	116
Order parameter dynamics via T ₁	123
NMR STUDIES OF MOLECULAR SOLIDS, POLYMERS AND GLASSES W. Müller-Warmuth	131
Introduction	131
Molecular solids	132
Polymers	139
Glasses	142
NMR IN METALS AND ALLOYS	
H. Alloul	157
Introduction	157
Theory of the Knight shift and spin lattice relaxation in metals	158
Knight shift and T ₁ in pure metals: Experimental results	164
Spin-spin interactions and NMR lineshapes in metals	172

xi

CONT	'EN	ΤS
------	-----	----

NMR in dilute alloys		177
Concentrated alloys		193
Summary		197

Chapter	111:	METHODS	8			
,		FOURIER RESONANC	TRANSFORM, CE	MULTIPLE	PULSE,	DOUBLE

THE FOURIER TRANSFORM IN NMR: I. WHY AND HOW P. Van Hecke	201
Introduction	201
Definitions	202
Time domain - Frequency domain	204
Pulsed Fourier transform or continuous wave	205
Discrete Fourier transform (DFT)	209
Windowing and resolution	211
Sampling rate and folding	212
Calculation of the discrete Fourier transform	214
calculation of the discrete Fourier transform	614
THE FOURIER TRANSFORM IN NMR: II. SIGNAL PROCESSING	
AND INSTRUMENTAL REQUIREMENTS P. Van Hecke	217
Filters and detectors	217
Analog-to-digital conversion. Time averaging	222
Optimization of the stored signal	224
Phase corrections on the spectrum	226
LINE NARROWING BY MULTIPLE PULSE TECHNIQUES: I. OBJECTIVES	
AND PRINCIPLES	
U. Haeberlen	229
LINE NARROWING BY MULTIPLE PULSE TECHNIQUES: II. THE REAL	
WORLD OF PULSES	020
U. Haeberlen	239
Phase transients	239
Finite nulse widths flip angle errors	242

CONTENTS	xiii
LINE NARROWING BY MULTIPLE PULSE TECHNIQUES: III. EXPERIMENTAL ASPECTS	
U. Haeberlen	251
PROBLEMS + REFERENCES ABOUT LINE NARROWING BY MULTIPLE PULSE TECHNIQUES	
U. Haeberlen	259
HIGH RESOLUTION DOUBLE RESONANCE DIRECT DETECTION OF RARE NUCLEI IN SOLIDS. METHOD AND TECHNIQUE	
P. Van Hecke	263
Introduction	263
Principles	264
Description of the method	266
A variation of the basic method. The single contact total transfer of polarization	272
Instrumental requirements	275
HIGH RESOLUTION DOUBLE RESONANCE IN SOLIDS. RECENT DEVELOPMENTS AND APPLICATIONS	
J. Tegenfeldt	281
Some introductory remarks	281
I spin preparation recipes	283
Cross polarization dynamics	288
Echoes	292
Resolution - Applications	294
WIDE LINE DOUBLE RESONANCE AND RELAXATION IN THE ROTATING AND LABORATORY FRAMES	
R. Blinc	303
Double resonance spectroscopy	303
Double resonance relaxation measurements	312
NUCLEAR MAGNETIC DOUBLE RESONANCE BASED ON STRONG RF MAGNETIC FIELD INDUCED COUPLING BETWEEN SPIN SYSTEMS	
R. Blinc	319
Introduction	319

The origin of the RF magnetic field induced coupling between spin systems	320
Theory of the RF magnetic field induced coupling between spin systems	326
Experimental	330
Analysis of the double resonance process	334
Experimental results	342
Discussion	345

Chapter IV: LIFE: PEPTIDES, PROTEINS, NUCLEIC ACIDS

NMR STUDIES OF STRUCTURE AND CONFORMATION IN PEPTIDES AND PROTEINS	
K. Wüthrich	347
Structure and conformation in peptides and proteins	347
Primary structure and NMR parameters	349
Manifestations of different molecular conformations in the NMR parameters	353
Dynamics of protein conformations	358
NMR STUDIES OF HEMOPROTEINS K. Wüthrich	361
Structure and biological roles of hemoproteins	361
¹ H-NMR spectra of hemoproteins	363
Local magnetic fields in hemoproteins	366
Protein conformations in single crystals and in solution	368
NMR studies of the electronic states in the heme groups	369
HIGH RESOLUTION NMR INVESTIGATION OF NUCLEIC ACID	
D.R. Kearns	375
Introduction	375
The assignment problem	377

xiv

Ţ

ł

Ţ)

Detailed interpretation of the low field NMR spectra of tRNA	380
Temperature dependence of low field NMR	387
Paramagnetic rare earth probes of tRNA structure	393
Conformation of DNA: poly d(A-T)	401
Determination of DNA structural parameters	405
Future NMR studies	407
PARAFFINIC CHAINS: THE OBSERVATION OF STATIC DIPOLAR INTERACTIONS IN THE PRESENCE OF ANISOTROPIC MOTIONAL NARROWING M. Guéron	409
Demonstration of a static dipolar interaction	412
Investigation of molecular motions	413

XV

PARTICIPANTS	421
SUBJECT INDEX	 425