LECTURE NOTES IN PHYSICS

J. Dolinšek
M. Vilfan
S. Žumer
(Eds.)

Novel NMR and EPR Techniques

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Editors

Professor Dr. Janez Dolinšek[+*]
Professor Dr. Marija Vilfan[*]
Professor Dr. Slobodan Žumer[+*]

[+]Physics Department
Faculty of Mathematics and Physics
University Ljubljana
Jadranska 19
1000 Ljubljana
Slovenia

[*]Jozef Stefan Institute
Jamova 39
1000 Ljubljana
Slovenia

E-mails:
jani.dolinsek@ijs.si
mika.vilfan@ijs.si
slobodan.zumer@fmf.uni-lj.si

J. Dolinšek et al., *Novel NMR and EPR Techniques*,
Lect. Notes Phys. 684 (Springer, Berlin Heidelberg 2006), DOI 10.1007/b11540830

Library of Congress Control Number: 2006921047

ISSN 0075-8450
ISBN-10 3-540-32626-X Springer Berlin Heidelberg New York
ISBN-13 978-3-540-32626-7 Springer Berlin Heidelberg New York

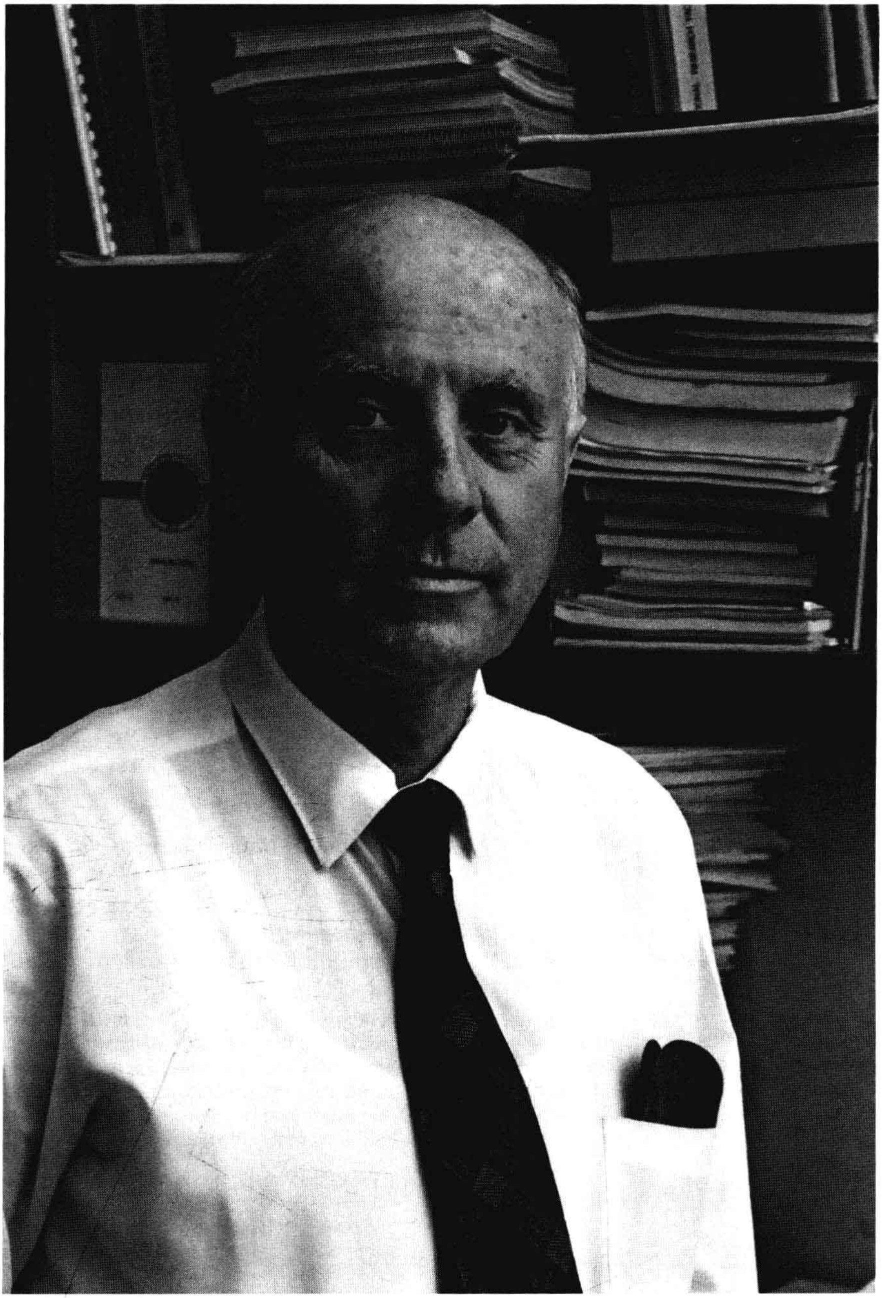
Springer is a part of Springer Science+Business Media
springer.com

