Nuclear Magnetic Resonance in Solids

Edited by

Lieven Van Gerven

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

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Preface

Plus est en vous ...
(Device of the Lords of Gruuthuse, Brugge, 15th century)

This book is based on, and contains the lectures of the NATO Advanced Study Institute *NUCLEAR MAGNETIC RESONANCE IN SOLIDS*, which was held August 26 to September 6, 1974, at the University of Leuven, Belgium.

The planning of the Leuven Institute developed over several years. The idea came into being around 1971 in the *A.E.I.O.U.*, the *Association Européenne pour une Interaction entre les Organismes Universitaires*. The first practical steps were undertaken exactly two years before it took place, on the evening of the 25th of August 1972 in a restaurant on the Eerikinkatu in Turku, Finland, during the 17th Congress AMPERE. Meeting - and eating, of course - that evening, in that most excellent restaurant, were Raymond Andrew, Karl Hausser, John Waugh and myself. From the beginning on it was decided to take as general theme of the Institute, the recent developments in high resolution and high sensitivity nuclear magnetic resonance in solids.

NMR has been, from the beginning on - 1946, when it was detected for the first time by Felix Bloch's team at the West coast of the U.S.A. and by Edward Purcell's team at the East coast - a powerful tool for studying internal static and dynamic properties of matter, in particular the finest details of structures and motions. When investigating solids, however, there is a severe restriction. Dipolar broadening, which is overwhelmingly important in solids - unlike in liquids and gases, where it is cancelled by rapid motions - has prevented for a long time high resolution and high sensitivity radiospectroscopy in solids. A lot of efforts have been made in recent years to solve the problem, or to get around it, by sophisticated techniques e.g., introducing some (real or fictive) random "motion" or interaction in the spin system. The results are very promising, and quite a number of contributions in the School and in the present book are devoted to these new developments. On the other hand the directors of the Institute wanted to provide the study of recent developments in NMR with a firm basis, and finally they also wanted to present new applications of modern NMR to all kind of solids, in chemistry and biology as well as in physics. The results of these efforts, of the really interdisci-

plinary School which was the NATO Advanced Study Institute in Leuven, are to be found in the present volume.

The presentation of this book gives me the opportunity to remind of the organizations and the people, who contributed to the organization of the Institute.

First of all our thanks are due to the *Scientific Affairs Division of the North Atlantic Treaty Organization* and to Dr. T. Kester, Director of the Division. The NATO Summer School program has been criticized from different sides, very often too by students organizations. However, as I remarked in my welcome speech at the Leuven School, one could, if one wants, blame NATO for many things, but one should not blame it for supporting and doing science. To a representative of one Eastern European country at the Congress AMPERE in Turku, who was not very happy about the possibility of having the NATO Summer School in Leuven linked to the next Congress AMPERE (the one in Nottingham), my reply was that I would welcome very much a joint effort of NATO *and* the Warsaw Pact in organizing the Leuven Summer School. Of course, this has not been realized! Nevertheless, we were happy to welcome in Leuven many participants and students also from Socialist Countries. Their presence made it clear that, at least in science, there is no iron curtain, nor any other curtain whatsoever.

Many others contributed to the success of the Institute, and in this way to the present book. We are grateful for the sponsorship of the *European Physical Society*, for the financial support of the *Ministery of Education and Flemish Cultural Affairs*, and for the grants provided by the *National Science Foundation* of the United States of America. Moreover several local and national - even multinational, why not! - industrial companies supported the Institute. We thank the N.V.'s *Philips, Brouwerijen Artois, Raychem, Bruker-Spectrospin, Varian-Benelux, Metallurgie Hoboken-Overpelt, Agfa-Gevaert, Bell Telephone Mfg. Co* and *Kredietbank*.

The Scientific Directors of the Institute, Professor E.R. Andrew and myself, have been very fortunate in having an effective Advisory Committee which helped us with the planning and the scientific organization of the School. Dr. P. Grobet and Dr. P. Van Hecke served as Secretaries; members of the International Advisory Committee were: R. Blinc, K. Hausser, J.Jeener, G.J. Martin, A. Redfield, C.P. Slichter, N. Trappeniers and J. Waugh. In addition Miss M.A. Jennes, Miss H. Van Gerven, Mr. A. Werner, Dr. G. Adriaenssens, Drs. A. Stesmans and Drs. G. Janssens have been very helpful in organizing and running the School. We are most grateful to all of them.

Many thanks also - last but not least - to the professors of the Advanced Study Institute: H. Alloul (Orsay), R. Blinc (Ljubljana), S. Clough (Nottingham), M. Guéron (Paris), U. Haeberlen (Heidelberg), J. Jeener (Bruxelles), D. Kearns (Riverside),

W. Müller-Warmuth (Münster), R. Orbach (Los Angeles), Ch. Slichter (Urbana), J. Tegenfeldt (Cambridge), P. Van Hecke (Leuven), K. Wüthrich (Zürich). Professor H.B.G. Casimir, President of the European Physical Society, gave an Opening Address on *Resonance*. They have put our School at a high level ... without losing contact with the students. They made this book.