Printed in The Netherlands

Typesetting: by the authors and techbooks using a Springer LaTeX macro package
Cover design: *design & production* GmbH, Heidelberg

Printed on acid-free paper SPIN: 11540830 54/techbooks 5 4 3 2 1 0

This book is dedicated to
Professor Robert Blinc,
with respect and kind regards



Professor Robert Blinc

Preface

This book is a collection of scientific articles on current developments of NMR and ESR techniques and their applications in physics and chemistry. It is dedicated to Professor Robert Blinc, on the occasion of his seventieth birthday, in appreciation of his remarkable scientific accomplishments in the NMR of condensed matter. He is a physicist commanding deep respect and affection from those who had the opportunity to work with him.

Robert Blinc was born on October 31, 1933, in Ljubljana, Slovenia. He graduated in 1958 and completed his Ph.D in 1959 in physics at the University of Ljubljana. His doctoral research on proton tunneling in ferroelectrics with short hydrogen bonds was supervised by Professor Dušan Hadži. After a postdoctoral year spent in the group of Professor John Waugh at M.I.T., Cambridge, Mass., Robert Blinc was appointed as a professor of physics at the University of Ljubljana at a time when there was scarce research in the field of condensed matter in Slovenia. With his far-sighted mind, Robert Blinc, together with Ivan Zupančič, started the NMR laboratory at the Jozef Stefan Institute in Ljubljana. He immediately realized the enormous potential of NMR methods in the research of structure, dynamics, and phase transitions in solids. In the subsequent years he made significant contributions in applying magnetic resonance to the research of ice, ferroelectric materials, liquid crystals, incommensurate systems, spin glasses, relaxors, fullerenes, and fullerene nanomagnets. His work led to the detailed understanding of the microscopic nature and properties of those materials. To mention only a few: Robert Blinc and coworkers elucidated the isotopic effect in ferroelectric crystals, predicted the Goldstone mode in ferroelectric liquid crystals, studied the impact of collective orientational fluctuations on spin relaxation, detected solitons and phasons in incommensurate systems using NMR, and determined the Edwards-Anderson order parameter in glasses and relaxors. He also pioneered the application of NMR to the nondestructive oil-content measurements in seeds and the development of the NMR measurements of the self-diffusion coefficient in broad-line materials. In the early stage of the double resonance technique, he succeeded in obtaining the first nitrogen NMR spectra in nucleic acids and peptides. An important achievement of Professor Robert Blinc, which attracted considerable attention in the broad scientific community, is the book *Soft Modes in Ferroelectrics and Antiferroelectrics* (North Holland), written by him and Boštjan Žekš in 1974. The book was translated into Russian (1975) and Chinese (1982) and belongs to the 600 most-cited scientific books in the world. Another of his books, written together with Igor Muševič and Boštjan Žekš, *The Physics of Ferroelectric and Antiferroelectric Liquid Crystals*, was published by World Scientific in 2000.

Apart from being professor of physics at the University of Ljubljana, the head of the Condensed Matter Physics Department at Jožef Stefan Institute and a member (and vice-president in the years 1980–1999) of Academy of Science and Arts of Slovenia, Robert Blinc maintained a wide range of contacts with scientists worldwide. There is an amazingly long list of his international scientific activities. To mention only a few of them, he was a visiting professor at the University of Washington in Seattle; ETH Zurich; Federal University of Minas Gerais in Belo Horizonte, Brazil; University of Vienna in Austria; University of Utah in Salt Lake City; Kent State University in Ohio, Argon National Laboratory, and several others. In the years 1988–1994 he was the president of the Groupement AMPERE (Atomes et Molecules Par Etudes Radio Electrique), and president of the European Steering Committee on Ferroelectrics (1990–1999). He is a member of seven foreign Academies of Sciences and has received several national and international scientific prizes and medals.

As the head of the Condensed Matter Physics Department at the Jožef Stefan Institute for more than 40 years, Robert Blinc promoted, in addition to NMR, other experimental techniques: ESR, dielectric measurements, optical spectroscopy. He also atomic force microscopy. He also took active part in solving theoretical problems related to the systems under study. He was the supervisor of 67 diploma works and 35 Ph. D. theses in the field of condensed matter physics in Ljubljana. He can therefore be recognized as the founder and tireless promoter of the condensed matter physics research in Slovenia.

Most of Robert Blinc's research is tightly related to nuclear magnetic resonance. Therefore we invited a number of prominent researchers in this field to write chapters on the recent condensed matter physics research based on new NMR and ESR techniques. The book covers:

- Adiabatic and nonadiabatic magnetization caused by rotation of solids with dipole-dipole coupled spins.
- Magnetic resonance techniques for studying spin-to-spin pair correlation in multi-spin systems.
- Studies of selectively deuterated semisolid materials and anisotropic liquids by deuterium NMR.
- Initial steps toward quantum computing with electron and nuclear spins in crystalline solids.

- Laser radiation-induced increase of the spin polarization in various magnetic resonance experiments.
- Multiple-photon processes in cw and pulse electron paramagnetice resonance spectroscopy.
- NMR and EPR for the determination of ion localization and charge transfer in metallo-endofullerenes.
- NMR shifts in metal nanoparticles of silver, platinum, and rhodium.
- NMR relaxation studies of different superconducting systems.
- Investigations of static and dynamic properties of low dimensional magnetic systems by NMR.
- NMR-NQR relaxation studies of spin fluctuations in two-dimensional quantum Heisenberg antiferromagnets.
- The dynamics of the deuteron glass in KDP type crystals studied by various one-dimensional and two-dimensional NMR techniques.
- Nuclear Magnetic Resonance cryoporometry based on depression of the melting temperature of liquids confined in pores.

We congratulate Professor Robert Blinc on his great scientific achievements and also express our deep gratitude for his continuous efforts in stimulating and supporting the NMR and condensed matter physics community.

Ljubljana
June 2005

Janez Dolinšek
Marija Vilfan
Slobodan Žumer

Contents

Nuclear Spin Analogues of Gyromagnetism: Case of the Zero-Field Barnett Effect

E.L. Hahn[1], B.K. Tenn[2] and M.P. Augustine[2]

[1] Department of Physics, University of California, Berkeley, CA 94720
hahn@socrates.berkeley.edu
[2] Department of Chemistry, One Shields Avenue, University of California, Davis CA 95616
augustin@chem.ucdavis.edu

Abstract. A short review of the history and elementary principles of gyromagnetic effects is presented. The Barnett effect is considered as a mechanism for inducing nuclear spin magnetization in solids by sample spinning in zero and low field. Simulations of rotation induced adiabatic and non-adiabatic magnetization derived from initial dipolar order in homonuclear dipole-dipole coupled spins are carried out. Aspects of the converse Einstein-de Haas effect are included.