I also would like to thank those who helped me in preparing the manuscripts, Guy Adriaenssens, Luc Parijs and in particular Marie-Anne Jennes. She contributed to the Institute from the early correspondence to the final stages. Her continued dedication, both to the Institute and to this book guaranteed success.

To say a final word about the book, as editor I have taken the liberty not to print the lectures in chronological order, as they were given at the Institute, but to collect them in four chapters: *Principles, Systems, Methods* and .... *Life*. Read and judge!

I hope this book will help you to get more information out of your NMR-spectra and to challenge them: *Plus est en vous* ...

Lieven Van Gerven

This seal, designed by Rijkhard Van Gerven, symbolizes the NATO Advanced Study Institute on Nuclear Magnetic Resonance in Solids, its place and subject. It represents the contours of the Gothic Town Hall of Leuven(finished in 1463), together with a semi-exponential decay pattern of transversal magnetization in nuclear magnetic resonance(recorded in Leuven in 1963).

Contents

DEDICATION

During the course of the preparation of my lectures I received the sad news of the death of a young, German scientist for whom I hold the highest admiration and regard, Dr. Horst Seidel. It was my great good fortune to have him as a guest in my laboratory for a year. My students and I had the benefit of his deep and contagious love of physics, his superb physical insight, his clever approach to the design of experiments, his profound ability to strip away theoretical complexity to reveal the essential physical concepts behind natural phenomena, and his humane and sensitive dealings with others in the laboratory. For his Ph. D. thesis at Stuttgart with Professor Wolf, he made a major breakthrough in the technique of electron-nuclear double resonance and applied it to the understanding of the structure of color centers. He is one of the major figures in the younger generation of European scientists who revolutionized the style of European experimental research. Building on the ancient tradition of superb experimentation, he added the new dimension of a thorough-going theoretical analysis of his own results. He was a scientist who knew and contributed to the truly international character of science.

This occasion, gathering scientists from many countries, focusing attention on those of you at the start of your careers, emphasizing the interplay of theory and experiment, and exploring the uses of magnetic resonance in physics, chemistry, and biology, strikes a chord exactly in tune with his spirit. I therefore dedicate my lectures to the memory of our beloved colleague, Horst Seidel.

C.P. SLICHTER

Chapter I

PRINCIPLES: TEMPERATURES, STRUCTURES, MOTIONS

GENERAL ASPECTS OF NUCLEAR MAGNETIC RESONANCE IN SOLIDS

C.P. Slichter

University of Illinois,

Urbana-Champaign (Illinois, U.S.A.)

INTRODUCTION

It is a great honour to be invited to lecture at NATO Summer School on NMR in solids. I have done so before - many of today's prominent resonators were in the class. I look on this summer school as the start of both a personal and professional acquaintance.

We do resonance in solids to study problems in physics, chemistry, or biology. The subject is as broad as the problems of interest to scientists in those fields. The task of your lecturers will be to draw on their experience as physicists, chemists, and biologists to bring out resonance concepts and methods which have been fruitful. I will try to launch the main themes to be presented by the other speakers.

THE CONTRAST WITH HIGH RESOLUTION NMR

Most chemists and biologists think of high resolution when they think of NMR. They deal with liquid samples in order that they have resonance lines which are narrow as a result of motional narrowing. The narrowness enables one to resolve the chemical shifts associated with different nuclear sites, and the indirect spin-spin couplings from which we learn what groups of nuclei are near one another in a molecule.

But one also gives up some things.

(1) The problem of interest may inherently be a solid state problem, e.g., superconductivity or solid state rate

processes (like determining the mechanisms whereby atoms can diffuse in solids).

(2) The liquid motion averages out some things which contain information because their effect depends on the orientation of H_o relative to crystal axes. Examples are:
(a) dipolar interactions (which reveal the orientation of H_2O molecules in solids - the famous Pake doublet [1])
(b) chemical shift anisotropy - basically the statement that local magnetic polarization is anisotropic
(c) electric quadrupole coupling
(d) anistropic coupling to electron spins (dipolar and pseudo dipolar).

(3) In solids the dipolar spin-spin coupling is often much stronger than the spin-lattice. This enables one to do trick experiments such as some of the double resonance schemes for getting very high sensitivity.

THE FLAVOR OF THE PROBLEMS STUDIED

We usually associate classification with the early stages of a scientific discipline - the period prior to establishment of a theoretical framework.

But names also evoke a whole host of associations, sometimes quite vivid. The words Jerusalem, Bethlehem and Mecca carry vivid connotations for most people. As scientists, names such as Leiden or the Cavendish Lab have special meaning and they stimulate our thoughts.

We might in this vein catalogue things to study - what aspects of solids people study by resonance. This listing is to stir the juices of the brain - to make you think "aha - that suggests a study".

Here's a physicist's list:
- static processes, rate processes
- perfect solids, imperfect solids (chemical impurities, misplaced atoms, dislocations)
- insulators, semiconductors, conductors, superconductors
- diamagnets, paramagnets, ferromagnets, ferrimagnets, antiferromagnets
- single crystals, powders, amorphous solids
- simple solids, multicomponent solids, alloys, molecular solids, polymers, biological molecules
- phase transitions (first order, second order).

Note these cut across the field in different ways. The above list being a physicist's list may be more like Sodom, Gomorrah, Waterloo, or Dunkirk to many of you.