1 Personal Tribute

We thank the editors for the invitation to write in honor of Robert Blinc and to celebrate his 70$^{\text{th}}$ birthday. Over his many years of international research collaborations and leadership of NMR research groups at the Josef Stefan Institute, he and his colleagues have generated a body of comprehensive experimental data leading to new concepts and clarifications concerning unusual solid state structures. These have involved topics such as ferroelectrics, disordered systems, and liquid crystals, often connected with phase transitions and modal behavior.

While continually devoting himself to his group as a pioneering research physicist working out new interpretations of experiments, Professor Blinc also served as a leader of Slovenian science, maintaining many personal contacts as a virtual "Science Ambassador" in Europe. During the Cold War and through its waning years, because of Robert's international connections in the East, he was able to arrange contacts with people from both the East and the West to attend conferences in Slovenia and on the Dalmation Coast. He has made it possible for many NMR research people from the Eastern block to interact with those of us from the West. His international influence has been unique in making the world a better place for scientific cooperation. Personally I can testify how much we have enjoyed Robert's hospitality, friendship, and

E.L. Hahn et al.: *Nuclear Spin Analogues of Gyromagnetism: Case of the Zero-field Barnett Effect*, Lect. Notes Phys. **684**, 1–19 (2006)
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stimulation provided by visitations to interact with his NMR research group at the Jozef Stefan Institute for which we are grateful. We wish him and his spouse many happy and fruitful years and that he should remain active and not really retire.

2 Introduction

The motivation of this work is the possibility of the ultra-sensitive detection of pico and femto-Tesla fields from the nuclear spin polarization induced in spinning solids at zero field caused by the Barnett effect. Both the Superconducting Quantum Interference Device (SQUID) [1] and non-linear optical Faraday rotation methods [2] of measuring magnetic fields with an ultimate sensitivity of about one femto-Tesla $\mathrm{Hz}^{-1/2}$ or $10^{-11}\,\mathrm{G\,Hz}^{-1/2}$ promise to detect these small fields generated by diamagnetic solids.

A brief review of well known elementary principles of gyromagnetic experiments [3, 4] sets the stage for discussion of coupling mechanisms in the Barnett effect that may account for momentum transfer from a mechanically spinning macroscopic body to microscopic nuclear spins within the body. Only a minute fraction of the total mechanical angular momentum of the spinning sample is transferred to the oriented macroscopic magnetic spin angular momentum, thus conserving the total angular momentum of the system. In the absence of diamagnetic effects, the ratio of the change of the macroscopic magnetism of a rotating body to this corresponding change in angular momentum of the body is well known as the effective gyromagnetic ratio $(q/2mc)\ g$ where q is the fundamental charge, m is the electron mass, c is the speed of light, and g is the empirical g factor.

The Barnett effect was first observed in 1914 [4] by detecting the magnetism due to the polarization of electron spins caused by rotation of a cylinder of soft unmagnetized iron. Although the Barnett effect is looked upon today as an archaic experiment, it was an important experiment of the old physics era. Today many people are not aware of the Barnett effect because it is referred to so little in the literature. It is interesting that even though the concept of electron spin did not exist at that time, the original Barnett experiment provided the first evidence that the electron had an anomalous magnetic moment with a g factor of 2. Today it is well known that the electron spin g factor can also differ significantly from the value of 2 (ignoring the small radiative correction) because of spin orbit coupling. Barnett concluded in 1914 that he measured the gyromagnetic ratio of classical rotating charges q to be q/mc, an anomalous value twice the classical value he expected.

In 1915 Einstein and de Haas [5] carried out the converse of the Barnett experiment. The reversal of an initially known magnetization M_0, or the growth of M_0 from zero, of an iron cylinder produces a small mechanical rotation of the cylinder. In contrast to Barnett's experiment, there is an apparent transfer of spin angular momentum from M_0 into mechanical rotation. Curiously

Einstein and de Haas reported $g = 1$ from their measurements, apparently rejecting data that deviated from the expected classical value of $g = 1$ to account for the orbital magnetism. In 1820 Ampere established that the current due to a charge q and mass m rotating in a circle of radius r, multiplied by circle area πr^2, expresses the classical orbital magnetic moment. This picture supported the idea of hidden classical Amperian currents in permanent magnets, a view that held sway into the early years of the 20$^{\text{th}}$ century. But this view of classical magnetism, and ultimately the Einstein and de Haas $g = 1$ experimental interpretation, was first challenged by a theorem formulated by Miss van Leeuwen [6] and Bohr, namely, that any confined configuration of free charges obeying classical laws of motion and precessing in any magnetic field must yield zero magnetic susceptibility. Finally the advent of momentum quantization and the concept of magnetic spin made possible a break away from the invalid classical picture of magnetism. The classical Amperian magnetic moment was replaced by the non-classical entity of magnetism, the Bohr magneton,

$$\mu = \frac{e\hbar}{2mc} = \gamma\hbar\,. \tag{1}$$

3 Parameter Rules for Interpretation of Gyromagnetic Experiments

Let the ratio $n\mu/n\hbar = M/\Omega = \gamma = e/2mc$ be defined from (1), where n is the number of polarized spins, or circulating charges in the old picture, lined up to define a macroscopic magnetic moment $M = n\mu$. The corresponding angular momentum is given by $\Omega = n\hbar$. By itself this ratio is a trivial identity, given that the Bohr magneton of every particle with $L = 1$ is $\mu = e\hbar/2mc$. The terms n and $\hbar$ contained in γ always cancel, implying in first order that the macroscopic body must display the same γ as a single spin would, and provide a measure of $e/2mc$ multiplied by any anomalous g factor. However this argument deserves a better physical justification, relating phenomenologically and still somewhat obscurely to the response of a gyroscope to torque. Sample rotation at a given frequency ω_r may be viewed as equivalent to a Larmor precession caused by a magnetic field H. As shown in Fig. 1, the imposed torque due to H tends to line up the spins. Changes in M and Ω evolve coaxially. They precess about H independent of the angle between H and M or Ω. A real magnetic field H causes spin precession of M about the direction of H while M develops and finally reaches equilibrium because of spin-lattice relaxation. However, if the sample is not left to rotate freely as in the Einstein-de Haas experiment, there can be no direct evidence of any mechanical exchange of momentum Ω no matter how minute. Except for certain special circumstances of macroscopic radiation damping, theories of spin relaxation keep track of energy degrees of freedom but not of elusive internal mechanisms of spin lattice momentum transfer.

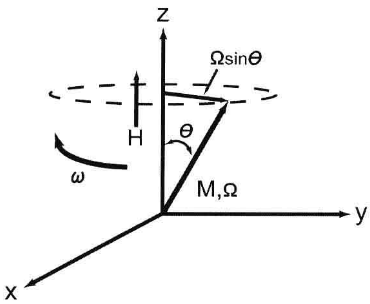

Fig. 1. Relationship of the magnetization M, rotational angular momentum Ω, and static magnetic field H used to discuss magnetomechanical rotation experiments

Before the development of gyromagnetic experiments, in 1861 Maxwell perceived Amperian currents as hidden gyroscopic sources of permanent magnetism. He tried to detect the precession of a permanent magnet in response to an outside torque, but the effect is too small to detect. His attempt relates to Fig. 1. In place of a mechanical torque, the magnetic field H subjects the magnetization M to the torque $T = M \sin\theta \; H = \Omega \sin\theta \; \omega_r$. Including the empirical factor g the ratio

$$\frac{M}{\Omega} = \frac{\omega_r}{H} = \left(\frac{e}{2mc}\right) g \tag{2}$$

defines values of M and Ω as final values representing changes from zero. As a gyromagnetic rule, M/Ω should be written as the ratio of changes $\Delta M/\Delta\Omega$ at any time in the evolution of the spin alignment. The Einstein-de Haas experiment measures the ratio of any imposed M change to the resulting sample rotation angular momentum which is observed. The Barnett experiment measures the ratio of ω_r to a calibrated H field that produces the same M caused by sample rotation at the frequency ω_r. Generation of a calibrated H in the pico to femto-Tesla range from a stable current source would be an extremely difficult requirement. No real field is present when the Barnett effect takes place. Instead, the field H in (2) acts like a "ghost" field H_{ghost}, having the same effect as a real field. Its definition relates to Larmor's theorem, where $H_{ghost} = \omega_r/\gamma$ is defined as an equivalent field. Equation (2) must follow from energy conservation arguments. A sample rotating at the rate ω_r and with moment of inertia I is endowed with rotational energy $U = I\omega_r^2/2$. Any small momentum transfer $\Delta\Omega = I\Delta\omega_r$ that might take place to the spins would require a corresponding increase in spin energy ΔMH. The total energy transferred between spin and rotation is then $\Delta U = I\omega_r\Delta\omega_r = \Delta\Omega\omega_r = \Delta MH$, a relation that immediately rearranges to express the gyroscopic rule given by (2).

4 Nuclear Spin Analogues

Prior to 1940, gyromagnetic experiments served as a measure of g values of electron spin systems in ferromagnetic and paramagnetic substances [4]. The Barnett magnetization, although at least a thousand times or more greater than nuclear spin magnetization in samples of comparable size, is very small, difficult to measure, and easily obscured by instrumental instabilities and stray fields. Even large magnetic fields in those days could not be measured to better than a fraction of a percent by rotating pick up coils. These methods are now obsolete, superseded by the application of magnetic resonance detection methods [7, 8, 9]. As a physical mechanism, the nuclear Barnett effect was invoked later by Purcell [10] to account for the observation of weakly polarized starlight. In that account, Purcell discusses the mechanism of differential light scattering from fast "suprathermal" rotating grains in interstellar space. Because of their rotation it is postulated that these grains become magnetized due to the nuclear Barnett effect. The common directivity and polarization of light scattering by the grains occurs over vast distances because the polarized grains in turn precess about the direction of weak interstellar magnetic fields.

Rather than discuss parameters of this very special unearthly case [11] of Barnett polarization, consider a more representative and yet marginal case on Earth. Here a $1\,\mathrm{cm}^3$ sample of $N = 10^{22}$ nuclear Bohr magnetons where $\mu_B = (9.27/1840) \times 10^{-21}\,\mathrm{erg\,G}^{-1}$ is rotated at the rate $\omega_r/2\pi = 4\,\mathrm{kHz}$ in zero applied magnetic field at $T = 300\,\mathrm{K}$. Assume that the sample acquires an equilibrium magnetization $M_0 = N\mu_B(\hbar\omega_r/kT)$ because of spin lattice relaxation in the ghost field $H_{ghost} = \omega_r/\gamma$. The resulting polarization field in the sample is about $4\pi M_0 \approx 10^{-10}$ G or about 1–10 femto-Tesla. Clearly rotation at higher speeds and at lower temperature could provide M_0 values 10 to 100 times larger, providing an extra margin for weak field detection [1, 2].

5 Homonuclear Dipole-Dipole Coupling

The crude estimate of the field due to a Barnett induced magnetization mentioned above assumes that the spins polarize in a ghost field $H_{ghost} = \omega_r/\gamma$ during a spin-lattice relaxation process as though it were a real field. However, the complexity of many momentum transfer relaxation mechanisms between spin and lattice thermal reservoirs is too difficult to handle. Some understanding can be gained from a specific example of momentum conservation by simulating the effect of sample spinning on dipolar interactions among nuclear spins. A rigid lattice firmament of spins is assigned only a spin temperature with lattice coordinates θ, r and ϕ independent of time in the absence of sample spinning. Since there is no lattice thermal reservoir in this picture, the source of magnetization is obtained from previously prepared dipolar order in zero field that is converted to magnetization by sample rotation. A simple starting point considers two identical spins I_1 and I_2